Quantum Physics II

Lecture notes of Professor Savona
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Chapter 1

Introduction to the Course

Considerations based on the symmetry of a physical system have always been used in the formulation of general principles and in solving physical problems. Thus, the reader has certainly already encountered several examples of the use of a symmetry principle. For instance, momentum is conserved for a system that is invariant under spatial translation, and angular momentum is conserved for a system that is invariant under rotation. More generally, symmetry properties of a system provide us with two advantages. Firstly, they allow us to establish *conservation laws*. Secondly, they introduce *selection rules* that greatly facilitate the calculation of the physical quantities of interest. However, it is not always intuitive how to take advantage of the symmetry properties. Therefore, it is necessary to introduce a formalism that systematically allows us to construct the link between symmetry properties and physical laws.

Most of the symmetry operations of a physical system are geometric transformations, such as rotations around a fixed axis, translations, or inversions about a center of symmetry (i.e., the transformation of each point $\mathbf{x}$ into the point $-\mathbf{x}$, with the point $\mathbf{x} = 0$ being the center of symmetry). If the application of a geometric transformation results in the transformed object being indistinguishable from the object in its initial state (same position, same shape, same orientation), then we say that the system is *invariant* under the considered transformation.

The set of operations for which a system is invariant forms a group in the mathematical sense. The mathematical theory of groups, therefore, naturally comes into play in a formal treatment of symmetry properties in physics. The application of group theory to physics was systematically developed only in the early 20th century. Among the most important contributions to this field, we highlight the work of Eugene Paul Wigner, who formalized the application of group theory to quantum mechanics in his book *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* in 1931.

The branch of group theory that applies to physics is called *group representation theory*. An important distinction within this theory is that between finite groups and infinite groups. Indeed, some symmetry properties imply a finite number of symmetry operations. For example, this is the case for the rotational symmetries of molecules. As an example, we introduce the ammonia molecule in the following paragraph. This molecule is characterized by six rotational symmetry operations: the identity transformation (a non-transformation is always a symmetry operation!), two 120-degree rotations, and three mirror operations. On the other hand, some systems are characterized by an infinite number of symmetry operations. For instance, a sphere is invariant under a rotation through an arbitrary angle about the center of the sphere as the fixed point. The theories of finite group representations and infinite group representations present significant differences that necessitate separate treatment of the two domains.

The primary goal of this course is to introduce the theory of finite group representations and its application to symmetry properties in molecular and solid-state physics. In the first part,

we will introduce the necessary mathematical concepts. In the second part, we will discuss the most important finite groups for our purposes and provide examples of the theory's application. We will briefly address the rotation-inversion group $O(3)$, which is an infinite group, and its applications.

1.1 An Example: Vibration Modes of a Molecule

In this section, we will address a physical problem using symmetry criteria. The goal is to show that symmetry properties can significantly simplify the search for a solution to a problem. At the current state of our knowledge, we will primarily use symmetry arguments *by hand*, meaning relying on intuition, without having a systematic method with a set of rules at our disposal. The ultimate goal of this course is to lay the foundations for such a method and provide examples of its application.

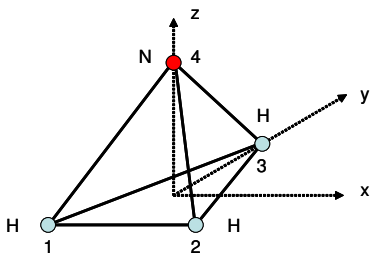

Figure 1.1: Scheme of the NH_3 molecule. In the figure, you can also see the numbering of the four atoms and the choice of the reference frame.

Let's consider the problem of the vibrations of the ammonia (NH_3) molecule. This molecule consists of three hydrogen atoms arranged in a triangle and one nitrogen atom located on the vertical axis passing through the center of the triangle (see Figure 1.1). In molecular physics, it is known that for small displacements from the equilibrium positions, the restoring forces on the four atoms are proportional to the displacements. The molecule behaves as a system of coupled harmonic oscillators with 12 degrees of freedom (three spatial coordinates for each atom). Let's denote $\mathbf{R}_1$, $\mathbf{R}_2$, $\mathbf{R}_3$, and $\mathbf{R}_4$ as the coordinates of the three hydrogen atoms and the nitrogen atom. If the equilibrium positions of the four atoms are $\mathbf{R}_j^{(0)}$, where $j = 1, \ldots, 4$, then the displacement vectors are given by $\mathbf{u}_j = \mathbf{R}_j - \mathbf{R}_j^{(0)}$. Let m_H and m_N be the masses of the hydrogen and nitrogen atoms, respectively.

To realistically describe the harmonic modes of the molecules, a precise parametrization of the elastic constants would be necessary. Such a parametrization should take into account that the force between two atoms will be characterized by different elastic constants, depending on whether the displacement direction is along the line connecting them or perpendicular to this line. In general, we cannot express the harmonic force on an atom as the sum of harmonic forces exerted by the other atoms because the harmonic constant for the force between two atoms will be influenced by the presence of the other atoms. However, in the context of this exercise, we can introduce a highly simplified model without fear, which allows us to familiarize ourselves with the symmetry properties. We will assume that the system is simply characterized by two harmonic constants: k_{HH} for the restoring force between two hydrogen atoms and k_{NH} for the force between a hydrogen atom and the nitrogen atom. We have made a strong approximation by assuming that the harmonic force between two atoms is isotropic. We will see that this approximation results in accidental degeneracies, which are not strictly imposed by the symmetry of the problem. Such degeneracies would not be present in a more realistic model of

harmonic forces. In the following notes, we will discuss the problem of accidental degeneracies in more detail and see that their existence is very rare: their occurrence is almost always a sign of a poor consideration of the symmetry properties of the system.

Once the masses and elastic constants are given, we can write the potential energy as follows:

$$\begin{aligned} V(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,\mathbf{u}_4) &= \frac{1}{2}k_{HH}\left[(\mathbf{u}_1-\mathbf{u}_2)^2+(\mathbf{u}_1-\mathbf{u}_3)^2+(\mathbf{u}_2-\mathbf{u}_3)^2\right] \\ &+ \frac{1}{2}k_{NH}\left[(\mathbf{u}_1-\mathbf{u}_4)^2+(\mathbf{u}_2-\mathbf{u}_4)^2+(\mathbf{u}_3-\mathbf{u}_4)^2\right]. \end{aligned} \tag{1.1}$$

The force acting on a given particle is obtained from the gradient of this potential with respect to the corresponding displacement variable:

$$\mathbf{F}_j = m_j\frac{\partial^2\mathbf{u}_j}{\partial t^2} = -\frac{\partial V}{\partial \mathbf{u}_j}, \tag{1.2}$$

which allows us to write the equations of motion for the system:

$$\begin{aligned} m_H\frac{\partial^2\mathbf{u}_1}{\partial t^2} &= -k_{HH}(\mathbf{u}_1-\mathbf{u}_2)-k_{HH}(\mathbf{u}_1-\mathbf{u}_3)-k_{NH}(\mathbf{u}_1-\mathbf{u}_4), \\ m_H\frac{\partial^2\mathbf{u}_2}{\partial t^2} &= -k_{HH}(\mathbf{u}_2-\mathbf{u}_1)-k_{HH}(\mathbf{u}_2-\mathbf{u}_3)-k_{NH}(\mathbf{u}_2-\mathbf{u}_4), \\ m_H\frac{\partial^2\mathbf{u}_3}{\partial t^2} &= -k_{HH}(\mathbf{u}_3-\mathbf{u}_1)-k_{HH}(\mathbf{u}_3-\mathbf{u}_2)-k_{NH}(\mathbf{u}_3-\mathbf{u}_4), \\ m_N\frac{\partial^2\mathbf{u}_4}{\partial t^2} &= -k_{NH}(\mathbf{u}_4-\mathbf{u}_1)-k_{NH}(\mathbf{u}_4-\mathbf{u}_2)-k_{NH}(\mathbf{u}_4-\mathbf{u}_3). \end{aligned} \tag{1.3}$$

In this simplified notation, it is implied that the variables $\mathbf{u}_j(t)$ depend on time. Such a system of coupled oscillators is characterized by "normal modes." A normal mode is a specific solution to the equations (1.3) where the 12 degrees of freedom depend on time according to the same harmonic law:

$$\mathbf{u}_j(t) = \mathbf{u}_j^{(0)}\sin(\omega t). \tag{1.4}$$

Here, $\mathbf{u}_j^{(0)}$ is a constant vector. By substituting the solution (1.4) into the set of equations (1.3), we obtain:

$$\begin{aligned} \omega^2\mathbf{u}_1^{(0)} &= \frac{1}{m_H}\left[k_{HH}(\mathbf{u}_1^{(0)}-\mathbf{u}_2^{(0)})+k_{HH}(\mathbf{u}_1^{(0)}-\mathbf{u}_3^{(0)})+k_{NH}(\mathbf{u}_1^{(0)}-\mathbf{u}_4^{(0)})\right], \\ \omega^2\mathbf{u}_2^{(0)} &= \frac{1}{m_H}\left[k_{HH}(\mathbf{u}_2^{(0)}-\mathbf{u}_1^{(0)})+k_{HH}(\mathbf{u}_2^{(0)}-\mathbf{u}_3^{(0)})+k_{NH}(\mathbf{u}_2^{(0)}-\mathbf{u}_4^{(0)})\right], \\ \omega^2\mathbf{u}_3^{(0)} &= \frac{1}{m_H}\left[k_{HH}(\mathbf{u}_3^{(0)}-\mathbf{u}_1^{(0)})+k_{HH}(\mathbf{u}_3^{(0)}-\mathbf{u}_2^{(0)})+k_{NH}(\mathbf{u}_3^{(0)}-\mathbf{u}_4^{(0)})\right], \\ \omega^2\mathbf{u}_4^{(0)} &= \frac{1}{m_N}\left[k_{NH}(\mathbf{u}_4^{(0)}-\mathbf{u}_1^{(0)})+k_{NH}(\mathbf{u}_4^{(0)}-\mathbf{u}_2^{(0)})+k_{NH}(\mathbf{u}_4^{(0)}-\mathbf{u}_3^{(0)})\right]. \end{aligned} \tag{1.5}$$

Subsequently, to simplify the notation, we will represent $\mathbf{u}_j^{(0)}$ as simply $\mathbf{u}_j$. We can define the vector in the 12-dimensional space as:

$$\mathbf{u} = (\mathbf{u}_1;\,\mathbf{u}_2;\,\mathbf{u}_3;\,\mathbf{u}_4)\,. \tag{1.6}$$

The system of equations (1.5) can be expressed in the compact form:

$$A\mathbf{u} = \omega^2 \mathbf{u}\,, \tag{1.7}$$

Here, A is the dynamic matrix of the system, obtained straightforwardly from the form (1.5) of the equation of motion.

Exercise: Write the matrix A.

The equation (1.7) represents an eigenvalue problem. The solutions are obtained by diagonalizing the matrix A. The eigenvalues ω^2 of A and the corresponding eigenvectors describe the normal modes of vibration of the molecule. These solutions form a complete set. Any other solution to the problem (1.3) with given initial conditions can be expressed as a linear combination of the normal modes found.

We note that the matrix A is not symmetric. This is due to the difference between the mass of hydrogen m_H and the mass of nitrogen m_N. To have a symmetric matrix, we would need to rewrite the problem with displacement vectors normalized by the masses, $\mathbf{q}_j = \sqrt{m_j}\mathbf{u}_j$, with $j = 1, \ldots, 4$, $m_j = m_H$ for the three hydrogens, and $m_j = m_N$ for nitrogen. We will not adopt this change of variables since the non-normalized vectors $\mathbf{u}_j$ provide us with a better intuition of the molecule's dynamics. It goes without saying that the matrix A describes the dynamics of a system of coupled harmonic oscillators, and therefore, all its eigenvalues will be real for physical reasons, regardless of its lack of symmetry.

The diagonalization of a 12×12 matrix cannot be solved analytically in the general case. One might think, "No problem! We can always solve it numerically with a computer." While this is true, such an approach can sometimes limit our understanding of the results. Furthermore, it should be noted that we have chosen an example in classical mechanics, where the number of degrees of freedom is finite. However, most of the time, we will deal with quantum mechanics, where the solution space is the Hilbert space of the wave function, a space of infinite dimensions. In such cases, the computer often cannot assist us, and simplifications must be introduced.

We will now show how symmetry arguments allow us to solve this problem analytically. Analytical mechanics allows us to make an initial consideration. A rigid body in a vacuum has six degrees of freedom: three for the translation of the center of mass and three for rotation about the principal axes of inertia. The molecule can, therefore, move through space at a constant velocity in an arbitrary direction and rotate about an axis at a constant angular velocity. We can always envision the molecule as a rigid body and place ourselves in the reference frame where it is at rest. These six degrees of freedom are characterized by a zero frequency $\omega = 0$.

For example, free translation along the x-axis (see Fig. 1.2(a)) is characterized by the displacement vector (normalized):

$$\mathbf{u} = \frac{1}{2}\,(1,\,0,\,0\,;\,1,\,0,\,0\,;\,1,\,0,\,0\,;\,1,\,0,\,0)\,. \tag{1.8}$$

Exercise: Verify that the vector (1.8) is an eigenvector of the matrix A with an eigenvalue of zero.

Free rotation around the z-axis (see Fig. 1.2(b)) is characterized by the displacement vector:

$$\mathbf{u} = \frac{1}{\sqrt{3}}\left(-\frac{1}{2},\,\frac{\sqrt{3}}{2},\,0\,;-\frac{1}{2},\,-\frac{\sqrt{3}}{2},\,0\,;\,1,\,0,\,0\,;\,0,\,0,\,0\right). \tag{1.9}$$

In reality, a finite-length displacement, as illustrated in Fig. 1.2(b), involves a deformation of the molecule and consequently a potential energy due to elastic forces. Such displacement cannot be an eigenvector with an eigenvalue of zero for the matrix A in our problem formulation.

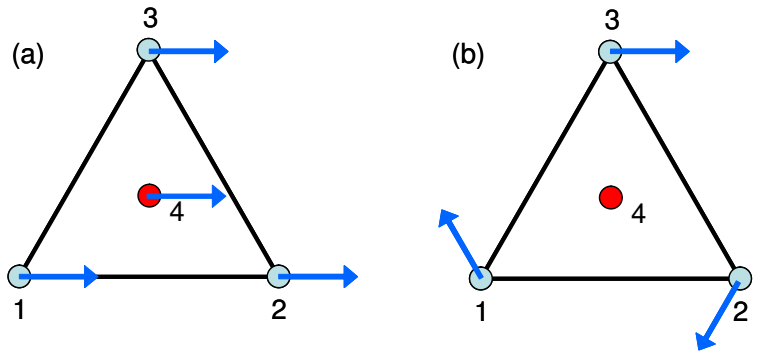

Figure 1.2: (a) Example of translation proper mode of the center of mass. The blue vectors are the displacement vectors $\mathbf{u}_j$. (b) Example of proper modes of free rotation around axis z.

In our problem formulation, the rotation modes are solutions to the eigenvalue problem, always in the form of a combination of rigid rotation and deformation of the molecule. In this way, the eigenvectors associated with these solutions have finite eigenvalues that correspond to the eigenvalues of the associated deformation. For example, we can verify that the displacement illustrated in Fig. 1.2(b) is composed of a rotation around the z-axis and a deformation in the radial mode (1.17), which we will describe later. The corresponding eigenvalue is the same as for this radial mode.

In principle, we can place ourselves in the space orthogonal to the one generated by these six vectors—three for translation and three for rotation—using the Gram-Schmidt orthogonalization process. The problem would then be reduced to diagonalizing a 6x6 matrix, which is still a challenge for an analytical approach.

Suppose we perform an orthogonal transformation of the positions $\mathbf{R}_j$ of the four atoms that make up the molecule. Let's denote the transformed vector as $\mathbf{R}'_j = S\mathbf{R}_j$. The matrix S is a three-dimensional orthogonal matrix. The orthogonality condition implies that $S^{-1}S = I$, and the elements of S are real. This transformation corresponds to an orthogonal transformation O of the 12-dimensional displacement vector $\mathbf{u}$, such that $\mathbf{u}' = O\mathbf{u}$ and $O^{-1}O = I$. For example, a counterclockwise rotation of $2\pi/3$ about the z-axis is given by:

$$O\mathbf{u} = (S\mathbf{u}_3\,;\, S\mathbf{u}_1\,;\, S\mathbf{u}_2\,;\, S\mathbf{u}_4) = \begin{pmatrix} 0 & 0 & S & 0 \\ S & 0 & 0 & 0 \\ 0 & S & 0 & 0 \\ 0 & 0 & 0 & S \end{pmatrix} \begin{pmatrix} \mathbf{u}_1 \\ \mathbf{u}_2 \\ \mathbf{u}_3 \\ \mathbf{u}_4 \end{pmatrix}, \tag{1.10}$$

where

$$S = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{1.11}$$

The inverse transformation is $\mathbf{u} = O^{-1}\mathbf{u}'$. By substituting it into the equation of motion (1.7), we obtain:

$$AO^{-1}\mathbf{u}' = \omega^2 O^{-1}\mathbf{u}'\,. \tag{1.12}$$

Let's multiply by O on the left side. We have:

$$A'\mathbf{u}' = OAO^{-1}\mathbf{u}' = \omega^2\mathbf{u}'\,, \tag{1.13}$$

where we've defined $A' = OAO^{-1}$.

The key point of this approach is to notice that there is a set of orthogonal transformations O that leave the matrix A unchanged, i.e., $A' = A$. For example, the rotation (1.10) superimposes the molecule on itself. The matrix does not change due to this transformation since it depends only on the spatial shape of the molecule with the atoms in their equilibrium positions. In other words, the rotation only involves a permutation of the identical hydrogen atoms and, therefore, cannot influence the dynamics of the oscillations.

Exercise: Verify that, under transformation (1.10), we have $OAO^{-1} = A$.

We can seek all the transformations that have this property of invariance. These transformations form a set $\{O_j\}$ where $j = 1, \ldots, N$, and N is the cardinality of this set. We will call them symmetry transformations of the system. An analysis of the shape of the molecule allows us to find all the symmetry transformations by inspection. They are summarized in the following scheme:

E	Identity
C_3	Counterclockwise rotation of $2\pi/3$ around the z-axis
C_3^{-1}	Clockwise rotation of $2\pi/3$ around the z-axis
σ_1	Mirror plane at $x = 0$
σ_2	Mirror plane at $x = \sqrt{3}y$
σ_3	Mirror plane at $x = -\sqrt{3}y$

We will see in the rest of the course that this set of transformations forms a group.

Exercise: Write the corresponding 12×12 matrices for the symmetry transformations in the displacement space. This set of matrices is called a *representation* of the symmetry group.

Let's now assume we have found a non-degenerate eigenvector $\mathbf{u}_p$ of the matrix A, such that $A\mathbf{u}_p = \omega_p^2 \mathbf{u}_p$. For each symmetry operation O_j, we have

$$O_j A O_j^{-1} \mathbf{u}_p = A\mathbf{u}_p = \omega_p^2 \mathbf{u}_p \,. \tag{1.14}$$

Let's multiply by O_j^{-1} on the left.

$$A(O_j^{-1}\mathbf{u}_p) = \omega_p^2 (O_j^{-1}\mathbf{u}_p) \,. \tag{1.15}$$

So the transformed vector $\mathbf{u}_p^j = O_j^{-1}\mathbf{u}_p$ is also an eigenvector of the matrix A with the same eigenvalue ω_p^2. Since we have assumed that $\mathbf{u}_p$ is a non-degenerate eigenvector, it follows necessarily that

$$\mathbf{u}_p^j = \alpha_j \mathbf{u}_p \,, \tag{1.16}$$

where $\alpha_j = \pm 1$. This must hold for all symmetry transformations O_j of the molecule's symmetry group. In fact, if there existed an O_l for which this property is not satisfied, we would have a vector $\mathbf{u}_p^l = O_l^{-1}\mathbf{u}_p$ that would be linearly independent of $\mathbf{u}_p$ and would simultaneously be an eigenvector of A with the same eigenvalue, which would contradict our assumption.

The relationship (1.16) is a very important property of non-degenerate eigenvectors. We can summarize it as follows: if $\mathbf{u}_p$ is a non-degenerate eigenvector of A, then for any symmetry transformation O_j, we have $O_j^{-1}\mathbf{u}_p = \pm\mathbf{u}_p$. Unfortunately, the reverse is not generally true. Indeed, suppose we have two non-degenerate eigenvectors $\mathbf{u}_1$ and $\mathbf{u}_2$ with eigenvalues $\omega_1^2 \neq \omega_2^2$.

Suppose also that these two vectors behave identically under the symmetry transformations of the group, i.e., $O_j^{-1}\mathbf{u}_1 = \alpha_j \mathbf{u}_1$ and $O_j^{-1}\mathbf{u}_2 = \beta_j \mathbf{u}_2$, where $\alpha_j = \pm 1$, $\beta_j = \pm 1$, and $\alpha_j = \beta_j$ for each j. In this case, any linear combination of the vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ would also satisfy the property (1.16) for each j, but by construction, it would not lead to an eigenvector of A. Therefore, we can use this property to more easily find the normal modes of vibration of the molecule, but we must always check that a vector found in this way is indeed an eigenvector of A.

To begin with, let's consider the vector corresponding to a displacement of the three hydrogen atoms in the radial direction, while the nitrogen atom remains in its equilibrium position, as illustrated in Figure 1.3(a). This vector is given by

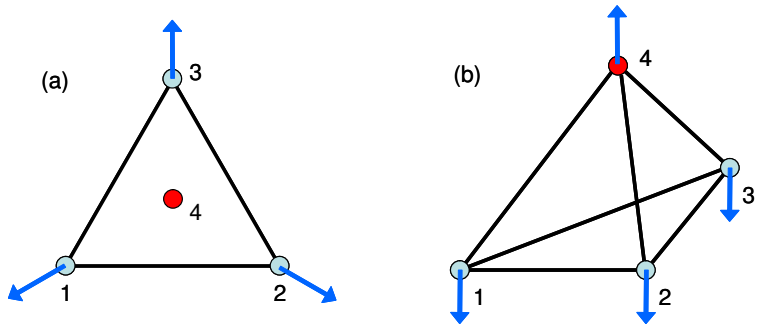

Figure 1.3: (a) Non-degenerate vibration mode in the $z = 0$ plane. (b) Non-degenerate vibration mode with vertical axis oscillation.

$$\mathbf{u}_p = \frac{1}{\sqrt{3}}\left(-\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\,;\, \frac{\sqrt{3}}{2}, -\frac{1}{2}, 0\,;\, 0, 1, 0\,;\, 0, 0, 0\right). \tag{1.17}$$

Exercise: Verify that for such a displacement, the center of mass of the molecule remains fixed. This assures us that it is a pure vibrational mode without a translational component.

It can be shown that $\mathbf{u}_p$ is invariant under the symmetry transformations of the molecule, i.e., σ_1, σ_2, σ_3, C_3, C_3^{-1}, E. So, $\mathbf{u}_p$ is a good candidate to become a proper mode of the system. To be sure, we need to verify it manually.

Exercise: Verify that the vector (1.17) is invariant under all the symmetry transformations of the molecule. In particular, check that in the relation (1.16), we have $\alpha_j = 1$ for each j. Verify that this vector is an eigenvector of the matrix A and derive the corresponding eigenvalue.

Now, let's consider the displacement along the vertical axis where the nitrogen atom is moved in the opposite direction to the plane of the three hydrogens, as illustrated in Figure 1.3(b). This displacement is defined by the vector

$$\mathbf{u}_p = \frac{1}{\sqrt{3+\mu^2}}\,(0, 0, 1\,;\, 0, 0, 1\,;\, 0, 0, 1\,;\, 0, 0, \mu)\,, \tag{1.18}$$

with $\mu{=}3m_H/m_N$ (under this condition, the center of mass remains fixed).

Exercise: As with the vector (1.17), verify the property of invariance of (1.18), that $\alpha_j = 1$ for each j, that it is an eigenvector of the matrix A, and derive the corresponding eigenvalue.

This vector is, therefore, an eigenvector of the system with an eigenvalue different from that of the vector (1.17), but with exactly the same symmetry (the same α_j) as the latter. As mentioned earlier, a linear combination of these two vectors would still be invariant under all the symmetry operations of the molecule but would not be an eigenvector of the system. This is why we need to verify that the found vectors are indeed eigenvectors. For another system, it might have been more difficult to guess their form, or the proper eigenvectors could have been linear combinations of these two vectors. Our symmetry considerations have still allowed us to restrict ourselves to a dimension-2 subspace that can be analytically diagonalized easily. This is the power of the method.

Now, suppose that an eigenvector $\mathbf{u}_{p1}$ of matrix A does not satisfy the property $O_j\mathbf{u}_{p1} = \pm\mathbf{u}_{p1}$ for all symmetry operations of the molecule. We have at least one transformation O_l such that $O_l\mathbf{u}_{p1} = \mathbf{u}_{p2}$ is a vector linearly independent of $\mathbf{u}_{p1}$. We have seen that $\mathbf{u}_{p2}$ must still be an eigenvector of A with the same eigenvalue ω_p^2 as vector $\mathbf{u}_{p1}$. So, we have found another degenerate eigenvector with the first. We can repeat this procedure by applying all symmetry operations to the two vectors found in this way. We have two possibilities.

(i) For all symmetry operations, the vectors $O_j\mathbf{u}_{p1}$ and $O_j\mathbf{u}_{p2}$ lie in the subspace generated by $\mathbf{u}_{p1}$ and $\mathbf{u}_{p2}$. In this case, we have defined an invariant subspace of dimension 2, i.e., all symmetry operations applied to a vector in this subspace result in a vector that belongs to the same subspace. To search for eigenvectors based on symmetry properties, we can proceed by analogy with the case of a non-degenerate eigenvector. If we manage to find two linearly independent vectors that generate an invariant subspace concerning the symmetry operations of the molecule, these two vectors are good candidates to be degenerate eigenvectors of the matrix A. We just need to verify that they are.

(ii) There is at least one symmetry operation of the molecule, O_l, such that $O_l\mathbf{u}_{p1}$ or $O_l\mathbf{u}_{p2}$ gives a vector $\mathbf{u}_{p3}$ that is linearly independent of $\mathbf{u}_{p1}$ and $\mathbf{u}_{p2}$. This vector is an eigenvector of matrix A, degenerate with the eigenvectors $\mathbf{u}_{p1}$ and $\mathbf{u}_{p2}$. We can repeat the reasoning and distinguish two more cases, depending on whether the 3-dimensional subspace found is invariant or not. The reverse procedure tells us that, once we have identified an invariant subspace of dimension 3, any three arbitrary linearly independent eigenvectors in this subspace are good candidates to be degenerate eigenvectors of the system.

With this procedure, we can decompose the 12-dimensional vector space of the problem into several subspaces that are invariant under the symmetry operations of the molecule. This procedure simplifies the task of finding the eigenvectors of the system. In the rest of the course, we will see that this approach is called the "decomposition into irreducible representations of the symmetry group of the system." We will learn techniques for performing this decomposition systematically and finding the eigenvectors of the system under study.

Now, let's go back to our ammonia molecule. Consider the displacement vector illustrated in Figure 1.4(a).

$$\mathbf{u}_{p1} = \frac{1}{\sqrt{3}}\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\,;\, \frac{1}{2}, -\frac{\sqrt{3}}{2}, 0\,;\, -1, 0, 0\,;\, 0, 0, 0\right), \tag{1.19}$$

Exercise: Verify that the vector (1.19) is an eigenvector of the matrix A. Verify that it is not invariant under the symmetry operations of the molecule.

Since this vector is not invariant, we can obtain other degenerate eigenvectors with the first one by applying the symmetry operations of the molecule. Note that the displacement (1.19) is only in the $z = 0$ plane, and all symmetry operations leave this plane invariant. Therefore, the invariant subspace cannot have more than two dimensions. Without the effort of generating the second vector by applying a symmetry operation, we can choose any second linearly independent

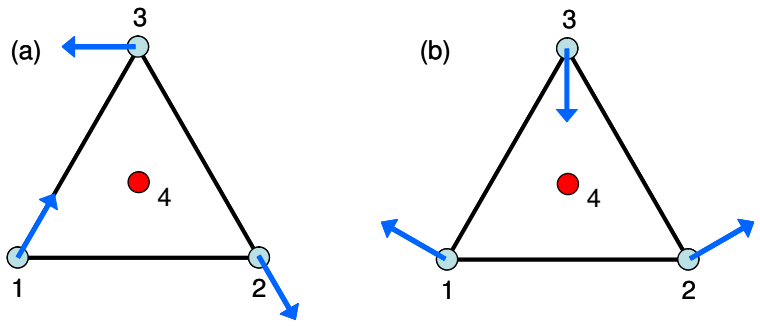

Figure 1.4: Proper vibration modes, degenerate in the plane $z = 0$. Displacements in (a) and (b) transform under symmetry operations of the molecules like the x and y components of a vector in the plane.

vector in the plane of the three hydrogens. Let's choose the vector orthogonal to the first one, obtained by a $\pi/2$ rotation of the vectors $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$, as illustrated in Figure 1.4(b).

$$\mathbf{u}_{p2} = \frac{1}{\sqrt{3}}\left(-\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\,; \frac{\sqrt{3}}{2}, \frac{1}{2}, 0\,; 0, -1, 0\,; 0, 0, 0\right), \tag{1.20}$$

This vector is also an eigenvector of the matrix A. This choice of the two vectors is not arbitrary. It could be shown that the two vectors (1.19) and (1.20) behave under the symmetry operations of the molecule as the x and y components of a vector in the $z = 0$ plane. This means, for example, that for each j, if $O_j\mathbf{u}_{p1} = a_j\mathbf{u}_{p1} + b_j\mathbf{u}_{p2}$, then the coefficients a_j and b_j are the same as for the rotation $S_j\hat{\mathbf{x}} = a_j\hat{\mathbf{x}} + b_j\hat{\mathbf{y}}$ in three-dimensional space. Later, we will see that, for molecules and solids, the invariant subspaces can be grouped into a very small number of categories - the irreducible representations - based on the transformation properties of vectors under the symmetry operations. We will learn to recognize these categories and derive the base vectors using systematic methods.

Our journey is nearly complete. We have found the three translational modes, the three rotational modes, and four proper vibrational modes. We could, through the Gram-Schmidt orthogonalization procedure, find the two remaining eigenvectors and diagonalize the problem in the corresponding subspace. The method used above further simplifies the task. Consider the mode illustrated in Figure 1.5(a) and (c).

$$\mathbf{u}_{p1} = \frac{1}{\sqrt{3 + 2b^2 + \mu^2}}\,(1, 0, b\,; 1, 0, -b\,; 1, 0, 0\,; -\mu, 0, 0)\,, \tag{1.21}$$

with $b = 3H/L$, where H and L are the height and side of the triangle formed by the three hydrogens. It is an eigenvector of matrix A, and we can verify that it is not invariant under all symmetry operations. Since we have only two dimensions left, it is clear that the invariant subspace for this vector is of dimension two. A second vector is illustrated in Figure 1.5(b) and (d).

$$\mathbf{u}_{p2} = \frac{1}{\sqrt{3 + 6a^2 + \mu^2}}\,(0, 1, a\,; 0, 1, a\,; 0, 1, -2a\,; 0, -\mu, 0)\,, \tag{1.22}$$

with $a = b/\sqrt{3}$. The constants a and b are chosen so that the two modes do not contain a rigid rotation of the molecule.

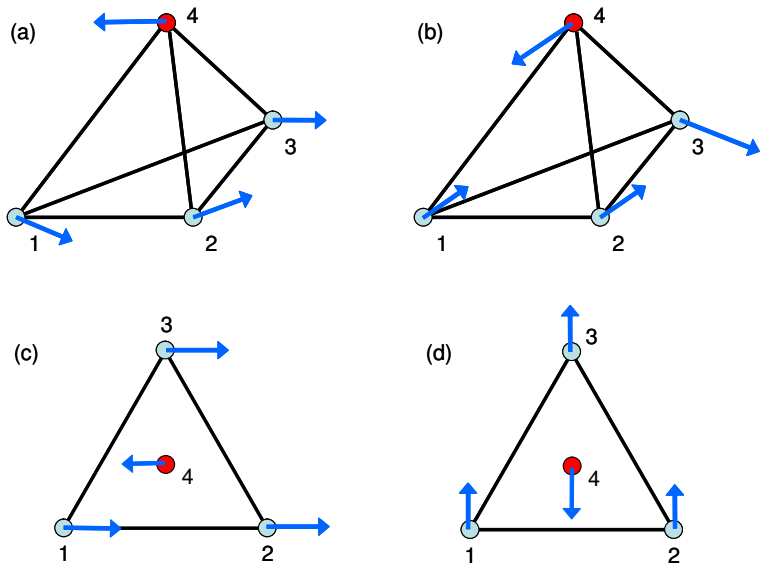

Figure 1.5: Degenerate vibrational eigenmodes. Since these two modes involve deformation in all three dimensions, we have depicted, for each component, the perspective view (top: (a) and (b) for both components) and the projected view on the horizontal plane (bottom: (c) and (d)).

Chapter 2

Mathematical Introduction

The purpose of this chapter is to summarize the algebraic concepts necessary for formulating the theory of group representations.

2.1 Applications and Binary Operations

Consider two sets, X and Y. A *function* (or *map*) f from X to Y is defined such that, for each element x belonging to X (denoted as $x \in X$), there exists a unique element y in Y associated with x. We represent this element as $y = f(x)$ and call it the image of x under the function f. We write it as:

$$f: \ X \to Y \quad , \quad x \mapsto y = f(x) \, . \tag{2.1}$$

The set X is called the *domain* of f, and Y is its *image*. The set of elements in Y, which are images under f of elements in X, is called the image of X under f and is denoted as $f(X)$.

In general, $f(X)$ is a subset of Y (we write $f(X) \subset Y$) and is not necessarily identical to Y.

The function f is *injective* if:

$$f(x) = f(x') \ \Rightarrow \ x = x' \, . \tag{2.2}$$

For an injective function, two elements of X cannot have the same image in Y. A function is *surjective* if $f(X) = Y$. For a surjective function, every element of Y is the image of at least one element of X. A function that is both injective and surjective is called *bijective*.

Let f be a function from X to Y and g be a function from Y to Z. The *composition* or *product* of these two functions $h : X \to Z$ is defined as:

$$h(x) = g\left(f(x)\right) \, . \tag{2.3}$$

The function h acts from X to Z and is denoted as:

$$h = g \cdot f \tag{2.4}$$

or simply gf when there is no possibility of confusion with other operations. It should be noted that $f \cdot g$ is not necessarily well-defined, and when it exists, it is not necessarily equal to $g \cdot f$. For example, consider real-valued functions $f(x) = x^2$ and $g(y) = \mathrm{e}^y$. We have:

$$(g \cdot f)(x) = g\left(x^2\right) = \mathrm{e}^{x^2} \tag{2.5}$$

and

$$(f \cdot g)(x) = f\left(\mathrm{e}^x\right) = \mathrm{e}^{2x} \, . \tag{2.6}$$

The composition of functions is associative, meaning that if u, v, and w are functions from X to Y, Y to Z, and Z to W, respectively, then:

$$(w \cdot (v \cdot u))(x) = ((w \cdot v) \cdot u)(x)\,. \tag{2.7}$$

For each $x \in X$, both sides of this equation correspond to the element:

$$w(v(u(x))) \tag{2.8}$$

in W. Therefore, we can write:

$$(w \cdot (v \cdot u))(x) = ((w \cdot v) \cdot u)(x) = w \cdot v \cdot u\,. \tag{2.9}$$

If $f : X \to Y$ is a bijective application, then for each element y in Y, there is a unique element x in X such that $f(x) = y$, and, naturally, each element x has an image in Y. Therefore, we can define a bijective application $Y \to X$, $y \mapsto x$ such that $y = f(x)$. This application is called the *inverse* of f and is denoted by f^{-1}.

Often, we consider applications from a set X to itself. An example is given by real (complex) functions of a real (complex) variable. We define the identity application as:

$$e : \ X \to X \quad , \quad x \mapsto e(x) = x\,. \tag{2.10}$$

This application is clearly bijective. If $f : X \to Y$ is a bijective application, f^{-1} exists, and we have:

$$(f^{-1} \cdot f)(x) = x \tag{2.11}$$

for each x. Therefore, we write:

$$f^{-1} \cdot f = e_X \tag{2.12}$$

where we denote the identity application of X by e_X. Note that we also have:

$$f \cdot f^{-1} = e_Y \tag{2.13}$$

Theorem. Let X and Y be two sets containing the same finite number n of elements[1]. The following three statements are equivalent:

(i) $f : X \to Y$ is surjective,

(ii) $f : X \to Y$ is injective,

(iii) $f : X \to Y$ is bijective.

Proof:

(i) $\Rightarrow f(X) = Y$. Thus, $f(X)$ is composed of n elements, which implies (ii).

(ii) $\Rightarrow f(X)$ is composed of n elements. It follows that $f(X) = Y$, which can be reduced to property (i).

Since (i) and (ii) are each a consequence of the other, (iii) is also true, and the theorem is thus proved.

The *cartesian product* $X \times Y$ of two sets X and Y is the set of all ordered pairs (x, y) where $x \in X$ and $y \in Y$. If $Y = X$, then $X \times Y$ is denoted by X^2. For example, if the set of real numbers is denoted by R, then R^2 is the set of points in a two-dimensional space (a plane). Similarly, we can define X^3, X^4, and so on. The graph of a function $f : X \to Y$ is the subset of $X \times Y$ that contains the ordered pairs $(x, f(x))$.

A *relation* $\mathcal{R}$ between elements of the sets X and Y is defined as a subset of $X \times Y$. We say that $x \in X$ is related by $\mathcal{R}$ to $y \in Y$ if $(x, y) \in \mathcal{R}$. In this case, we write $x\mathcal{R}y$.

[1]Note that this theorem is not valid for two sets with different numbers of elements.

An *equivalence relation* - denoted by $x \sim y$ - is a relation between elements of a set X that satisfies the following three conditions:

(i) $x \sim x$ for each $x \in X$ (reflexivity).

(ii) $x \sim y \Rightarrow y \sim x$ (symmetry).

(iii) $x \sim y$ and $y \sim z \Rightarrow x \sim z$ (transitivity).

If in a set S we have defined an equivalence relation, then the set of $y \in S$ that are equivalent to x is called the *equivalence class* of x. We denote this set by:

$$C_x = \{y;\, y \sim x\}\,. \tag{2.14}$$

Naturally, C_x contains the element x.

Theorem. An equivalence relation among the elements of a set S divides the set into disjoint equivalence classes. This means that

(i) $x \in C_x$,

(ii) $x \sim y \Leftrightarrow C_x = C_y \Leftrightarrow C_x \cap C_y \neq \varnothing$

Proof: (i) is evident. We demonstrate (ii) in three steps.

a. $x \sim y \Rightarrow C_x = C_y$. Indeed, if $z \in C_y$, $y \sim z$, by transitivity $z \sim x$, and thus $z \in C_x$. Therefore, every element of C_y is also an element of C_x. In the same way, we can demonstrate that every element of C_x is also an element of C_y. Consequently, $C_x = C_y$.

b. $C_x = C_y \Rightarrow C_x \cap C_y \neq \varnothing$ since $x \in C_x$ and $x \in$C$_y$, implying $C_x \cap C_y \neq \varnothing$.

c. $C_x \cap C_y \neq \varnothing \Rightarrow x \sim y$. Since $C_x \cap C_y \neq \varnothing$, it contains at least one element, let's say z. So, $z \in C_x$ and $z \in C_y$, which implies $z \sim x$ and $z \sim y$, from which we deduce that $x \sim y$.

These three implications complete the proof of the theorem.

Consider a set S. An internal binary operation on S is a function

$$f : S \times S \to S\,. \tag{2.15}$$

This means that for each ordered pair (x, y) of elements from $S \times S$, we assign a unique element $z \in S : z = f(x, y)$. This operation is typically denoted by xy and is called the *product* of x and y (in that order). Here are examples of internal binary operations:

(i) Real number multiplication $(x, y \in R)$

$$(x, y) \mapsto xy \in R\,. \tag{2.16}$$

(ii) Real number addition

$$(x, y) \mapsto x + y\,. \tag{2.17}$$

An internal binary operation is called *commutative* if

$$xy = yx \tag{2.18}$$

for all $x, y \in S$. It is called *associative* if, for all $x, y, z \in S$,

$$x(yz) = (xy)z\,. \tag{2.19}$$

In this case, the parentheses are redundant, and we can represent the result of the operation as xyz. We also define $x^2 = xx$, $x^3 = xxx$, and so on.

Let S be a set, and $\mathcal{R}$ an equivalence relation. The equivalence classes form a set called the *quotient* $S/\mathcal{R}$ of S by $\mathcal{R}$. The function

$$S \to S/\mathcal{R} \tag{2.20}$$

defined by

$$x \mapsto C_x \tag{2.21}$$

is surjective since every element of $S/\mathcal{R}$ is an equivalence class.

Let S be a set with an internal binary operation. If elements e_R and e_L exist in S such that $xe_R = x$ and $e_L x = x$ for every $x \in S$, then we call these elements the *right identity* and *left identity*, respectively. If e_L and e_R exist at the same time, then they coincide, and we call this unique element e. In this case, we have $xe = ex = x$ for every $x \in S$. In fact, from the definition of e_L and e_R, we have $e_L e_R = e_L = e_R$. If there were two distinct identity elements e and e' such that $ex = xe = x$ and $e'x = xe' = x$ for every x, then $e = e'e = e'$. If an element x in S has a right inverse element x'_R such that $xx'_R = e$, we say that x'_R is a *right inverse* of x. Similarly, a *left inverse* is defined as an element x'_L such that $x'_L e = e$. If x'_R and x'_L exist at the same time, and the operation is associative, then $x'_R = x'_L$. Indeed,

$$x'_R = ex'_R = (x'_L x)x'_R = x'_L(xx'_R) = x'_L e = x'_L \,. \tag{2.22}$$

Therefore, for an associative binary operation, x' is a right inverse of x if

$$xx' = x'x = e \,. \tag{2.23}$$

The inverse of x is unique. Indeed, if x'' was another inverse of x, we would have,

$$x'' = x''e = x''(xx') = (x''x)x' = ex' = x' \,. \tag{2.24}$$

We denote the inverse of x as x^{-1}. For example, in the set of real numbers R, 0 and 1 are respectively the identities (also called neutral elements) for addition and multiplication. The inverse of x for addition is $-x$. The inverse for multiplication is $1/x$ if $x \neq 0$.

Theorem. Consider a set S with an associative internal binary operation and an identity element e. If x and y have inverses x^{-1} and y^{-1}, then xy has an inverse, and

$$(xy)^{-1} = y^{-1}x^{-1} \,. \tag{2.25}$$

Proof:

$$(xy)(y^{-1}x^{-1}) = x(yy^{-1})x^{-1} = xex^{-1} = xx^{-1} = e \tag{2.26}$$

and

$$(y^{-1}x^{-1})(xy) = y^{-1}(x^{-1}x)y = y^{-1}ey = y^{-1}y = e \tag{2.27}$$

2.2 Abstract Group Theory

A set G, equipped with an associative internal binary operation, is called a *group* if it contains an identity element (also called a neutral element) and the inverse of each of its elements.

To ensure that G is a group, the following must be verified:

(i) The binary operation is internal, meaning G is closed under this operation,

(ii) The operation is associative,

(iii) There exists an identity element $e \in G$, meaning $xe = ex = x$ for each $x \in G$,

(iv) $x \in G \Rightarrow x^{-1} \in G$.

If the binary operation is commutative (i.e., $xy = yx$ for every $x, y \in G$), then the group is called *Abelian*. If a group contains n elements, it is said to be of *order* n. Such a group is called *finite*. A group that is not finite is called *infinite*.

Examples of groups:

(i) The set R of real numbers equipped with addition is an Abelian group. The identity element is 0, and the inverse of x is $-x$.

(ii) The set R of real numbers equipped with multiplication is not a group. Indeed, the element 0 has no inverse. However, $R - \{0\}$ equipped with multiplication is an Abelian group. The identity element is 1, and the inverse of x is $1/x$ if $x \neq 0$. If C is the set of complex numbers and Q is the set of rational numbers, then $C - \{0\}$ and $Q - \{0\}$ equipped with multiplication are Abelian groups.

(iii) The set Z of integers equipped with addition is a group. It is not a group when equipped with multiplication.

(iv) The set $\{1, -1\}$ equipped with multiplication is a group.

(v) If n is a positive integer and $\omega = e^{2\pi i/n}$, then the set

$$\{1, \omega, \omega^2, \ldots, \omega^{n-1}\}$$

equipped with multiplication is a group. The identity element is 1, and the inverse of ω^k $(0 \leq k \leq n-1)$ is ω^{n-k}. Multiplication by $e^{i\phi}$ transforms the complex number

$$z = re^{i\theta}$$

into

$$z' = e^{i\phi} z = re^{i(\theta+\phi)} .$$

This operation is a rotation of all points in the complex plane by an angle ϕ around the origin. The numbers $1, \omega, \omega^2, \ldots, \omega^{n-1}$ represent rotations by $0, 2\pi/n, 2(2\pi/n), \ldots, (n-1)(2\pi/n)$ around the origin. The rotations by these angles around a fixed axis thus form an Abelian group.

Let G be a group with the identity element e and H be a subset of G. We say that H is a subgroup of G (equipped with the same binary operation as G if

(i) $x, y \in H \Rightarrow xy \in H$,

(ii) $x \in H \Rightarrow x^{-1} \in H$.

Clearly, properties (i) and (ii) imply that $e \in H$. Examples of subgroups include:

(i) G is a subgroup of G,

(ii) $\{e\}$ is a subgroup of G,

(iii) If $G = R$ equipped with addition, then Z is a subgroup of G.

(iv) If $G = R - \{0\}$ equipped with multiplication, then $\{1, -1\}$ is a subgroup of G.

Rearrangement Theorem. Let G be a group, and m one of its elements. The mappings

$$G \to G : x \mapsto mx ,$$
$$x \mapsto xm$$

are bijective.

Proof:

(i) The mapping $x \mapsto mx$ is surjective because for every $y \in G$, $m^{-1}y \in G$, and $m(m^{-1}y) = y$. Therefore, y is the image of $m^{-1}y$ under this mapping.

(ii) The mapping $x \mapsto mx$ is injective because $mx = mx' \Rightarrow m^{-1}mx = m^{-1}mx' \Rightarrow x = x'$.

The proof is similar for the second mapping. This shows that the sets mG and Gm are rearrangements of the elements of G. This theorem allows us to write multiplication tables for finite groups of small order. The multiplication tables are written as follows:

	a	b	c	$\dots$
a	a^2	ab	ac	$\dots$
b	ba	b^2	bc	$\dots$
c	ca	cb	c^2	$\dots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	

The Rearrangement Theorem states that each row and each column of the table contains all the elements of the group. No element is repeated on a row or column. Therefore, each row or column is a rearrangement of the group's elements. As an example, we can write the only possible multiplication tables for groups of order two and three.

	e	a
e	e	a
a	a	e

	e	a	b
e	e	a	b
a	a	b	e
b	b	e	a

The Rearrangement Theorem shows that a group of order n is a subgroup of the permutation group of n objects (Cayley's theorem). This theorem is very important as it significantly reduces the number of possibilities for writing the multiplication table of a group. Thanks to this theorem, we have seen that a group of order 3 is unique, and we could write its multiplication table without specifying the nature of its elements or the internal operation. More generally, we can construct multiplication tables using two fundamental criteria. Firstly, the table must satisfy the Rearrangement Theorem. Secondly, the resulting table must also satisfy the associative property, i.e., $a(bc) = (ab)c$, for all elements. In Exercise 2 of the Series, we will see how, based on these two criteria, we can obtain the only two non-equivalent groups of order 6.

Consider an element a of a finite group G. The set $\{e, a, a^2, \dots\}$ is a subset of G, and it is therefore finite. Hence, there exist integers m and k, with $m > k$, such that $a^m = a^k$ or $a^{m-k} = a^n = e$, where $n = m - k$. Thus, it is always possible to find a power of a equal to the identity element e. Let n be the smallest positive integer for which this property is satisfied. Then, we have

$$H = \{e, a, a^2, \dots, a^{n-1}\} \tag{2.28}$$

is a subgroup of G. We say that H is generated by a. A group in the form of H is called a "cyclic" group. It is clearly abelian.

A "proper" subgroup of G is a subgroup other than $\{e\}$ and G.

Let G be a group, and let H be one of its proper subgroups. We define an equivalence relation among the elements of G as follows: if $x, y \in G$ and $x^{-1}y \in H$, then x and y are equivalent, and we write $x \sim y$. Let's prove that this is indeed an equivalence relation.

(i) $x \sim x$ since $x^{-1}x = e \in H$.

(ii) $x \sim y \Rightarrow y \sim x$, since $x^{-1}y \in H \Rightarrow (x^{-1}y)^{-1} = y^{-1}x \in H$.

(iii) $x \sim y$ and $y \sim z \Rightarrow x \sim z$, since $x^{-1}y \in H$ and $y^{-1}z \in H \Rightarrow x^{-1}yy^{-1}z = x^{-1}z \in H$.

This equivalence relation allows us to divide the elements of G into disjoint classes. If $x^{-1}y \in H$, then y is equal to an element of H multiplied on the left by x. We denote the set constructed in this way by the symbol

$$C_x = xH \tag{2.29}$$

and call it the "left coset." The map $H \to xH$ is bijective. Indeed, each element $z \in xH$ is the image of $x^{-1}z \in H$, which implies that the map is surjective. It is also injective, as for $y, y' \in H$, we have $xy = xy' \Rightarrow y = y'$.

We can also define a second equivalence relation $x \sim y$ if $yx^{-1} \in H$. We can thus introduce the concept of a "right coset" (Hx) in the same way.

Theorem. If G is a finite group and H is a proper subgroup of G, then the order of H is a divisor of the order of G.

Proof: Consider the left cosets of H. They are either all disjoint or identical (since they are equivalence classes). If there are n distinct left cosets, their union is G. Therefore, if we denote the orders of G and H as g and h, respectively, then $g = nh$, and the theorem is proved. A simple corollary is that a group of prime order has no proper subgroups.

We will now introduce the concept of a "homomorphism." A group G is said to be "homomorphic" to a group H if there exists a mapping $h : H \to G$ such that

(i) h is surjective, i.e., $h(H) = G$.

(ii) $h(xy) = h(x)h(y)$ for every pair of elements x, y in H.

Note that if $H = \{e, x, y, \ldots\}$, the elements $h(e)$, $h(x)$, $h(y)$ in G are not necessarily distinct. The only necessary condition is that each element of G is the image of at least one element of H. The mapping h is called a "homomorphism" and is denoted by $G = \hom H$. For example, if G consists of a single element e', then $h(x) = e'$ for all $x \in H$ is a homomorphism. The group $G = \{1, -1\}$ equipped with multiplication is homomorphic to $Z = \{\ldots, -3, -2, -1, 0, 1, 2, \ldots\}$ equipped with addition, with

$$h(x) = \begin{cases} 1 & \text{if } x \text{ is even} \\ -1 & \text{if } x \text{ is odd}\,. \end{cases} \tag{2.30}$$

Theorem. If the group $G = \{e', a', b', \ldots\}$ is homomorphic to $H = \{e, a, b, \ldots\}$ by the homomorphism h, then

$$h(e) = e' \tag{2.31}$$

and

$$h(x^{-1}) = h^{-1}(x)\,, \tag{2.32}$$

for all $x \in H$. **Proof:**

$$\begin{aligned} h(x) &= h(xe) = h(x)h(e) \\ h(x) &= h(ex) = h(e)h(x) \end{aligned}$$

where

$$h(e)h(x) = h(x)h(e) = h(x) \tag{2.33}$$

which implies that $h(e)$ is the neutral element of G and it is necessarily equal to e'.

$$\begin{aligned} h(xx^{-1}) &= h(x)h(x^{-1}) = h(e) = e' \\ h(x^{-1}x) &= h(x^{-1})h(x) = h(e) = e' \end{aligned}$$

which implies

$$h(x)h(x^{-1}) = h(x^{-1})h(x) = e' \tag{2.34}$$

and thus $h(x^{-1})$ is the inverse of $h(x)$ in G.

We also introduce the concept of an "isomorphism." Two groups, H and G, are isomorphic if there exists a bijective mapping $h : H \to G$ such that $h(xy) = h(x)h(y)$ for all $x, y \in H$. Clearly, if G is homomorphic to H and H is homomorphic to G, then H and G are isomorphic.

Theorem. Let $G = \hom H$. The set of all $x \in H$ such that $h(x) = e'$ is a subgroup of H called the kernel of h. We denote it as $\ker h$.

Proof:

(i) $e \in \ker h$ since $h(e) = e'$.

(ii) $x \in \ker h \Rightarrow h(x) = e' \Rightarrow h(x^{-1}) = h^{-1}(x) = e'$.

(iii) $x, y \in \ker h \Rightarrow h(xy) = h(x)h(y) = e' \Rightarrow xy \in \ker h$.

Now, let's introduce the concept of a "conjugacy class." In a group G, if x and y are elements of G, we say that y is a conjugate of x if there exists an element u in G such that

$$y = u^{-1}xu. \tag{2.35}$$

The relation we have just defined is an equivalence relation. Indeed:

(i) $x = e^{-1}xe$, meaning $x \sim x$,

(ii) $y = u^{-1}xu \Rightarrow x = uyu^{-1} = (u^{-1})^{-1}yu^{-1} \Rightarrow x \sim y$ if $y \sim x$,

(iii) $x \sim y$ and $y \sim z \Rightarrow$ there exist u and v in G such that $x = u^{-1}yu$ and $y = v^{-1}zv$. This implies $x = u^{-1}v^{-1}zvu = (vu)^{-1}z(vu) \Rightarrow x \sim z$.

By this theorem, the conjugation relation divides the elements of the group G into distinct sets called "conjugacy classes" or simply "classes." In the following, we will use the term "class" without further qualification to refer to a conjugacy class. We denote the set composed of elements conjugate to x by the symbol C_x.**Please note that in general**, C_x **is not a group**. Also, notice that the class C_e consists only of the element e: $C_e = \{e\}$. The function f_u defined as

$$f_u : C_a \to C_a \,;\, x \mapsto f_u(x) = u^{-1}xu \tag{2.36}$$

with $x \in C_a$ and $u \in G$ is bijective. Specifically, f_u is surjective because if $x \sim a$, then x is the image of $uxu^{-1} \sim a$ under f_u. It is also injective as $f_u(x) = f_u(x') \Rightarrow u^{-1}xu = u^{-1}x'u \Rightarrow x = x'$.

Hence, the set $u^{-1}C_au$ is just a rearrangement of C_a. Thus, we can write

$$u^{-1}C_au = C_a. \tag{2.37}$$

A subgroup N of a group G is called an "invariant subgroup" or a "normal divisor" of G if it consists only of entire conjugacy classes. This means that the conjugation of all elements of an invariant subgroup by an element u of G simply rearranges its elements, i.e.,

$$u^{-1}Nu = N. \tag{2.38}$$

We can also write

$$Nu = uN. \tag{2.39}$$

Thus, the right and left cosets of an invariant subgroup are equal. Consider now a set $\mathcal{F}$ composed of the right cosets of N:

$$C_u = Nu. \tag{2.40}$$

We now define a composition law for the elements C_u. Consider C_u and C_v and construct the set containing all products of an element of C_u by an element of C_v. This way, we have constructed the set C_uC_v that contains elements of G. Please note that we do not account for element repetitions: in C_uC_v, each element is contained only once. If x and y are elements of N, then a typical element of C_u is xu, and a typical element of C_uC_v is $xuyv$. This composition operation satisfies the property

$$C_uC_v = C_{uv}. \tag{2.41}$$

In fact,

$$\begin{aligned} C_uC_v &= (Nu)(Nv) = (Nu)(Nu^{-1}uv) = (N)(uNu^{-1})uv \\ &= (N)(Nuv) = (NN)(uv) = Nuv = C_{uv}, \end{aligned} \tag{2.42}$$

where we could use $NN = N$ thanks to the rearrangement theorem. Equipped with this internal operation, the set $\mathcal{F}$ forms a group. Furthermore, $\mathcal{F}$ is homomorphic to G. We call $\mathcal{F}$ the "quotient" of G by N, and write

$$\mathcal{F} = G/N. \tag{2.43}$$

The group $\mathcal{F}$ is also known as the "factor group" of G with respect to the invariant subgroup N.

We now introduce a new type of multiplication between two sets. First, let's establish the notation $[S]$ to indicate that if there are repeated elements in the set S, we keep them. For example, if $[S] = \{a, a, b, c, c, c\}$, then $S = \{a, b, c\}$.

We have seen that if C is a conjugacy class of a group G and $x \in G$, then $x^{-1}Cx = C$. Let $[\mathcal{R}]$ be a set of elements of G composed solely of entire classes. By this, we mean that if an element $x \in G$ is contained in $[\mathcal{R}]$ n times, then each of its conjugate elements will also be contained in $[\mathcal{R}]$ an equal number of times. Then, for each $u \in G$, we have

$$u^{-1}[\mathcal{R}]u = [\mathcal{R}]\,. \tag{2.44}$$

Conversely, if $[\mathcal{R}]$ satisfies this relation for each $u \in G$, then $[\mathcal{R}]$ is composed of entire classes. This last implication is demonstrated as follows. Suppose that $[\mathcal{R}]$ is not composed of entire classes. Let $[\mathcal{R}']$ be the largest subset of $[\mathcal{R}]$ composed of entire classes. Since

$$u^{-1}[\mathcal{R}']u = [\mathcal{R}'], \tag{2.45}$$

for each $u \in G$, then it follows that the residual set

$$[\mathcal{R}''] = [\mathcal{R}] - [\mathcal{R}'] \tag{2.46}$$

satisfies

$$u^{-1}[\mathcal{R}'']u = [\mathcal{R}'']. \tag{2.47}$$

We must now show that the set $[\mathcal{R}'']$ is empty. $[\mathcal{R}'']$ cannot contain e, since e alone constitutes an entire class. Suppose that $[\mathcal{R}'']$ is not empty, and let x be an element of $[\mathcal{R}'']$. Since $[\mathcal{R}'']$ does not contain entire classes, there must be an element y in G, conjugate to x and not contained in $[\mathcal{R}'']$" but $y = u^{-1}xu$ for some $u \in G$, and since $u^{-1}[\mathcal{R}'']u = [\mathcal{R}'']$, then y belongs to $[\mathcal{R}'']$. We have reached a contradiction. Therefore, we necessarily have

$$[\mathcal{R}''] = \varnothing. \tag{2.48}$$

We can thus formulate the following theorem.

Theorem:: A necessary and sufficient condition for $[\mathcal{R}]$ to be composed solely of entire classes of a group G is that for each $u \in G$,

$$u^{-1}[\mathcal{R}]u = [\mathcal{R}]. \tag{2.49}$$

Let H be a finite group of order h, and $C_1 = \{e\}$, $C_2, \ldots, C_\mu, \ldots, C_{N_C}$ be its classes. We indicate by n_μ the number of elements in class C_μ and by N_C the total number of classes. We have, therefore,

$$\sum_{\mu=1}^{N_C} n_\mu = h. \tag{2.50}$$

Let X and Y be two subsets of H. We build the products xy of elements x from X and y from Y, keeping the repeated elements. We define the set

$$X \cdot Y = [xy], \tag{2.51}$$

which contains all these elements. Let C_μ and C_ν be two classes of H. We take the product

$$C_\mu \cdot C_\nu = [uv]\,, \tag{2.52}$$

where u and v are respectivly elements of C_μ and C_ν. For all $x \in H$ we have

$$x^{-1} C_\mu \cdot C_\nu x = [x^{-1} uvx] = [x^{-1} uxx^{-1} vx] = C_\mu \cdot C_\nu\,. \tag{2.53}$$

Therefore $C_\mu \cdot C_\nu$ is composed only of entire classes and we can write

$$C_\mu \cdot C_\nu = \sum_{\lambda=1}^{N_C} n_{\mu\nu\lambda} C_\lambda\,, \tag{2.54}$$

where $n_{\mu\nu\lambda}$ are non-negative integers. The sum indicates the collection of classes where each element C_λ is repeated $n_{\mu\nu\lambda}$ times. The coefficients $n_{\mu\nu\lambda}$ satisfy the following symmetry property:

$$n_{\mu\nu\lambda} = n_{\nu\mu\lambda}\,. \tag{2.55}$$

This follows from

$$C_\mu \cdot C_\nu = C_\nu \cdot C_\mu\,. \tag{2.56}$$

In fact,

$$C_\mu \cdot C_\nu = [uv] = [uvu^{-1}u] = C_\nu \cdot C_\mu\,, \tag{2.57}$$

since uvu^{-1} is a typical element of C_ν and, when v traverses the elements of C_ν, uvu^{-1} traverses the same elements in a different order. Since $C_1 = \{e\}$, then

$$C_1 \cdot C_\nu = C_\nu \tag{2.58}$$

which implies

$$n_{1\nu\lambda} = n_{\nu 1\lambda} = \delta_{\nu\lambda}\,. \tag{2.59}$$

Chapter 3

Theory of Representations

The purpose of this chapter is to formulate the theory of representations of discrete groups.

3.1 Representations

Consider a group H. Now, suppose we have a set G of linear transformations in a vector space, and this set forms a group under the composition of transformations. Let's also assume that the group G is homomorphic to the group H. The group G of linear transformations is then called a *representation* of the group H.

We can always express linear transformations in terms of square matrices defined with respect to a basis for the vector space in question. In this case, the group operation for the group G is simply matrix multiplication. Let $H = \{e, x, y, \ldots\}$ and $G = \{\Gamma(e), \Gamma(x), \Gamma(y), \ldots\}$. Since the mapping Γ is a homomorphism, we have

$$\Gamma(xy) = \Gamma(x)\Gamma(y)\,. \tag{3.1}$$

We call the *dimension* of a representation the dimension of the vector space in which the representation is defined.

Here are some examples of representations:

(i) $\Gamma(x) = \mathbf{1}$, the identity transformation, for all $x \in H$. This representation is called the identity representation or totally symmetric representation.

(ii) Consider the group $O(3)$ of orthogonal transformations in three-dimensional space. This group consists of all rotations and inversions (thus it is an infinite group). These transformations are represented by 3×3 orthogonal matrices. These matrices form a representation of the group $O(3)$. Another possible representation of the group $O(3)$ is defined in one-dimensional space. It associates with each element x of the group $O(3)$ the linear transformation that amounts to multiplying a one-dimensional vector by $\det(R_x)$, where R_x is the 3×3 matrix related to the three-dimensional representation defined above. This one-dimensional representation is often called the determinant representation.

(iii) Consider the 12×12 matrices defined by (1.10) and (1.11), as well as in point (iii) of Exercise Set 1. When an ammonia molecule undergoes a rotation in space, these matrices represent the effect of such a rotation in the 12-dimensional space of displacement vectors of the atoms composing the molecule. We have verified in Exercise Set 1 that these matrices form a group that is homomorphic to the group C_{3v}. These matrices are, therefore, a representation of the group C_{3v} in a 12-dimensional space. We will see that, in general, the first step in applying group theory to physics is to find the representation of the

symmetry group in the vector space of system configurations. For vibrational modes of a molecule, this is the space generated by displacement vectors. For a quantum system, on the other hand, it will be the Hilbert space of the quantum states of the system.

Theorem. Let $H = \{e, x, y, \ldots\}$ be a group and $\Gamma(x)$ a representation of H. The set of elements in H such that $\Gamma(x) = \Gamma(e)$, where $\Gamma(e)$ is the identity for the representation Γ, forms an invariant subgroup of H.

Proof: In the group theory review of the previous chapter, we saw that for a homomorphism Γ, $\Gamma(e)$ is the identity, and $\Gamma(x^{-1}) = \Gamma^{-1}(x)$. The set of elements such that $\Gamma(x) = \Gamma(e)$ is an invariant subgroup because:

(i) It is a group. $\Gamma(x) = \Gamma(e)$ and $\Gamma(y) = \Gamma(e) \Rightarrow \Gamma(xy) = \Gamma(e)$; it has a neutral element $\Gamma(e)$ and, if $\Gamma(x) = \Gamma(e)$, then $\Gamma(x^{-1} = \Gamma^{-1}(x) = \Gamma(e)$.

(ii) The group is invariant because if $\Gamma(x) = \Gamma(e)$, then for every $u \in H$, we have $\Gamma(u^{-1}xu) = \Gamma(u^{-1})\Gamma(e)\Gamma(u) = \Gamma(u^{-1}u) = \Gamma(e)$.

Definition. The representations $\Gamma(x)$ and $\Gamma'(x)$ of a group $H = \{e, x, y, \ldots\}$ are said to be *equivalent* if a non-singular transformation S exists, such that

$$\Gamma'(x) = S^{-1}\Gamma(x)S\,, \tag{3.2}$$

for each $x \in H$.

Theorem. Every representation Γ of a finite-order group H is equivalent to a unitary representation.

Proof: Let ψ and ϕ be two arbitrary vectors in the vector space of transformations $\Gamma(x)$ defined by the representation of H. Define

$$\{\psi|\phi\} = \frac{1}{h}\sum_{x\in H}\langle\Gamma(x)\psi|\Gamma(x)\phi\rangle\,, \tag{3.3}$$

where $\langle\xi|\eta\rangle$ is the ordinary inner product between vectors ξ and η. It can be verified that the operation $\{\psi|\phi\}$ is an inner product. Recall that an inner product must satisfy three properties:

(i) $\langle\xi|\eta\rangle = \langle\eta|\xi\rangle^*$ for every ξ, η,

(ii) $\langle\xi|a\eta + b\nu\rangle = a\langle\xi|\eta\rangle + b\langle\xi|\nu\rangle$ for every ξ, η, ν, with a, b complex,

(iii) $\langle\xi|\xi\rangle > 0$ for every $\xi \neq 0$.

We can, therefore, build an orthonormal basis $\{\epsilon_i\}$ according to the inner product $\langle\xi|\eta\rangle$. This basis provides an orthonormal basis according to the inner product $\{\psi|\phi\}$ (for example, using the Gram-Schmidt orthogonalization procedure). For each $y \in H$, we have

$$\begin{aligned}\{\Gamma(y)\psi|\Gamma(y)\phi\} &= \frac{1}{h}\sum_{x\in H}\langle\Gamma(x)\Gamma(y)\psi|\Gamma(x)\Gamma(y)\phi\rangle \\ &= \frac{1}{h}\sum_{x\in H}\langle\Gamma(xy)\psi|\Gamma(xy)\phi\rangle \\ &= \{\psi|\phi\}\,,\end{aligned} \tag{3.4}$$

where the last equality follows from the rearrangement theorem. This means that $\Gamma(y)$ ($y \in H$) is a unitary operator according to the inner product $\{\psi|\phi\}$. We can explicitly construct the unitary transformation S that relates the representation Γ to a unitary representation according

to the ordinary inner product. Consider the initial basis $\{\epsilon_i\}$ and the target basis defined by $\phi_i = S\epsilon_i$. If

$$\xi = \sum_i \alpha_i \epsilon_i \tag{3.5}$$

and

$$\eta = \sum_i \beta_i \epsilon_i \,, \tag{3.6}$$

then

$$\begin{aligned} \{S\xi|S\eta\} &= \sum_{ij} \alpha_i^* \beta_j \{S\epsilon_i|S\epsilon_j\} \\ &= \sum_{ij} \alpha_i^* \beta_j \{\phi_i|\phi_j\} \\ &= \sum_i \alpha_i^* \beta_i \\ &= \langle \xi|\eta\rangle \,. \end{aligned} \tag{3.7}$$

Therefore

$$\begin{aligned} \langle S^{-1}\Gamma(x)S\psi|S^{-1}\Gamma(x)S\phi\rangle &= \{\Gamma(x)S\psi|\Gamma(x)S\phi\} \\ &= \{S\psi|S\phi\} = \langle\psi|\phi\rangle \,. \end{aligned} \tag{3.8}$$

This proves that the representation

$$\Gamma'(x) = S^{-1}\Gamma(x)S \tag{3.9}$$

is unitary.

A representation Γ of dimension l can be regarded as a set of linear transformations in the complex vector space $\mathbb{C}^l$ formed by complex vectors with l components. If $\{\phi_i\}$ is an orthonormal basis in $\mathbb{C}^l$, we can express a vector ξ as

$$\xi = \sum_{i=1}^{l} \alpha_i \phi_i \,. \tag{3.10}$$

The operators $\Gamma(x)$ applied to the basis vectors yield

$$\Gamma(x)\phi_i = \sum_{j=1}^{l} \phi_j \Gamma_{ji}(x) \,, \tag{3.11}$$

where $\Gamma_{ji}(x)$ are the components of an $l \times l$ matrix. We can write the transformed vector as

$$\xi' = \Gamma(x)\xi = \sum_{i=1}^{l} \alpha_i \Gamma(x)\phi_i = \sum_{j=1}^{l} \phi_j \sum_{i=1}^{l} \alpha_i \Gamma_{ji}(x) \,. \tag{3.12}$$

The components of $\xi' = \sum_i \alpha_i' \phi_i$ are

$$\alpha_i' = \sum_{j=1}^{l} \Gamma_{ij}(x)\alpha_j \,. \tag{3.13}$$

Let $\Gamma^{(1)}, \Gamma^{(2)}, \ldots, \Gamma^{(n)}$ be representations of a group. We can find a new representation by constructing matrices of the form:

$$\Gamma(x) = \begin{pmatrix} \Gamma^{(1)}(x) & 0 & 0 & \ldots & 0 \\ 0 & \Gamma^{(2)}(x) & 0 & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \ldots & \Gamma^{(n)}(x) \end{pmatrix} . \tag{3.14}$$

If the representations $\Gamma^{(i)}$ have dimensions l_i, then the representation Γ has a dimension

$$l = \sum_{i=1}^{n} l_i \tag{3.15}$$

We symbolically denote the representation Γ as

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \ldots \oplus \Gamma^{(n)} \,. \tag{3.16}$$

Some of the representations among $\Gamma^{(i)}$ may be identical. If, for example, the representation $\Gamma^{(i)}$ appears twice, we indicate it as $2\Gamma^{(i)}$. It is clear that there is no limit to the number of representations that can be constructed. The structure of representation (3.14) is a block structure, with the i-th block given by the matrix related to the representation $\Gamma^{(i)}$. It is crucial to note that for the representation Γ, the homomorphism with the group H only exists if such a block structure is valid for each element x of the group. If we now perform a unitary transformation

$$\Gamma'(x) = S^{-1}\Gamma(x)S \,, \tag{3.17}$$

where S is a unitary matrix of size $l \times l$, the matrices $\Gamma'(x)$ will generally no longer have a block structure, while the representation Γ' is equivalent to the representation Γ.

If, on the other hand, given a representation Γ, we can find a unitary transformation S such that the matrices of the new representation $\Gamma'(x) = S^{-1}\Gamma(x)S$ all have the same block structure, we say that we have reduced the representation Γ into a sum of representations. The possibility of reducing a representation is at the heart of representation theory and its applications in physics. We will now discuss this concept more rigorously.

Let $\{\phi_i\}$ be an orthonormal basis in the vector space related to a representation Γ. Consider the vector $\xi = \sum_{i=1}^{l} \alpha_i \phi_i$ and study the effect of $\Gamma(x)$ on ξ. Suppose we find that if $\alpha_i = 0$ for $i \geq l_1 + 1$, then the application of $\Gamma(x)$ to ξ produces vectors for which such a property remains valid, and this holds for all x. We then say that the subspace generated by the vectors $\phi_1, \phi_2, \ldots, \phi_{l_1}$ is invariant under the transformations $\Gamma(x)$.

Now, let's imagine having a group H and a representation $\Gamma(x)$ in an n-dimensional space V_n. Suppose there exists an invariant proper subspace M in V_n with dimension $l < n$ under all transformations $\Gamma(x)$. Let $\{\phi_1, \phi_2, \ldots, \phi_l\}$ be a basis for M. The invariance of M implies that

$$\Gamma(x)\phi_i = \sum_{j=1}^{l} \Gamma_{ji}(x)\phi_j \;,\; i = 1, 2, \ldots, l \,. \tag{3.18}$$

We can construct a basis for the vector space V_n that contains the vectors $\phi_1, \phi_2, \ldots, \phi_l$ as a subset. Such a basis includes the vectors $\phi_1, \phi_2, \ldots, \phi_l$ and the remaining $n - l$ basis vectors $\phi_{l+1}, \phi_{l+2}, \ldots, \phi_n$. We have

$$\Gamma(x)\phi_i = \sum_{j=1}^{l} \Gamma_{ji}(x)\phi_j + \sum_{j=l+1}^{n} \Gamma_{ji}(x)\phi_j \;,\; i = l+1, l+2, \ldots, n \,. \tag{3.19}$$

This shows that, in such a basis, the matrices of the representation have the form:

$$\Gamma(x) = \begin{pmatrix} P & Q \\ 0 & T \end{pmatrix} , \tag{3.20}$$

Where P and T are square matrices with dimensions $l \times l$ and $(n-l) \times (n-l)$ respectively. If such an invariant subspace M can be found, we say that the representation Γ is *reducible*. In other words, a representation Γ defined in an n-dimensional vector space V_n is reducible if there exists

a non-empty proper eigenspace of V_n that is invariant under all group transformations. If such a subspace does not exist, the representation Γ is called *irreducible*. A representation is called *completely reducible* if, for every non-empty proper eigenspace M invariant under group transformations, the orthogonal complement N of M is also invariant. Clearly, a **unitary** representation of a group that is reducible is automatically also completely reducible. Unitary transformations $\Gamma(x)$, by definition, preserve orthogonality. Since the subspaces with bases $\phi_1, \phi_2, \ldots, \phi_l$ and $\phi_{l+1}, \phi_{l+2}, \ldots, \phi_n$ are orthogonal, they will remain so after applying the transformations $\Gamma(x)$. In expression (3.20), the block Q is identically zero. We have seen that for finite groups, each representation is equivalent to a unitary representation. Therefore, for finite groups, there is no need to distinguish between the concepts of reducibility and complete reducibility. So, from now on, when we say reducible, we will imply a completely reducible representation.

Now, let's develop criteria for establishing the irreducibility of a representation. These criteria take the form of two *Schur's Lemmas*.

Schur's Lemma 1. A transformation that commutes with all the transformations of an irreducible representation of a group is a constant transformation, i.e., a multiple of the identity.

Proof: Let H be the group, and x be one of its elements. Let $\Gamma(x)$ be the transformation associated with x in the irreducible representation Γ. Let M be a transformation in the domain space of Γ. We need to show that if

$$M\Gamma(x) = \Gamma(x)M \tag{3.21}$$

for all $x \in$H, then M is a multiple of the identity operator. If $M = 0$, the lemma is proved. Suppose $M \neq 0$. Let S be the domain vector space of Γ. If $\xi \in S$, the set $\{M\xi\}$ forms a vector space, which we denote as $M(S)$. In general, $M(S)$ is a subspace of S. From equation (3.21), we deduce that

$$M\Gamma(x)\xi = \Gamma(x)M\xi \tag{3.22}$$

for each x. Therefore, $\Gamma(x)$ applied to $M\xi$ results in an element of $M(S)$. This means that $M(S)$ is invariant under Γ. Since Γ is irreducible, $M(S)$ cannot be a proper subspace of S. Moreover, since $M \neq 0$, $M(S)$ cannot be the set $\{0\}$ containing only the zero vector. It follows that $M(S) = S$. This result shows that the set of vectors ξ for which $M\xi = 0$ contains only the zero vector. Therefore, M is nonsingular. Let λ_m be an eigenvalue of M, and ϕ_m its corresponding eigenvector. Define $M' = M - \lambda_m \mathbf{1}$. The operator M' satisfies condition (3.21) for each x, and if $M' \neq 0$, then $M'(S)$ is an invariant subspace of S under Γ. However, $M'(S)$ does not contain the vectors generated by ϕ_m. That would imply that Γ is reducible, which contradicts the initial assumption. So, $M' = 0$, which implies

$$M = \lambda_m \mathbf{1}\,, \tag{3.23}$$

proving the lemma.

Schur's lemma 2. Consider a group H and two non-equivalent irreducible representations $\Gamma^{(1)}$ and $\Gamma^{(2)}$, defined in vector spaces S_1 and S_2 of dimensions l_1 and l_2, respectively. Let M be a linear map from S_1 to S_2 that satisfies the property

$$M\Gamma^{(1)}(x) = \Gamma^{(2)}(x)M \tag{3.24}$$

for each $x \in H$. Then, $M = 0$.

Proof: Suppose $M \neq 0$. In general, the image of M applied to S_1 is a subspace $M(S_1)$ of S_2. If $\xi \in S_1$, then

$$M\Gamma^{(1)}(x)\xi = \Gamma^{(2)}(x)M\xi \tag{3.25}$$

implies that $M(S_1)$ is an invariant subspace of S_2 under $\Gamma^{(2)}$. Since $\Gamma^{(2)}$ is irreducible and $M \neq 0$, we have

$$M(S_1) = S_2 \,. \tag{3.26}$$

As the dimension of $M(S_1)$ is $\leq l_1$, we deduce that $l_2 \leq l_1$. Suppose for now that $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are unitary. Let's take the Hermitian conjugate of both sides of equation (3.24). We obtain

$$\Gamma^{(1)}(x)M^\dagger = M^\dagger \Gamma^{(2)}(x) \,. \tag{3.27}$$

By the same argument as before, we have $M^\dagger(S_2) = S_1$, and $l_1 \leq l_2$. But then, $l_1 = l_2$, and M is non-singular. This would imply that $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are equivalent, which contradicts our initial assumption. We can remove the constraint on the unitarity of $\Gamma^{(1)}$ and $\Gamma^{(2)}$. If these representations are not unitary, we can show that $\Gamma^{(1)\dagger}(x^{-1})$ and $\Gamma^{(2)\dagger}(x^{-1})$ are irreducible representations. In fact, for each $\Gamma(x)$, we can define

$$D(x) = \Gamma^\dagger(x^{-1}) \,. \tag{3.28}$$

The transformation thus defined is irreducible. $D^{(1)}(x)$ and $D^{(2)}(x)$ are defined in the dual spaces of $\Gamma^{(1)}$ and $\Gamma^{(2)}$. They are representations since

$$\begin{aligned} D(x)D(y) &= \Gamma^\dagger(x^{-1})\Gamma^\dagger(y^{-1}) \\ &= (\Gamma(x^{-1})\Gamma(y^{-1}))^\dagger \\ &= (\Gamma(y^{-1}x^{-1}))^\dagger \\ &= \Gamma^\dagger((xy)^{-1}) \\ &= D(xy) \,. \end{aligned} \tag{3.29}$$

Equation (3.24) gives us

$$D^{(1)}(x)M^\dagger = M^\dagger D^{(2)}(x) \tag{3.30}$$

for each $x \in H$, and the proof proceeds as before.

Corollary. A necessary and sufficient condition for an irreducible unitary representation Γ of a group H is that all transformations M such that, for each $x \in H$,

$$M\Gamma(x) = \Gamma(x)M \,, \tag{3.31}$$

are multiples of the identity.

Proof: As a consequence of the first Schur's lemma, the condition is necessary. To prove that it is also sufficient, we assume, for the sake of contradiction, that all linear transformations M satisfying condition (3.31) are multiples of the identity, but that Γ is reducible. Let S be the vector space of the definition of Γ, and let S_1 be a non-empty proper invariant subspace under $\Gamma(x)$ for every x. Since Γ is reducible, we are certain that such a subspace exists. Furthermore, as Γ is unitary, the orthogonal complement of S_1, denoted as S_2, is also invariant. Now, consider a linear operator M such that

$$M\xi_1 = m_1\xi_1 \tag{3.32}$$

and

$$M\xi_2 = m_2\xi_2 \,, \tag{3.33}$$

where $\xi_1 \in S_1$, $\xi_2 \in S_2$, and $m_1 \neq m_2$. Clearly, M commutes with all $\Gamma(x)$, but it is not a multiple of the identity. This leads to a contradiction to the initial assumption. It follows that Γ must be irreducible.

Great orthogonality theorem. Let $\Gamma^{(1)}$ and $\Gamma^{(2)}$ be two non-equivalent irreducible unitary representations of a finite group H of order h. We have

$$\text{(i)} \qquad \sum_{x\in H} \Gamma^{(1)*}_{ij}(x)\Gamma^{(2)}_{kl}(x) = 0\,, \tag{3.34}$$

$$\text{(ii)} \qquad \sum_{x\in H} \Gamma^{(1)*}_{ij}(x)\Gamma^{(1)}_{kl}(x) = \frac{h}{l_1}\delta_{ik}\delta_{jl}\,, \tag{3.35}$$

where l_1 and l_2 are the dimensions of representations $\Gamma^{(1)}$ and $\Gamma^{(2)}$, respectively.

Proof: (i) Consider an arbitrary matrix X with l_1 rows and l_2 columns. Construct

$$M = \sum_{x\in H} \Gamma^{(1)}(x^{-1})X\Gamma^{(2)}(x)\,. \tag{3.36}$$

For each element y in H, we have

$$\begin{aligned} M\Gamma^{(2)}(y) &= \sum_{x\in H} \Gamma^{(1)}(y)\Gamma^{(1)}(y^{-1})\Gamma^{(1)}(x^{-1})X\Gamma^{(2)}(x)\Gamma^{(2)}(y) \\ &= \Gamma^{(1)}(y)\sum_{x\in H} \Gamma^{(1)}((xy)^{-1})X\Gamma^{(2)}(xy) \\ &= \Gamma^{(1)}(y)M\,, \end{aligned} \tag{3.37}$$

where in the last equality, we used the theorem of rearrangement. According to Schur's second lemma, $M = 0$, and this is valid for an arbitrary matrix X. By expanding the indices, we can rewrite $M = 0$ as

$$\sum_{x\in H}\sum_{i,k} \Gamma^{(1)*}_{ij}(x)X_{ik}\Gamma^{(2)}_{kl}(x) = 0\,. \tag{3.38}$$

By setting $X_{ik} = 0$ for all i and k except for a given pair i, k for which $X_{ik} = 1$, we obtain (3.34).

(ii) If representation $\Gamma^{(2)}$ is identical to $\Gamma^{(1)}$, using a similar procedure as before, we can conclude that the linear operation

$$M = \sum_{x\in H} \Gamma^{(1)}(x^{-1})X\Gamma^{(1)}(x) \tag{3.39}$$

commutes with all $\Gamma^{(1)}(y)$ $(y \in H)$. According to Schur's first lemma, the matrix M is a multiple of the identity

$$M = c(X)\mathbf{1}\,, \tag{3.40}$$

where $c(X)$ is a number depending on the choice of X. Now, let's derive $c(X)$. For that, we express M by expanding its indices. We have

$$\sum_{x\in H}\sum_{i,k} \Gamma^{(1)}_{ji}(x^{-1})X_{ik}\Gamma^{(1)}_{kl}(x) = c(X)\delta_{jl}\,. \tag{3.41}$$

Now, let's set $l = j$ and sum over j,

$$\sum_{x\in H}\sum_{i,k} X_{ik}\sum_{j} \Gamma^{(1)}_{kj}(x)\Gamma^{(1)}_{ji}(x^{-1}) = l_1 c(X)\,. \tag{3.42}$$

Since $\Gamma^{(1)}(x)\Gamma^{(1)}(x^{-1})$ is the identity matrix, we obtain

$$c(X) = \frac{h}{l_1}\mathrm{Tr}(X)\,. \tag{3.43}$$

Choose X as before, such that $X_{ik} = 1$ for a given pair i, k and $X_{ik} = 0$ for the others. We obtain exactly relation (3.35). We can combine (i) and (ii) as follows:

$$\sum_{x\in H} \left(\frac{l_i}{h}\right)^{\frac{1}{2}} \Gamma^{(i)*}_{kl}(x) \left(\frac{l_j}{h}\right)^{\frac{1}{2}} \Gamma^{(j)*}_{mn}(x) = \delta_{ij}\delta_{km}\delta_{ln}\,, \tag{3.44}$$

$$\sum_{x\in H} \Gamma^{(i)*}_{kl}(x)\Gamma^{(j)*}_{mn}(x) = \frac{h}{l_i}\delta_{ij}\delta_{km}\delta_{ln}\,, \tag{3.45}$$

where $\Gamma^{(i)}$ and $\Gamma^{(j)}$ are two unitary irreducible representationsof H; $\delta_{ij} = 0$ if $\Gamma^{(i)}$ and $\Gamma^{(j)}$ are not equivalent while $\delta_{ij} = 1$ if $\Gamma^{(i)} \equiv \Gamma^{(j)}$

We can view equation (3.44) as the expression of orthogonality for a set of orthonormal vectors whose components are given by

$$\left(\frac{l_i}{h}\right)^{\frac{1}{2}} \Gamma^{(i)}_{kl}(x)\,. \tag{3.46}$$

Notice that the index of the components of this vector is the element x that runs through the elements of the group H. These vectors are defined in a vector space of dimension h, denoted as $\mathbb{C}^h$. Since there cannot be more than h mutually orthogonal vectors in $\mathbb{C}^h$, the number of non-equivalent irreducible representations is finite and cannot exceed h. Let N_Γ be the number of non-equivalent irreducible representations. If the i-th irreducible representation has dimension l_i, then the total number of these orthonormal vectors is

$$l_1^2 + l_2^2 + \ldots + l_{N_\Gamma}^2 \leq h\,. \tag{3.47}$$

Next, we will demonstrate that in all cases, we have $l_1^2 + l_2^2 + \ldots + l_{N_\Gamma}^2 = h$ (Burnside's Theorem).

3.2 Characters

Definition: Consider a representation Γ of a group H. The trace of the matrices $\Gamma(x)$ is denoted as

$$\chi(x) = \sum_i \Gamma_{ii}(x)\,. \tag{3.48}$$

In a representation Γ, all elements that are in the same class have the same trace. Indeed, let y be an element of the group H equivalent to the element x, meaning there exists an element $u \in H$ such that

$$y = u^{-1}xu\,. \tag{3.49}$$

Then

$$\Gamma(y) = \Gamma(u^{-1}xu) = \Gamma(u^{-1})\Gamma(x)\Gamma(u)\,, \tag{3.50}$$

and

$$\begin{aligned}\chi(y) &= \mathrm{Tr}[\Gamma(u^{-1})\Gamma(x)\Gamma(u)] \\ &= \mathrm{Tr}[\Gamma(x)\Gamma(u)\Gamma(u^{-1})] \\ &= \mathrm{Tr}[\Gamma(x)] = \chi(x)\,,\end{aligned} \tag{3.51}$$

where we used the property that the trace of a product of matrices is invariant under a cyclic permutation of the matrices in the product. The set $\{\chi(x)\}$ of traces for all x is called the *character* of the representation Γ. It is evident that two equivalent representations Γ and Γ' have the same character since if

$$\Gamma'(x) = S^{-1}\Gamma(x)S\,, \tag{3.52}$$

then

$$\begin{aligned}\chi'(x) &= \mathrm{Tr}[\Gamma'(x)] \\ &= \mathrm{Tr}[S^{-1}\Gamma(x)S] \\ &= \mathrm{Tr}[\Gamma(x)SS^{-1}] = \chi(x)\,.\end{aligned} \tag{3.53}$$

From equation (3.45), setting $l = k$ and $n = m$ and summing over k and m ($k = 1, 2, \ldots, l_i$), ($m = 1, 2, \ldots, l_j$), we have

$$\sum_{x\in H} \chi^{(i)*}(x)\chi^{(j)}(x) = h\delta_{ij}\,. \tag{3.54}$$

If we denote the classes of H by C_μ ($\mu = 1, 2, \ldots, N_C$) and the number of elements in C_μ by n_μ, equation (3.54) can be rewritten in the form

$$\sum_{\mu=1}^{N_C} n_\mu \chi^{(i)*}(C_\mu)\chi^{(j)}(C_\mu) = h\delta_{ij}\,. \tag{3.55}$$

In this equation, we have denoted by $\chi^{(i)}(c_\mu)$ the trace of an element of the class C_μ in the irreducible representation $\Gamma^{(i)}$.

The equation (3.55) represents the **little orthogonality theorem**. It can be interpreted as an orthogonality relation among the N_Γ vectors with components

$$(n_\mu/h)^{1/2}\chi^{(i)}(C_\mu) \tag{3.56}$$

in a vector space of dimension N_C. Since there cannot be more than N_C linearly independent vectors in such a space, we can establish the following inequality

$$N_\Gamma \le N_C\,. \tag{3.57}$$

We will see later on that it is always equality that is satisfied.

Theorem. A necessary and sufficient condition for two irreducible representations of a finit group to be equivalent, is that their character be the same.

Proof:

(i) We have already proven that the condition is necessary.

(ii) The condition is sufficient because if $\chi^{(1)}(x) = \chi^{(2)}(x)$ for all x, but $\Gamma^{(1)}$ is not equivalent to $\Gamma^{(2)}$, then by the grand orthogonality theorem (3.45), we have

$$\sum_{x\in H} |\chi^{(1)}(x)|^2 = 0$$

which represents a contradiction since at least the class containing the identity has a character that is different from zero.

Thanks to the characters, we now have a tool to reduce an arbitrary representation of a finite group H. Consider a representation Γ. We can formally write its reduction into irreducible representations as follows:

$$\Gamma = b_1\Gamma^{(1)} \oplus b_2\Gamma^{(2)} \oplus \ldots \oplus b_{N_\Gamma}\Gamma^{(N_\Gamma)}\,, \quad b_i = 0,\, 1,\, 2, \ldots\,. \tag{3.58}$$

It is clear that for all $x \in H$,

$$\chi(x) = \sum_{i=1}^{N_\Gamma} b_i \chi^{(i)}(x)\,, \tag{3.59}$$

or

$$\chi(C_\mu) = \sum_{i=1}^{N_\Gamma} b_i \chi^{(i)}(C_\mu)\,. \tag{3.60}$$

Multiply both sides of equation (3.60) by $n_\mu \chi^{(j)*}(C_\mu)$ and sum over μ. Thanks to the little orthogonality theorem (3.55), we obtain

$$b_i = \frac{1}{h}\sum_{\mu=1}^{N_C} n_\mu \chi^{(i)^*}(C_\mu)\chi(C_\mu)\,. \tag{3.61}$$

Equation (3.61) is the fundamental formula for reducing an arbitrary representation into irreducible representations.

From equation (3.61), we obtain

$$\sum_{\mu=1}^{N_C} n_\mu |\chi(C_\mu)|^2 = \sum_{i,j} b_i b_j \sum_{\mu=1}^{N_C} n_\mu \chi^{(i)*}(C_\mu)\chi^{(j)}(C_\mu) = h\sum_{i=1}^{N_\Gamma} b_i^2\,. \tag{3.62}$$

This equation allows us to prove the following theorem.

Theorem. A necessary and sufficient condition for a representation Γ, with character $\chi(C_\mu)$, to be irreducible is that

$$\sum_{\mu=1}^{N_C} n_\mu |\chi(C_\mu)|^2 = h\,. \tag{3.63}$$

Proof: Indeed, if the representation Γ is irreducible, then only one of the b_i in equation (3.62) is equal to 1, with all others being zero. The condition is therefore necessary. On the other hand, if equation (3.63) holds, then we can deduce from equation (3.62) that

$$\sum_{i=1}^{N_\Gamma} b_i^2 = 1 \quad i = 0,\, 1,\, 2, \ldots\,. \tag{3.64}$$

This relation can only be satisfied in the case where one of the b_i is equal to 1, with all others being zero.

In the group theory review, we saw how to write a multiplication table for a finite group. In particular, we constructed the multiplication table by placing the product xy in the cell corresponding to the intersection of the row labeled with x and the column labeled with y. The elements of the group appear in the same order in both the row and column labels. Alternatively, we can use a different labeling scheme by designating the rows as $x_1 = e$, $x_2, \ldots, x_h$, and the columns as $x_1^{-1} = e$, $x_2^{-1}, \ldots, x_h^{-1}$. It is clear that the sequence of inverses $\{x_i^{-1}\}$ contains all the elements of the group in a different order. The multiplication table obtained using this labeling scheme is as follows:

H	$x_1^{-1} = e$	x_2^{-1}	x_3^{-1}	$\ldots$	x_h^{-1}
$x_1 = e$	e	$x_1x_2^{-1}$	$x_1x_3^{-1}$	$\ldots$	$x_1x_h^{-1}$
x_2	x_2	$x_2x_2^{-1} = e$	$x_2x_3^{-1}$	$\ldots$	$x_2x_h^{-1}$
x_3	x_3	$x_3x_2^{-1}$	$x_3x_3^{-1} = e$	$\ldots$	$x_3x_h^{-1}$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
x_h	x_h	$x_hx_2^{-1}$	$x_hx_3^{-1}$	$\ldots$	$x_hx_h^{-1} = e$

We now construct a set of matrices $\{\Gamma(x_i)\}$, one for each element x_i of the group, as follows: the matrix $\Gamma(x_i)$ is of dimensions $h \times h$ and consists of zeros everywhere except at positions corresponding to the element x_i in the multiplication table we have just written. The set of matrices obtained in this way is a representation of the group H, as we will see later. It is called the *regular representation* of the group and is denoted as $\Gamma^{(R)}$. We can summarize the definition of this representation as follows:

$$\Gamma^{(R)}_{ij}(x) = \begin{cases} 1 & \text{if } x_i x_j^{-1} = x \\ 0 & \text{otherwise.} \end{cases} \tag{3.65}$$

We can immediately see that $\Gamma^{(R)}(e)$ is the identity matrix of dimension h. Let's now show that $\Gamma^{(R)}$ is a representation. Indeed,

$$[\Gamma^{(R)}(x)\Gamma^{(R)}(y)]_{ij} = \sum_k \Gamma^{(R)}_{ik}(x)\Gamma^{(R)}_{kj}(y)\,. \tag{3.66}$$

For a given i and j, the term in k in this sum is nonzero if and only if

$$x_i x_k^{-1} = x \tag{3.67}$$

and

$$x_k x_j^{-1} = y\,. \tag{3.68}$$

Each of these two conditions uniquely determines x_k. For both conditions to be satisfied simultaneously, it is necessary to have $x^{-1}x_i = yx_j$, which means

$$x_i x_j^{-1} = xy\,. \tag{3.69}$$

In this case, the sum on the right-hand side of equation (3.66) contains a term for which $\Gamma^{(R)}_{ik}(x)\Gamma^{(R)}_{kj}(y) = 1$, with all other terms in the sum being zero. If, on the other hand, condition (3.69) is not met, then the terms $\Gamma^{(R)}_{ik}(x)\Gamma^{(R)}_{kj}(y)$ in the sum (3.66) are identically zero. In summary,

$$[\Gamma^{(R)}(x)\Gamma^{(R)}(y)]_{ij} = \begin{cases} 1 & \text{if } x_i x_j^{-1} = xy \\ 0 & \text{otherwise.} \end{cases} \tag{3.70}$$

But this is exactly the definition of the matrix $\Gamma^{(R)}(xy)$. Therefore, we have

$$[\Gamma^{(R)}(x)\Gamma^{(R)}(y)]_{ij} = \Gamma^{(R)}_{ij}(xy)\,, \tag{3.71}$$

which proves that $\Gamma^{(R)}$ is a representation of the group H.

Theorem. The regular representation of a finit group H contains each irreducible representation of the group, as many times as its dimension, this is to say:

$$\Gamma^{(R)} = l_1\Gamma^{(1)} \oplus l_2\Gamma^{(2)} \oplus \ldots \oplus l_{N_\Gamma}\Gamma^{(N_\Gamma)}\,. \tag{3.72}$$

Proof: Let

$$\Gamma^{(R)} = b_1\Gamma^{(1)} \oplus b_2\Gamma^{(2)} \oplus \ldots \oplus b_{N_\Gamma}\Gamma^{(N_\Gamma)}\,. \tag{3.73}$$

The equation (3.61) for the reduction of a representation using its characters gives us:

$$\begin{aligned} b_i &= \frac{1}{h}\sum_{\mu=1}^{N_C} n_\mu \chi^{(i)^*}(C_\mu)\chi^{(R)}(C_\mu) \\ &= \frac{1}{h}\chi^{(i)}(e)h = l_i\,, \end{aligned} \tag{3.74}$$

Here, we have used the obvious property that all the $\chi^{(R)}(C_\mu)$ are zero except for $\chi^{(R)}(e) = h$. Using (3.60), we have:

$$\chi^{(R)}(C_\mu) = \sum_{i=1}^{N_\Gamma} l_i\chi^{(i)}(C_\mu)\,. \tag{3.75}$$

This relation is very useful in the particular case where $C_\mu = \{e\}$. In this case, indeed, we have $\chi^{(i)}(e) = l_i$ and:

$$\sum_{i=1}^{N_\Gamma} l_i^2 = h\,. \tag{3.76}$$

This proves that in the relation (3.47), equality is always satisfied.

Theorem. Let Γ be an irreducible representation. The sum of $\Gamma(x)$ matrices over all x belonging to an equivalence class is a multiple of the identity matrix.

Proof: Let $\{x_1, x_2, \ldots, x_n\}$ be the elements of a class of a group H. Consider the matrix:

$$M = \sum_{i=1}^{n}\Gamma(x_i)\,. \tag{3.77}$$

By the definition of a conjugacy class, we have:

$$\Gamma(y^{-1})M\Gamma(y) = \sum_{i=1}^{n}\Gamma(y^{-1}x_iy) = M\,, \tag{3.78}$$

where we have used the theorem of rearrangement of a class. So we have:

$$M\Gamma(y) = \Gamma(y)M \tag{3.79}$$

for each $y \in H$. By the first Schur's lemma, M is a multiple of the identity. We notice that this result is valid for infinite groups as well, as long as n remains finite.

For each irreducible representation $\Gamma^{(i)}$ and for each class C_μ of a finite group H, we can construct the matrix:

$$M_\mu^{(i)} = \sum_{k=1}^{n_\mu} \Gamma^{(i)}(x_k^{(\mu)}) = m_\mu^{(i)} \mathbf{1}^{(i)} , \tag{3.80}$$

where $x_k^{(\mu)}$ is an element of the class C_μ ($k = 1, 2, \ldots, n_\mu$), $m_\mu^{(i)}$ is a number, and $\mathbf{1}^{(i)}$ is the identity matrix acting on the l_i-dimensional space of the representation $\Gamma^{(i)}$. Sometimes, the matrices $M_\mu^{(i)}$ are called "Dirac characters." Taking the trace of both sides of equation (3.80), we obtain:

$$n_\mu \chi^{(i)}(C_\mu) = l_i m_\mu^{(i)} . \tag{3.81}$$

The product of two matrices $M_\mu^{(i)}$ and $M_\nu^{(i)}$, from the same representation but different classes C_μ and C_ν, yields:

$$M_\mu^{(i)} M_\nu^{(i)} = \sum_{k=1}^{n_\mu} \sum_{l=1}^{n_\nu} \Gamma^{(i)}(x_k^{(\mu)} x_l^{(\nu)}) . \tag{3.82}$$

The collection $[x_k^{(\mu)} x_l^{(\nu)}]$ (see group theory review, Chapter 2) contains all products of an element from class C_μ with an element from class C_ν (with repeated elements). In Chapter 2, we denoted this collection as $C_\mu \cdot C_\nu$. Using formula (2.54) derived in the previous chapter, we can deduce:

$$M_\mu^{(i)} M_\nu^{(i)} = \sum_{\lambda=1}^{N_C} n_{\mu\nu\lambda} M_\lambda^{(i)} , \tag{3.83}$$

Here, the non-negative integers $n_{\mu\nu\lambda}$ indicate the number of times class C_λ appears in the collection $C_\mu \cdot C_\nu$. We can now use equation (3.80) to obtain.

$$m_\mu^{(i)} m_\nu^{(i)} \mathbf{1}^{(i)} = \sum_{\lambda=1}^{N_C} n_{\mu\nu\lambda} m_\lambda^{(i)} \mathbf{1}^{(i)} . \tag{3.84}$$

Equation (3.81) allows us to write

$$n_\mu n_\nu \chi^{(i)}(C_\mu) \chi^{(i)}(C_\nu) = l_i \sum_{\lambda=1}^{N_C} n_{\mu\nu\lambda} n_\lambda \chi^{(i)}(C_\lambda) , \tag{3.85}$$

Where the coefficients $n_{\mu\nu\lambda}$ are the same as those defining the class product expansion (2.54). This relation is the most important result of this chapter because it will allow us to derive the characters of all the irreducible representations of a finite group.

We can also define the Dirac character of any representation Γ as:

$$M_\mu = \sum_{k=1}^{n_\mu} \Gamma(x_k^{(\mu)}) , \tag{3.86}$$

where $x_k^{(\mu)}$ is an element of class C_μ ($k = 1, 2, \ldots, n_\mu$). Now, consider the transformation S that reduces the representation Γ into irreducible representations. The matrices $\Gamma'(x) = S^{-1}\Gamma(x)S$ will have a block structure (3.14), with each block being the matrix of an irreducible representation $\Gamma^{(i)}$ of the group. Let's write the reduction of Γ as follows:

$$\Gamma = \Gamma^{(i_1)} \oplus \Gamma^{(i_2)} \oplus \ldots \oplus \Gamma^{(i_n)} \tag{3.87}$$

where n is the total number of irreducible representations involved in the reduction of Γ. Note that the indices i_j can be equal. For example, if $i_1 = i_2 = i_3 = 1$, it means that representation

$\Gamma^{(1)}$ is contained three times in the reduction of Γ. Since the matrices M_μ are sums of matrices $\Gamma(x)$, in the basis that reduces the representation Γ, the new matrices $M'_\mu = S^{-1}M_\mu S$ will also have a block structure. Moreover, we have just shown that in each subspace related to an irreducible representation, the corresponding block of the matrix M'_μ must be a multiple of the identity. We thus obtain a matrix of the form:

$$M'_\mu = \begin{pmatrix} m_\mu^{(i_1)}\mathbf{1}^{(i_1)} & 0 & 0 & \dots & 0 \\ 0 & m_\mu^{(i_2)}\mathbf{1}^{(i_2)} & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & m_\mu^{(i_n)}\mathbf{1}^{(i_n)} \end{pmatrix}, \tag{3.88}$$

where $m_\mu^{(i_j)}$ are complex numbers, and $\mathbf{1}^{(i_j)}$ are identity matrices in each subspace corresponding to an irreducible representation of the group. It is clear that the transformation $M'_\mu = S^{-1}M_\mu S$ simultaneously diagonalizes the matrices M_μ.

This result will be very important for applications of representation theory in physics. For instance, when studying the symmetry group of a quantum mechanical system, the Dirac characters in the Hilbert space of the system's wave functions are observables that can be simultaneously diagonalized with the Hamiltonian. Such operators represent physically conserved quantities within each subspace that is invariant under the symmetry group's operations. Representation theory provides a tool for finding these observables based on the system's symmetries.

Now, let's prove another fundamental orthogonality theorem regarding the characters.

Orthogonality theorem by column. Vectors of dimension N_Γ (the number of irreducible representation of a group H) given by

$$(n_\mu/h)^{1/2}\chi^{(i)}(C_\mu) \;\; ; \;\; i = 1, 2, \dots, N_\Gamma \;\; , \;\; \mu = 1, 2, \dots, N_C\,, \tag{3.89}$$

are orthonormal,

$$\sum_{i=1}^{N_\Gamma} \chi^{(i)*}(C_\mu)\chi^{(i)}(C_\nu) = \frac{h}{n_\mu}\delta_{\mu\nu} \tag{3.90}$$

where $\delta_{\mu\nu}$ is the Kroeneker delta equal to 1 if the classes C_μ and C_ν coincide, else is 0.

Before proving the theorem, let's consider the collection $C_\mu \cdot C_\nu$. This set contains the neutral element e if and only if there exists an element x in C_μ such that $x^{-1} \in C_\nu$. If this is the case, then for all other elements y in the class C_μ, the inverse element y^{-1} is contained in the class C_ν. In fact, for $y \in C_\mu$, there exists an element $u \in H$ such that $y = u^{-1}xu$. Consequently, $y^{-1} = u^{-1}x^{-1}u \in C_\nu$. It follows that the collection $C_\mu \cdot C_\nu$ contains the neutral element e of the group H if and only if the classes C_μ and C_ν are composed of mutually inverse elements. In this case, the number of times the element e – and hence the class $C_1 = \{e\}$ – is contained in $C_\mu \cdot C_\nu$ is $n_{\mu\nu 1} = n_\mu$, which is the number of elements in the class C_μ. We denote the class that contains the inverses of the elements of class C_μ as $C_{\mu'}$. The property that has just been proven can be summarized by the notation:

$$n_{\mu\nu 1} = n_\mu \delta_{\mu'\nu} \tag{3.91}$$

Note that the classes C_μ and $C_{\mu'}$ contain the same number of elements, i.e., $n_{\mu'} = n_\mu$. In some cases, the classes C_μ and $C_{\mu'}$ are actually the same class. We will see later, for example, that this is the case for the class denoted by $8C_3$ in the tetrahedral group T_d. In contrast, the same rotations occupy two different classes, $4C_3$ and $4C_3^2$, in the group T, which, compared to T_d, does not contain spatial inversion.

At this point, it is useful to emphasize another important property of the characters. Since a representation of a finite group is always equivalent to a unitary representation, and the characters of two equivalent representations are the same, we can write:

$$\begin{aligned}\chi^{(i)}(C_{\mu'}) &= \mathrm{Tr}(\Gamma^{(i)}(x^{-1})) \\ &= \mathrm{Tr}(\Gamma^{(i)\dagger}(x)) \\ &= \chi^{(i)*}(C_\mu) \end{aligned} \tag{3.92}$$

We can also deduce that if $C_{\mu'} \equiv C_\mu$, then the character for this class must be real, since we have $\chi^{(i)}(C_\mu) = \chi^{(i)*}(C_\mu)$.

Proof of the orthogonality by column theorem. We are now able to prove the theorem of column orthogonality. Consider equation (3.85) and sum over all the irreducible representations of the group H. We have:

$$\sum_{i=1}^{N_\Gamma} n_{\mu'} n_\nu \chi^{(i)}(C_{\mu'})\chi^{(i)}(C_\nu) = \sum_{\lambda=1}^{N_C} n_{\mu'\nu\lambda} n_\lambda \sum_{i=1}^{N_\Gamma} l_i \chi^{(i)}(C_\lambda) \tag{3.93}$$

We have seen that:

$$\sum_{i=1}^{N_\Gamma} l_i \chi^{(i)}(C_\lambda) \tag{3.94}$$

is nothing but the trace of the regular representation of an element of the class C_λ. It follows that this quantity is zero for all C_λ except for $C_1 = \{e\}$, for which it equals:

$$\sum_{i=1}^{N_\Gamma} l_i \chi^{(i)}(C_1) = \sum_{i=1}^{N_\Gamma} l_i^2 = h \tag{3.95}$$

Thus:

$$\sum_{i=1}^{N_\Gamma} n_{\mu'} n_\nu \chi^{(i)}(C_{\mu'})\chi^{(i)}(C_\nu) = n_{\mu'\nu 1} h \tag{3.96}$$

Using relations (3.91) and (3.92), and the property $n_{\mu'} = n_\mu$, we obtain equation (3.90), and the theorem is thus proved.

Since the set of vectors with N_Γ components $(n_\mu/h)^{1/2}\chi^{(i)}(C_\mu)$ ($i = 1, 2, \ldots, N_\Gamma$) is orthonormal, it must necessarily be:

$$N_\Gamma \leq N_C \tag{3.97}$$

But the little theorem of orthogonality (which essentially states that the characters of irreducible representations are orthonormal by rows) allowed us to establish the inequality in the reverse direction (3.57). We have, therefore, demonstrated that:

$$N_\Gamma = N_C \tag{3.98}$$

The properties of the characters that we have demonstrated allow us to construct, for each finite group H, the character table in the following way.

H	$C_1 = \{e\}$	C_2	C_3	$\ldots$	C_{N_Γ}
$\Gamma^{(1)}$	1	1	1	$\ldots$	1
$\Gamma^{(2)}$	l_2	$\chi^{(2)}(C_2)$	$\chi^{(2)}(C_3)$	$\ldots$	$\chi^{(2)}(C_{N_\Gamma})$
$\Gamma^{(3)}$	l_3	$\chi^{(3)}(C_2)$	$\chi^{(3)}(C_3)$	$\ldots$	$\chi^{(3)}(C_{N_\Gamma})$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
$\Gamma^{(N_\Gamma)}$	l_{N_Γ}	$\chi^{(N_\Gamma)}(C_2)$	$\chi^{(N_\Gamma)}(C_3)$	$\ldots$	$\chi^{(N_\Gamma)}(C_{N_\Gamma})$

In this character table, each row contains the characters of an irreducible representation, and each column represents a conjugacy class of the group. The first row contains the character of the identity irreducible representation, for which $\Gamma^{(1)}(x) = 1$, and thus $\chi^{(1)}(x) = 1$ for every element x of H. The first column contains the character for the class $C_1 = \{e\}$ for each irreducible representation. We have seen that the representation $\Gamma(e)$ of the group's neutral element is always the identity in the representation's defining space. The character is, therefore, equal to the dimension of the space. For the irreducible representations $\Gamma^{(i)}$, we have indicated the dimensions of the defining spaces by l_i. Since $N_C = N_\Gamma$, the character table is square.

The character table can generally be deduced from equation (3.85). This equation defines an algebra of characters from the algebra of classes. To determine the characters, proceed as follows:

(i) From the group H multiplication table, deduce the conjugacy classes C_μ ($\mu = 1, 2, \ldots, N_C$).

(ii) Build all possible multiplications $C_\mu \cdot C_\nu$ of two classes (keeping repeated elements) and determine the numbers $n_{\mu\nu\lambda}$ that appear in the expansion (2.54)

$$C_\mu \cdot C_\nu = \sum_{\lambda=1}^{N_C} n_{\mu\nu\lambda} C_\lambda \,.$$

(iii) Once the $n_{\mu\nu\lambda}$ are determined, use equation (3.85) to determine algebraic relations between the characters $\chi^{(i)}(C_\mu)$ for each possible value of l_i. For example, by setting $l_i = 1$ in (3.85) and choosing all possible pairs μ, ν, we obtain a system of algebraic equations for the characters of possible irreducible representations of dimension 1.

(iv) We know that such a procedure can be repeated a maximum of N_C times, after which all rows of the character table will be filled.

(v) In general, it is not necessary to repeat procedure (iii) for all irreducible representations. At a certain point in the derivation, we can often deduce the remaining characters using the orthogonality theorems (3.55) and (3.90), and relations (3.63), (3.92), and Burnside's theorem (3.76).

Once the character table is obtained, we have the tools to reduce any arbitrary representation Γ of a finite group to a direct sum of irreducible representations. Suppose we have a representation Γ expressed in the form of matrices $\Gamma(x)$ for each element x of the group. From the matrices $\Gamma(x)$, we can immediately calculate their trace and hence the characters $\chi(C_\mu)$ of the representation Γ. Then, using equation (3.61) and the knowledge of the group's character table, we can calculate the coefficients b_i in the reduction

$$\Gamma = b_1\Gamma^{(1)} \oplus b_2\Gamma^{(2)} \oplus \ldots \oplus b_{N_\Gamma}\Gamma^{(N_\Gamma)} \,. \tag{3.99}$$

The final step of the problem is to find the transformation S that reduces the representation Γ to a block structure. We will describe a systematic method for finding this transformation in the chapter concerning applications in physics.

Chapter 4

Applications in Physics

The purpose of this chapter is to demonstrate how the theory of representations applies to a problem in physics.

We can often formulate a physical problem in the mathematical form of an eigenvalue problem in a suitable vector space. As we saw in the first chapter, for example, the problem of classical mechanics of the vibrational modes of a molecule can be reduced to an eigenvalue problem in the vector space of displacements of the atoms that make up the molecule. The most important example is the solution of a problem in quantum mechanics. In this case, we seek the eigenvectors and eigenvalues of the Hamiltonian operator in a Hilbert space of functions. In all these cases, the exact solution of the problem is often very difficult to find. It is useful to have a rigorous method that allows us to simplify the problem. The method that arises from the symmetry properties of the system and the representations of groups is a very powerful method in this regard. We will see later that it allows us to predict the degeneracy of an energy eigenvalue and restrict ourselves to subspaces of limited dimension in the search for eigenstates.

In the rest of this chapter, we will develop this method. For this, we will consider an example of a problem in quantum mechanics. The extension to other types of problems, for example, in classical mechanics, will be discussed in examples. We will also restrict ourselves to symmetry operations of rotation or rotation-inversion, which form the group of rotation-inversion $O(3)$. This group will be described in detail in the following chapters. It should not be forgotten that other symmetry operations in physics are possible. Namely, (i) translation operations, (ii) permutation operations in the case of systems with multiple identical particles, (iii) time reversal, and (iv) charge conjugation.

4.1 Symmetries in Quantum Mechanics

A system with N particles (without spin) in quantum mechanics is characterized by its wave function $\psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, where the $\mathbf{x}_i$ are vectors in three-dimensional space $\mathbb{R}^3$. Consider a transformation R from the three-dimensional rotation-inversion group $O(3)$. The operator R is a three-dimensional orthogonal matrix. If the system is transformed by an operation R, then each position vector $\mathbf{x}_i$ is transformed into a new vector as follows:

$$\mathbf{x}_i \to \mathbf{x}'_i = R\mathbf{x}_i \,. \tag{4.1}$$

We define a new function $P_R\psi(\mathbf{x}'_1, \mathbf{x}'_2, \ldots, \mathbf{x}'_N)$ such that its value at position $\{\mathbf{x}'_i\}$ is equal to the value of the old function at position $\{\mathbf{x}_i\}$, meaning:

$$\begin{aligned} P_R\psi(\mathbf{x}'_1, \mathbf{x}'_2, \ldots, \mathbf{x}'_N) &= \psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \\ &= \psi(R^{-1}\mathbf{x}'_1, R^{-1}\mathbf{x}'_2, \ldots, R^{-1}\mathbf{x}'_N) \,. \end{aligned} \tag{4.2}$$

Such a definition makes physical sense as it corresponds to performing a rotation of the system in space. Since we do not consider particle permutation operations, the operations R act independently on each position $\mathbf{x}_i$. Without loss of generality, we can consider a single-particle system. In this case, the definition (4.2) becomes simply:

$$P_R\psi(\mathbf{x}) = \psi(R^{-1}\mathbf{x})\,. \tag{4.3}$$

Subsequently, to simplify the notation, we will omit the prime in the expression $\mathbf{x}'$ when it is not necessary, and we will indicate $\mathbf{x}$ as the position after the transformation.

Now consider a finite group $G = \{R_i\}$ of orthogonal transformations. Associated with this group, there is a group of operations $\{P_{R_i}\}$. To prove that it is a group, we will apply two successive transformations, R and S, from the group. The first operation transforms $\mathbf{x}$ into $\mathbf{x}' = R\mathbf{x}$, and the second transforms $\mathbf{x}'$ into $\mathbf{x}'' = S\mathbf{x}' = (SR)\mathbf{x}$. We have:

$$\begin{aligned} P_S P_R\psi(\mathbf{x}'') &= P_R\psi(\mathbf{x}') \\ &= \psi(\mathbf{x}) \\ &= \psi((SR)^{-1}\mathbf{x}'') \\ &= P_{SR}\psi(\mathbf{x}'')\,, \end{aligned} \tag{4.4}$$

hence:

$$P_S P_R = P_{SR}\,. \tag{4.5}$$

Consider the inner product in the space of functions $\psi(\mathbf{x})$ defined as:

$$\langle\psi|\phi\rangle = \int d\mathbf{x}\psi^*(\mathbf{x})\phi(\mathbf{x}) \tag{4.6}$$

for each pair of complex functions $\psi(\mathbf{x})$ and $\phi(\mathbf{x})$. We deduce that P_R is a unitary operator. Indeed, we have

$$\begin{aligned} \langle P_R\psi|P_R\phi\rangle &= \int d\mathbf{x}(P_R\psi(\mathbf{x}'))^*(P_R\phi(\mathbf{x}')) \\ &= \int d\mathbf{x}\left|\frac{\partial(x_1',x_2',x_3')}{\partial(x_1,x_2,x_3)}\right|\psi^*(\mathbf{x})\phi(\mathbf{x}) \\ &= \langle\psi|\phi\rangle\,, \end{aligned} \tag{4.7}$$

since the Jacobian

$$\left|\frac{\partial(x_1',x_2',x_3')}{\partial(x_1,x_2,x_3)}\right| \tag{4.8}$$

of the transformation is equal to 1 for an orthogonal transformation.

As an example, consider an operation P_R that corresponds to a rotation by an angle θ around the x_3 axis. The coordinate transformation is

$$\begin{aligned} x_1' &= x_1\cos(\theta) - x_2\sin(\theta) \\ x_2' &= x_1\sin(\theta) + x_2\cos(\theta) \\ x_3' &= x_3\,. \end{aligned} \tag{4.9}$$

We have

$$P_R\psi(x_1,x_2,x_3) = \psi(x_1\cos(\theta) + x_2\sin(\theta), -x_1\sin(\theta) + x_2\cos(\theta), x_3)\,. \tag{4.10}$$

However, please note that in this expression, the coordinates x_1, x_2, x_3 are the coordinates of the point after the transformation and should be denoted as x_1', x_2', x_3'. Nevertheless, we have

chosen to denote it as $\mathbf{x}$, which represents an arbitrary position after the transformation. For example, if $\psi(x_1, x_2, x_3) = x_1^2 - x_2^2$, then

$$P_R\psi(x_1, x_2, x_3) = \psi(x_1, x_2, x_3)\cos(2\theta) + \phi(x_1, x_2, x_3)\sin(2\theta)\,, \tag{4.11}$$

where

$$\phi(x_1, x_2, x_3) = 2x_1x_2\,. \tag{4.12}$$

On the other hand, if $\psi(x_1, x_2, x_3) = x_1^2 + x_2^2$, then we obtain

$$P_R\psi(x_1, x_2, x_3) = \psi(x_1, x_2, x_3)\,. \tag{4.13}$$

Now, let's consider the Hamiltonian operator $H(\mathbf{x})$. This operator, for a spinless particle, generally depends on both the position $\mathbf{x}$ and the momentum, which, in the position representation, is given by $\mathbf{p} = -i\hbar\nabla_{\mathbf{x}}$. It's evident that the components of $\mathbf{p}$ follow the same transformation law as $\mathbf{x}$, subject to a transformation R. According to the definition, the operator P_R acts on the function $H(\mathbf{x})\psi(\mathbf{x})$ as

$$P_R(H(\mathbf{x})\psi(\mathbf{x})) = H(R^{-1}\mathbf{x})\psi(R^{-1}\mathbf{x})\,. \tag{4.14}$$

We say that the system is invariant under a transformation R if the Hamiltonian of the transformed system is identically the same as for the system before the transformation. This implies that $H(R^{-1}\mathbf{x}) = H(\mathbf{x})$. The expression (4.14) gives us

$$\begin{aligned} P_R(H(\mathbf{x})\psi(\mathbf{x})) &= H(\mathbf{x})\psi(R^{-1}\mathbf{x}) \\ &= H(\mathbf{x})P_R\psi(\mathbf{x})\,, \end{aligned} \tag{4.15}$$

which, in compact notation, is written as

$$[H, P_R] = HP_R - P_RH = 0\,. \tag{4.16}$$

We have thus proven that if a physical system is invariant under a transformation R, it is equivalent to saying that the commutator of its Hamiltonian with the transformation operator P_R is zero. We call R a symmetry of the system. Based on this definition, it's evident that the set $\{R\}$ of all symmetry transformations of the system forms a group. In this case, it is referred to as the symmetry group of the system. As we have seen, the set of operations P_R also forms a group that is isomorphic to the group $\{R\}$.

Consider a system characterized by a Hamiltonian H and a symmetry group $G = \{R\}$. Suppose that ϕ is an eigenstate of H with eigenvalue E. Then $P_R\phi$ is also an eigenstate of H with the same eigenvalue. Indeed,

$$HP_R\phi = P_RH\phi = EP_R\phi\,. \tag{4.17}$$

If the eigenvalue E is non-degenerate, this implies that $P_R\phi$ is equal to ϕ, up to a complex numerical factor (with absolute value 1). If, on the other hand, E is l-fold degenerate, then we can define a set of orthonormal vectors $\{\phi_k\}$ ($k = 1, 2, \ldots, l$), which are eigenvectors of H with eigenvalue E. These vectors generate a subspace S. In this case, the vector $P_R\phi_k$ is still an eigenstate with eigenvalue E and must be a linear combination of the vectors $\{\phi_k\}$, i.e.,

$$P_R\phi_k = \sum_{n=1}^{l} \phi_n\Gamma_{nk}(R)\,. \tag{4.18}$$

The complex numbers $\Gamma_{nk}(R) = \langle\phi_n|P_R|\phi_k\rangle$ are the elements of a unitary matrix (since the operator P_R is unitary), denoted as $\Gamma(R)$. The set of matrices $\{\Gamma(R)\}$ for each R forms a

unitary representation of the group G. If we choose another orthonormal basis $\{\psi_k\}$ for the subspace S of eigenstates of H with eigenvalue E, this basis is related to the old one by a unitary transformation, and the representation it generates is equivalent to $\Gamma(R)$. Consider now the subspace S of eigenstates of H with eigenvalue E. Suppose there are no proper subspaces of S that are invariant under the operations $\{P_R\}$. In this case, the representation $\Gamma(R)$ related to S is, by definition, irreducible. The degeneracy of the energy level E is then called "necessary." If, on the other hand, there exists a proper subspace of S that is invariant under the $\{P_R\}$, then the representation $\Gamma(R)$ is reducible, and the degeneracy is called "accidental." Such a denomination is clearly justified by the considerations we have made. If a subspace is invariant under the symmetry group $\{P_R\}$, then all vectors in that subspace must necessarily have the same eigenvalue. Indeed, given a vector $\phi \in S$, the vectors $\{P_R\phi\}$ for all R generate the subspace S and are all degenerate by (4.17). The symmetry group G, on the other hand, does not impose any degeneracy between two eigenstates of H belonging to different invariant subspaces. In this case, degeneracy would be of an accidental nature.

In general, in nature, we rarely have accidental degeneracies. If an accidental degeneracy appears in the system under analysis, most of the time, it is due to a misidentification of the symmetry group of the system. In such situations, additional symmetries are often found that have gone unnoticed and can explain the observed degeneracies. A very well-known example is that of the s and p states of an electron in the hydrogen atom. The $2p$ states have the form $-(1/\sqrt{2})(x+iy)f(r)$, $zf(r)$, $(1/\sqrt{2})(x-iy)f(r)$, where $f(r)$ is a function of $r = |\mathbf{r}|$. They generate a three-dimensional function space that defines an irreducible representation of the spherical group $O(3)$ (it's an infinite group, so we can't apply all the properties seen here). Similarly, the $2s$ state has the form $f(r)$ and generates the identity representation of the group $O(3)$. These two representations are irreducible and distinct. However, we know that the $2s$ and $2p$ levels (in general, the ns, np, etc. levels) are degenerate. The degeneracy in this case is accidental, given the symmetry group of rotation-inversion $O(3)$. In reality, it is possible to show that the hydrogen atom is characterized by an additional symmetry, and the symmetry group is $SO(4)$ instead of $O(3)$. This hidden symmetry of the hydrogen atom is one of the most interesting aspects of symmetries in physics and highlights the utility of the formalism we are dealing with here.

Theorem. Consider two subspaces S_i and S_j, not necessarily distinct or orthogonal, defining two unitary irreducible representations $\Gamma^{(i)}$ and $\Gamma^{(j)}$, of dimensions l_i and l_j, respectively, of a finite group G. Consider two sets of orthonormal vectors $\{\phi_k^{(i)}\}$ $(k = 1, 2, \ldots, l_i)$ and $\{\psi_k^{(j)}\}$ $(k = 1, 2, \ldots, l_j)$ that are bases for S_i and S_j, respectively. We say that the vector $\phi_k^{(i)}$ *transforms* like the k-th basis function of the i-th irreducible representation. The following orthogonality relation is satisfied

$$\langle \phi_k^{(i)} | \psi_m^{(j)} \rangle = \alpha^{(i)} \delta_{ij} \delta_{km} \,, \tag{4.19}$$

where $\alpha^{(i)}$ is a complex number.

Proof: Consider the $l_i \times l_j$ matrix defined by $M_{km} = \langle \phi_k^{(i)} | \psi_m^{(j)} \rangle$. For each element R of the symmetry group, we can establish the following relations

$$\begin{aligned} \langle \phi_k^{(i)} | \psi_m^{(j)} \rangle &= \langle P_R \phi_k^{(i)} | P_R \psi_m^{(j)} \rangle \\ &= \langle \phi_k^{(i)} \Gamma^{(i)}(R) | \psi_m^{(j)} \Gamma^{(j)}(R) \rangle \\ &= \Gamma^{(i)\dagger}(R) \langle \phi_k^{(i)} | \psi_m^{(j)} \rangle \Gamma^{(j)}(R) \\ &= (\Gamma^{(i)}(R))^{-1} \langle \phi_k^{(i)} | \psi_m^{(j)} \rangle \Gamma^{(j)}(R) \,, \end{aligned} \tag{4.20}$$

where the first equality follows from the unitarity of P_R, the second from the definition of the representation, the third from the definition of the scalar product, and the fourth from the

unitarity of the representation. For each element R of the group, we therefore have $\Gamma^{(i)}(R)M = M\Gamma^{(j)}(R)$. By the two Schur's lemmas, we have that, if $i \neq j$, then M is identically zero, while, if $i = j$, then M is a multiple of the identity matrix.

This theorem tells us that, after classifying the states of a quantum system according to the irreducible representations of the symmetry group, two states can only have a non-zero inner product if they transform like the same basis function of the same irreducible representation. This is very important for establishing *selection rules* in quantum mechanics, for example.

Another theorem that follows from the theory of representations is Unsöld's theorem, which allows us to construct quantities that are invariant under the symmetry operations of the system.

Theorem (Unsöld's Theorem). If $\{\phi_n^{(i)}\}$ and $\{\psi_n^{(i)}\}$ $(n = 1, 2, \ldots, l_i)$ are two orthonormal bases of the same unitary irreducible representation $\Gamma^{(i)}$ of a group G, then for each operation P_R of the group and for an arbitrary pair of vectors ξ and η, we have

$$\sum_{n=1}^{l_i} \langle \xi | \psi_n^{(i)} \rangle \langle \phi_n^{(i)} | \eta \rangle = \sum_{n=1}^{l_i} \langle \xi | P_R \psi_n^{(i)} \rangle \langle P_R \phi_n^{(i)} | \eta \rangle \,. \tag{4.21}$$

We can interpret this result as follows. Consider the operator

$$\sum_{n=1}^{l_i} |\psi_n^{(i)}\rangle \langle \phi_n^{(i)}| \,. \tag{4.22}$$

With this notation, we indicate the operator that, when applied to a vector ξ, gives us the vector

$$\xi' = \sum_{n=1}^{l_i} \psi_n^{(i)} \langle \phi_n^{(i)} | \xi \rangle \,. \tag{4.23}$$

Unsöld's theorem states that an operator constructed in this way is invariant under all transformations P_R, meaning

$$P_R^{-1} \left(\sum_{n=1}^{l_i} |\psi_n^{(i)}\rangle \langle \phi_n^{(i)}| \right) P_R = \sum_{n=1}^{l_i} |\psi_n^{(i)}\rangle \langle \phi_n^{(i)}| \,, \tag{4.24}$$

where we used the unitarity property $P_R^{-1} = P_R^\dagger$.

Proof: We have

$$P_R \phi_n^{(i)} = \sum_{m=1}^{l_i} \phi_m^{(i)} \Gamma_{mn}^{(i)}(R) \,, \tag{4.25}$$

and the same relation is also valid for the $\{\psi_n^{(i)}\}$. Then

$$\begin{aligned} \sum_{n=1}^{l_i} \langle \xi | P_R \psi_n^{(i)} \rangle \langle P_R \phi_n^{(i)} | \eta \rangle &= \sum_{pqn} \langle \xi | \psi_p^{(i)} \rangle \langle \phi_q^{(i)} | \eta \rangle \Gamma_{pn}^{(i)*}(R) \Gamma_{qn}^{(i)}(R) \\ &= \sum_{pq} \langle \xi | \psi_p^{(i)} \rangle \langle \phi_q^{(i)} | \eta \rangle \sum_n \Gamma_{qn}^{(i)}(R) \Gamma_{np}^{(i)}(R^{-1}) \\ &= \sum_{p} \langle \xi | \psi_p^{(i)} \rangle \langle \phi_q^{(i)} | \eta \rangle \,, \end{aligned} \tag{4.26}$$

where we used the property $\Gamma^{(i)}(R)\Gamma^{(i)}(R^{-1}) = \Gamma^{(i)}(RR^{-1}) = I$.

Notice that for the proof, we didn't use the orthogonality theorem. Unsöld's theorem is therefore valid for infinite groups as well. This theorem plays a fundamental role in quantum mechanics, allowing us to construct operators that are invariant under the symmetry operations of the system under consideration.

Let us now consider a vector ϕ in a vector space. By applying the operator P_R associated with the transformations of the group G, we obtain a set of vectors $\{P_R\phi\}$. In general, these vectors are not linearly independent. They generate a subspace S of the vector space, in which we can define an orthonormal basis $\{\phi_k\}$. From this basis, we have seen how to construct the representation Γ of the group G related to this subspace. If the subspace S is the smallest subspace invariant under the transformations P_R, then the representation Γ is irreducible, and the vectors $\{\phi_k\}$, by definition, transform like the basis functions of this representation. If the subspace S can be further reduced into smaller invariant subspaces, we can perform the change of basis that accomplishes such a reduction. For the representation Γ, we have the general relation

$$\Gamma = b_1\Gamma^{(1)} \oplus b_1\Gamma^{(1)} \oplus \ldots \oplus b_{N_\Gamma}\Gamma^{(N_\Gamma)} . \tag{4.27}$$

We indicate the basis that reduces Γ by $\{\phi_k^{(i,j)}\}$ with $i = 1, \ldots, N_\Gamma$, $j = 1, \ldots, b_i$, and $k = 1, \ldots, l_i$, to emphasize that the vector $\phi_k^{(i,j)}$ transforms like the k-th basis function of the i-th irreducible representation. We can thus state the following theorem:

Theorem. A vector ϕ in a vector space closed under transformations P_R can be written as a linear combination of vectors $\{\psi_k^{(i)}\}$.

$$\phi = \sum_{i=1}^{N_\Gamma} \sum_{k=1}^{l_i} \psi_k^{(i)} . \tag{4.28}$$

Here, by $\psi_k^{(i)}$, we indicate a vector that transforms like the k-th basis function of the i-th irreducible representation of the group G.

Proof: We have already seen that the subspace, of which $\{\phi_k^{(i,j)}\}$ is a basis, is generated by the vector ϕ. Therefore, ϕ is a linear combination of these basis vectors.

$$\phi = \sum_{i=1}^{N_\Gamma} \sum_{k=1}^{l_i} \sum_{j=1}^{b_i} c_k^{(i,j)} \phi_k^{(i,j)} . \tag{4.29}$$

Since the basis is orthonormal, the coefficients $c_k^{(i,j)}$ are obtained as follows

$$\begin{aligned} \langle \phi_k^{(i,j)} | \phi \rangle &= \sum_{p=1}^{N_\Gamma} \sum_{m=1}^{l_p} \sum_{n=1}^{b_p} \langle \phi_k^{(i,j)} | \phi_m^{(p,n)} \rangle c_m^{(p,n)} \\ &= \sum_{p=1}^{N_\Gamma} \sum_{m=1}^{l_p} \sum_{n=1}^{b_p} \delta_{ip}\delta_{jn}\delta_{km} c_m^{(p,n)} \\ &= c_k^{(i,j)} \end{aligned} \tag{4.30}$$

Let's define

$$\psi_k^{(i)} = \sum_{j=1}^{b_i} c_k^{(i,j)} \phi_k^{(i,j)} , \tag{4.31}$$

and we finally obtain the expression (4.28).

So we can decompose any vector ϕ into the basis vectors of irreducible representations, provided we know these basis vectors for the subspace generated by the vector ϕ. Now, we will learn how to determine these basis vectors. Suppose we have found one, denoted by $\psi_k^{(i)}$. By applying the operations P_R, we generate the irreducible representation $\Gamma^{(i)}$, which means

$$P_R \psi_k^{(i)} = \sum_{n=1}^{l_i} \psi_n^{(i)} \Gamma_{nk}^{(i)}(R) . \tag{4.32}$$

Multiply both sides of this expression by $\Gamma^{(j)}_{n'k'}(R)$ and sum over the elements R of the group. By the great orthogonality theorem, we have

$$\begin{aligned}\sum_R \Gamma^{(j)}_{n'k'}(R) P_R \psi^{(i)}_k &= \sum_{n=1}^{l_i} \psi^{(i)}_n \sum_R \Gamma^{(j)}_{n'k'}(R)\Gamma^{(i)}_{nk}(R) \\ &= \frac{h}{l_i}\delta_{ij}\delta_{k'k}\psi^{(j)}_{n'} \,. \end{aligned} \tag{4.33}$$

Therefore, the operator

$$\Pi^{(j)}_{nk} = \frac{l_j}{h}\sum_R \Gamma^{(j)}_{nk}(R) P_R \tag{4.34}$$

applied to $\psi^{(j)}_m$ gives $\delta_{ij}\delta_{km}\psi^{(j)}_n$. It follows that if we know the matrices of the irreducible representations, then from just one of these basis vectors, say $\psi^{(j)}_k$, we can generate the others using the formula

$$\psi^{(j)}_n = \Pi^{(j)}_{nk}\psi^{(j)}_k \,. \tag{4.35}$$

The operators $\Pi^{(j)}_{nn}$, in particular, act as projectors on states that transform like the n-th basis function of the j-th irreducible representation.

We now know how to accomplish the two main tasks involving basis vectors of irreducible representations. First, suppose we need to find the decomposition (4.28) of any vector ϕ. This decomposition is obtained simply using projectors $\Pi^{(j)}_{nn}$ as follows

$$\begin{aligned}\phi &= \sum_{i=1}^{N_\Gamma}\sum_{k=1}^{l_i}\psi^{(i)}_k \,, \\ \psi^{(i)}_k &= \Pi^{(i)}_{kk}\phi \,. \end{aligned} \tag{4.36}$$

More generally, suppose we have decomposed a representation Γ defined in a vector space S into irreducible representations $\Gamma = \sum_{i=1}^{N_\Gamma} b_i\Gamma^{(i)}$. We want to find the basis vectors $\{\phi^{(i,j)}_k\}$ for this decomposition. To find, for example, the vectors $\phi^{(i,j)}_k$ for a given k and i and for $j = 1,\ldots,b_i$, it will be sufficient to arbitrarily choose a vector $\phi \in S$ (for example, from the vectors of any basis of S) and apply the projector $\Pi^{(i)}_{kk}$ to this vector. This procedure must be repeated until a set of b_i linearly independent vectors is obtained. By applying an orthonormalization procedure, we will have obtained the vectors $\phi^{(i,j)}_k$ for $j = 1,\ldots,b_i$. The vectors $\phi^{(i,j)}_n$ that transform like the other basis functions of $\Gamma^{(i)}$ can be obtained using the operators $\Pi^{(i)}_{nk}$ applied to the already found vectors. We now know how to systematically find the basis vectors of a decomposition into irreducible representations of a given representation.

To understand the utility of these recent developments, we recall that for a quantum system characterized by a Hamiltonian H, the basis of the Hilbert space that diagonalizes the Hamiltonian is a basis whose elements transform like the basis functions of the irreducible representations of the symmetry group of the system. Suppose the vector space in which we want to solve the Hamiltonian problem is of finite dimension. In quantum mechanics, this is generally not the case, since the Hilbert space of square-integrable wave functions is of infinite dimension. However, very often, to search for the eigenstates of the system, we restrict ourselves to subspaces of finite dimension. Let V be such a finite-dimensional space. For the formalism of group representation theory to be applicable, the basic assumption is that all symmetry operations of the system, P_R, are internal to the space V, which means that if $\phi \in V$, then $P_R\phi \in V$ for every P_R in the symmetry group. An example of such a finite-dimensional space is given by polynomials of degree n in the variables x, y, and z and the rotation operations. A rotation

is a linear transformation of the three variables x, y, and z, so the transformation applied to a function $\psi(x,y,z) = x^\alpha y^\beta z^\gamma$, with $\alpha+\beta+\gamma = n$, always results in a linear combination of monomials of the same degree n. A space of functions defined in this way is obviously of finite dimension.

In general, the space V generates a representation Γ of the symmetry group. This representation decomposes into irreducible representations as $\Gamma = b_1\Gamma^{(1)} \oplus b_2\Gamma^{(2)} \oplus \ldots \oplus b_{N_\Gamma}\Gamma^{(N_\Gamma)}$. We have already seen how to calculate the coefficients b_i using the characters. Let the basis (currently unknown) in which the Hamiltonian is diagonal be denoted by $\phi_k^{(i,j)}$, where $i = 1,\ldots,N_\Gamma$, $j = 1,\ldots,b_i$, and $k = 1,\ldots,l_i$. We seek this basis, and without the help of symmetries, we would have to diagonalize an eigenvalue problem of dimension $\sum_i b_i l_i$, the dimension of space V. The advantage of knowing how to classify states with respect to their symmetry properties, and therefore to say that such a state transforms like the k-th basis function of the i-th irreducible representation, allows us to significantly simplify the problem. Suppose we have a state $\psi_n^{(m)}$ that transforms like the n-th basis function of the m-th irreducible representation. In general, we can express this state in the chosen basis. We have

$$\psi_n^{(m)} = \sum_{i,j,k} c_k^{(i,j)} \phi_k^{(i,j)} \,, \tag{4.37}$$

where the coefficients $c_k^{(i,j)}$ are obtained from the inner products

$$c_k^{(i,j)} = \langle \phi_k^{(i,j)} | \psi_n^{(m)} \rangle \,. \tag{4.38}$$

But we know from the theorem on the orthogonality of basis functions of irreducible representations, equation (4.19), that in this expression, only the terms with $k = n$ and $i = m$ survive, with all others being zero. Therefore, the previous expansion is reduced to

$$\psi_n^{(m)} = \sum_{j=1}^{b_m} c_n^{(m,j)} \phi_n^{(m,j)} \,, \tag{4.39}$$

In other words, any vector that transforms like a given basis function of an irreducible representation is a linear combination exclusively of the basis vectors of the space with the same symmetry. This leads to a very important property. If we have two arbitrary vectors, $\psi_n^{(m)}$ and $\psi_k^{(j)}$, transforming as basis functions of the irreducible representations of the symmetry group of the system, suppose $k \neq n$ or $j \neq m$. The expansion (4.39) and the fact that the Hamiltonian is diagonal in the basis $\phi_k^{(i,j)}$ ensure that

$$\langle \psi_k^{(j)} | H | \psi_n^{(m)} \rangle = 0 \,. \tag{4.40}$$

This is a *selection rule* for the matrix elements of the Hamiltonian and, in effect, it's a partial diagonalization of the problem. It tells us that the Hamiltonian problem is restricted to each subspace of all states that transform like the same basis function of the same irreducible representation.

Consider, for example, the k-th basis function of the i-th irreducible representation. We can find a set of linearly independent vectors that generate this subspace, denoted as $S_k^{(i)}$, by applying the projector $(l_i/h)\sum_R \Gamma_{kk}^{(i)}(R) P_R$ to all elements of the initial space V (for example, to vectors from any basis of that space). The Hamiltonian operator has no nonzero matrix elements between vectors from $S_k^{(i)}$ and those in its orthogonal complement in V. We can diagonalize the Hamiltonian H in this subspace, which has a dimension of b_i. Therefore, we have reduced the dimension of the problem from $\sum_i b_i l_i$ to b_i without loss of generality. Furthermore, since the

degeneracy imposed by symmetry is necessary, the eigenvalues found in this subspace will be the same as those in other subspaces $S_m^{(i)}$ belonging to the same irreducible representation $\Gamma^{(i)}$.

The reduction of the vector space of a Hamiltonian problem is the first of the simplifications introduced by the theory of group representations. Another significant simplification is in the calculation of probability amplitudes, where we can systematically take advantage of the selection rules imposed by symmetry. We will discuss this in detail in the following paragraph.

4.2 Direct Product of Representations

We will now introduce the concept of a direct product of representations, an essential tool for constructing group representations and for applications in physics. Consider two vector spaces S_1 and S_2 with elements, respectively, $\{\xi_1, \eta_1, \zeta_1, \ldots\}$ and $\{\xi_2, \eta_2, \zeta_2, \ldots\}$. The direct product $S_1 \times S_2$ consists of all pairs composed of a vector from S_1 and a vector from S_2. Such pairs have the form $\{\xi_1, \eta_2\}$, which we simply denote as $\xi_1\eta_2$. This set is a vector space, provided we define addition and scalar multiplication in such a way that we have

$$(a_1\xi_1 + b_1\eta_1)(a_2\xi_2 + b_2\eta_2) = a_1a_2\xi_1\xi_2 + a_1b_2\xi_1\eta_2 + a_2b_1\eta_1\xi_2 + b_1b_2\eta_1\eta_2\,, \tag{4.41}$$

for arbitrary complex numbers a_1, a_2, b_1, b_2.

Suppose two linear transformations, A and B, respectively transform S_1 and S_2 into S_1' and S_2' as follows:

$$\begin{aligned} A:&\ \ \xi_1 \to \xi_1' = A\xi_1 \\ B:&\ \ \xi_2 \to \xi_2' = B\xi_2\,. \end{aligned} \tag{4.42}$$

We can define the direct product $A \times B$ of the two transformations as an application from $S_1 \times S_2$ to $S_1' \times S_2'$ that acts as follows

$$A \times B:\ \ \xi_1\xi_2 \to \xi_1'\xi_2' = (A \times B)(\xi_1\xi_2) = (A\xi_1)(B\xi_2)\,. \tag{4.43}$$

In most cases, we are interested in linear transformations from a space S to the same space S. We will consider applications A from S_1 to S_1 and applications B from S_2 to S_2. Let $\{\phi_i\}$ and $\{\psi_j\}$ be two orthonormal bases of vector spaces S_1 and S_2, respectively. We can write the transformations A and B in these bases as follows:

$$\begin{aligned} A\phi_i &= \sum_m \phi_m A_{mi} \\ B\psi_j &= \sum_n \psi_n B_{nj}\,. \end{aligned}$$

The direct product $A \times B$ in the basis $\{\phi_i\psi_j\}$ of $S_1 \times S_2$ takes the form

$$(A \times B)\phi_i\psi_j = (A\phi_i)(B\psi_j) = \sum_{mn} \phi_m\psi_j A_{mi}B_{nj}\,. \tag{4.44}$$

It follows that the application $A \times B$ is characterized by a matrix representation

$$(A \times B)_{mn;ij} = A_{mi}B_{nj}\,. \tag{4.45}$$

In this expression, $A \times B$ is a $l_1l_2 \times l_1l_2$ matrix, where l_1 and l_2 are the dimensions of S_1 and S_2, respectively. Note that the rows and columns of this matrix are now indicated by two indices instead of one: in the notation $(A \times B)_{mn;ij}$, the terms mn and ij denote pairs of indices, not products.

The trace of the matrix $A \times B$ is

$$\chi(A \times B) = \sum_{ij} (A \times B)_{ij;ij} = \sum_i A_{ii} \sum_j B_{jj} = \chi(A)\chi(B)\,. \tag{4.46}$$

So, the trace of a direct product of linear transformations is equal to the product of their traces. If we have two transformations, A and A', from S_1 to S_1, and two other transformations, B and B', from S_2 to S_2, then the direct product of transformations AA' and BB' is simply written as

$$(AA')(BB') = (A \times B)(A' \times B')\,. \tag{4.47}$$

The proof is very straightforward:

$$\begin{aligned} [(AA')(BB')]_{mn;ij} &= (AA')_{mi}(BB')_{nj} \\ &= \textstyle\sum_{p=1}^{l_1} A_{mp}A'_{pi} \sum_{q=1}^{l_2} B_{nq}B'_{qj} \\ &= \textstyle\sum_{pq} (A \times B)_{mn;pq}(A' \times B')_{pq;ij} \end{aligned} \tag{4.48}$$

Direct products allow us to construct new representations of a group from known representations. Consider a group $H = \{e, x, y, \ldots\}$ and two representations of this group, Γ and Γ', defined in the subspaces S and S', with bases $\{\phi_i\}$ and $\{\phi'_i\}$, respectively. The dimensions of the subspaces are l and l', respectively. We have

$$\begin{aligned} \Gamma(x)\phi_i &= \sum_{m=1}^{l} \phi_m \Gamma_{mi}(x) \\ \Gamma'(x)\phi'_j &= \sum_{n=1}^{l'} \phi'_n \Gamma'_{nj}(x)\,. \end{aligned}$$

This allows us to define the direct product representation $\Gamma \times \Gamma'$ as follows:

$$\begin{aligned} (\Gamma(x) \times \Gamma'(x))(\phi_i\phi'_j) &= \sum_{m=1}^{l} \sum_{n=1}^{l'} \phi_m\phi'_n \Gamma_{mi}(x)\Gamma'_{nj}(x) \\ &= \sum_{m,n} \phi_m\phi'_n (\Gamma(x) \times \Gamma'(x))_{mn;ij}\,. \end{aligned} \tag{4.49}$$

The direct product of the transformations $\Gamma(x) \times \Gamma'(x)$ forms a representation of the group H with a dimension of $l \times l'$. Indeed, the group's composition law is satisfied by the matrices of the product representation, as we can verify:

$$\begin{aligned} (\Gamma(x) \times \Gamma'(x))(\Gamma(y) \times \Gamma'(y)) &= (\Gamma(x)\Gamma(y)) \times (\Gamma'(x)\Gamma'(y)) \\ &= \Gamma(xy) \times \Gamma'(xy)\,. \end{aligned} \tag{4.50}$$

The character of this representation is given by the product of the characters, as in (4.46):

$$\chi^{\Gamma\times\Gamma'}(x) = \chi^{\Gamma}(x)\chi^{\Gamma'}(x)\,. \tag{4.51}$$

In general, the representation obtained by the direct product of two irreducible representations is reducible. Let's take, for example, the representation $\Gamma_3 \times \Gamma_3$ of C_{3v}. Its character is

$$\begin{aligned} \chi^{\Gamma_3\times\Gamma_3}(E) &= 4 \\ \chi^{\Gamma_3\times\Gamma_3}(2C_3) &= 1 \\ \chi^{\Gamma_3\times\Gamma_3}(3\sigma) &= 0 \end{aligned}$$

Using equation (3.61), we have

$$\Gamma_3 \times \Gamma_3 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3\,. \tag{4.52}$$

4.3 Selection Rules

We will now study the constraints imposed by symmetry on probability amplitudes in quantum mechanics.

From time-dependent perturbation theory in quantum mechanics, we know that for a system in a state $|\psi\rangle$ at time t_0, the probability that it is in a state $|\phi\rangle$ at time $t > t_0$ is related to a quantity called the "probability amplitude." This quantity is expressed as the "matrix element":

$$\langle\phi|V(t)|\psi\rangle\,, \tag{4.53}$$

where $V(t)$ is the Hamiltonian operator of the physical perturbation inducing the transition between the two states. For example, for a transition induced by an electromagnetic field $E(t) = E_0\exp(-i\omega t)$ with a long wavelength, this operator is the electric dipole operator: $V(t) = \sum_i E_0 q_i \mathbf{r}_i \exp(-i\omega t)$, where the sum is over all charged particles in the system, $\mathbf{r}_i$ are their positions, and q_i are their charges. In general, for a complex system, one needs to calculate these matrix elements for several pairs of states, and it turns out that, for symmetry reasons, most of these quantities are zero. It is very useful to establish "selection rules" that tell us when a probability amplitude is zero without having to calculate it explicitly.

Let's consider the operator V that describes, for example, a perturbation on a quantum system. This operator, in general, can be written as a sum of operators $V_m^{(i)}$ that transform like the m-th basis function of the i-th irreducible representation of the system's symmetry group. For example, the dipole operator mentioned above has the symmetry of a position vector. For a system with C_{3v} symmetry, we know that the z component of this vector transforms as the identity representation, while the two components x and y transform as the two basis functions of the irreducible representation Γ_3. Suppose we want to calculate the matrix elements of these components $V_m^{(i)}$ between states $\phi_n^{(j)}$ $(n = 1, 2, \ldots, l_j)$ and $\psi_p^{(k)}$ $(p = 1, 2, \ldots, l_k)$, which are also classified according to the irreducible representations of the symmetry group. We want to calculate the matrix elements:

$$\langle\phi_n^{(j)}|V_m^{(i)}|\psi_p^{(k)}\rangle\,. \tag{4.54}$$

We have seen that the vectors $V_m^{(i)}|\psi_p^{(k)}\rangle$ generate the $l_i\times l_k$-dimensional representation $\Gamma^{(i)}\times\Gamma^{(k)}$ of the symmetry group. We can decompose this representation into irreducible representations:

$$\Gamma^{(i)}\times\Gamma^{(k)} = \sum_{p=1}^{N_\Gamma} b_p\Gamma^{(p)}\,, \tag{4.55}$$

where b_p is the number of times the representation $\Gamma^{(p)}$ appears in the reduction. The theorem (4.28) tells us that the vector $V_m^{(i)}|\psi_p^{(k)}\rangle$ can be written as:

$$V_m^{(i)}|\psi_p^{(k)}\rangle = \sum_{p=1}^{N_\Gamma}\sum_{q=1}^{l_p}|\xi_q^{(p)}\rangle\,, \tag{4.56}$$

where the vectors $|\xi_q^{(p)}\rangle$ are linear combinations of eigenstates of the Hamiltonian, as we saw in equation (4.39):

$$|\xi_q^{(p)}\rangle = \sum_{r=1}^{b_p} c_q^{(p,r)}|\xi_q^{(p,r)}\rangle\,. \tag{4.57}$$

Replacing this decomposition in the matrix element expression, we get:

$$\langle\phi_n^{(j)}|V_m^{(i)}|\psi_p^{(k)}\rangle = \sum_{p=1}^{N_\Gamma}\sum_{q=1}^{l_p}\sum_{r=1}^{b_p} c_q^{(p,r)}\langle\phi_n^{(j)}|\xi_q^{(p,r)}\rangle\,. \tag{4.58}$$

We can now apply theorem (4.19), which ensures that most of the dot products in this expression are zero. Only dot products between vectors that transform like the same basis function of the same irreducible representation are different from zero. Therefore, we obtain:

$$\langle \phi_n^{(j)} | V_m^{(i)} | \psi_p^{(k)} \rangle = \sum_{r=1}^{b_j} c_n^{(j,r)} \langle \phi_n^{(j)} | \xi_n^{(j,r)} \rangle \,. \tag{4.59}$$

Furthermore, the same theorem tells us that the number of independent constants of the form $\langle \phi_n^{(j)} | \xi_n^{(j,r)} \rangle$ is equal to b_j. It follows that to calculate the $l_i \times l_j \times l_k$ matrix elements of the form $\langle \phi_n^{(j)} | V_m^{(i)} | \psi_p^{(k)} \rangle$, it is sufficient to calculate the quantities $\langle \phi_n^{(j)} | \xi_n^{(j,r)} \rangle$, the number of which is only b_j. This constitutes a significant simplification of the problem.

For example, consider the ground electronic state $\psi^{(1)}$ of the ammonia molecule. We know that this state is totally symmetric and thus belongs to the Γ_1 representation of the symmetry group C_{3v}. Now, consider a dipole-order induced transition by the electromagnetic field to a higher energy state $\psi^{(2)}$ that transforms like the Γ_2 representation. The dipole operator $\mathbf{d} = (d_x, d_y, d_z)$ is a three-dimensional vector, and its components are operators that transform like the components of a vector in Cartesian space. For a system with C_{3v} symmetry, such a vector decomposes into the component d_z, which belongs to the Γ_1 representation, and the two components (d_x, d_y), which transform like the basis functions of Γ_3. The matrix element $\langle \psi^{(2)} | \mathbf{d} | \psi^{(1)} \rangle$ is therefore given by a constant $\langle \psi^{(2)} | \xi^{(2)} \rangle$, where $|\xi^{(2)}\rangle$ is a vector that transforms like Γ_2 and appears in the decomposition of $\mathbf{d}|\psi^{(1)}\rangle$. However, we know that $\mathbf{d}|\psi^{(1)}\rangle$ belongs to the representation $(\Gamma_1 \oplus \Gamma_3) \times \Gamma_1 = \Gamma_1 \oplus \Gamma_3$. No component of this vector will have symmetry Γ_2, and the matrix element we seek is zero. Such a transition is said to be forbidden at the dipole order. This selection rule has been derived solely by the application of group theory and demonstrates the scope of this method.

Chapter 5

The Orthogonal Group and Point Groups

In this chapter, we will describe the properties of the group of rotations and rotation-inversions in three dimensions. We will then derive the finite subgroups known as the *crystallographic point groups* that represent the rotational symmetries of crystals and molecules.

5.1 The Orthogonal Group in Three Dimensions

The orthogonal group consists of all linear transformations of a vector in three dimensions that preserve the norm of the vector. Before discussing this group in detail, let's establish the nomenclature that will be used later. Consider linear transformations of vectors of the form $\xi = (x_1, x_2, \ldots, x_n) \in \mathbb{C}^n$, where $x_1, x_2, \ldots, x_n$ are complex numbers. A linear transformation A takes the form:

$$\xi \to \xi' = A\xi\,, \tag{5.1}$$

where the components of ξ' are:

$$x_i' = \sum_j A_{ij} x_j\,. \tag{5.2}$$

So, A is represented by an $n \times n$ matrix $A = (A_{ij})$. The set of all non-singular $n \times n$ matrices (i.e., those for which inverses are defined) obviously forms a group called the *general linear group* in n dimensions, denoted as $GL(n)$. The *special linear group* $SL(n)$ is the subgroup of $GL(n)$ that contains matrices with a determinant equal to 1.

The unitary group in n dimensions, denoted as $U(n)$, is composed of all matrices U such that:

$$\langle U\xi | U\xi \rangle = \langle \xi | \xi \rangle \tag{5.3}$$

for each $\xi \in \mathbb{C}^n$. By applying this definition to the vectors $\xi + \eta$ and $\xi + i\eta$, we can deduce that, for arbitrary ξ and η, we have:

$$\langle U\xi | U\eta \rangle = \langle \xi | \eta \rangle \tag{5.4}$$

and, therefore, $U^\dagger U = I$, the identity matrix. It follows that the determinant of U is a complex number with a unit modulus, and:

$$U^\dagger = U^{-1}\,. \tag{5.5}$$

The *special unitary group* $SU(n)$ is the subgroup of $U(n)$ that contains all matrices with a determinant equal to 1.

The orthogonal group in n dimensions $O(n)$ is defined like $U(n)$, but it contains linear transformations of real vectors in n dimensions in the space $\mathbb{R}^n$. Therefore, $O(n)$ contains non-singular matrices with real components. If R is an element of $O(n)$, then the components of $\xi' = R\xi$ are:

$$x_i' = \sum_j R_{ij} x_j \,. \tag{5.6}$$

In this case, the invariance of the vector's norm implies:

$$\sum_i (x_i')^2 = \sum_{jk} \sum_i R_{ij} R_{ik} x_j x_k = \sum_j x_j^2 \,, \tag{5.7}$$

for each vector $\xi = (x_1, x_2, \ldots, x_n)$. It is, therefore, necessary that:

$$R_{ij} R_{ik} = \delta_{jk} \tag{5.8}$$

or:

$$R^t R = I \,. \tag{5.9}$$

It follows that the determinant of R can only take the values ± 1 and:

$$R^{-1} = R^t \,. \tag{5.10}$$

A matrix that satisfies such a condition is called an orthogonal matrix. The *special orthogonal group* $SO(n)$ is the subgroup of $O(n)$ composed of matrices with a determinant equal to 1.

We can now discuss the orthogonal group in three dimensions $O(3)$. Consider three orthonormal vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$, and $\hat{\mathbf{e}}_3$ in three-dimensional space. Orthogonality implies:

$$\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j = \delta_{ij} \,. \tag{5.11}$$

The vectors are oriented according to the right-hand rule, that is:

$$\hat{\mathbf{e}}_1 \cdot (\hat{\mathbf{e}}_2 \times \hat{\mathbf{e}}_3) = 1 \,. \tag{5.12}$$

An orthogonal transformation $R \in O(3)$ preserves the norm of all vectors and, therefore, the angles between vectors. In fact, consider the vector $\mathbf{x} + \mathbf{y}$. Since its norm is conserved, we have:

$$|R(\mathbf{x} + \mathbf{y})|^2 = |R\mathbf{x} + R\mathbf{y}|^2 = |\mathbf{x} + \mathbf{y}|^2 \,. \tag{5.13}$$

This is true for arbitrary $\mathbf{x}$ and $\mathbf{y}$, which necessarily implies:

$$(R\mathbf{x}) \cdot (R\mathbf{y}) = \mathbf{x} \cdot \mathbf{y} \,, \tag{5.14}$$

leading to the preservation of the angle between the two vectors. Therefore, by defining:

$$\hat{\mathbf{e}}_i' = R\hat{\mathbf{e}}_i \,, \tag{5.15}$$

We find that the three vectors $\hat{\mathbf{e}}_1'$, $\hat{\mathbf{e}}_2'$, and $\hat{\mathbf{e}}_3'$, like the old $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$, and $\hat{\mathbf{e}}_3$, are orthonormal. We can express an arbitrary vector in the basis formed by the three vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$, and $\hat{\mathbf{e}}_3$:

$$\mathbf{x} = \sum_{i=1}^{3} x_i \hat{\mathbf{e}}_i \,. \tag{5.16}$$

The transformed vector becomes:

$$\mathbf{x}' = R\mathbf{x} = \sum_{i=1}^{3} x_i \hat{\mathbf{e}}_i' \,. \tag{5.17}$$

The components of $\mathbf{x}'$ in the new basis $\hat{\mathbf{e}}'_1$, $\hat{\mathbf{e}}'_2$, and $\hat{\mathbf{e}}'_3$ are the same as those of $\mathbf{x}$ in the old basis. We seek the components of the transformed vector $\mathbf{x}'$ with respect to the old basis. They are given by the dot products of the vector with the three basis vectors:

$$x'_i = \mathbf{x}' \cdot \hat{\mathbf{e}}_i = \sum_{j=1}^{3} x_j \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}'_j = \sum_{j=1}^{3} R_{ij} x_j \,, \tag{5.18}$$

which establishes the law of transformation of components. For the last equality, we used the relation:

$$R_{ij} = \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}'_j \,, \tag{5.19}$$

which easily follows from the definition (5.15). The transformation law of the basis vectors is also immediately derived from (5.15):

$$\hat{\mathbf{e}}'_i = \sum_{j=1}^{3} \hat{\mathbf{e}}_j R_{ji} \,. \tag{5.20}$$

Let's now calculate the product $\hat{\mathbf{e}}'_1 \cdot (\hat{\mathbf{e}}'_2 \times \hat{\mathbf{e}}'_3)$:

$$\begin{aligned} \hat{\mathbf{e}}'_1 \cdot (\hat{\mathbf{e}}'_2 \times \hat{\mathbf{e}}'_3) &= \sum_{ijk} R_{i1} R_{j2} R_{k3} \hat{\mathbf{e}}_i \cdot (\hat{\mathbf{e}}_j \times \hat{\mathbf{e}}_k) \\ &= \sum_{ijk} \epsilon_{ijk} R_{i1} R_{j2} R_{k3} \\ &= \det(R) \,, \end{aligned} \tag{5.21}$$

where we introduced the Levi-Civita tensor ϵ_{ijk}, which is equal to 1 if (i, j, k) is an even permutation of $(1, 2, 3)$, -1 if the permutation is odd, and zero otherwise. We have shown that the vectors $\hat{\mathbf{e}}'_1$, $\hat{\mathbf{e}}'_2$, and $\hat{\mathbf{e}}'_3$ are ordered according to the right-hand or left-hand rule, depending on whether the determinant of R is 1 or -1. In particular, the inversion operator:

$$i: \quad \mathbf{x} \to \mathbf{x}' = -\mathbf{x} \,, \tag{5.22}$$

represented by the matrix

$$R_i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} , \tag{5.23}$$

having a determinant equal to -1 transforms a right-handed oriented basis into a left-handed one. Given a transformation $R \in O(3)$, two cases are possible: (i) $\det(R) = +1$, and thus R is also an element of $SO(3)$. (ii) $\det(R) = -1$, and therefore, R is given by an element of $SO(3)$ multiplied by R_i.

Now, consider rotations about a fixed point. These rotations form a group. This group is isomorphic to $SO(3)$. To demonstrate this, we need to show that each rotation is represented by an element of $SO(3)$ and that for each orthogonal matrix in $SO(3)$, there corresponds to a rotation. A rotation of an angle ϕ around an axis parallel to the unit vector $\hat{\mathbf{e}}$ passing through the origin O transforms the vector $\mathbf{x}$ into the vector $\mathbf{x}'$ given by:

$$\mathbf{x}' = \mathbf{x} \cos\phi + \hat{\mathbf{e}}(\mathbf{x} \cdot \hat{\mathbf{e}})(1 - \cos\phi) + (\hat{\mathbf{e}} \times \mathbf{x}) \sin\phi \,. \tag{5.24}$$

This expression can be easily deduced from a graphical representation like the one shown in Figure 5.1. This transformation is clearly linear and of the form (5.18) with components:

$$R_{ij}(\phi) = \delta_{ij} \cos\phi + e_i e_j (1 - \cos\phi) - \sum_k \epsilon_{ijk} e_k \sin\phi \,. \tag{5.25}$$

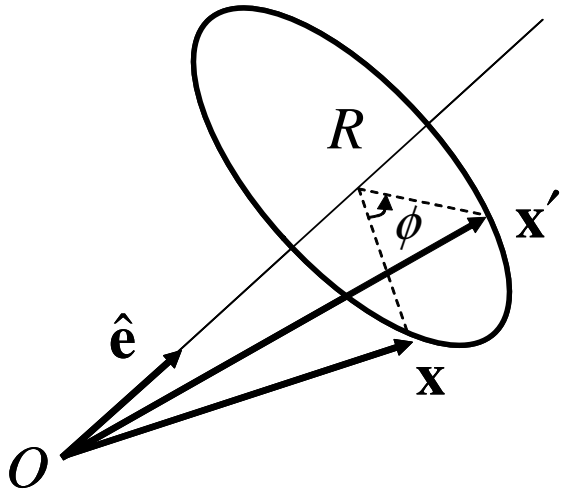

Figure 5.1: Diagram of a rotation by an angle ϕ of a vector $\mathbf{x}$.

The elements $R_{ij}(\phi)$ form an orthogonal matrix since $R_{ij}(\phi) = R_{ji}(-\phi)$, and thus, the inverse matrix is equal to the transposed matrix. Its determinant is equal to 1. We can demonstrate this as follows. For $\phi = 0$, we clearly have $\det(R(0)) = 1$. Moreover, $\det(R(\phi))$ is a continuous function of the variable ϕ. If there exists an angle for which $\det(R(\phi)) = -1$, then by continuity, the function $\det(R(\phi))$ must take all values between 1 and -1. This is impossible since the determinant of an orthogonal matrix can only take the two values ± 1.

We have yet to prove that all elements of $SO(3)$ represent rotations. Let $R \in SO(3)$. We first show that there exists at least one direction $\hat{\mathbf{e}}_3$ invariant under R, meaning

$$R\hat{\mathbf{e}}_3 = \hat{\mathbf{e}}_3 \,. \tag{5.26}$$

To prove this, consider the eigenvalue problem

$$R\mathbf{x} = \lambda\mathbf{x} \,. \tag{5.27}$$

The eigenvalues λ are solutions to the secular equation

$$\det(R - \lambda I) = 0 \,. \tag{5.28}$$

Since this is a third-degree equation with real coefficients in λ, it has at least one real solution. Let λ_3 be this solution, and $\hat{\mathbf{e}}_3$ the corresponding eigenvector. Since R is an orthogonal matrix, we have

$$(R\hat{\mathbf{e}}_3) \cdot (R\hat{\mathbf{e}}_3) = \lambda_3^2 \hat{\mathbf{e}}_3 \cdot \hat{\mathbf{e}}_3 = 1 \,, \tag{5.29}$$

implying $\lambda_3 = \pm 1$. The product of the three solutions $\lambda_1\lambda_2\lambda_3$ is the determinant of the matrix and must be equal to 1. If λ_1 and λ_2 are real, then they must be equal to 1 or -1. Two cases are possible: (i) $\lambda_1 = \lambda_2 = \pm 1$ and $\lambda_3 = 1$; (ii) $\lambda_1 = -\lambda_2 = \pm 1$ and $\lambda_3 = -1$. In both cases, we have found an eigenvalue equal to $+1$. If, on the other hand, λ_1 and λ_2 are complex, then we must have $\lambda_2 = \lambda_1^*$ for the determinant to be real. In this latter case, the determinant condition gives $|\lambda_1|^2\lambda_3 = 1$, implying $\lambda_3 = +1$. Therefore, the existence of the invariant direction $\hat{\mathbf{e}}_3$ is proved. We now choose two unit vectors $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$, orthogonal to each other and both orthogonal to $\hat{\mathbf{e}}_3$, oriented according to the right-hand rule. The three vectors $R\hat{\mathbf{e}}_1$, $R\hat{\mathbf{e}}_2$, and $R\hat{\mathbf{e}}_3 = \hat{\mathbf{e}}_3$ are also oriented according to the right-hand rule, and the first two lie in the plane defined by $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$. Let ϕ be the angle between $\hat{\mathbf{e}}_1$ and $R\hat{\mathbf{e}}_1$ (which is also the angle between $\hat{\mathbf{e}}_2$ and $R\hat{\mathbf{e}}_2$, due

to the orthogonality of the matrix). The angles formed by $\hat{\mathbf{e}}_1$ and $R\hat{\mathbf{e}}_2$, and by $\hat{\mathbf{e}}_2$ and $R\hat{\mathbf{e}}_1$, are $\phi \pm \pi/2$. It follows that

$$\begin{aligned} R\hat{\mathbf{e}}_1 &= \hat{\mathbf{e}}_1 \cos\phi + \hat{\mathbf{e}}_2 \sin\phi \\ R\hat{\mathbf{e}}_2 &= -\hat{\mathbf{e}}_1 \sin\phi + \hat{\mathbf{e}}_2 \cos\phi \,. \end{aligned} \tag{5.30}$$

The matrix R thus represents a rotation by an angle ϕ around $\hat{\mathbf{e}}_3$. This proves the isomorphism between $SO(3)$ and the group of proper rotations in three dimensions.

The elements of the matrix $R_{lm}(\phi)$ [Eq. (5.25] can be expressed in terms of three Hermitian matrices.

$$\begin{aligned} J_1 &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \\ J_2 &= \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \\ J_3 &= \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \end{aligned} \tag{5.31}$$

These matrices obey the commutation laws

$$\begin{aligned} [J_l, J_m] &= J_l J_m - J_m J_l \\ &= i \sum_k \epsilon_{lmk} I_k \,. \end{aligned} \tag{5.32}$$

The element lm of the matrix

$$\mathbf{J} \cdot \hat{e} = \sum_{k=1}^{3} J_k e_k \tag{5.33}$$

is given by

$$(\mathbf{J} \cdot \hat{e})_{lm} = -i \sum_k \epsilon_{lmk} \,. \tag{5.34}$$

Here we have formally defined a vector $\mathbf{J} = \{J_1, J_2, J_3\}$, where its components are the three matrices defined in (5.31). This definition allows us to write linear combinations of these matrices in a compact form, such as the expression (5.33). From (5.34), we deduce that

$$\begin{aligned} (\mathbf{J} \cdot \hat{e})^2_{lm} &= -\sum_{n,k,p} \epsilon_{lnk} e_k \epsilon_{nmp} e_p \\ &= -\sum_{n,k,p} \epsilon_{kln} e_k \epsilon_{mpn} e_p \\ &= \sum_{k,p} (\delta_{kp}\delta_{lm} - \delta_{km}\delta_{lp}) e_k e_p \\ &= \delta_{lm} - e_l e_m \,, \end{aligned} \tag{5.35}$$

where we have used the properties of the Ritchie tensor ϵ_{ijk}, and

$$(\mathbf{J} \cdot \hat{e})^3 = \mathbf{J} \cdot \hat{e} \,. \tag{5.36}$$

These last two results allow us to write the matrix, whose elements are given by (5.25), in the following form

$$\begin{aligned} R_{\hat{e}}(\phi) &= I - i\mathbf{I}\cdot\hat{e}\sin(\phi) - (\mathbf{I}\cdot\hat{e})^2(1-\cos(\phi)) \\ &= \exp(-i\phi\mathbf{J}\cdot\hat{e})\,, \end{aligned} \tag{5.37}$$

, where we have used the Taylor series expansion of the exponential function. This expression in terms of an exponential function allows us to call the matrices J_1, J_2, J_3 the generators of rotations in three dimensions.

5.2 Subgroups of $O(3)$

Transformations of the orthogonal group are often denoted by special symbols. The two commonly used notations are Schönflies notation and international notation.

In Schönflies notation, the following symbols are used:

(i) C_n indicates a rotation by an angle of $2\pi/n$. If the rotation axis is not clear from the context, it should be specified. If not specified, it's normally assumed to be the **z**-axis.

(ii) i indicates inversion with respect to the origin: $\mathbf{x} \to \mathbf{x}' = -\mathbf{x}$.

(iii) σ indicates a mirror reflection across a plane. Often, several types of mirrors are distinguished, depending on their relation to the other symmetry elements of the object of interest. A mirror whose plane contains the axis of highest symmetry is called a "vertical" mirror and is denoted by σ_v. A mirror whose plane is orthogonal to the axis of highest symmetry is called a "horizontal" mirror and is denoted by σ_h. Finally, a mirror whose plane contains the axis of highest symmetry and at the same time bisects two orthogonal C_2 axes to the axis of highest symmetry is called a "dihedral" mirror and is denoted by σ_d.

(iv) S_n indicates an improper rotation by an angle of $2\pi/n$. It is a rotation of $2\pi/n$ about an axis $\hat{\mathbf{e}}$, followed by a mirror whose plane is orthogonal to $\hat{\mathbf{e}}$. So,

$$S_n = \sigma_h C_n = C_n \sigma_h\,, \tag{5.38}$$

since these two operations commute. It's worth noting that $i = S_2$.

In international notation (which we won't use but is often found in the literature), the operation C_n is simply indicated by the symbol n, "*and a mirror by* m." A rotation-inversion operation of the form iC_n in Schönflies notation is denoted as $\bar{n}$. So, $i = \bar{1}$. A system that has a principal axis of symmetry $\hat{\mathbf{e}}$ with symmetry C_n and orthogonal C_2 axes to $\hat{\mathbf{e}}$ is indicated as $n2$. The combinations (C_n, σ_h) and (C_n, σ_v) are denoted as $\frac{n}{m}$"*and*nm," respectively.

We will now state the commutation rules between transformations belonging to $O(3)$ and the theorems of membership in conjugacy classes. These properties will be useful for the study of irreducible representations of rotation groups and can be easily derived from (5.37).

Theorem. The only pairs R_1, R_2 of operations belonging to $O(3)$ such that $R_1R_2 = R_2R_1$ are:

- Two rotations about the same axis.
- Two mirrors σ with respect to orthogonal planes.
- Two rotations of π (180 degrees) about orthogonal axes.

- One rotation and one mirror σ with respect to the plane orthogonal to the axis of rotation.
- Inversion i and any element of $O(3)$.

It should be noted that these rules are valid only for rotations applied to position functions $\mathbf{x}$ as well as vector or tensor fields. We will see later that they do not apply to spinors, which are vectors in the Hilbert space that describe the spin degree of freedom of a quantum system.

Theorem. Let G be a rotation group. Two rotations $R(\phi, \hat{e})$ and $R(\phi', \hat{e}')$ are in the same conjugacy class if $\phi = \phi'$ and there exists a rotation $R(\theta, \hat{n}) \in G$ such that $\hat{e}' = R(-\theta, \hat{n})\hat{e}$.

Corollary. Let G be a rotation group. Two rotations $R(\phi, \hat{e})$ and $R(-\phi, \hat{e})$ are in the same conjugacy class if there exists a rotation $R(\theta, \hat{n}) \in G$ such that $-\hat{e} = R(-\theta, \hat{n})\hat{e}$.

Corollary. Let $G = SO(3)$. All rotations $R(\phi, \hat{e})$, for a given ϕ and arbitrary $\hat{e}$, are in the same conjugacy class. Similarly, the rotations $R(-\phi, \hat{e}) = R(\phi, -\hat{e})$ are in the same class. We can summarize this property by saying that all rotations with the same $|\phi|$ belong to the same class.

We may now describe the principal finite groups that intervene in solid and molecular physics.

Cyclic Groups C_n. These are cyclic groups generated by a rotation of $2\pi/n$ about a given axis. They have the form

$$\{E,\ C_n,\ C_n^2, \ldots,\ C_n^{n-1}\}$$

where, of course, $E = C_n^n$ is the identity operator. They are indicated by C_n, which is the same symbol used to denote a rotation operation of $2\pi/n$. So, one must be careful, but most of the time, the distinction can be deduced from the context. In Schoenflies notation, these groups are simply indicated by n (which creates even more confusion!).

Groups C_{nv}. These are groups that contain the operations C_n and n vertical mirrors σ_v with respect to vertical planes that contain the rotation axis. They have the form

$$\{E,\ C_n,\ C_n^2, \ldots,\ C_n^{n-1},\ \sigma_{v1}, \ldots, \sigma_{vn}\}$$

It is clear that the composition of a mirror σ_{vj} with a rotation C_n^l results in another mirror σ_{vk}. The group C_{3v} frequently used in these notes as an example belongs to this category.

Groups C_{nh}. These groups are generated by a rotation C_n and a horizontal mirror σ_h with respect to a plane orthogonal to the C_n axis. Note that these groups contain not only operations C_n^l and σ_h since the composition of these two types of operations leads to improper rotations S_m. For example, $S_2 = \sigma_h C_2 = C_2\sigma_h = i$. This implies that for even n, inversion i is contained in C_{nh}.

Improper Rotation Groups S_n. These groups are generated by an improper rotation S_n. Again, one must distinguish between the group and the operation, both unfortunately indicated by the same symbol. Since $S_n = \sigma_h C_n = C_n\sigma_h$, then $S_n^2 = C_n^2$, $S_n^n = E$ for even n, and $S_n^n = \sigma_h$ for odd n. So, one must be careful because, for odd n, the groups S_n coincide with the groups C_{nh} since they contain $\sigma_h = S_n^n$ and $C_n = \sigma_h S_n$. However, for even n, S_n is not the same group as C_{nh}, but it contains the cyclic group $C_{(n/2)}$ as a subgroup.

Dihedral Groups D_n. These groups are generated by a principal rotation C_n about a given axis and n rotations C_2 about axes orthogonal to the principal axis of rotation C_n. We can better understand the nature of these groups by noting that they represent the groups of proper symmetries (proper rotations) of regular polygons with n sides in three dimensions.

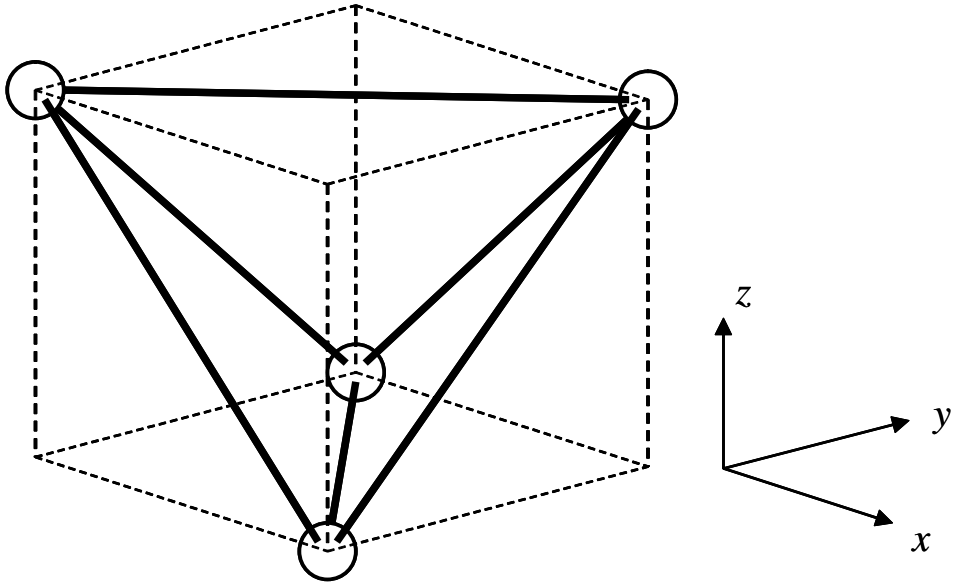

Figure 5.2: Diagram of a tetrahedral.

Dihedral Groups with Dihedral Mirrors D_{nd}. These groups consist of the elements of D_n plus n dihedral mirrors σ_d. Recall that a mirror is dihedral when the mirror plane bisects the angle between two adjacent C_2 operations. The groups D_{nd} are the symmetry groups (including improper rotations) of regular polygons with n sides in three dimensions.

Dihedral Groups with Horizontal Mirrors D_{nh}. These groups consist of the elements of D_n plus a horizontal mirror σ_h.

Cubic Groups. There are five so-called cubic groups. These groups are of fundamental importance in solid-state physics, as many crystalline solids have one of these groups as their point symmetry group of rotations. Let's start with the T group. It represents the proper rotational symmetry group of a tetrahedron about its geometric center. The tetrahedron is shown in Figure 5.2. We can see that it is inscribed in a cube, which explains the name of this category of groups.

We can imagine that the vertices of the tetrahedron represent four atoms constituting the fundamental cell of a crystal (e.g., diamond). The six edges of the tetrahedron are the diagonals of the faces of the cube. The rotations that leave the tetrahedron invariant include the identity E, four rotations of $2\pi/3$ about the axes $\hat{e}_1 = 3^{-1/2}(\hat{x}+\hat{y}+\hat{z})$, $\hat{e}_2 = 3^{-1/2}(\hat{x}-\hat{y}-\hat{z})$, $\hat{e}_3 = 3^{-1/2}(-\hat{x}+\hat{y}-\hat{z})$, and $\hat{e}_4 = 3^{-1/2}(-\hat{x}-\hat{y}+\hat{z})$; the inverses of these four rotations, which also correspond to rotations of $4\pi/3$; and three rotations of π about the axes $\hat{x}$, $\hat{y}$, and $\hat{z}$. Typically, this group is denoted as:

$$T = \{E,\ 4C_3,\ 4C_3^2,\ 3C^2\},$$

where we have highlighted the class structure. The second cubic group is T_h. It is generated by the elements of T plus inversion i. Its structure is:

$$T_h = \{E,\ 4C_3,\ 4C_3^2,\ 3C_2,\ i,\ 4S_6^{-1},\ 4S^6,\ 3\sigma_h\},$$

where $S_6^{-1} = iC_3$, $S_6 = iC_3^2$, and $\sigma_h = iC_2$. Note that the tetrahedron is not invariant under all operations of T_h. On the other hand, the group T_d is the group of symmetries, both proper and

improper, of the tetrahedron and describes the symmetry of many crystalline solids. It contains the elements of T plus six dihedral mirror planes bisecting the $(\hat{y},\hat{z})$, $(\hat{z},\hat{x})$, and $(\hat{x},\hat{y})$ planes, respectively, and six improper rotations S_4 about the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes. These new operations form the $6\sigma_d$ and $6S_4$ classes. Since these new operations can change the sign of the $\hat{e}_j$ axes, $(j = 1,\ldots,4)$, the operations C_3 and C_3^2 now belong to the same class, unlike in the group T. The class structure of the group T_d is therefore:

$$T_d = \{E,\ 8C_3,\ 3C_2,\ 6\sigma_d,\ 6S_4\}\,.$$

The group O is the group of proper rotations that leave a cube invariant. These operations include the identity E, C_3 rotations about the $\hat{e}_j$ axes, $(j = 1,\ldots,4)$, C_2 rotations about the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes, C_2 rotations about the $(\hat{x}+\hat{y})/\sqrt{2}$, $(\hat{x}-\hat{y})/\sqrt{2}$, $(\hat{y}+\hat{z})/\sqrt{2}$, $(\hat{y}-\hat{z})/\sqrt{2}$, $(\hat{z}+\hat{x})/\sqrt{2}$,and $(\hat{z}-\hat{x})/\sqrt{2}$ axes, and C_4 rotations about the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes. The latter operations also generate $C_2 = C_4^2$, but they are not in the same class. The class structure is:

$$O = \{E,\ 8C_3,\ 3C_2,\ 6C_2',\ 6C_4\}\,.$$

We conclude this list with the group O_h, generated by the elements of the group O plus inversion i. It represents the complete group of symmetries (both proper and improper) of a cube. Since i commutes with all other operations, the class structure is duplicated compared to the class structure of O:

$$O_h = \{E,\ 8C_3,\ 3C_2,\ 6C_2',\ 6C_4, i,\ 8S_6,\ 3\sigma_h,\ 6\sigma_d,\ 6S_4\}\,.$$

The irreducible representations and character tables for all these groups can be found in most books on the applications of group theory in physics.

We conclude this chapter by stating a fundamental theorem in solid-state physics, known as the "crystallographic restriction."

Theorem (Crystallographic Restriction). In a three-dimensional periodic crystalline solid, the only possible proper point symmetry rotations are C_n with $n = 2, 3, 4,$ and 6.

This theorem is crucial because it limits the possible point symmetry operations to these rotations, mirrors, and improper rotations generated by these two. We do not provide the proof of this theorem here, but it arises from the three-dimensional periodicity of the crystal. An important consequence of this theorem is that, for a crystalline solid, only 32 point groups are possible. These are the 32 point groups. We list them in the following table.

C_n	$n = 1, 2, 3, 4, 6$
C_{nh}	$n = 1, 2, 3, 4, 6$
C_{nv}	$n = 2, 3, 4, 6$
S_n	$n = 2, 4, 6$
D_n	$n = 2, 3, 4, 6$
D_{nh}	$n = 2, 3, 4, 6$
D_{nd}	$n = 2, 3$
T	
T_d	
T_h	
O	
O_h	

Table 5.1: The 32 ponctual groups of symmetry for periodic crystals

Chapter 6

Perturbation Theory

When it becomes impractical to calculate the eigenstates and eigenenergies of the Hamiltonian governing a problem, it is customary to resort to approximation techniques. These techniques differ depending on whether there is or isn't a time dependence, whether there is or isn't degeneracy in the eigenstates, as well as depending on the relevance of the sought-after approximation and the available computational power...

6.1 Time-Independent Perturbation Theory

We consider a physical problem governed by a Hamiltonian $\hat{H}$, which we decompose as $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ is a Hamiltonian with known eigenenergies and eigenstates, and the additional term $\hat{V}$ is treated as a *perturbation* of the system.

6.1.1 Non-degenerate Case:

Hereafter, we will denote $|\phi_n\rangle$ as the basis of *known* eigenstates of $\hat{H}_0$ and ϵ_n as the associated eigenenergies. The goal of this section is to establish techniques to determine the eigenenergies of the total Hamiltonian $\hat{H}$ and to compare their variation with respect to the eigenenergies of $\hat{H}_0$. For sufficiently small perturbations, it is reasonable to assume that the eigenstates $|\psi_n\rangle$ of $\hat{H}$ will be "close" to $|\phi_n\rangle$, and the associated energies E_n will be close to ϵ_n.

In fact, we are dealing with a more general problem here by introducing a parameter $\lambda \in \mathbb{R}$ such that $\hat{H} = \hat{H}_0 + \lambda\hat{V}$. We are studying the limit of this problem as λ tends to 0 (i.e., focusing on very small variations). In the limit of very small λ, the solution can certainly be expanded in powers of λ:

$$|\psi_n\rangle = |\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \lambda^2\,|\psi_n^{(2)}\rangle + \cdots \tag{6.1}$$

$$E_n = \epsilon_n + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots. \tag{6.2}$$

The Schrödinger equation is written as follows:

$$\begin{aligned}\left(\hat{H}_0 + \hat{V}\right)\left(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \lambda^2\,|\psi_n^{(2)}\rangle + \cdots\right) \\ = \left(\epsilon_n + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\right)\left(|\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \lambda^2\,|\psi_n^{(2)}\rangle + \cdots\right)\end{aligned} \tag{6.3}$$

Please note that if the radius of convergence of these series is greater than or equal to 1, we will have a good approximation to the problem for $\lambda = 1$, i.e., for our initial problem. We choose the normalization of the basis $|\psi_n\rangle$ for any value of λ by imposing $\langle\phi_n|\psi_n\rangle = 1$, which is equivalent to imposing

$$\langle\phi_n|\psi_n^{(j)}\rangle = 0, \tag{6.4}$$

for all $j \in \mathbb{N}$, including the fact that the states $|\psi_n\rangle$ are not orthonormal.

The equation 6.3 must be satisfied at each order in λ:

1. At order 0, we have :
$$\hat{H}_0 |\phi_n\rangle = \epsilon_n |\phi_n\rangle,$$

2. At order 1 :
$$\hat{H}_0 |\psi_n^{(1)}\rangle + \hat{V} |\phi_n\rangle = \epsilon_n |\psi_n^{(1)}\rangle + E_n^{(1)} |\phi_n\rangle, \tag{6.5}$$
which gives us, if we apply the scalar product with $|\phi_n\rangle$:
$$\underbrace{\langle\phi_n|\hat{H}_0|\psi_n^{(k+1)}\rangle}_{=0} + \underbrace{\langle\phi_n|\hat{V}|\phi_n\rangle}_{=1} = \epsilon_n \underbrace{\langle\phi_n|\psi_n^{(1)}\rangle}_{=0} + E_n^{(1)} \underbrace{\langle\phi_n|\phi_n\rangle}_{=1}.$$
In other words :
$$\langle\phi_n|\hat{V}|\phi_n\rangle = E_n^{(1)}. \tag{6.6}$$

3. At order $k \geq 2$:
$$\hat{H}_0 |\psi_n^{(k)}\rangle + \hat{V} |\psi_n^{(k-1)}\rangle = \epsilon_n |\psi_n^{(k)}\rangle + E_n^{(1)} |\psi_n^{(k-1)}\rangle + \cdots + E_n^{(k-1)} |\psi_n^{(1)}\rangle + E_n^{(k)} |\psi_n\rangle,$$
and once the scalar product with $|\psi_n\rangle$ done, we obtain:
$$E_n(k) = \langle\phi_n|\hat{V}|\psi_n^{(k-1)}\rangle.$$

So, we know how to determine, at a fixed n, the energies $E_n^{(1)}, \cdots, E_n^{(k)}$, once we know $|\psi_n^{(1)}\rangle, \cdots, |\psi_n^{(k-1)}\rangle$. However, we still need to determine $|\psi_n^{(k)}\rangle$ based on $|\psi_n^{(1)}\rangle, \cdots, |\psi_n^{(k-1)}\rangle$. To do this, we use the condition 6.4: if we know the projection of $|\psi_n^{(k)}\rangle$ onto all ϕ_m for $m \neq n$, we can access $|\psi_n^{(k)}\rangle$. To achieve this, we present two approaches here: the Rayleigh-Schrödinger theory and the Brillouin-Wigner theory.

Rayleigh-Schrödinger theory:

We have :
$$\begin{aligned}\langle\phi_m|\hat{H}_0|\psi_n^{(k)}\rangle + \langle\phi_m|\hat{V}|\psi_n^{(k-1)}\rangle \\ = \epsilon_n \langle\phi_m|\psi_n^{(k)}\rangle + E_n^{(1)}\langle\phi_m|\psi_n^{(k-1)}\rangle + \cdots + E_n^{(k)}\langle\phi_m|\phi_n\rangle,\end{aligned}$$
which gives :
$$\begin{aligned}\epsilon_m\langle\phi_m|\psi_n^{(k)}\rangle + \langle\phi_m|\hat{V}|\psi_n^{(k-1)}\rangle \\ = \epsilon_n \langle\phi_m|\psi_n^{(k)}\rangle + E_n^{(1)}\langle\phi_m|\psi_n^{(k-1)}\rangle + \cdots + E_n^{(k-1)}\langle\phi_m|\psi_n^{(1)}\rangle.\end{aligned}$$

Thus :

$$\langle\phi_m|\psi_n^k\rangle = \frac{1}{\epsilon_n - \epsilon_m}\left(\langle\phi_m|\hat{V}|\psi_n^{(k-1)}\rangle - E_n^{(1)}\langle\phi_m|\psi_n^{(k-1)}\rangle - \cdots - E_n^{(k-1)}\langle\phi_m,|\psi_n^{(1)}\rangle\right)$$

We notice that $|\psi_n^{(k)}\rangle$ is entirely determined by the values of $E_n^{(1)},\cdots,E_n^{(k-1)}$ and the states $|\psi_n^{(1)}\rangle,\cdots,|\psi_n^{(k-1)}\rangle$. To illustrate, let's consider the calculation at the 2^{nd} order: we need to determine $E_n^{(1)}$ and $\psi_n^{(1)}$. The first-order approximation of E_n is given by 6.6, but we still need to determine $\psi_n^{(1)}$. We take the dot product of equation 6.5 with $|\psi_m\rangle$, and we get:

$$\langle\phi_m|\hat{H}_0|\psi_m^{(1)}\rangle + \langle\phi_m|\hat{V}|\phi_n\rangle = \epsilon_n\langle\phi_m|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\phi_m|\phi_n\rangle,$$

from which

$$\langle\phi_m|\psi_n^{(1)}\rangle = \frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}.$$

Thus,

$$\begin{aligned}|\psi_n\rangle &= |\phi_n\rangle + \lambda\,|\psi_n^{(1)}\rangle + \mathcal{O}(\lambda)\\ &= |\phi_n\rangle + \lambda\sum_{m\neq n}\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}\,|\phi_m\rangle + \mathcal{O}(\lambda),\end{aligned}$$

which gives us $E_n^{(2)}$:

$$\begin{aligned}E_n^{(2)} &= \langle\phi_n|\hat{V}|\psi_n^{(1)}\rangle\\ &= \sum_m \langle\phi_n|\hat{V}|\phi_m\rangle\,\langle\phi_m|\psi_n^{(1)}\rangle\\ &= \sum_{m\neq n}\langle\phi_n|\hat{V}|\phi_m\rangle\,\langle\phi_m|\psi_n^{(1)}\rangle,\end{aligned}$$

from where

$$E^{(2)} = \sum_{m\neq n}\frac{\left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2}{\epsilon_n - \epsilon_m}.$$

Note 6.1.1.

1. If $|\phi_n\rangle$ is the ground state, then $\epsilon_n - \epsilon_m$ is always strictly negative (as we assumed the states are non-degenerate). Thus, the energy of the ground state is always lowered by the second-order correction.

2. The presence of a denominator in $\epsilon_n - \epsilon_m$ immediately rules out the use of such a method in the case of a degenerate level.

As previously mentioned, the states $|\psi_n\rangle$ obtained in this way are not orthonormal. We use 6.2:

$$\langle\psi_n|\psi_n\rangle = 1 + \sum_{k,l=1}^{\infty}\lambda^{k+l}\langle\psi_n^{(k)}|\psi_m^{(l)}\rangle.$$

In other words, the norm always entails a higher-order correction in λ. In particular, the first term is of order 2 and is given by:

$$\langle\psi_n|\psi_n\rangle = 1 + \lambda^2\sum_{m\neq n}\frac{\left|\langle\psi_n^{(k)}|\psi_m^{(l)}\rangle\right|^2}{(\epsilon_n - \epsilon_m)^2}.$$

Let's focus on the conditions for the validity of such a method. As mentioned at the beginning of this section, it is necessary for the radius of convergence of the energy series to be greater

than or equal to 1. However, it is impossible to verify this condition since the series is not explicitly determined. To address this issue, we impose that the coefficient of the λ^2 term is small compared to the coefficient of λ. Let Δ be the energy difference between ϵ_n and the nearest energy level; we have:

$$\begin{aligned}
\left|E_n^{(2)}\right| &= \Big|\sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2}{(\epsilon_n-\epsilon_m)}\Big| \\
&\leq \sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2}{(\epsilon_n-\epsilon_m)} \\
&\leq \frac{1}{\Delta}\sum_{m\neq n} \left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2 \\
&= \frac{1}{\Delta}\left(\sum_m \langle\phi_m|\hat{V}|\phi_n\rangle\,\langle\phi_m|\hat{V}|\phi_n\rangle - \left|\langle\phi_n|\hat{V}|\phi_n\rangle\right|^2\right) \\
&= \frac{1}{\Delta}\left(\sum_m \langle\phi_n|\hat{V}^2|\phi_n\rangle - \langle\phi_n|\hat{V}|\phi_n\rangle^2\right).
\end{aligned}$$

The condition $|E_n^{(2)}| \ll |E_n^{(1)}|$ is satisfied as long as:

$$\Big|\frac{\langle\phi_n|\hat{V}^2|\phi_n\rangle}{\langle\phi_n|\hat{V}|\phi_n\rangle} - \langle\phi_n|\hat{V}|\phi_n\rangle\Big| \ll \Delta.$$

A more restrictive but also easier-to-verify condition would be to require that the elements of the perturbation matrix are small compared to the energy level spacing. In other words, we impose:

$$\Big|\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n-\epsilon_m}\Big| \ll 1.$$

Example 6.1.2. Potential of a Diatomic Molecule

The system's Hamiltonian is given by $\hat{H} = \hat{H}_0 + \hat{V}$ with:

$$\begin{cases} \hat{H}_0 = \frac{\hat{p}^2}{2} + \frac{\hat{x}^2}{2}, \\ \hat{V} = c\hat{x}^3 + q\hat{x}^4, \end{cases}$$

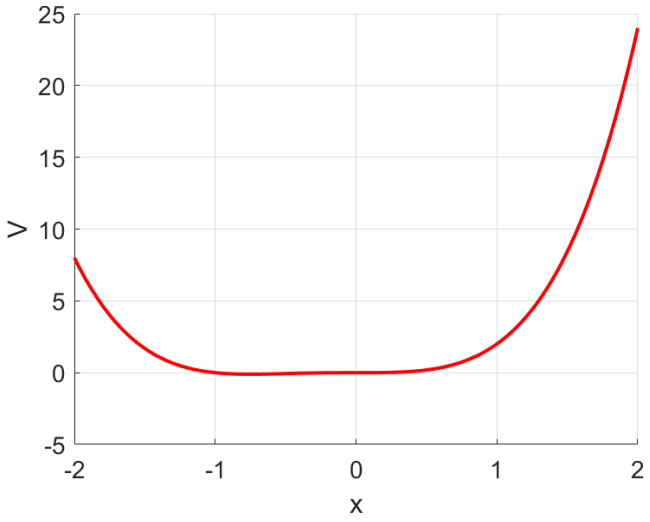

Figure 6.1: Correction to the potential

The energy and eigenstates of $\hat{H}_0$ for the system are already known, especially $\epsilon_n = (n + \frac{1}{2})$. The goal is to determine the $E_n^{(k)}$ for a fixed n. For example:

$$E_n^{(1)} = \langle n|c\hat{x}^3 + q\hat{x}^4|n\rangle \,.$$

We introduce the creation and annihilation operators in such a way that $\hat{x} = \hat{a}^\dagger + \hat{a}$. It is immediately noticed that the term $c\hat{x}^3$ does not contribute because only terms with the same number of $\hat{a}$ and $\hat{a}^\dagger$ operators give rise to non-zero coefficients. Furthermore, the graph 6.1.2 indicates that the coefficient q must be negative, and:

$$\begin{aligned}
\hat{x}^4 &= \left(\hat{a}^\dagger + \hat{a}\right)^4 = \left(\left(\hat{a}^\dagger\right)^2 + \hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger + \hat{a}^2\right)^2 \\
&= (\hat{a}^\dagger)^4 + (\hat{a}^\dagger)^2\hat{a}^2 + (\hat{a}^\dagger)^3\hat{a} + (\hat{a}^\dagger)^2\hat{a}\hat{a}^\dagger \\
&+ \hat{a}^2(\hat{a}^\dagger)^2 + \hat{a}^4\hat{a}^2\hat{a}^\dagger\hat{a} + \hat{a}^3\hat{a}^\dagger + \hat{a}^\dagger\hat{a}(\hat{a}^\dagger)^2 \\
&+ \hat{a}^\dagger\hat{a}^3 + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}(\hat{a}^\dagger)^3 \\
&+ \hat{a}\hat{a}^\dagger\hat{a}^2 + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger \\
&= \left(\hat{a}^\dagger\right)^2\hat{a}^2 + \hat{a}^2\left(\hat{a}^\dagger\right)^2 + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger,
\end{aligned}$$

Where the last equality is obtained using the preceding note on the terms contributing in non trivial ways Recall that

$$\begin{cases} \hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle, \\ \hat{a}^\dagger\,|n\rangle = \sqrt{n-1}\,|n+1\rangle, \end{cases}$$

which gives us

$$\begin{aligned}
&\langle n|\left(\hat{a} + \hat{a}^\dagger\right)^4|n\rangle \\
&= \langle n|\left(\hat{a}^\dagger\right)^2\hat{a}^2|n\rangle + \langle n|\hat{a}^2\left(\hat{a}^\dagger\right)^2|n\rangle + \langle n|\hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger|n\rangle + \langle n|\hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a}|n\rangle + \langle n|\hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a}|n\rangle + \langle n|\hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger|n\rangle \\
&= \left(\sqrt{n}\right)^2\left(\sqrt{n-1}\right)^2\langle n-2|n-2\rangle + \left(\sqrt{n-1}\right)^2\left(\sqrt{n}\right)^2\langle n-2|n-2\rangle \\
&+ \left(\sqrt{n-1}\right)^2\left(\sqrt{n}\right)^2\langle n+2|n+2\rangle + 2\sqrt{n-2}\sqrt{n-1}\sqrt{n}\sqrt{n+1}\langle n|n\rangle + \left(\sqrt{n-1}\right)^2\left(\sqrt{n+1}\right)^2\langle n|n\rangle \\
&= 6\left(n^2 + n - \frac{1}{2}\right) + \mathcal{O}().
\end{aligned}$$

Note that the energy correction is negative and that when n increases, the potential increases as well, thus energy levels get closer when n increases

Brillouin-Wigner Theory:

The practical limitations of the previous method become very clear in the previous example and in series exercises: except for very particular cases, calculations at orders higher than 2 quickly become much too complicated. The Brillouin-Wigner theory offers an alternative to this technique by treating the components $\langle\phi_m|\psi_n\rangle$, with $m \neq n$, as $\mathcal{O}(\lambda)$. This choice seems reasonable since the components $\langle\phi_m|\psi_n\rangle$ become arbitrarily small as λ tends to 0. We start with the Schrödinger equation for an eigenstate $|\psi_n\rangle$:

$$\left(\hat{H}_0 + \lambda\hat{V}\right)|\psi_n\rangle = E_n\,|\psi_n\rangle\,. \tag{6.7}$$

Using 6.4, we notice that such a state decomposes into the unperturbed basis:

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} |\phi_m\rangle\langle\phi_m|\psi_n\rangle.$$

We take the inner product of 6.7 with $|\phi_m\rangle$:

$$\begin{aligned}
&\langle\phi_m|\left(\hat{H}_0 + \lambda\hat{V}\right)|\psi_n\rangle = E_n\langle\phi_m|\psi_n\rangle \\
\implies &(E_n - \epsilon_m)\langle\phi_m|\psi_n\rangle = \lambda\,\langle\phi_m|\hat{V}|\psi_n\rangle\,.
\end{aligned}$$

This provides an expression for $|\psi_n\rangle$ in the unperturbed basis:

$$\begin{aligned}
|\psi_n\rangle &= |\phi_n\rangle + \lambda\sum_{m\neq n}|\phi_m\rangle\frac{\langle\phi_m|\hat{V}|\psi_n\rangle}{E_n-\epsilon_m}, \\
&= |\phi_n\rangle + \lambda\sum_{m\neq n}|\phi_m\rangle\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{E_n-\epsilon_m} + \lambda^2\sum_{m\neq n,j\neq n}|\phi_m\rangle\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{E_n-\epsilon_m}\frac{\langle\phi_j|\hat{V}|\phi_n\rangle}{E_n-\epsilon_j} + \cdots,
\end{aligned}$$

allowing us to obtain an expression for energy at an arbitrary order. In fact, all that is needed is to project equation 6.7 onto the state $|\psi_n\rangle$:

$$\begin{aligned}
&\langle\phi_n|\left(\hat{H}_0 + \lambda\hat{V}\right)|\psi_n\rangle = E_n\langle\phi_n|\psi_n\rangle \\
\implies &(E_n - \epsilon_n) = \lambda\,\langle\phi_n|\hat{V}|\psi_n\rangle\,,
\end{aligned}$$

and to combine this expression with the representation of $|\phi_n\rangle$ in the non-degenerate basis:

$$\begin{aligned}
E_n = \epsilon_n + \lambda\,\langle\phi_n|\lambda\hat{V}|\psi_n\rangle\; &+ \lambda^2\sum_{m\neq n}\langle\phi_n|\hat{V}|\phi_m\rangle\frac{1}{E_n-\epsilon_m}\langle\phi_m|\hat{V}|\phi_n\rangle \\
&+ \lambda^3\sum_{m\neq n,j\neq n}\langle\phi_n|\hat{V}|\phi_m\rangle\frac{1}{E_n-\epsilon_m}\langle\phi_m|\hat{V}|\phi_j\rangle\frac{1}{E_n-\epsilon_j}\langle\phi_j|\hat{V}|\phi_n\rangle + \cdots.
\end{aligned}$$

Note 6.1.3.

1. If we truncate the expression for E_n at a given order, the solution coincides with that given by Rayleigh-Schrödinger theory. Examples are provided in the series.

2. At a given order, it is observed that the expression for energy contains all higher-order terms, which provides a better approximation than the result obtained by Rayleigh-Schrödinger theory.

6.1.2 Degenerate Case:

As mentioned earlier, the Rayleigh-Schrödinger theory fails when $\hat{H}_0$ has a degenerate eigenvalue ϵ_n, due to the presence of terms of the form $\frac{1}{\epsilon_n - \epsilon_m}$ in the expression for E_n for all $m \neq n$. To solve this problem, let's observe that the degenerate states associated with an energy ϵ_n form a finite vector subspace of the Hilbert space. Suppose this subspace is generated by the eigenstates $|\phi_{n_i}\rangle$, for $i \in \{1, \cdots, k\}$ of H_0, which are chosen to be orthonormal. The problematic terms in the expression for $\psi_n^{(1)}$ are of the form $\frac{\langle \phi_{n_i}|\hat{V}|\phi_{n_j}\rangle}{\epsilon_{n_i} - \epsilon_{n_j}}$ with $i \neq j$. In other words, if we can diagonalize $\hat{V}$ in the basis of states $|\phi_{n_i}\rangle$, the problem disappears.

First-Order Calculation:

The eigenstates of the perturbed problem are a priori decomposed in the basis of unperturbed states as follows:

$$|\psi_n\rangle = \sum_{j=1}^{k} \underbrace{\langle \phi_{n_j}|\psi_n\rangle}_{\mathcal{O}()} |\psi_{n_j}\rangle + \sum_{m \neq n} \underbrace{\langle \phi_m|\psi_n\rangle}_{\mathcal{O}(\lambda)} |\phi_m\rangle .$$

From now on, and for the rest of this section, we will use the notation $|\phi_m\rangle$ to denote the eigenstates of H_0 that do not correspond to the eigenvalue ϵ_m.

If we project the Schrödinger equation for the eigenstate ψ_n of the perturbed problem onto a degenerate unperturbed state $\langle \phi_{n_i}|$, we find:

$$(E_n - \epsilon_n)\langle \phi_{n_i}|\psi_n\rangle = \lambda \sum_j \langle \phi_{n_i}|\hat{V}|\phi_{n_j}\rangle \langle \phi_{n_j}|\psi_n\rangle + \lambda \sum_{m \neq n_j} \langle \phi_{n_i}|\hat{V}|\phi_m\rangle \langle \phi_m|\psi_n\rangle, \tag{6.8}$$

which gives the following expression in the order in λ :

$$(E_n - \epsilon_n) \langle \phi_{n_i}|\psi_n\rangle = \lambda \sum_j \langle \phi_{n_i}|\hat{V}|\phi_{n_j}\rangle \langle \phi_{n_j}|\psi_n\rangle + \mathcal{O}(\lambda). \tag{6.9}$$

Note that solving this system of k equations is, as introduced, equivalent to a matrix diagonalization problem. Indeed, if we introduce $\mathbf{u}$, the vector with components $(\langle \phi_{n_i}|\psi_n\rangle)$, and $M^{(1)}$, the $(k \times k)$ matrix with components $M_{ij}^{(1)} = \lambda \langle \phi_{n_i}|\hat{V}|\phi_{n_j}\rangle$, problem 6.9 can be rewritten as:

$$M^{(1)}\mathbf{u} = (E_n - \epsilon_n)\, \mathbf{u}.$$

Let $E_{n,i}^{(1)}$ be the k eigenvalues of $M^{(1)}$, and $\mathbf{u}^i$ the associated eigenvectors. We have:

$$\begin{cases} E_{n,i} = \epsilon_n + E_{n,i}^{(1)} \sim \mathcal{O}(\lambda), \\ u_j^i = \langle \phi_{n_j}|\psi_{n,i}\rangle \sim \mathcal{O}(), \end{cases}$$

where the $|\psi_{n,i}\rangle$, with $i \in \{1, \cdots, k\}$, form a basis of the subspace of degenerate states with energy ϵ_n, such that $\hat{V}$ is diagonal in this basis, i.e. for all $i,\ j \in \{1, \cdots, k\}$:

$$\langle \psi_{n,i}|\hat{V}|\psi_{n,j}\rangle = E_{n,i}\delta_{ij}.$$

Note 6.1.4. 1. If we explicitly write down the eigenvalue equation for the eigenvalue $E_{n,i}^{(1)}$, we have, for $l \in \{1, \cdots, k\}$:

$$\sum_{j=1}^{k} \lambda \langle \phi_{n_l}|\hat{V}|\phi_{n_j}\rangle \langle \phi_{n_j}|\psi_{n,i}\rangle = (E_{n,i} - \epsilon_n) \langle \phi_{n_l}|\psi_{n,i}\rangle.$$

It is clear that, in general, $E_{n,i}^{(1)} \neq \langle \phi_{n_i}|\hat{V}|\phi_{n_i}\rangle$.

2. In general, a perturbation allows us to *lift degeneracy*, i.e., obtain energy corrections $E_{n,i}^{(1)}$ that are all different. Any remaining degeneracies are actually due to intrinsic symmetries, directly related to the physics of the problem.

3. Note that in the context of perturbation theory for a non-degenerate physical system, the perturbation appears at order 1 in λ, while here it appears already at order 0.

4. So, we started with a system described by a Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where:

$$\begin{pmatrix} 0 & 0 & \cdots & & & & & & \\ \epsilon_0 & 0 & & & & & & & \\ 0 & \epsilon_1 & \ddots & & & & & & \\ \vdots & 0 & \epsilon_2 & & & & & & \\ & & \ddots & \ddots & & & & & \\ & & & & \epsilon_n & & & & \\ & & & & & \ddots & & & \\ & & & & & & \epsilon_n & & \\ & & & & & & & \epsilon_{n+1} & \\ & & & & & & & & \ddots \end{pmatrix}$$

   A first order perturbation in λ comes to diagonalizing the block I. But at order 2 and higher, we can no longer neglect the contributions of A, B, C and D.

Higher-order Calculations:

Starting from the problem 6.8:

$$(E_n - \epsilon_n)\langle\phi_{n_i}|\psi_n\rangle = \lambda \sum_j \langle\phi_{n_i}|\hat{V}|\phi_{n_j}\rangle\langle\phi_{n_j}|\psi_n\rangle + \lambda \sum_{m\neq n_j} \langle\phi_{n_i}|\hat{V}|\phi_m\rangle\langle\phi_m|\psi_n\rangle,$$

Also, consider the projection of the Schrödinger equation onto an eigenstate $|\psi_m\rangle$ of $\hat{H}_0$ not corresponding to the eigenenergy ϵ_n, we have:

$$(E_n - \epsilon_m)\langle\phi_m|\psi_n\rangle = \lambda\langle\phi_m|\hat{V}|\psi_n\rangle$$

i.e.:

$$\langle\phi_m|\psi_n\rangle = \lambda\frac{\langle\phi_m|\hat{V}|\psi_n\rangle}{E_n - \epsilon_m},$$

with $E_n = \epsilon_n + \mathcal{O}(\lambda)$. Furthermore, the orthonormality of the family $\{|\psi_{n_i}\rangle\}_{i=1}^k$ allows us to write:

$$|\psi_n\rangle = \mathbb{1}|\psi_n\rangle = \left(\sum_{j=1}^k |\phi_{n_j}\rangle\langle\phi_{n_j}| \sum_m |\psi_m\rangle\langle\psi_m|\right)|\psi_n\rangle = \sum_{j=1}^k |\phi_{n_j}\rangle\langle\phi_{n_j}|\psi_n\rangle + \mathcal{O}(\lambda).$$

Thus,

$$\langle\phi_m|\psi_n\rangle = \lambda\sum_{j=1}^k \frac{\langle\phi_m|\hat{V}|\phi_{n_j}\rangle\langle\phi_{n_j}|\psi_n\rangle}{\epsilon_n - \epsilon_m} + \mathcal{O}(\lambda).$$

Injecting this expression into equation 6.8, we get:

$$(E_n - \epsilon_n)\langle\phi_{n_j}|\psi_n\rangle = \lambda\sum_{j=1}^k \langle\phi_{n_i}|\hat{V}|\phi_{n_j}\rangle\langle\phi_{n_j}|\psi_n\rangle \tag{6.10}$$

$$+ \lambda^2 \sum_{j=1}^k \sum_m \frac{1}{\epsilon_n - \epsilon_m}\langle\phi_{n_i}|\hat{V}|\phi_m\rangle\langle\phi_m|\hat{V}|\phi_{n_j}\rangle\langle\phi_{n_j}|\psi_m\rangle. \tag{6.11}$$

As before, this leads us to an eigenvalue problem by introducing the matrix $M^{(2)}$, which is a $(k \times k)$ matrix with components:

$$M_{ij}^{(2)} = \lambda \langle \phi_{n_i} | \hat{V} | \phi_{n_j} \rangle + \lambda^2 \sum_m \frac{1}{\epsilon_n - \epsilon_m} \langle \phi_{n_i} | \hat{V} | \phi_m \rangle \langle \phi_m | \hat{V} | \phi_{n_j} \rangle .$$

If we denote $E_{n,i}^{(2)}$ as the k eigenvalues of $M^{(2)}$, and $\mathbf{v}^i$ as the associated eigenvectors, we have this time:

$$\begin{cases} E_{n,i} = \epsilon_n + E_{n,i}^{(2)} \sim \mathcal{O}(\lambda), \\ v_j^i = \langle \phi_{n_j} | \psi_{n,i} \rangle \sim \mathcal{O}() + \mathcal{O}(\lambda), \end{cases}$$

where the $|\psi_{n,i}\rangle$, with $i \in \{1, \cdots, k\}$, form a basis for the subspace of degenerate states with energy ϵ_n, such that $\hat{V}$ is diagonal in this basis, i.e., for all $i,\ j \in \{1, \cdots, k\}$:

$$\langle \psi_{n,i} | \hat{V} | \psi_{n,j} \rangle = E_{n,i} \delta_{ij}.$$

Note 6.1.5.

1. With this method, we must directly calculate the perturbation to the desired order starting from order 0 (unlike non-degenerate perturbation theory, which is iterative).

2. In the case of one-dimensional problems, degeneracy *never* occurs if the potential diverges at infinity. In particular, in this case, the ground state is non-degenerate.

Example 6.1.6. Two-Dimensional Square Potential Well: Consider a particle confined in a square region of side length a. The potential is zero inside the "box" and infinite at the "walls." The eigenenergies of the system are known and have the form $\epsilon_{p,q} = \frac{\hbar^2 \pi^2}{2ma^2}(p^2 + q^2)$ with p and $q \in \mathbb{N}^*$. Note that the ground state, denoted as $|1,1\rangle$ and corresponding to $p = 1 = q$, is non-degenerate, unlike the states $|1,2\rangle$ and $|2,1\rangle$, which both have an energy of $5\frac{\hbar^2 \pi^2}{2ma^2}$. The corresponding wavefunctions are given by:

$$\phi_{1,2}(x,y) = \frac{2}{a} \cos(\frac{\pi x}{a}) \sin(\frac{2\pi y}{a}),$$

$$\phi_{2,1}(x,y) = \frac{2}{a} \cos(\frac{2\pi x}{a}) \sin(\frac{\pi y}{a}).$$

To lift this degeneracy, we introduce a perturbation corresponding to a potential $V(x,y) = -k(x^2 - y^2)$, where k is a positive constant. We aim to diagonalize the matrix:

$$M^{(1)} = \begin{pmatrix} \langle 1,2|\hat{V}|1,2\rangle & \langle 1,2|\hat{V}|2,1\rangle \\ \langle 2,1|\hat{V}|1,2\rangle & \langle 2,1|\hat{V}|2,1\rangle \end{pmatrix}.$$

Note that the diagonal terms are zero since the potential $\hat{V}$ is an odd function in x and y (hence zero upon integration). We need to determine the off-diagonal terms:

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$$\begin{aligned}
\langle 1,2|\hat{V}|2,1\rangle &= -\frac{4k}{a^2}\int_{-\frac{a}{2}}^{\frac{a}{2}} dx \int_{-\frac{a}{2}}^{\frac{a}{2}} dy(x^2-y^2)\cos\left(\frac{\pi x}{a}\right)\cos\left(\frac{2\pi x}{a}\right)\sin\left(\frac{\pi y}{a}\right)\sin\left(\frac{2\pi y}{a}\right) \\
&= -\frac{4k}{a^2}\int_{-\frac{a}{2}}^{\frac{a}{2}} dx \int_{-\frac{a}{2}}^{\frac{a}{2}} dy(x^2-y^2)\frac{1}{4}\left(\cos(\beta x)+\cos(\gamma x)\right)\left(\cos(\gamma y)-\cos(\beta y)\right) \\
&= -\frac{1}{4}\frac{4k}{a^2}\int_{-\frac{a}{2}}^{\frac{a}{2}} dx\left(x^2\left[\frac{\sin(\gamma y)}{\gamma}-\frac{\sin(\beta y)}{\beta}\right]-\left[\frac{y^2\sin(\gamma y)}{\gamma}+\frac{2\gamma\sin(\gamma y)}{\gamma^2}-\frac{2\sin(\gamma y)}{\gamma^3}\right]\right. \\
&\quad \left.+\left[\frac{y^2\sin(\beta y)}{\beta}+\frac{2\beta\sin(\beta y)}{\beta^2}-\frac{2\sin(\beta y)}{\beta^3}\right]\right)\left(\cos(\gamma x)+\cos(\beta x)\right)\Big|_{y=-\frac{a}{2}}^{y=\frac{a}{2}} \\
&= -\frac{16}{9\pi^2}ka^2 = -\Delta.
\end{aligned}$$

where we have used $\beta = \frac{3\pi}{a}$ and $\gamma = \frac{\pi}{a}$ for clarity.

Thus, the Hamiltonian $\hat{H} = \begin{pmatrix} \epsilon & -\Delta \\ -\Delta & \epsilon \end{pmatrix}$ has eigenvalues

$$\lambda_\pm = \frac{1}{2}\left(2\epsilon \pm \sqrt{4\Delta^2}\right) = \frac{1}{2}\left(2\epsilon \pm 2\Delta\right) = \epsilon \pm \Delta,$$

in the subspace of degenerate states, and the associated eigenvectors are given by $v_\pm = \begin{pmatrix} \epsilon \\ -\Delta - \lambda_\pm. \end{pmatrix}$
As mentioned throughout this chapter, this method remains valid as long as the perturbation is small enough that nearby energy levels do not significantly overlap. In other words, the results established above are valid as long as $|\Delta| \ll \frac{\hbar^2\pi^2}{2ma^2}$, i.e., as long as $1 \sim \frac{16}{9\pi^2}ka^2 \ll \frac{\hbar^2\pi^2}{2ma^2}$. In other words, it requires that $k \ll \frac{\hbar^2}{2ma^4}$.

6.2 Time-Dependent Perturbation Theory

So far, we have focused on approximating the eigenstates and eigenvalues of systems described by time-independent Hamiltonians. What happens when we can no longer neglect time dependence?

We want to solve the equation:

$$i\hbar\frac{\partial}{\partial t}|\phi(t)\rangle = \hat{H}(t)|\phi(t)\rangle. \tag{6.12}$$

Note that this is a first-order differential equation. According to Picard's theorem, if the system's state is known at a given time, then it is known at every moment. This allows us to introduce a time evolution operator $\hat{U}(t,t_0)$ such that

$$|\phi(t)\rangle = \hat{U}(t,t_0)|\phi(t_0)\rangle. \tag{6.13}$$

If the Hamiltonian is time-independent, it has the form

$$\hat{U}(t,t_0) = e^{-i\frac{\hat{H}(t-t_0)}{\hbar}}, \tag{6.14}$$

but when there is explicit time dependence, we cannot use such an expression. We need to reconsider the reasoning that led us to establish the previous form of the Hamiltonian.

The time evolution operator is obtained by solving the system:

$$\begin{cases} i\hbar\frac{\partial}{\partial t}\hat{U}(t,t_0) = \hat{H}(t)\hat{U}(t,t_0), \\ \hat{U}(t_0,t_0) = \mathbb{1}. \end{cases} \tag{6.15}$$

Integrate the equation from t_0 to t, and you get:

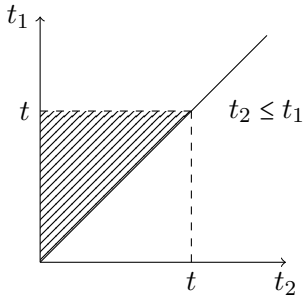
$$\begin{aligned} i\hbar\int_{t_0}^{t} dt_1 \frac{\partial}{\partial t}\hat{U}(t_1,t_0) &= \int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0) \\ \implies i\hbar\left(\hat{U}(t,t_0)-\mathbb{1}\right) &= \int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0). \end{aligned}$$

Therefore,

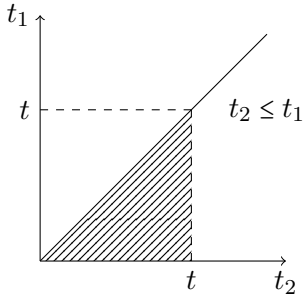
$$\begin{aligned} \hat{U}(t,t_0) &= \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0) \\ &= \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1) + \left(-\frac{1}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2)\hat{U}(t_2,t_0) \\ &= \mathbb{1} + \sum_{i=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{H}(t_1)\cdots\hat{H}(t_n) \end{aligned}$$

Example 6.2.1. Integral on a triangle

We want to compute the term $\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2)$, in other words, we are looking for the area of the "lined over" area, in the following figure:



Which is strictly equivalent to finding the area of the "lined over" area of the following figure (change of variable $t_2 \mapsto t_1$ and reciprocally) :



In other words

$$\begin{aligned}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2) &= \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 \hat{H}(t_1)\hat{H}(t_2) \\ &= \int_{t_0}^{t} dt_1 \int_{t_2}^{t} dt_2 \hat{H}(t_2)\hat{H}(t_1),\end{aligned}$$

Where the last equality is found thanks to the change of variable used above. We thus have :

$$\begin{aligned}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2) &= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 \hat{H}(t_1)\hat{H}(t_2) + \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 \hat{H}(t_1)\hat{H}(t_2) \\ &= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \left(\hat{H}(t_1)\hat{H}(t_2)\mathcal{O}(-) + \hat{\mathcal{H}}()\hat{\mathcal{H}}()\mathcal{O}(-)\right) \\ &= \frac{1}{2}\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \hat{T}\left(\hat{H}(t_1)\hat{H}(t_2)\right).\end{aligned}$$

The operator $\hat{T}$ introduced in the last equality is called the *t-ordered* or *time-ordered operator*. For $n = 2$:

$$\hat{T}\left(\hat{H}(t_1)\hat{H}(t_2)\right) = \begin{cases} \hat{H}(t_1)\hat{H}(t_2) \text{ if } t_1 \geq t_2, \\ \hat{H}(t_2)\hat{H}(t_1) \text{ if } t_2 \geq t_1. \end{cases}$$

In general, for any $n \in \mathbb{N}$:

$$\hat{T}\left(\hat{H}(t_{\sigma(1)})\cdots\hat{H}(t_{\sigma(n)})\right) = \hat{H}(t_1)\cdots\hat{H}(t_n) \text{ if } t_1 > \cdots > t_n,$$

where σ denotes a permutation of $\{1, \cdots, n\}$. In other words, the operator $\hat{T}$ reorders the operators $H(t_i)$ on which it acts into chronological order. This allows us to rewrite the time evolution operator in the form:

$$\hat{U}(t, t_0) = \mathbb{1} + \sum_{i=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{1}{n!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{T}\left(\hat{H}(t_1)\cdots\hat{H}(t_n)\right). \tag{6.16}$$

Note the presence of the corrective factor $\frac{1}{n!}$ due to the fact that the integral over each of the $n!$ possible combinations of the positions of t_i remains the same because the operator $\hat{T}$ always rearranges the t_i in such a way that they return to their initial positions. It is customary to condense the expression 6.16 into the form:

$$\hat{U}(t, t_0) = \hat{T}\left(e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1)}\right). \tag{6.17}$$

Note 6.2.2. 1. If the Hamiltonian $\hat{H}$ is independent of time, then necessarily $[\hat{H}(t_i), \hat{H}(t_j)] = 0$ for all t_i, t_j. In other words, the operator $\hat{T}$ acts trivially on the product $\left(\hat{H}(t_{\sigma(1)}) \cdots \hat{H}(t_{\sigma(n)})\right)$ for any permutation σ of n elements. In particular:

$$\begin{aligned}\hat{U}(t, t_0) &= \mathbb{1} + \sum_{i=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{1}{n!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{T}\left(\hat{H}(t_1)\cdots\hat{H}(t_n)\right) \\ &= \mathbb{1} + \sum_{i=1}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{1}{n!}\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{H}(t_1) \cdots \hat{H}(t_n),\end{aligned}$$

which, in exponential notation, gives $\hat{U}(t, t_0) = e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1)}$. Moreover, since $\hat{H}$ is independent of time, $\int_{t_0}^{t} dt' \hat{H}(t') = \hat{H}(t - t_0)$, and the time evolution operator can be rewritten as $\hat{U}(t, t_0) = \hat{T}\left(e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}\right)$. Thus, we indeed recover the expression 6.14.

2. In general, there is no guarantee that $\hat{T}\left(e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1)}\right) = e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{H}(t_1)}$. One needs to go back to the uncompressed expression 6.16 for $\hat{U}$ and explicitly compute each term of the expansion before summing them. Unless a recurrence relation between all the terms is found, which is highly unlikely, and in addition, a convergent series is obtained, such calculations are practically infeasible. Therefore, we focus on situations where we can limit the expansion to a few terms. In our case, it concerns problems described by a Hamiltonian of the form:
$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$
where the perturbation is assumed to be small compared to $\hat{H}_0$. Let's look more closely at what this implies for the different terms in the sum 6.16. For example, for $n = 2$, we have:
$$\hat{H}(t_1)\hat{H}(t_2) = (\hat{H}_0 + V)(\hat{H}_0 + V) = H_0^2 + 2\hat{H}_0\hat{V} + \hat{V}^2.$$
The term of order $\hat{V}^2$ is thus generated by the terms of order $\hat{V}^0$ and $\hat{V}^1$. More generally, each term of order $\hat{V}^n$ in the expansion 6.16 is determined by terms of order $m < n$ in the expansion of $\hat{H}(t_i)$. To obtain a direct power series expansion in $\hat{V}(t)$, we must change the representation; this is the focus of the next section.

6.2.1 Interaction Representation

In the preceding chapters, we have already developed the formalism of quantum mechanics from the perspectives of Heisenberg and Schrödinger. In this section, we introduce a new representation called the *interaction representation.*

Let's begin with some reminders:

1. In the Schrödinger representation, it is the states $|\phi_S(t)\rangle$ that explicitly depend on time. The evolution is governed by the following equation:
$$i\hbar\frac{\partial}{\partial t}|\phi_S(t)\rangle = \hat{H}(t)|\phi_S(t)\rangle.$$
In this representation, observables are fixed operators, and any time dependence they have, if at all, is intrinsic and not governed by $\hat{H}$.

2. In the Heisenberg viewpoint, the time dependence is instead transferred to the operators. The state vectors are assumed to be fixed, and their time dependence is intrinsic. The system's time evolution is governed by:
$$\begin{cases} |\phi_H(t)\rangle = |\phi_S(t_0)\rangle, \\ \hat{O}_H(t) = \hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0) \end{cases}$$

3. If we combine these two definitions, we recover $|\phi_H(t)\rangle = \hat{U}_S^\dagger(t,t_0)|\phi_S(t)\rangle$, which leads to:
$$\begin{aligned} \langle\phi_H(t)|\hat{O}_H(t)|\phi_H(t)\rangle &= \langle\phi_H(t)|\hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0)|\phi_H(t)\rangle \\ &= \langle\hat{U}_S^\dagger(t,t_0)\phi_S(t)|\hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0)|\hat{U}_S^\dagger(t,t_0)\phi_S(t)\rangle \\ &= \langle\hat{U}_S(t,t_0)\hat{U}_S^\dagger(t,t_0)\phi_S(t)|\hat{O}_S(t)|\hat{U}_S(t,t_0)\hat{U}_S^\dagger(t,t_0)\phi_S(t)\rangle \\ &= \langle\phi_S(t)|\hat{O}_S(t)|\phi_S(t)\rangle. \end{aligned}$$

In other words, the expectations are the same, regardless of the adopted representation.

The interaction representation is a kind of "blend" of these two points of view. We start with a problem described by a Hamiltonian of the form:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t),$$

where the time dependence due to the perturbation $\hat{V}$ is transferred to the states, while the time dependence due to $\hat{H}_0$ is transferred to the observables. In other words, and noting that $\hat{H}_0$ is independent of time, the temporal evolution of the system is governed by the following equations:

$$\begin{cases} \hat{O}_I(t) = e^{i\frac{\hat{H}(t-t_0)}{\hbar}} \hat{O}_S(t) e^{-i\frac{\hat{H}(t-t_0)}{\hbar}}, \\ \\ |\phi_I(t)\rangle = e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} |\phi_S(t)\rangle. \end{cases} \tag{6.18}$$

For the representation to be consistent, we must have $|\phi_I(t_0)\rangle = |\phi_S(t_0)\rangle = |\phi_H\rangle$. We introduce the interaction evolution operator $\hat{U}_I(t, t_0)$, defined for each t as:

$$|\phi_I(t)\rangle = \hat{U}_I(t, t_0) |\phi_I(t_0)\rangle.$$

This, combined with the second equation in 6.18, gives us an explicit expression for $\hat{U}_I(t, t_0)$:

$$\hat{U}_I(t, t_0) = e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \hat{U}_S(t, t_0). \tag{6.19}$$

We still need to determine how such an operator evolves. We have:

$$\begin{aligned} \frac{\partial}{\partial t}\hat{U}_I(t, t_0) &= e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \frac{i\hat{H}_0}{\hbar} \hat{U}_S(t, t_0) + e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \hat{U}_S(t, t_0) \left(\frac{-i}{\hbar}\right) \hat{H}(t) \hat{U}_S(t, t_0) \\ &= e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \left(\frac{-i}{\hbar}\right) \left(\hat{H}(t) - \hat{H}_0\right) \hat{U}_S(t, t_0) \\ &= e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \left(\frac{-i}{\hbar}\right) \left(\hat{V}(t)\right) \hat{U}_S(t, t_0) \\ &= \left(\frac{-i}{\hbar}\right) e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \left(\hat{V}(t)\right) e^{-i\frac{\hat{H}_0(t-t_0)}{\hbar}} e^{i\frac{\hat{H}_0(t-t_0)}{\hbar}} \hat{U}_S(t, t_0) \\ &= \left(\frac{-i}{\hbar}\right) \left(\hat{V}_I(t)\right) \hat{U}_I(t, t_0). \end{aligned}$$

From this, we derive the differential equation:

$$i\hbar \frac{\partial}{\partial t}\hat{U}_I(t, t_0) = \left(\hat{V}_I(t)\right) \hat{U}_I(t, t_0). \tag{6.20}$$

We find an equation identical to the one governing the evolution of the operator $\hat{U}_S(t, t_0)$ in the Schrödinger representation. However, this time, it's the perturbation $\hat{V}_I$, expressed from the interaction representation's point of view, that plays the role of $\hat{H}$. If we push the analogy a bit further, we can use similar reasoning to obtain an expansion of $\hat{U}_I(t, t_0)$:

$$\begin{aligned} \hat{U}_I(t, t_0) &= \mathbb{1} + \sum_{i=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \left(\hat{V}_I(t_1) \cdots \hat{V}_I(t_{n-1})\right) \\ &= \mathbb{1} + \sum_{i=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{T}\left(\hat{V}_I(t_1) \cdots \hat{V}_I(t_n - 1)\right), \end{aligned}$$

Which we can put in a more condensed version:

$$\hat{U}_I(t,t_0) = \hat{T}\left(e^{\frac{-i}{\hbar}\int_{t_0}^{t} dt' \hat{V}_I(t')}\right).$$

Using 6.19, we deduce that $\hat{U}_S(t,t_0) = e^{-i\frac{\hat{H}_0(t-t_0)}{\hbar}}\hat{U}_I(t,t_0)$, which gives us the desired expansion of $\hat{U}_S(t,t_0)$ in powers of $\hat{V}(t)$. As mentioned earlier, such an expansion is only meaningful if it is possible to truncate the sum from a certain term onwards. This is feasible when $\hat{V}(t)$ is a small perturbation. It should be noted that perturbations have always been assumed to be finite in the reasoning conducted so far. We will discuss this assumption in the following paragraph.

6.2.2 Transition Probabilities

Consider a system described by a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t),$$

where $\hat{V} = \begin{cases} 0 \text{ if } t \leq t_0 \\ \hat{V}(t) \text{ if } t > t_0. \end{cases}$ and let $|n\rangle$, E_n be the states and eigenvalues of the unperturbed Hamiltonian. Suppose the system is in the initial state $|i\rangle$ at $t = t_0$, so its temporal evolution is determined by:

$$|\phi_S(t)\rangle = U_S(t,t_0)\,|i\rangle = \sum_{n=0}^{\infty} c_n(t)\,|n\rangle\,,$$

where $\sum_{n=0}^{\infty}|c_i|^2 = 1$. Since the states $|n\rangle$ are orthonormal, projecting the state $|\phi_S\rangle$ onto the state $|n\rangle$ determines the coefficient c_n, and this holds for any $n \in \mathbb{N}$:

$$\begin{aligned} c_n(t) = \langle n|\phi_S(t)\rangle &= \langle n|\hat{U}_S(t,t_0)|i\rangle \\ &= \langle n|e^{-i\frac{\hat{H}_0(t-t_0)}{\hbar}}\hat{U}_I(t,t_0)|\,|i\rangle\rangle \\ &= e^{-i\frac{E_n(t-t_0)}{\hbar}}\,\langle n|\hat{U}_I(t,t_0)|i\rangle\,. \end{aligned}$$

This allows us to access the transition probability $P_{i\to n}$ from the initial state $|i\rangle$ to any eigenstate $|n\rangle$ of $\hat{H}_0$:

$$P_{i\to n} = |\langle n|\phi_S(t)\rangle|^2 = |c_n(t)|^2 = \left|\langle n|\hat{U}_I(t,t_0)|i\rangle\right|^2.$$

Note that by assumption $\hat{V}(t) = 0$ for all $t \leq t_0$, so $|i\rangle$ is not only an eigenstate of $\hat{H}_0$ but also of $\hat{H}$. Let's determine the expression of the transition probability at the first order in $\hat{V}$. Note that in the first order:

$$\hat{U}_I(t,t_0) = \mathbb{1} - \frac{i}{\hbar}\int_{t_0} t dt_1 \hat{V}_I(t_1),$$

thus :

$$\begin{aligned} \langle n|\hat{U}_I(t,t_0)|\,|i\rangle\rangle &= -\frac{i}{\hbar}\int_0^t dt_1\,\langle n|\hat{V}_I(t,t_0)|i\rangle \\ &= -\frac{i}{\hbar}\int_0^t dt_1\,\langle n|e^{\frac{i}{\hbar}\hat{H}_0)(t_1-t_0)}\hat{V}(t,t_0)e^{\frac{-i}{\hbar}(\hat{H}_0)(t_1-t_0)}|\,|i\rangle\rangle \\ &= -\frac{i}{\hbar}\int_0^t dt_1 e^{-\frac{i}{\hbar}(E_n-E_i)(t_1-t_0)}\,\langle n|\hat{V}(t,t_0)|i\rangle\,, \end{aligned}$$

and finally

$$P_{i\to n} = \left|-\frac{i}{\hbar}\int_0^t dt_1 e^{-\frac{i}{\hbar}(E_n-E_i)(t_1-t_0)}\,\langle n|\hat{V}(t_1,t_0)|i\rangle\right|^2. \tag{6.21}$$

6.2.3 Particular cases :

1. Let us apply what precedes to the special case, when the potential does not depend on time. We get

$$\hat{V} = \begin{cases} 0 \text{ si } t \leq t_0 \\ \hat{V} \text{ si } t > t_0, \end{cases}$$

and 6.21 becomes:

$$\begin{aligned} P_{i\to n}(t) &= \frac{1}{\hbar^2}\left|\langle n|\hat{V}|i\rangle \int_0^t dt_1 e^{-\frac{i}{\hbar}(E_n-E_i)(t_1-t_0)}\right|^2 \\ &= \frac{1}{\hbar^2}\left|\frac{\hbar}{i}\langle n|\hat{V}|i\rangle \frac{e^{-\frac{i}{\hbar}(E_n-E_i)(t-t_0)}-1}{E_n.-E_i}\right|^2 \\ &= \left|\langle n|\hat{V}|i\rangle\right|^2 \left|\frac{1-e^{-\frac{i}{\hbar}(E_n-E_i)(t-t_0)}}{E_n-E_i}\right|^2 \\ &= \left|\langle n|\hat{V}|i\rangle\right|^2 \frac{4}{(E_n-E_i)^2}\sin^2\left(\frac{(E_n-E_i)(t-t_0)}{2\hbar}\right). \end{aligned}$$

With no loss of generality take $t_0 = 0$ and re-writting the preceding expression $P_{i\to n}(t)$ in the form

$$P_{i\to n}(t) = \frac{1}{\hbar^2}\left|\langle n|\hat{V}|i\rangle\right|^2 f\left(\frac{E_n-E_i}{\hbar}\right), \tag{6.22}$$

with $f(\omega) = \frac{4}{\omega^2}\sin\left(\frac{\omega t}{2}\right)$ et $\omega = \frac{E_n-E_i}{\hbar}$. Note that $\lim_{t\to 0} f(\omega) = t^2$ and

$$f(\omega) = \begin{cases} 0 \text{ for } \omega = \frac{2k\pi}{t},\ k \in \mathbb{Z}^* \\ \\ \frac{4}{\omega^2} \text{ if } \frac{\omega t}{2} = \frac{\pi}{2} + k\pi, \end{cases}$$

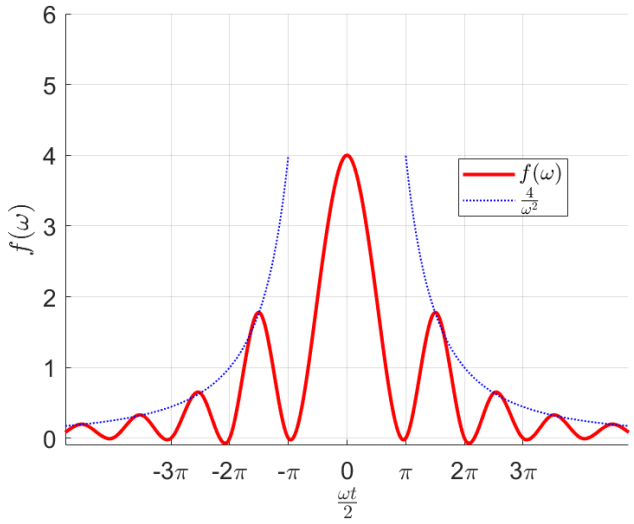


Figure 6.2: $f(\omega)$

At a fixed time t, the most favored transitions satisfy $\omega \leq \frac{2\pi}{t}$. With what precision can we determine the energy difference between an initial state and a final state after

a perturbation has been applied to the system for a time Δt? Transitions can occur to energy states $E_n - E_i \leq \frac{2\pi\hbar}{\Delta t}$. In other words, the measurement precision is at best of the order of $\Delta E \simeq \frac{2\pi\hbar}{\Delta t}$. This leads to:

$$\Delta E \Delta t \geq 2\pi\hbar, \tag{6.23}$$

which recalls the uncertainty relation $\Delta x \Delta p \geq \frac{\hbar}{2}$. Note that this is a purely mathematical resemblance, as energy and time are not observables.

For any value of ω, it is necessarily the case that $f(\omega) \leq \frac{4}{\omega^2}$. Furthermore, note that $\lim_{\Delta t \to \infty} \frac{\sin^2(\omega)\Delta t}{\omega^2 \Delta t} = \pi\delta(\omega)$ where δ is the Dirac delta function.
Indeed:

$$\begin{aligned}
\lim_{t\to\infty} \frac{1}{t} \int_{-\infty}^{+\infty} \frac{1}{\omega^2} \sin^2(\omega t)\phi(\omega) d\omega &= \lim_{t\to\infty} \frac{1}{t} \int_{-\infty}^{+\infty} \frac{t^2}{x^2} \sin^2(x)\phi(\frac{x}{t}) \frac{dx}{t} \\
&= \lim_{t\to\infty} \int_{-\infty}^{+\infty} \frac{1}{x^2} \sin^2(x)\phi(\frac{x}{t}) dx \\
&= \phi(0) \int_{-\infty}^{+\infty} \frac{\sin^2(x)}{x^2} dx \\
&= \pi\phi(0).
\end{aligned}$$

Thus replacing ω by $E_n - E_i$ and t by $\frac{t}{2\hbar}$ we obtain the *Fermi golden rule* :

$$P_{i\to n}(t) = \frac{2\pi}{\hbar} \Delta t \left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i). \tag{6.24}$$

It is sometimes more usefult to work with a *transition probability per unit time* : $\omega_{i\to n}(t) = \frac{\partial P_{i\to n}(t)}{\partial t}$, in our example

$$\omega_{i\to n}(t) = \frac{2\pi}{\hbar} \left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i).$$

2. if now the potential is given by $\hat{V} = \begin{cases} 0 \text{ if } t \leq t_0 \\ \hat{V}(t)e^{i\omega t} + \hat{V}^\dagger e^{-i\omega t} \text{ if } t > t_0. \end{cases}$

Equation 6.21 is now given by :

$$\begin{aligned}
P_{i\to n} &= \left| -\frac{i}{\hbar} \int_0^t dt_1 e^{i(E_n - E_i)\frac{t_1}{\hbar}} \left(\langle n|\hat{V}|i\rangle e^{i\omega t_1} + \langle n|\hat{V}^\dagger|i\rangle e^{-i\omega t_1} \right) \right|^2 \\
&= \left| \frac{1 - e^{-i\left(\frac{E_n - E_i}{\hbar} + \omega\right)t}}{E_n - E_i + \hbar\omega} \langle n|\hat{V}|i\rangle + \frac{1 - e^{-i\left(\frac{E_n - E_i}{\hbar} - \omega\right)t}}{E_n - E_i - \hbar\omega} \langle n|\hat{V}^\dagger|i\rangle \right|^2.
\end{aligned}$$

At long times, transitions to energy states with $E_n = E_i \pm \hbar\omega$ are favored, and we find:

$$\omega_{i\to n}(t) = \frac{2\pi}{\hbar} \left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i + \hbar\omega) + \frac{2\pi}{\hbar} \left|\langle n|\hat{V}^\dagger|i\rangle\right|^2 \delta(E_n - E_i + \hbar\omega).$$

Notice that the first term in the sum corresponds to an energy loss by the system, while the second term represents an energy gain by the system due to the perturbation. We can observe that the harmonic part induces transitions with $\Delta E = \pm\hbar\omega$. More precisely, the

term $\propto e^{-i\omega t}$ is the positive-energy part that allows transitions to final states with $E_n > E_i$, while $e^{+i\omega t}$ is the negative-energy term, allowing transitions to states with $E_n < E_i$.

This Fermi's golden rule is very important, as it explains how optical transitions occur in the presence of an oscillating external electromagnetic field, for instance, between levels of an atom or a solid.

3. Let's now consider the second-order effects. We will use a slightly different method to obtain the Dirac delta of the golden rule.

$$c_n(t) = e^{-\frac{i}{\hbar}E_n t} \langle n|\hat{U}_I(t,t_0)|i\rangle$$

where we have omitted the constant phase $e^{iE_n t_0/\hbar}$. Instead of turning on the perturbation at time t_0, we will assume that it turns on very slowly from $t = -\infty$.

4. Case of a nearly constant perturbation

$$\hat{V}(t) = \hat{V}e^{\epsilon t/\hbar} \qquad\qquad \epsilon > 0 \text{ real}$$

The idea is to take the limit $\epsilon \to 0$ at the end of the calculation to describe a constant perturbation. Let's write the perturbative expansion of $\hat{U}_I(t,-\infty)$. For the sake of calculation simplicity, which will become clear later, we will use the first form, the one used before the introduction of the time-ordered operator:

$$\hat{U}_I(t,-\infty) = \hat{I} - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1 \hat{V}_I(t_1) - \frac{1}{\hbar^2}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \hat{V}_I(t_1)\hat{V}_I(t_2) + \cdots$$

from which

$$e^{\frac{i}{\hbar}E_n t}c_n(t) = \underbrace{-\frac{i}{\hbar}\int_{-\infty}^{t} dt_1 \langle n|\hat{V}_I(t_1)|i\rangle}_{I_1} \underbrace{-\frac{1}{\hbar^2}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt2 \langle n|\hat{V}_I(t_1)|i\rangle \langle n|\hat{V}_I(t_2)|i\rangle}_{I_2}$$

Let's start with the first integral. Recall that

$$\begin{aligned}\hat{V}_I(t) &= e^{i\hat{H}_0 t/\hbar}\hat{V}(t)e^{-i\hat{H}_0 t\hbar} \\ &= e^{i\hat{H}_0 t/\hbar}\hat{V}e^{\epsilon t}e^{-i\hat{H}_0 t\hbar}\end{aligned}$$

Using the property of the eigenstate:

$$\begin{aligned}I_1 &= \int_{-\infty}^{t} dt_1 \langle n|\hat{V}_I(t_1)|i\rangle = \langle n|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 e^{i[(E_n-E_i)t_1 - i\epsilon t_1]/\hbar} \\ &= \langle n|\hat{V}|i\rangle \left.\frac{\exp\left(\frac{i}{\hbar}((E_n-E_i)t_1 - i\epsilon t_1)\right)}{\frac{i}{\hbar}(E_n - E_i - i\epsilon}\right|_{-\infty}^{t}\end{aligned}$$

If we were to stop at the first order, we would find the golden rule as follows:

$$P_{i\to n} = |c_n(t)|^2 = |\langle n|\hat{V}|i\rangle|^2 \frac{e^{2\epsilon t/\hbar}}{(E_n - E_i)^2 + \epsilon^2}$$

But

$$\lim_{\alpha\to 0}\frac{2\alpha}{x^2+\alpha^2} = 2\pi\delta(x), \text{ here } \alpha = \frac{\epsilon}{\hbar}$$
$$\lim_{\epsilon\to 0}\frac{dP_{i\to n}}{dt} = |\langle n|\hat{V}|i\rangle|^2$$
$$\Rightarrow \lim_{\epsilon\to 0}\frac{e^{2\epsilon t/\hbar}2\epsilon/\hbar}{(E_n-E_i)^2+\epsilon^2}$$
$$= \frac{2\pi}{\hbar}|\langle n|\hat{V}|i\rangle|^2\delta(\frac{E_n-E_i}{\hbar})$$
$$= \frac{2\pi}{\hbar}|\langle n|\hat{V}|i\rangle|^2\delta(E_n-E_i) = \omega_{i\to n} \quad \square$$

We have retrieved the previous result. Now let's calculate I_2:

$$I_2 = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_m \langle n|\hat{V}_I(t_1)|m\rangle\langle m|\hat{V}_I(t_2)|i\rangle$$

where we have introduced $\hat{I}$ as $\sum_m |m\rangle\langle m|$

$$I_2 = \sum_m \langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \exp\left(\frac{i}{\hbar}(E_n-E_m-i\epsilon)t_1\right)\exp\left(\frac{i}{\hbar}(E_m-E_i-i\epsilon)t_2\right)$$
$$= \sum_m \langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \exp\left(\frac{i}{\hbar}(E_n-E_m-i\epsilon)t_1\right)\frac{\exp\left(\frac{i}{\hbar}(E_m-E_i-i\epsilon)t_2\right)}{\frac{i}{\hbar}(E_m-E_i-i\epsilon)}\Bigg|_{-\infty}^{t_1}$$
$$= \sum_m \langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \exp\left(\frac{i}{\hbar}(E_n-E_m-i\epsilon)t_1\right)\frac{\exp\left(\frac{i}{\hbar}(E_m-E_i-i\epsilon)t_1\right)}{\frac{i}{\hbar}(E_m-E_i-i\epsilon)}$$
$$= -\hbar^2\sum_m \frac{\langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle\exp\left(\frac{i}{\hbar}(E_n-E_i-2i\epsilon)t\right)}{(E_m-E_i-i\epsilon)(E_n-E_i-2i\epsilon)}$$

The term $\exp\left(\frac{i}{\hbar}(E_n-E_i-2i\epsilon)t\right)/(E_n-E_i-2i\epsilon)$ is the same as in I_1 (except for $\epsilon\to 2\epsilon$, which doesn't change anything in the limit $\epsilon\to 0$). If we start from

$$\exp\left(\frac{i}{\hbar}E_n t\right)c_n(t) = \hat{I} - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\hat{V}_I(t_1) - \frac{1}{\hbar^2}\int_{-\infty}^{t} dt_1\int_{-\infty}^{t_1} dt_2\hat{V}_I(t_1)\hat{V}_I(t_2)$$

and replace the two previous results, we have

$$P_{i\to n} = |c_t(t)|^2 = \left|\frac{i}{\hbar}\int_{-\infty}^{t} dt_1\hat{V}_I(t_1) + \frac{1}{\hbar^2}\int_{-\infty}^{t} dt_1\int_{-\infty}^{t_1}\hat{V}_I(t_1)\hat{V}_I(t_2)\right|^2$$
$$= \left|\langle n|\hat{V}|i\rangle + \sum_m \frac{\langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle}{E_m-E_i-i\epsilon}\right|^2\frac{e^{2\epsilon t/\hbar}}{(E_n-E_i)^2+\epsilon^2}$$

and

$$\lim_{\epsilon\to 0}\frac{dP_{i\to n}}{dt} = \omega_{i\to n} = \frac{2\pi}{\hbar}\left|\langle n|\hat{V}|i\rangle + \sum_m \frac{\langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle}{E_m-E_i-i0^+}\right|^2\delta(E_n-E_i)$$

which is the second-order transition rate for a time-independent perturbation $\hat{V}$. Note the sum over intermediate states $|m\rangle$ typical of second-order perturbation. Here, a very suggestive image is that the system undergoes "virtual" transitions to states $|m\rangle$ without conserving energy since they occur in an arbitrarily short time before going to state $|n\rangle$.

The term $1/(x+i0^+)$ has a well-defined meaning, which is non-trivial when the states form an uncountable continuous spectrum. Here, we just need to be careful with the term $m = i$. This term has a singularity. It is simply due to the assumption that $\hat{V} = cste$ until $t = -\infty$. Indeed, in the integral, we would have a contribution:

$$\lim_{\epsilon\to 0}\int_{t_0}^{t} dt_2 \exp\left(\epsilon t_2/\hbar\right) = t - t_0 \Rightarrow |c_n(t)| \propto (t-t_0)^2 \Rightarrow \omega_{i\to n} \propto t - t_0$$

In the case of a real active perturbation from t_0 to t, we can assume $t_0 \to -\infty$ but keep t_0 finite only in the case $m = i$. Alternatively, we can project $\hat{V}$ onto $|i\rangle$ in $\hat{H}_0$:

$$\begin{aligned} \hat{H}_0 &\to \hat{H}_0 + \hat{P}_i\hat{V}\hat{P}_i \qquad & \hat{P}_i &= |i\rangle\langle i| \\ \hat{V} &\to \hat{V} - \hat{P}_i\hat{V}\hat{P}_i \end{aligned}$$

Thus, for the new $\hat{V}$, $\langle i|\hat{V}|i\rangle = 0$, and we no longer have the singularity problem.

In the case of a harmonic perturbation, we can follow the same path. For simplicity, let's assume we have only the term with positive energy:

$$\hat{V}(t) = \hat{V}e^{-i\omega t}e^{\epsilon t/\hbar}$$

Thus, we will have:

$$\omega_{i\to n} = \frac{2\pi}{\hbar}\left|\langle n|\hat{V}|i\rangle \frac{\exp\left(\frac{i}{\hbar}((E_n - E_i - \hbar\omega)t - i\epsilon t)\right)}{E_n - E_i - \hbar\omega - i\epsilon}\right.$$
$$\left. + \sum_m \frac{\langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle}{E_m - E_i - \hbar\omega - i\epsilon} \frac{\exp\left(\frac{i}{\hbar}(E_n - E_i - 2\hbar\omega - 2i\epsilon)t\right)}{E_n - E_i - 2\hbar\omega - 2i\epsilon}\right|^2$$

This time, the two Dirac deltas have different arguments due to the factor of 2ω. The limit as $\epsilon \to 0$ is not simple in general. Let's assume the case where the perturbation is zero at the first order:

$$\omega_{i\to n} = \frac{2\pi}{\hbar}\left|\sum_m \frac{\langle n|\hat{V}|m\rangle\langle m|\hat{V}|i\rangle}{E_m - E_i - \hbar\omega - i0^+}\right| \delta(E_n - E_i - 2\hbar\omega)$$

Once again, this form suggests a physical problem: each virtual transition "absorbs" a quantum of energy $\hbar\omega$. Therefore, the real transition will occur between states separated by an energy of $2\hbar\omega$ due to the second-order perturbation.

6.2.4 Continuous Spectrum

Simple considerations allow us to generalize these results to the case with a continuous spectrum.

discrete case	continuous case
$\|\phi_s(t)\rangle = \sum_n c_n(t)\|n\rangle$	$\|\phi_s(t)\rangle = \int dE\, c_E(t)\|E\rangle$

Here, the eigenstates of $\hat{H}_0$. $|E\rangle$ are normalized such that $\langle E|E'\rangle = \delta(E - E')$. Therefore, the state $|E\rangle$ is no longer dimensionless. Its dimensions are $[|E\rangle] = [1/\sqrt{E}]$.

If we assume $|\phi_s(t)\rangle$ is normalized to 1, we see from the previous relation that $[c_E(t)] = [1/\sqrt{E}]$. In our perturbative expressions, $|c_E(t)|^2$ always appears, which has dimensions of $1/E$. This is a transition probability per unit of energy. Therefore, we can retain all the previous formulas by replacing sums with integrals in dE, simply stating:

$$\omega_{i\to n}(\text{discrete case}) \to \frac{d\omega_{i\to E}}{dE}(\text{continuous case})$$

Example Fermi's golden rule under harmonic perturbation:

$$\frac{d\omega_{i\to E}}{dE} = \frac{2\pi}{\hbar}|\langle E|\hat{V}|i\rangle|^2\delta(E - E_i - \hbar\omega)$$

Chapter 7

Multi-Particle Systems

7.1 Symmetry Postulate

So far, we have limited ourselves to describing the laws governing the spatial and temporal evolution of a single particle. How can we generalize the Schrödinger equation for a single particle:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}^2}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{7.1}$$

to systems composed of multiple particles?

Consider, for example, a system with two particles labeled as 1 and 2. Suppose that each one-particle subsystem is described by wave functions $\phi_i(r_i)$ for $i \in \{1, 2\}$. The most naive response, which would suggest that the product of one-particle wave functions satisfies the Schrödinger equation, fails in the general case. Indeed, such a solution, on the one hand, assumes that the probabilities of particle presence are entirely independent (which amounts, among other things, to neglecting all interactions between particles), and, on the other hand, potentially violates the linearity of the Schrödinger equation. More generally, for a system of two interacting particles through a potential $U(\mathbf{r_1}, \mathbf{r_2})$, writing

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial {\mathbf{r_1}}^2} - \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial {\mathbf{r_2}}^2} + \hat{V}(\mathbf{r_1}) + \hat{V}(\mathbf{r_2}) + \hat{U}(r_1, r_2)\right)\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}) = E\psi_1(\mathbf{r_1})\psi_2(\mathbf{r_2}),$$

presupposes that the two-particle Schrödinger equation:

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial {\mathbf{r_1}}^2} - \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial {\mathbf{r_2}}^2} + \hat{V}(\mathbf{r_1}) + \hat{V}(\mathbf{r_2}) + \hat{U}(r_1, r_2)\right)\psi(\mathbf{r_1}, \mathbf{r_2}) = E\psi(\mathbf{r_1}, \mathbf{r_2}), \tag{7.2}$$

is separable, which is not necessarily true. We must find a way to describe the system using a single wave function that depends on all coordinates.

Suppose the particles are indistinguishable. This implies, among other things, that the probability $|\psi(\mathbf{r_1}, \mathbf{r_2})|^2$ of finding one particle at point $\mathbf{r_1}$ and the other at point $\mathbf{r_2}$ must be equal to $|\psi(\mathbf{r_2}, \mathbf{r_1})|^2$. In other words, we must have:

$$\begin{aligned}
&\psi(\mathbf{r_2}, \mathbf{r_1}) = e^{i\phi}\psi(\mathbf{r_1}, \mathbf{r_2}) \\
\implies &\psi(\mathbf{r_1}, \mathbf{r_2}) = e^{i\phi}\psi(\mathbf{r_2}, \mathbf{r_1}) = e^{i2\phi}\psi(\mathbf{r_1}, \mathbf{r_2}) \\
\implies &e^{i2\phi} = 1 \\
\implies &e^{i\phi} = \pm 1.
\end{aligned}$$

Let $\mathbb{P}_{12}$ be the operator that acts on the system by interchanging particles 1 and 2, i.e.:

$$\mathbb{P}_{1,2}\psi(\mathbf{r_1},\mathbf{r_2}) = \psi(\mathbf{r_2},\mathbf{r_1}).$$

In the case of indistinguishable particles, this operator has eigenvalues ± 1, and the corresponding wave functions are either symmetric (particles described by these functions are *bosons*) or antisymmetric (particles described by these functions are *fermions*).

This reasoning generalizes to systems of n particles, where $n \in \mathbb{N}$. Let $\psi(r_1,\cdots,r_n)$ be the wave function of the system. First of all, note that exchanging particle j and particle k for $j,\ k \in \{1,\cdots,n\}$ is equivalent to exchanging particle k and particle j, i.e., $\mathbb{P}_{j,k} = \mathbb{P}_{k,j}$. Furthermore,

$$\begin{aligned}\mathbb{P}_{j,k}\left(\mathbb{P}_{j,k}\psi(r_1,\cdots,r_j,\cdots,r_k,\cdots,r_n)\right) &= \mathbb{P}_{j,k}\left(\psi(r_1,\cdots,r_j,\cdots,r_k,\cdots,r_n)\right)\\ &= \psi(r_1,\cdots,r_j,\cdots,r_k,\cdots,r_n)\\ &= \mathbb{1}\left(\psi(r_1,\cdots,r_j,\cdots,r_k,\cdots,r_n)\right),\end{aligned}$$

so, $\mathbb{P}_{j,k}\mathbb{P}_{j,k} = \mathbb{1}$, and $\mathbb{P}_{j,k}^{-1} = \mathbb{P}_{j,k} = \mathbb{P}_{k,j}$. Finally, the sign of the operator $\mathbb{P}_{j,k}$ must be the same for all $j,\ k \in \{1,\cdots,n\}$. In fact:

$$\mathbb{P}_{j,k} = \mathbb{P}_{1,j}\mathbb{P}_{2k}\mathbb{P}_{1,2}\mathbb{P}_{2k}\mathbb{P}_{1,j}.$$

Notice that this has important consequences in the description of the physics of the system. Consider, for example, an arbitrary observable $\hat{O}$ of the system. Using the above, its average value must satisfy, for all $j,\ k \in \mathbb{N}$:

$$\langle\psi|\hat{O}|\psi\rangle = \langle\psi|\mathbb{P}_{j,k}^{\dagger}\hat{O}\mathbb{P}_{j,k}|\psi\rangle\,,$$

which implies $\hat{O} = \mathbb{P}_{j,k}^{\dagger}\hat{O}\mathbb{P}_{j,k}$, and the operator $\mathbb{P}_{j,k}$ commutes with all observables. In particular, if $\hat{H}$ is the system's Hamiltonian, $[\mathbb{P}_{jk},\hat{H}] = [\hat{H},\mathbb{P}_{jk}]$ for all $j,\ k \in \mathbb{N}$. Physically, this result is expected: since the particles are assumed to be indistinguishable, there is no reason for the system's Hamiltonian to be modified by the exchange of two particles.

A "permutation operator" is an operator of the form $\mathbb{P} = \prod \mathbb{P}_{j,k}$. As per what was previously discussed, since all $\mathbb{P}_{j,k}$ have the same sign, we can always simultaneously diagonalize $\mathbb{P}$ and $\hat{H}$. In other words, $[\mathbb{P},\hat{H}] = 0$ for any operator $\mathbb{P}$.

We have seen that the wavefunctions corresponding to eigenvalues of a permutation operator are either symmetric or antisymmetric. Let's demonstrate that this result generalizes to any wavefunction, ψ.

Consider the group $\mathcal{S}_n$ of permutations on n objects and define the operators $\hat{S} = \sum_{\mathbb{P}\in\mathcal{S}_n}\mathbb{P}$ and $\hat{A} = \sum_{\mathbb{P}\in\mathcal{S}_n}\text{sign}(\mathbb{P})\mathbb{P}$. Apply these operators to the wavefunction ψ: $\hat{S}\psi = \psi_S$ and $\hat{A}\psi = \psi_A$, where ψ_S and ψ_A satisfy $\mathbb{P}_{j,k}\psi_S = \psi_S$ and $\mathbb{P}_{j,k}\psi_A = -\psi_A$, respectively. Since $\mathbb{P}_{j,k}$ is self-adjoint, using what was previously mentioned, we have:

$$\langle\psi_S|\psi_A\rangle = \langle\psi_S|\mathbb{P}_{j,k}^{\dagger}|\psi_A\rangle = \langle\psi_S|\mathbb{P}_{j,k}|\psi_A\rangle = \langle\psi_S|\mathbb{P}_{j,k}\psi_A\rangle = -\langle\psi_S|\psi_A\rangle,$$

which means that $\langle\psi_S|\psi_A\rangle$ is a wavefunction that is either completely symmetric or completely antisymmetric. This is the *symmetry postulate*, which can be restated as follows:

Postulat 7.1.1 (Symmetry Postulate)**.** *The Hilbert space of a set of n identical particles is either even or odd under transpositions $P_{j,k}$.*

In the rest of this chapter, we aim to describe the physics of these systems. From this point forward, $\mathcal{H}_1$ denotes the Hilbert space of one-particle states of a system of n particles, and the set $\{\phi_{n_i}(x_i)\}_{i=1}^n$ is an orthonormal basis for these spaces. Any wavefunction ψ of the system can be decomposed in this basis as follows:

$$\begin{aligned}\psi(x_1,\cdots,x_n) &= \langle x_1| \otimes \cdots \otimes \langle x_n| \, |\psi\rangle \\ &= \langle x_1| \otimes \cdots \otimes \langle x_n| \sum_{n_1,\cdots,n_n} c_{n_1,\cdots,n_n} |\phi_{n_1}\rangle \cdots |\phi_{n_n}\rangle \\ &= \sum_{n_1,\cdots,n_n} c_{n_1,\cdots,n_n} \langle x_1|\phi_{n_1}\rangle \cdots \langle x_n|\phi_{n_n}\rangle \\ &= \sum_{n_1,\cdots,n_n} c_{n_1,\cdots,n_n} \phi_{n_1}(x_1)\cdots\phi_{n_n}(x_n),\end{aligned}$$

which is neither symmetric nor antisymmetric, as predicted by the symmetry postulate. Therefore, we can specify the form of ψ a bit further.

7.2 Bosons

Bosons are particles described by a symmetric wave function ψ, which implies the following system:

$$\begin{aligned}\psi(x_1,\cdots,x_n) = \hat{S}\psi(x_1,\cdots,x_n) &= \sum_{\mathbb{P}\in\mathcal{S}_n} \mathbb{P}\psi(x_1,\cdots,x_n) \\ &= \sum_{\mathbb{P}\in\mathcal{S}_n} \mathbb{P}\left(\sum_{n_1,\cdots,n_n} c_{n_1,\cdots,n_n}\phi_{n_1}(x_1)\cdots\phi_{n_n}(x_n)\right) \\ &= \sum_{\mathbb{P}\in\mathcal{S}_n} c_{n_1,\cdots,n_n}\phi_{n_1}(x_{\mathbb{P}(1)})\cdots\phi_{n_n}(x_{\mathbb{P}(n)}).\end{aligned}$$

The normalization of the states requires $\psi(x_1,\cdots,x_n) = \frac{1}{\sqrt{n!}\sqrt{\prod_k n_k!}} \sum_{\mathbb{P}\in\mathcal{S}_n} \phi_{n_1}(x_{\mathbb{P}(1)})\cdots\phi_{n_n}(x_{\mathbb{P}(n)})$.

7.3 Fermions

Fermions are particles described by an antisymmetric wave function ψ, which implies the following system:

$$\begin{aligned}\psi(x_1,\cdots,x_n) = -\hat{A}\psi(x_1,\cdots,x_n) &= -\sum_{\mathbb{P}\in\mathcal{S}_n} \mathrm{sign}(\mathbb{P})\mathbb{P}\psi(x_1,\cdots,x_n) \\ &= -\sum_{\mathbb{P}\in\mathcal{S}_n} \mathrm{sign}(\mathbb{P})\mathbb{P}\left(\sum_{n_1,\cdots,n_n} c_{n_1,\cdots,n_n}\phi_{n_1}(x_1)\cdots\phi_{n_n}(x_n)\right) \\ &= -\sum_{\mathbb{P}\in\mathcal{S}_n} \mathrm{sign}(\mathbb{P})c_{n_1,\cdots,n_n}\phi_{n_1}(x_{\mathbb{P}(1)})\cdots\phi_{n_n}(x_{\mathbb{P}(n)}).\end{aligned}$$

We recognize the expression of a determinant. If we also impose the normalization of the states, we obtain:

$$\psi(x_1,\cdots,x_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_{n_1}(x_1) & \cdots & \phi_{n_n}(x_n) \\ \vdots & & \vdots \\ \phi_{n_n}(x_1) & \cdots & \phi_{n_n}(x_n)\end{vmatrix}.$$

From properties of the determinant, it can be directly deduced that the fermion wave function is identically zero if two one-particle wave functions are identical, meaning that *two particles cannot simultaneously be in the same state.* This is known as the *Pauli exclusion principle.*

7.3.1 Non-interacting Fermions:

In the particular case of a system of n identical non-interacting particles, the system is described as a sum of n-particle Hamiltonians: $\hat{H} = \sum_{i=1}^{n} \hat{H}_i$, where $\hat{H}_i$ acts on coordinate i. Let ϕ_n be the wavefunctions corresponding to the eigenstates of $\hat{H}$ and E_n the corresponding energies: $\hat{H}_i\phi_n(x_i) = E_n\phi_n(x_i)$. Since the particles are identical, all $\hat{H}_i$ are necessarily identical:

$$\hat{H}\phi_{n_1}(x_1)\cdots\phi_{n_n}(x_n) = (E_{n_1} + \cdots + E_{n_n})\left(\phi_{n_1}(x_1)\cdots\phi_{n_n}(x_n)\right),$$

and the sum of energies remains unchanged under coordinate permutations:

$$\hat{H}\phi_{n_1}(x_{\mathbb{P}(1)})\cdots\phi_{n_n}(x_{\mathbb{P}(n)}) = (E_{n_1} + \cdots + E_{n_n})\left(\phi_{n_1}(x_{\mathbb{P}(1)})\cdots\phi_{n_n}(x_{\mathbb{P}(n)})\right).$$

In other words, we have the following equality:

$$\psi(x_1,\cdots,x_n) = \hat{H}\begin{vmatrix} \phi_{n_1}(x_1) & \cdots & \phi_{n_n}(x_n) \\ \vdots & & \vdots \\ \phi_{n_n}(x_1) & \cdots & \phi_{n_n}(x_n) \end{vmatrix} = (E_{n_1} + \cdots + E_{n_n})\begin{vmatrix} \phi_{n_1}(x_1) & \cdots & \phi_{n_n}(x_n) \\ \vdots & & \vdots \\ \phi_{n_n}(x_1) & \cdots & \phi_{n_n}(x_n) \end{vmatrix}.$$

7.3.2 Exchange Terms:

Consider a two-fermion state:

$$\psi(x_1,x_2) = \frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right)$$

with wave functions ϕ_1 and ϕ_2. The expectation value of any observable of the system is:

$$\begin{aligned}\langle\psi|\hat{O}|\psi\rangle = \int dx_1 \int dx_2 &\left(\frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right)\right)^* \hat{O}(x_1,x_2) \\ &\times \left(\frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right)\right) \\ = \frac{1}{2}\int dx_1 \int dx_2 \Big(&\phi_1^*(x_1)\phi_2^*(x_2)\hat{O}(x_1,x_2)\phi_1(x_1)\phi_2(x_2) \\ &+ \phi_1^*(x_2)\phi_2^*(x_1)\hat{O}(x_1,x_2)\phi_1(x_2)\phi_2(x_1) \\ &- \phi_1^*(x_1)\phi_2^*(x_2)\hat{O}(x_1,x_2)\phi_1(x_2)\phi_2(x_1) \\ &- \phi_1^*(x_2)\phi_2^*((x_1)\hat{O}(x_1,x_2)\phi_1(x_1)\phi_2(x_2)\Big).\end{aligned}$$

The last two terms are *exchange terms.*

7.4 Second Quantization:

Second quantization is an approach used to represent systems composed of multiple particles. We consider a situation where the number of particles can potentially change, noting that a particle's state is entirely determined by the one-particle functions in the basis of $\mathcal{H}_1$. We construct the *Fock space* where kets indicate the number of times a wave function is involved. It's worth noting that for bosons, the n_i appearing in $|n_1, n_2, \cdots\rangle$ can be arbitrary, while for fermions, they can only take the values 0 or 1 due to the Pauli exclusion principle.

We introduce creation and annihilation operators to increase or decrease the number of particles. We distinguish between the cases where the particles are fermions or bosons:

- Fermionic Case:

$$\begin{cases} \hat{c}_i^\dagger \left|n_1, \cdots, n_i, \cdots\right\rangle = (-1)^{n_1+\cdots+n_{i-1}} (1-n_i) \left|n_1, \cdots, n_i+1, \cdots\right\rangle, \\ \hat{c}_i \left|n_1, \cdots, n_i, \cdots\right\rangle = (-1)^{n_1+\cdots+n_{i-1}} n_i \left|n_1, \cdots, n_i-1, \cdots\right\rangle, \end{cases}$$

  Let's define the *anticommutator* of two operators A and B: $\{A, B\} = AB + BA$. It can be shown that creation and annihilation operators in the fermionic case satisfy:

  - $\{c_i, c_j\} = \{c_i^\dagger, c_j^\dagger\} = 0$
  - $\{c_i, c_j^\dagger\} = \delta_{ij}$.

- Bosonic Case:

$$\begin{cases} \hat{c}_i^\dagger \left|n_1, \cdots, n_i, \cdots\right\rangle = \sqrt{n_i+1} \left|n_1, \cdots, n_i+1, \cdots\right\rangle, \\ \hat{c}_i \left|n_1, \cdots, n_i, \cdots\right\rangle = \sqrt{n_i} \left|n_1, \cdots, n_i-1, \cdots\right\rangle, \end{cases}$$

  It can be shown that creation and annihilation operators in the bosonic case satisfy:

  - $[c_i, c_j] = [c_i^\dagger, c_j^\dagger] = 0$
  - $[c_i, c_j^\dagger] = \delta_{ij}$.

  We observe in the bosonic case an analogy with the results obtained in the study of the harmonic oscillator.

Chapter 8

Variational Principle

8.1 General Idea:

Consider a physical system described by a Hamiltonian $\hat{H}$. Let $\mathcal{H}$ be the Hilbert space associated with the system's states and $\{\phi_n\}$ be an orthonormal basis of wave functions, with E_n as the energies associated with the corresponding states. For any state $|\psi\rangle$ of the system, the following inequality, known as the *variational principle*, is always satisfied:

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0,$$

where E_0 represents the energy of the system's ground state. Furthermore, equality holds if and only if $|\psi\rangle = |\phi_0\rangle$, and ϕ_0 is non-degenerate. We provide a proof of this fact in the discrete case, and the continuous case easily follows by using properties of the integral. In the basis of eigenstates, the system's Hamiltonian is rewritten as $\hat{H} = \sum_{n=0}^{\infty} E_n |\phi_n\rangle\langle\phi_n|$, so:

$$\begin{aligned}
\langle\psi|\hat{H}|\psi\rangle &= \sum_{n=0}^{\infty} E_n |\langle\psi|\phi_n\rangle|^2 \\
&\geq E_0 \sum_{n=0}^{\infty} |\langle\psi|\phi_n\rangle|^2 \\
&= E_0 \sum_{n=0}^{\infty} \langle\psi|\phi_n\rangle\langle\phi_n|\psi\rangle \\
&= E_0\langle\psi|\psi\rangle.
\end{aligned}$$

Idea: The previous relation will help us approximate the ground state. The method will be as follows: we start by approximating a certain wave function corresponding to a state $|\psi\rangle$, and then we use the variational principle to find the parameter values that minimize ψ.

This method generalizes to excited states. For any $|\psi\rangle \in \mathcal{H}$ such that $\langle\phi_0|\psi\rangle = 0$, the following inequality is always satisfied:

$$\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_1.$$

The proof of this fact is identical to the proof of the variational principle for the ground state since the term involving $|\phi_0\rangle$ drops out by the choice of ψ.

Example 8.1.1 (One-Dimensional Harmonic Oscillator). The system's Hamiltonian is given by:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}}_{=\hat{T}} + \underbrace{\frac{1}{2}m\omega^2x^2}_{=\hat{V}}. \tag{8.1}$$

We introduce a trial function $\psi_a(x) = \frac{1}{x^2+a}$ with $a > 0$. Note that this choice has no physical validity since the solution should decrease exponentially at infinity. Let $I_n = \int_{-\infty}^{\infty} dx \frac{1}{(x^2+a)^n}$ for any $n \in \mathbb{N}$. We calculate:

$$I_1 = \int_{-\infty}^{+\infty} dx \frac{1}{x^2+a} = \frac{1}{\sqrt{a}} \arctan\left(\frac{x}{\sqrt{a}}\right)\Big|_{-\infty}^{\infty} = \frac{\pi}{\sqrt{a}},$$

$$\frac{dI_n}{da} = -nI_{n+1}.$$

Therefore $I_2 = \frac{\pi}{2}a^{-\frac{3}{2}}$, $I_3 = \frac{3\pi}{8}a^{-\frac{5}{2}}$ et $I_4 = \frac{5\pi}{16}a^{-\frac{7}{2}}$. After repeated integration by parts, we find :

$$\langle\psi|\hat{T}|\psi\rangle = \int_{-\infty}^{\infty} dx \frac{1}{x^2+a}\frac{d^2}{dx^2}\frac{1}{x^2+a} = \underbrace{\frac{1}{x^2+a}\frac{d}{dx}\frac{1}{x^2+a}\Big|_{\infty}^{\infty}}_{=0} - \int_{-\infty}^{\infty}\left(\frac{d}{dx} - \frac{1}{x^2+a}\right)^2 dx = -4(I_3 - aI_4)\left(-\frac{\hbar}{2m}\right)$$

$$\langle\psi|\hat{V}|\psi\rangle = \int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^4} = (I_1 - aI_2)\left(\frac{1}{2}m\omega^2\right) \text{ et } \langle\psi|\psi\rangle = I_2.$$

The energy corresponding to a state $|psi_a\rangle$ is given by

$$E(a) = \frac{\langle\psi_a|\hat{H}|\psi_a\rangle}{\langle\psi_a|\psi_a\rangle} = \frac{\hbar^2}{4m}\frac{1}{a} + \frac{1}{2}m\omega^2 a,$$

and we seek a such that the energy is minimal:

$$\frac{dE(a)}{da} = 0 \implies \frac{1}{2}m\omega^2 a^2 = \frac{\hbar^2}{4m} \implies a = \frac{\hbar}{m\omega\sqrt{2}}.$$

The energy of the ground state is given by $E(\frac{\hbar}{m\omega\sqrt{2}}) = \frac{\hbar\omega}{\sqrt{2}} \simeq 0.72\hbar\omega$. Note that the approximate value is considerably higher than the exact (known in the case of the harmonic oscillator) ground state energy: $0.72\hbar\omega > 0.5\hbar\omega$.

Note 8.1.2. In our case, since we are approximating states, it is impossible to strictly impose $\langle\phi_0|\psi\rangle$. If $|\psi_0\rangle$ is the approximation of the ground state, at best we have $\langle\psi_0|\psi\rangle = 0$. This implies the introduction of additional errors.

Example 8.1.3 (One-Dimensional Harmonic Oscillator:). Now, we want to determine the first excited state of the one-dimensional harmonic oscillator. The Hamiltonian is still given by equation 8.1. Let's set $\psi_a(x))\frac{x}{(x^2+a)^2}$ with $a > 0$. This function is odd under the inversion $x \to -x$. Therefore, it will be orthogonal to the ground state $\psi_0(x)$, which is even.

Note 8.1.4. We have chosen to divide by $(x^2+a)^2$ rather than (x^2+a^2). This is due to the fact that even if $x/(x^2+a^2)$ is square-integrable, the potential term would eventually diverge.

For the computation, we will need the following integrations :

$$I_4 = \int_{-\infty}^{\infty} dx \frac{1}{(x^2+a)^4} = \frac{5\pi}{16}a^{-7/2} \qquad I_5 = \frac{35\pi}{128}a^{-9/2}$$

$$J_4 = \int_{-\infty}^{\infty} \frac{x^2}{(x^2+a)^4} = \frac{\pi}{16}a^{-5/2} \qquad I_6 = \frac{63\pi}{256}a^{-11/2}$$

$$k_4 = \int_{-\infty}^{\infty} dx \frac{x^4}{(x^2+a)^4} = \frac{\pi}{16}a^{-3/2}$$

Kinetic term:

$$\begin{aligned}
\langle\phi_a|\hat{T}|\phi_a\rangle &= -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^2}\frac{d^2}{dx^2}\frac{x^2}{(x^2+a)^2} = \cdots \\
&= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx \left(\frac{d}{dx}\frac{x}{(x^2+a)^2}\right)^2 \\
&= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx \left(-\frac{1}{(x^2+a)^2} - \frac{4x^2}{(x^2+a)^3}\right)^2 \\
&= \frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx \left(-\frac{3}{(x^2+a)^2} + \frac{4a}{(x^2+a)^3}\right)^2 \\
&= \frac{\hbar^2}{2m}\left(9I_4 - 24aI_5 + 16a^2 I_6\right) \\
&= \frac{\hbar^2}{2m}\left(\frac{45\pi}{16} - \frac{105\pi}{16} + \frac{63\pi}{16}\right)a^{-7/2} \\
&= \frac{3}{16}\pi\frac{\hbar^2}{2m}a^{-7/2}
\end{aligned}$$

Potential

$$\begin{aligned}
\langle\phi_a|\hat{V}|\phi_a\rangle &= \frac{1}{2}m\omega^2\int_{-\infty}^{\infty} dx \frac{x^4}{(x^2+a)^4} \\
&= \frac{1}{2}m\omega^2 k_4 \\
&= \frac{\pi}{32}m\omega^2 a^{-3/2}
\end{aligned}$$

Finally, the norm is

$$\begin{aligned}
\langle\phi_a|\phi_a\rangle &= \int_{-\infty}^{\infty} dx \frac{x^2}{(x^2+a)^2} = J_4 = \frac{\pi}{16}a^{-5/2} \\
E(a) &= \frac{1}{2}\left(\frac{3\hbar^2}{m}a^{-7/2} + m\omega^2 a^{-3/2}\right)\cdot\left(a^{-5/2}\right)^{-1} \\
&= 3\frac{\hbar^2}{2m}\frac{1}{a} + \frac{1}{2}m\omega^2 a \\
\frac{dE(a)}{da} &= -3\frac{\hbar^2}{2m}\frac{1}{a^2} + \frac{1}{2}m\omega^2 \\
\frac{dE(a)}{da} &= 0 \Rightarrow \frac{3\hbar^2}{2m}\frac{1}{a^2} = \frac{1}{2}m\omega^2 \\
\Rightarrow a^2 &= \frac{3\hbar^2}{m^2\omega^2} \\
a = &= \sqrt{3}\frac{\hbar}{m\omega} \\
E_1(a) &= \frac{3\hbar^2}{2m}\frac{m\omega}{\hbar\sqrt{3}} + \frac{\sqrt{3}}{2}\hbar\omega
\end{aligned}$$

We find $E(a) = \frac{3\hbar^2}{2ma} + \frac{1}{2}m\omega^2 a$ and the minimization of the energy gives us $a = \sqrt{3}\frac{\hbar}{m\omega}$ which allows us to approximate the energy of the first excited state :

$$E_1(a) = \sqrt{3}\hbar\omega \simeq 1,732\hbar\omega,$$

which is much superior to the effective value, known of the energy of the first excited state of the oscillator, that is $E_1^{\text{eff}} = 1,5\hbar\omega$.

More generally, if one cannot use a symmetry argument, one can always seek a state $|\phi\rangle$ that minimizes the energy expectation value, $E = \langle\phi|\hat{H}|\phi\rangle / \langle\phi|\phi\rangle$ with the constraint $\langle\phi|\psi\rangle = 0$, where $|\psi\rangle$ is the variational solution found for the ground state. If $|\psi\rangle$ is a good approximation, then its component orthogonal to $|0\rangle$ will be minimal. In this case, there is a high probability that the variational solution $|\phi\rangle$ will be almost orthogonal to $|0\rangle$ and will also provide a relatively good approximation to $|1\rangle$.

Note 8.1.5. Note that the variational approach makes error calculations extremely complicated: finding a lower bound for the sought-after energy assumes that a better approximation to the state is known, which makes any error calculation for the first approximation absurd. Furthermore, for any arbitrary wave function ψ, minimizing the error actually leads to restoring the Schrödinger equation.

We can try to find the exact solution to the problem using the variational approach. Consider a Hamiltonian $\hat{H}$ and an arbitrary state $\psi(x)$. The energy expectation value is given by

$$E[\psi, \psi^*] = \langle\psi|\hat{H}|\psi\rangle = \int dx \psi^* \hat{H} \psi$$

Since ψ is a complex-valued function, we consider E to be a function of ψ and ψ^* (i.e., of $\Re(\psi)$ and $\Im(\psi)$).

Introduce an infinitesimal variation $\delta\psi^*(x)$ of $\psi^*(x)$, with $\delta\psi^*(x) \to 0$. We are treating ψ and ψ^* as two independent variables, and thus

$$E[\psi, \psi^* + \delta\psi^*] = \int dx \psi^* \hat{H} \psi + \int dx \delta\psi^* \hat{H} \psi$$

and

$$\delta E = E[\psi, \psi^* + \delta\psi^*] - E[\psi, \psi^*] = \int dx \delta\psi^* \hat{H} \psi$$

It is necessary to introduce the concept of a functional derivative at this point. Alternatively, we can imagine a function ψ "discretized" on a grid x_j, $j = -\infty, \cdots, 1, 2, \cdots$. In this case, we can interpret this problem in a variational context with an infinite number of parameters $\delta\psi_j^* = \delta^*(x_j)$. This way, we recover the concept of a traditional derivative.

To minimize E, we need $\delta E = 0$. Now,

$$\delta E = \int dx \delta\psi^* \hat{H} \psi$$

In the discretized version,

$$\delta E = \sum_j \delta\psi_j^* \hat{H} \psi_j$$

and the (true) derivative of E with respect to ψ_j^* is

$$\frac{\partial E}{\partial \psi_j^*} = \hat{H}\psi_j$$

The minimization condition is then

$$\frac{\partial E}{\partial \psi_j^*} = 0 \ \forall j \Rightarrow \hat{H}\psi_j = 0 \ \forall j \Rightarrow \psi_j = 0$$

and similarly for ψ_j^*.

This is a pathological result, explained by our omission of the norm constraint: we want $\langle\psi|\psi\rangle = 1$.

To find a constrained minimum, we use the Lagrange multipliers. We want to minimize $\langle\psi|\hat{H}|\psi\rangle$ with the constraint $\langle\psi|\psi\rangle = 1$. We introduce the functional

$$E[\psi, \psi^*, \lambda] = \int dx \psi^* \hat{H}\psi - \lambda\left(\int dx \psi^*\psi - 1\right)$$

As before:

$$\delta E = \int dx \delta\psi^* \hat{H}\psi - \lambda \int dx \delta\psi^*\psi$$

The condition $\delta E = 0$ for arbitrary variation $\delta\psi^*(x)$ implies equality of the integrands:

$$\hat{H}\psi = \lambda\psi$$

It's the Schrödinger equation! The variational principle, without additional conditions, should lead to the exact solution of the problem.

Reminder 8.1.6. (Harmonic Oscillator) We have

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

with $[\hat{x}, \hat{p}] = i\hbar$. Let's introduce

$$\hat{a}^\dagger \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}$$
$$\hat{a} \equiv \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - i\frac{1}{\sqrt{2m\hbar\omega}}\hat{p}$$
$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger)$$
$$\hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}(\hat{a} - \hat{a}^\dagger)$$

We note

$$[\hat{a}^\dagger, \hat{a}] = \hat{a}^\dagger\hat{a} - \hat{a}\hat{a}^\dagger = 1$$

Why is this commutator so important? Let's try to define $\hat{a}^\dagger \to 2\hat{a}^\dagger$ and $\hat{a} \to 2\hat{a}$.

Note 8.1.7. If $|\phi\rangle$ such that $\hat{a}\hat{a}^\dagger|\phi\rangle = \lambda|\phi\rangle$ then

$$\hat{a}\hat{a}^\dagger(\hat{a}^\dagger|\phi\rangle) = (\lambda - 1)(\hat{a}^\dagger|\phi\rangle)$$

the choice of $\hat{a}^\dagger$ and $\hat{a}$ ensures that $\hat{a}\hat{a}^\dagger$ is the operator $\hat{N}$, not $\alpha\hat{N}$.

There is a ground state $|\phi_0\rangle$ such that

$$\hat{a}^\dagger|\phi_0\rangle = 0$$

Demo.

$$\hat{a}\hat{a}^\dagger \underbrace{(\hat{a}^2|\phi_n\rangle)}_{|\phi_0\rangle} = (n - n)\hat{a}^n|\phi_n\rangle = 0$$
$$\|\hat{a}^{n+1}|\phi_n\rangle\|^2 = 0$$
$$\Rightarrow \hat{a}^{n+1}|\phi_n\rangle \propto \hat{a}^\dagger|\phi_0\rangle = 0$$

□

The spectrum is

$$\hat{H}\,|\phi_n\rangle = \hbar\omega(n+\frac{1}{2})\,|\phi_n\rangle$$

The norms are

$$\hat{a}\,|\phi_n\rangle = \sqrt{n+1}\,|\phi_{n+1}\rangle$$
$$\hat{a}^\dagger\,|\phi_n\rangle = \sqrt{n}\,|\phi_{n-1}\rangle$$
$$|\phi_n\rangle = \frac{(\hat{a})^n}{\sqrt{n!}}\,|\phi_0\rangle$$

The $\{|\phi_n\rangle\}$ are non-degenerate, we thus have $\langle\phi_i|\phi_j\rangle = \delta_{ij}$.

Note 8.1.8.

$$\langle\phi_n|\hat{x}|\phi_n\rangle = \langle\phi_n|\hat{\rho}|\phi_n\rangle = 0$$

and

$$\langle\phi_n|\hat{x}^2|\phi_n\rangle = \cdots = \frac{\hbar}{2m\omega}(2n+1)$$
$$\langle\phi_n|\hat{p}^2|\phi_n\rangle = \cdots = \frac{m\hbar\omega}{2}(2n+1)$$

for $n=0$ we have $\Delta\hat{x}\Delta\hat{p} = \dfrac{\hbar}{2}$

For a Harmonic oscillator in isotropic 3D, we have

$$\hat{H} = \frac{|\hat{\mathbf{p}}|^2}{2m} + \frac{1}{2}m\omega^2|\hat{\mathbf{r}}|^2$$

Note 8.1.9.

$$|\hat{\mathbf{p}}|^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$$
$$|\hat{\mathbf{x}}|^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2$$

thus

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$
$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$
$$\hat{H} = \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2$$
$$\hat{H} = \frac{\hat{p}_z^2}{2m} + \frac{1}{2}m\omega^2\hat{z}^2$$

Separable hamiltonian:

$$\psi(x,y,z) = \psi_n(x)\phi_m(y)\xi_l(z)$$

where $\hat{H}_x\psi_n(x) = E_n\psi(x)$, with $E_n = \hbar\omega(n+\dfrac{1}{2})$, similarly for $\hat{y}$ and $\hat{z}$. Thus $\hat{H}\psi = E_{nml}\psi$, with $E_{nml} = \hbar\omega(n+m+l+\dfrac{3}{2})$ Why is the harmonic oscillator so important?

1. Except for pathological cases, all systems admit a harmonic approximation.

   Example 8.1.10. Central Potential We have

   $$V = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{L^2}{2mr^2} - \frac{\alpha}{r}$$

   One could start from the solution of the harmonic problem and calculate more accurate solutions using perturbation theory.

2. Quantum Field Theory for Multi-Body Systems. The state of a free particle with momentum $\hbar k$ corresponding to one quantum of energy can be written as $|1\rangle$. Thus, two particles in the same state will have twice the energy, which can be understood as the state $|2\rangle$ of the harmonic oscillator, and so on. The states of N free particles are described as an infinite set of harmonic oscillators, one for each $\hbar\mathbf{k}$.

   More formally, this result can be obtained from the consideration that the wave function $\psi(\mathbf{r})$ can be treated as a dynamic variable, and thus as an additional operator, denoted by $\hat{\psi}$ and $\hat{\psi}^\dagger$. This procedure is called second quantization.

8.2 Hartree-Fock Theory

We consider a system of N spinless fermions. As in the previous chapter, we work within the Hilbert space $\mathcal{H}_1$ of single-particle states, where the set $\{\phi_{n_i}\}_{i=1}^N$ represents an orthonormal basis of single-particle wave functions. Under these considerations, any wave function for N particles ψ can be expressed as:

$$\psi(x_1, \cdots, x_N) = \frac{1}{N!}\begin{vmatrix} \phi_{n_1}(x_1) & \cdots & \phi_{n_n}(x_n) \\ \vdots & & \vdots \\ \phi_{n_n}(x_1) & \cdots & \phi_{n_N}(x_n) \end{vmatrix},$$

In light of the above, we can consider the ϕ_{n_i} as variational parameters. The Hartree-Fock approximation involves representing the ground state as a single Slater determinant, so we need to choose the ϕ_{n_i} that provide the best approximation.

The Hamiltonian of the system is given by $\hat{H} = \hat{T} + \hat{V}$, where

- The operator $\hat{T}$ is the total kinetic energy of the system, which is the sum of the kinetic energies of the N particles:

  $$\hat{T} = \sum_{j=1}^{N} \hat{t}_j = \sum_{j=1}^{N} -\frac{\hbar}{2m}\nabla_j^2$$

- The operator $\hat{V}$ represents the potential energy of the N particles, given as the sum of potential energies of each pair of particles:

  $$\hat{V} = \sum_{\substack{i,j \\ i\neq j}} \hat{V}_{i,j},$$

  where $\hat{V}_{i,j} = \hat{V}(x_i, x_j)$.

We work within the Fock space. We have:

$$\langle\psi|\hat{T}|\psi\rangle = \sum_{j=1}^{N} \langle\phi_{n_j}|\hat{T}|\phi_{n_j}\rangle = \sum_{j=1}^{N} \int dx \phi_{n_j}^*(x) T(x) \phi_{n_j}(x), \tag{8.2}$$

and

$$\langle\psi|\hat{V}|\psi\rangle = \frac{1}{2}\sum_{i,j=1}^{N}\left(\langle\phi_{n_i}\phi_{n_j}|\hat{V}|\phi_{n_i}\phi_{n_j}\rangle - \langle\phi_{n_i}\phi_{n_j}|\hat{V}|\phi_{n_j}\phi_{n_i}\rangle\right) \tag{8.3}$$

$$= \frac{1/2}{\sum}^{N}_{i,j=1}\int dx_1 dx_2\Big(\phi^*_{n_i}(x_1)\phi^*_{n_j}(x_2)\hat{V}(x_1,x_2)\phi_{n_i}(x_1)\phi_{n_j}(x_2) \tag{8.4}$$

$$- \phi^*_{n_j}(x_1)\phi_{n_i^*(x_2)}\hat{V}(x_1,x_2)\phi_{n_i}(x_1)\phi_{n_j}(x_2)\Big). \tag{8.5}$$

The first term in the expression for $\langle\psi|\hat{V}|\psi\rangle$ is called the "direct term," while the second is the "exchange term."

The goal is to minimize $\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T}|\psi\rangle + \langle\psi|\hat{V}|\psi\rangle$ subject to the n^2 constraints: $\langle\phi_{n_i}|\phi_{n_j}\rangle = \delta_{i,j}$. We use the theorem of constrained extrema:

Theorem 8.2.1 (Constrained Extrema)**.** *Seeking the extrema of a function $F(x,y)$ under a constraint $f(x,y)=0$ is equivalent to searching for those of the function:*

$$H(x,y,\lambda) = F(x,y) - \lambda f(x,y).$$

Therefore, a priori, we should introduce n^2 Lagrange multipliers. In fact, it can be shown that $\lambda_{i,j} = \lambda^*_{i,j}$.

We consider ϕ and ϕ^* as independent variables. As an example, the variations with respect to $\phi^*_{n_i}$ yield:

$$\begin{aligned}\delta\hat{T} &= \delta\left(\sum_j\int dx\phi^*_{n_j}(x)\hat{t}\phi_{n_j}(x)\right)\\ &= \sum_j\int dx\delta\phi^*_{n_j}(x)\hat{t}\phi_{n_j}(x).\end{aligned}$$

Similarly, the variations in $\hat{V}$ are:

$$\begin{aligned}\delta\hat{V} = \sum_{j\neq i}\int dx_1\int dx_2\Big(&\delta\phi^*_{n_i}(x_1)\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x_1)\phi_{n_j}(x_2)\\ &- \delta\phi^*_{n_i}(x_2)\phi^*_{n_j}(x_1)\hat{V}\phi_{n_i}(x_1)\phi_{n_j}(x_2)\Big).\end{aligned}$$

and

$$\delta\sum_{i,j}\lambda_{i,j}\left(\langle\phi_{n_i}|\phi_{n_j}\rangle - 1\right) = \sum_{i,j}\lambda_{i,j}\int dx\delta\phi^*_i(x)\phi_j(x).$$

We want to minimize $F = \langle\psi|\hat{H}|\psi\rangle - \sum_{i,j}\lambda_{i,j}\left(\langle\phi_{n_i}|\phi_{n_j}\rangle - 1\right)$ with respect to ϕ_{n_i}. We, therefore, impose $\frac{\delta F}{\delta\phi^*_{n_i}} = 0$ for all i, which leads to the equation:

$$\hat{t}\phi_{n_i}(x) + \sum_{j=1}^{N}\int dx_2\Big(\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2) - \phi^*_{n_j}(x)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2)\Big) = \sum_{j=1}^{N}\lambda_{i,j}\phi_{n_j}(x). \tag{8.6}$$

With no loss of generality $\lambda_{i,j} = \epsilon_i\delta_{i,j}$, we end up with *the Hartree-Fock equation* :

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{n_i}(x) + \sum_{j=1}^{N}\int dx_2\Big(\phi^*_{n_j}(x_2)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2) - \phi^*_{n_j}(x)\hat{V}\phi_{n_i}(x)\phi_{n_j}(x_2)\Big) = \epsilon_i\phi_{n_i}(x). \tag{8.7}$$

8.3 Hartree equation

The term directly from the potential 8.5 leads to the Hartree term in equation 8.7 :

$$\hat{V}_H(x)\phi_{n_i}(x) := \sum_{j=1}^{N} \int dx_2 \phi^*_{n_j}(x_2)\hat{V}(x,x_2)\phi_{n_j}(x_2)\phi_{n_i}(x).$$

In the Hartree-Fock equation, the term $\hat{V}_H(x)$ can be interpreted as a mean-field term, i.e., a potential of the form $\hat{v}(x_1,x_2) = \frac{e^2}{|x_1-x_2|}$. Thus, we can rewrite the Hartree term as:

$$\begin{aligned}\hat{V}_H(x) &= \sum_{j=1}^{N} \int dx_2 e^2 \frac{\left|\phi_{n_j}(x_2)\right|^2}{|x-x_2|} \\ &= \int dx_2 e^2 \frac{\sum_{j=1}^{N}\left|\phi_{n_j}(x)\right|^2}{|x-x_2|} \\ &= \int dx_2 e^2 \frac{\rho(x_2)}{|x-x_2|},\end{aligned}$$

leading to the Hartree equation:

$$-\frac{\hbar^2}{2m}\nabla^2\phi_{n_i}(x) + \hat{V}_H(x)\phi_{n_i}(x) = \epsilon_i\phi_{n_i}(x). \tag{8.8}$$

Note that the potential differs for each ϕ_i. The Hartree energy is given by:

$$E = \sum_{i=1}^{N}\langle\phi_{n_i}|\hat{t}|\phi_{n_i}\rangle + \frac{1}{2}\sum_{i,j}\langle\phi_{n_i}\phi_{n_j}|\hat{v}|\phi_{n_i}\phi_{n_j}\rangle \tag{8.9}$$

$$= \sum_{i=1}^{N}\langle\phi_{n_i}|\hat{t}|\phi_{n_i}\rangle + \frac{1}{2}\int dx_1 \int dx_2 e^2 \frac{\rho(x_1)\rho(x_2)}{|x_1-x_2|}. \tag{8.10}$$

It should be noted that the *Hartree potential energy is a functional of the density* $\rho(x)$, as ρ is a function of a single variable. If the exchange term is negligible, the initial N-body problem reduces to a one-body problem.

8.4 Thomas-Fermi Approximation:

The goal is to approximate the total kinetic energy of the system using a "well-chosen" functional of the density. We introduce

$$T^{TF}(\rho(x)) = \frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{\frac{2}{3}}\int d^3x\rho(x)^{\frac{5}{3}}$$

We want to minimize $E(\rho(x))$ subject to the constraint $\int dx^3\rho(x) = N$, which leads to the equation:

$$\delta\left(E(\rho) - \lambda\left(\int d^3x\rho(x) - N\right)\right) = 0,$$

from which we derive the *Thomas-Fermi equation*:

$$\frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{\frac{2}{3}}\int d^3x\rho(x)^{\frac{5}{3}} + V(x) + e^2\int dx_2\frac{\rho(x)}{|x-x_2|} - \mu = 0, \tag{8.11}$$

where $V(x)$ is an external potential.

8.5 Density Functional Theory:

The Hohenberg-Kohn theorem generalizes the ideas from the previous sections:

Theorem 8.5.1 (First Hohenberg-Kohn Theorem)**.** *The energy E of the ground state of an N-particle system defined by $\hat{H}$ is an unknown functional of the density $\rho(x)$.*

The Kohn-Sham theorem, formulated shortly after, allows reformulating the problem in terms of a Fermi-Thomas expansion differential equation. For one-particle states $\phi_i(x)$:

$$(t(x) + V(x))\,\phi_i(x) + V_{CE}(x)\phi_i(x) = \epsilon_i\phi_i(x),$$

where V_{CE} is the correlation and exchange potential, which is unknown.

Chapter 9

Density Operator and Open Quantum Systems

9.1 Density Operator:

Consider a system composed of two subsystems, A and B. Let $\{|i\rangle, i \in \mathbb{N}\}$ be a basis of states for A, and $\{|\mu\rangle, \mu \in \mathbb{N}\}$ be a basis of states for B. An overall state ψ of this system can be decomposed in the basis of the eigenstates of the subsystems as follows:

$$|\psi\rangle = \sum_{i,\mu} \alpha_{i,\mu} |i\rangle \otimes |\mu\rangle .$$

If $\hat{O}$ is an observable of the system A, then $\hat{O} \otimes \mathbb{1}_B$ is an observable of the total system, and the average value of $\hat{O}$ in the total space is given by:

$$\begin{aligned}
\left\langle \hat{O} \right\rangle &= \left\langle \hat{O} \otimes \mathbb{1}_B \right\rangle = \left\langle \psi \right| \hat{O} \otimes \mathbb{1}_B \left| \psi \right\rangle \\
&= \sum_{j,\nu} \sum_{i,\mu} \alpha^*_{j,\nu} \alpha_{i,\mu} \left(\langle j| \otimes \langle \nu| \right) \left(\hat{O} |i\rangle \right) \otimes \left(\mathbb{1}_B |\mu\rangle \right) \\
&= \sum_{j,\nu} \sum_{i,\mu} \alpha^*_{j,\nu} \alpha_{i,\mu} \langle j|\hat{O}|i\rangle \, \delta_{\mu\nu} \\
&= \sum_{i,j} \underbrace{\sum_{\mu} \alpha^*_{j,\mu} \alpha_{i,\mu}}_{\rho_{ij}} \langle j|\hat{O}|i\rangle \\
&= \sum_{i,j} \rho_{ij} \langle j|\hat{O}|i\rangle \\
&= \sum_{i,j} \rho_{ij} \hat{O}_{ji} \\
&= \mathrm{Tr}(\rho_A \hat{O}),
\end{aligned}$$

where the last equality is obtained by defining an operator ρ_A acting on subsystem A, and its matrix in the chosen basis $\{|i\rangle, i \in \mathbb{N}\}$ is given by the coefficients

$$\rho_{ij} = \sum_{\mu} \alpha^*_{j,\mu} \alpha_{i,\mu} = \sum_{\mu} \langle i\mu|\psi\rangle\langle\psi|j\mu\rangle.$$

In other words, ρ_A takes the form:

$$\rho_A = \sum_{i',j'} \sum_{\mu} |i'\rangle \langle i'| \otimes \langle \mu| \left(|\psi\rangle \langle \psi| \right) |j'\rangle \otimes |\mu\rangle \langle j'| .$$

This operator is called the *density operator*. Formally, it can be seen as the quantum physics equivalent of phase space density. Note that since the trace of an operator is invariant under a change of basis, the use of a density operator to calculate the average value of $\hat{O}$ does not depend on the choice of the basis used to define this operator. Also, note that we have the following properties:

Property 9.1.1. *1. The density operator is self-adjoint, that is to say,* $\rho_A^\dagger = \rho_A$,

2. $\mathrm{Tr}(\rho_A) = \sum_i \rho_{ii} = \sum_{i,\mu} |\alpha_{i,\mu}|^2 = \|\psi\|^2 = 1$,

3. The density operator is positive semidefinite, i.e. $\langle\phi|\rho_A|\phi\rangle \geq 0$ *for all* $|\phi\rangle \in A$.

Demo. 1. We have:

$$\rho_{ij} = \sum_\mu \alpha^*_{i,\mu}\alpha_{j,\mu}$$
$$\rho_{ji} = \sum_\mu \alpha^*_{j,\mu}\alpha_{i,\mu}$$

One should see that

$$\rho_{ij} = \overline{\rho_{ji}}$$

2. We compute:

$$\begin{aligned}\sum_i \rho_{ii} = \sum_i \sum_\mu \alpha^*_{i,\mu}\alpha_{i,\mu} &= \sum_i \sum_\mu \langle i\mu|\psi\rangle\langle\psi|i\mu\rangle \\ &= \sum_{i,\mu} |\langle i\mu|\psi\rangle|^2\end{aligned}$$

The $|i\rangle$ and $|\mu\rangle$ form a basis of A and B, respectively. Thus, the sum over i and μ give the norm of $|\psi\rangle$, which is by definition normalized to 1.

3. We compute :

$$\begin{aligned}\langle\phi|\rho_A|\phi\rangle &= \sum_{i,j}\sum_\mu \langle\phi|i\rangle\langle j|\phi\rangle\langle i\mu|\psi\rangle\langle\psi|j\mu\rangle \\ &= \sum_\mu \beta_\mu\beta^*_\mu \\ &= \|\beta\|^2 \geq 0,\end{aligned}$$

where $\beta_\mu = \langle\phi|i\rangle\langle i\mu|\psi\rangle$

□

Notice that these properties imply, in particular:

- There exists a basis in which ρ_A is diagonal (from point 1),
- Furthermore, points 2 and 3 impose a particular form on the diagonal representation of the operator ρ_A:

$$\rho_A = \sum_j p_j |j\rangle\langle j|,$$

where $p_j \geq 0$ and $\sum p_j = 1$. Thus,

$$\langle\hat{O}\rangle = \mathrm{Tr}(\rho_A\hat{O}) = \sum_j p_j \langle j|\hat{O}|j\rangle = \sum_j p_j \langle\hat{O}\rangle_{|j\rangle},$$

where $\langle\hat{O}\rangle_{|j\rangle}$ denotes the average value of $\hat{O}$ for the subsystem consisting of state $|j\rangle$.

So far, we have described the state of a system using an element $|\psi\rangle$ from the Hilbert space. Note that it is also possible to describe this state using the density operator $\rho = |\psi\rangle\langle\psi|$. A density operator of this form is called a pure state of the system; otherwise, it is referred to as a mixed state or statistical mixture.

In the case of a pure state, the average value of an observable $\hat{O}$ is given by:

$$\begin{aligned}\left\langle \hat{O} \right\rangle &= \mathrm{Tr}(|\psi\rangle\langle\psi|\,\hat{O}) \\ &= \sum_{i,\mu} \langle i,\mu|\psi\rangle\,\langle\psi|\hat{O}|i,\mu\rangle \\ &= \langle\psi|\hat{O}|\sum_{i,\mu} i,\mu\rangle\,\langle i,\mu|\psi\rangle \\ &= \langle\psi|\hat{O}|\psi\rangle\,.\end{aligned}$$

Furthermore, if a density operator describes a pure state, then it is a projector, i.e., $\rho^2 = \rho$. In fact, the two properties are equivalent: if $\rho^2 = \rho$, the eigenvalues of the density operator must necessarily be 0 or 1. But since the sum of the eigenvalues of a density operator must be equal to 1, there must be a single eigenvalue of the density operator that equals 1, and it is unique. Let $|\psi_n\rangle$ be the associated eigenstate. We have $\rho = |\psi_n\rangle\langle\psi_n|$.

In this chapter, we have introduced 2 density operators, $\rho_A : \mathcal{H}_A \to \mathcal{H}_A$ and $\rho : \mathcal{H}_A \otimes \mathcal{H}_B \to \mathcal{H}_A \otimes \mathcal{H}_B$, is there a link between them? We will show $\rho_A = \mathrm{Tr}_B(\rho)$.

Demo. We have

$$\rho = |\psi\rangle\langle\psi| = \sum_{i\mu;j\nu} \alpha_{i\mu}\alpha^*_{j\nu}\,|i\mu\rangle\,\langle j\nu|$$

But $\rho_{i\mu,j\nu} = \alpha_{i\mu}\alpha^*_{j\nu}$. By definition

$$\rho_A = \sum_{\mu} \alpha_{i\mu}\alpha^*_{j\nu}$$

thus, defining

$$\mathrm{Tr}_B(\rho) = \sum_{\mu'} \langle\mu'|\rho|\mu'\rangle$$

We have

$$\begin{aligned}\sum_{ij}\sum_{\mu} \alpha_{i\mu}\alpha^*_{j\nu}\,|i\rangle\langle j| &= \sum_{\mu'}\sum_{i\mu,j\nu} \alpha_{i\mu}\alpha^*_{j\nu}\delta_{\mu\mu'}\delta_{\nu\mu'}\,|i\rangle\langle j| \\ &= \sum_{\mu'}\sum_{i\mu,j\nu} \alpha_{i\mu}\alpha^*_{j\nu}\,\langle\mu'|\,(|i\rangle\otimes|\mu\rangle)(\langle j|\otimes\langle\nu|)\,|\mu'\rangle \\ &= \sum_{\mu'} \langle\mu'|\rho|\mu'\rangle = \mathrm{Tr}_B(\rho) = \rho_A\end{aligned}$$

□

Example 9.1.2. Consider a state $|\psi\rangle = \alpha\,|00\rangle + \beta\,|01\rangle + \gamma\,|10\rangle + \delta\,|11\rangle$. We have:

$$\rho = |\psi\rangle\,\langle\psi| = \begin{pmatrix} |\alpha|^2 & \alpha^*\beta & \alpha^*\gamma & \alpha^*\delta \\ \beta^*\alpha & |\beta|^2 & \beta^*\gamma & \beta^*\delta \\ \gamma^*\alpha & \gamma^*\beta & |\gamma|^2 & \gamma^*\delta \\ \delta^*\alpha & \delta^*\beta & \delta^*\gamma & |\delta|^2 \end{pmatrix},$$

and

$$\rho_A = \mathrm{Tr}_B(\rho) = \sum_{x=0,1} \langle x|\psi\rangle\langle\psi|x\rangle = \begin{pmatrix} |\alpha|^2 + |\beta|^2 & \alpha^*\gamma + \beta^*\delta \\ \beta^*\alpha + \gamma^*\beta & |\gamma|^2 + |\delta|^2 \end{pmatrix}.$$

9.2 Time Evolution:

Let's consider a density operator in diagonal form at $t = 0$:

$$\rho(t=0) = \sum_j \alpha_j |\psi_j(0)\rangle \langle\psi_j(0)|$$

We are interested in determining the laws governing its time evolution. We assume that the statistical mixture does not change over time. In other words, α_i does not depend on t, and

$$\rho(t) = \sum_j \alpha_j |\psi_j(t)\rangle \langle\psi_j(t)| .$$

The time evolution of a state has already been characterized as:

$$|\psi_j(t)\rangle = e^{-i\frac{\hat{H}t}{\hbar}} |\psi_j(0)\rangle$$

Using these two equations, we obtain:

$$\rho(t) = \sum_j \alpha_j e^{-i\frac{\hat{H}t}{\hbar}} |\psi_j(0)\rangle \langle\psi_j(0)| e^{-i\frac{\hat{H}t}{\hbar}}$$

We differentiate:

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &= \sum_j \alpha_j \left(-i\frac{\hat{H}}{\hbar}\right) e^{-i\frac{\hat{H}t}{\hbar}} |\psi_j(0)\rangle \langle\psi_j(0)| e^{-i\frac{\hat{H}t}{\hbar}} \\
&+ \sum_j \alpha_j e^{-i\frac{\hat{H}t}{\hbar}} |\psi_j(0)\rangle \langle\psi_j(0)| \left(i\frac{\hat{H}}{\hbar}\right) e^{-i\frac{\hat{H}t}{\hbar}} \\
&= \left(-i\frac{\hat{H}}{\hbar}\right)\rho + \rho\left(i\frac{\hat{H}}{\hbar}\right)
\end{aligned}$$

which leads to the equation:

$$i\hbar\frac{\partial\rho}{\partial t} = -[\hat{H}, \rho], \tag{9.1}$$

describing the time evolution of the density operator. Note that ρ does not define an observable physical quantity!

Examples 9.2.1.

1. Consider the Hilbert space of states $\{|-\rangle, |+\rangle\}$. The operator $\hat{S}_z$ acts on this basis as $\hat{S}_z|+\rangle = \frac{\hbar}{2}|+\rangle$ and $\hat{S}_z|-\rangle = -\frac{\hbar}{2}|-\rangle$. The state $|\psi\rangle = |+\rangle$ is a pure state of the system, and the corresponding density operator ρ is given by:

$$\rho = |\psi\rangle\langle\psi| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

2. Now, consider the Hilbert space composed of eigenstates of the x-component of spin: $\{|+\rangle_x, |-\rangle_x\}$. We have $\hat{S}_x|+\rangle_x = \frac{\hbar}{2}|+\rangle_x$ and $\hat{S}_x|-\rangle_x = -\frac{\hbar}{2}|-\rangle_x$. Furthermore:

$$|+\rangle_x = \frac{|+\rangle + |-\rangle}{\sqrt{2}}, \text{ and } |-\rangle_x = \frac{|+\rangle - |-\rangle}{\sqrt{2}}.$$

The states $|\psi\rangle = |\pm\rangle_x$ are pure states, and the corresponding density operator is given by:

$$\rho = |\pm\rangle_x \langle\pm|_x = \frac{1}{2}\left(|+\rangle_x \pm |-\rangle_x\right)\left(\langle+|_x \pm \langle-|_x\right).$$

In the basis $\{|+\rangle, |-\rangle\}$, the operator ρ is written as:

$$\rho = \begin{pmatrix} \frac{1}{2} & \pm\frac{1}{2} \\ \pm\frac{1}{2} & \frac{1}{2} \end{pmatrix}.$$

3. What would be the density operator associated with a statistical mixture composed of 50% of $|+\rangle$ and 50% of $|-\rangle$? We have $\rho = \frac{1}{2}|+\rangle\langle+| + \frac{1}{2}|-\rangle\langle-| = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$.

4. Bell States: $\psi = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)$. In the basis of states $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$, the density operator $\rho = |\psi\rangle\langle\psi|$ is given by:

$$\rho = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

Additionally,

$$\rho_A = \mathrm{Tr}_B(\rho) = \sum_{j=0}^{1} {}_B\langle j|\rho|j\rangle_B = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

and

$$\rho_B = \mathrm{Tr}_A(\rho) = \sum_{j=0}^{1} {}_A\langle j|\rho|j\rangle_A = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

What would be the density matrix of a union of two systems? Naively, we might want to write $\rho = \rho_A \otimes \rho_B$. After calculations, we obtain:

$$\mathrm{Tr}_B\, \rho_A \oplus \rho_B = \rho_A$$

and

$$\mathrm{Tr}_A\, \rho_A \oplus \rho_B = \rho_B.$$

In the case of a pure state $|\psi\rangle = |\psi_A\rangle \otimes |\psi_B\rangle$, we can write $\rho_A = |\psi_A\rangle\langle\psi_A|$ and $\rho_B = |\psi_B\rangle\langle\psi_B|$. We indeed have $\rho = |\psi\rangle\langle\psi| = \rho_A \otimes \rho_B$.

In fact,

$$\rho = |\psi\rangle\langle\psi| = (|\psi_A\rangle \otimes |\psi_B\rangle)(\langle\psi_A| \otimes \langle\psi_B|) = |\psi_A\rangle\langle\psi_A| \otimes |\psi_B\rangle\langle\psi_B| = \rho_A \otimes \rho_B$$

$$\rho = |\psi\rangle\langle\psi| = (|\psi_A\rangle \otimes |\psi_B\rangle)(\langle\psi_A| \otimes \langle\psi_B|) = |\psi_A\rangle\langle\psi_A| \otimes |\psi_B\rangle\langle\psi_B| = \rho_A \otimes \rho_B$$

given the properties of the tensor product.

But as soon as there is entanglement, things become more complicated: let's revisit the example of the Bell state and consider the state $\psi = \frac{|01\rangle - |10\rangle}{\sqrt{2}}$. If indeed we had $\rho = \rho_A \otimes \rho_B$, then the density operator should be of the form:

$$\rho = \frac{1}{4}\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix},$$

which contradicts the results obtained in the example above.

In fact, given the density matrices of two systems once they come into contact, it is a priori impossible to access the density operator of the total system.

Examples 9.2.2 (Quantum Bits).

1. Systems with a single quantum bit: We consider a state $|\psi\rangle = \lambda|0\rangle + \mu|1\rangle$, where $|\lambda|^2 + |\mu|^2 = 1$. As seen previously, the density matrix of the system is given by:
$$\rho_A = |\psi\rangle\langle\psi| = \begin{pmatrix} |\lambda|^2 & \mu^*\lambda \\ \lambda^*\mu & |\mu|^2 \end{pmatrix},$$
We notice that in the case of a pure state, the density matrix provides the maximum information about the system.

2. Systems with two quantum bits: We consider a system composed of two subsystems with a single quantum bit A and B.

   - We are interested in the density matrix associated with the state $|\psi\rangle = |\phi_A\rangle \otimes |\phi_B\rangle$, where $|\psi_A\rangle = \lambda|0_A\rangle + \mu|1_A\rangle$ and $|\psi_B\rangle = \chi|0_B\rangle + \beta|1_B\rangle$. The matrix ρ_A has been determined in the previous section:
   $$\rho_A = |\psi\rangle\langle\psi| = \begin{pmatrix} |\lambda|^2 & \mu^*\lambda \\ \lambda^*\mu & |\mu|^2 \end{pmatrix},$$
   and $\rho_A \otimes \rho_B$ is a 4×4 matrix consisting of blocks:
   $$\rho_A \otimes \rho_B = |\psi\rangle\langle\psi| = \begin{pmatrix} |\lambda|^2\rho_B & \mu^*\lambda\rho_B \\ \lambda^*\mu\rho_B & |\mu|^2\rho_B \end{pmatrix},$$
   - Now, if we consider the state $|\psi\rangle = \lambda|00\rangle + \mu|11\rangle$. The density matrix is given by:
   $$\rho = |\psi\rangle\langle\psi| = \begin{pmatrix} |\lambda|^2 & 0 & 0 & \mu^*\lambda \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \lambda^*\mu & 0 & 0 & |\mu|^2 \end{pmatrix},$$
   and $\rho_A = \mathrm{Tr}_B(\rho) = \begin{pmatrix} |\lambda|^2 & 0 \\ 0 & |\mu|^2 \end{pmatrix}$. Thus, the average value of any observable of the system satisfies:
   $$\langle\hat{O}\rangle = |\lambda|^2\langle\hat{O}\rangle_0 + |\mu|^2\langle\hat{O}\rangle_1.$$

We are interested in the temporal evolution of a system composed of two subsystems, A and B, described by Hamiltonians $\hat{H}_A$ and $\hat{H}_B$, such that $\hat{H} = \hat{H}_A \otimes \mathbb{1}_B + \mathbb{1}_A \otimes \hat{H}_B = \hat{H}_A \oplus \hat{H}_B$. In other words, the two subsystems do not interact with each other. The time evolution operator is given by:

$$\hat{U}(t,t') = e^{i\frac{(\hat{H}_A\oplus\hat{H}_B)(t-t')}{\hbar}} = \hat{U}_A \otimes \hat{U}_B, \tag{9.2}$$

so any state of the system, denoted as $|\psi(t)\rangle = |\psi_A(t)\rangle \otimes |\psi_B(t)\rangle$, will evolve according to the equation:

$$|\psi(t)\rangle = |\psi_A(t)\rangle \otimes |\psi_B(t)\rangle = \left(\hat{U}_A \otimes \hat{U}_B\right)\left(|\psi_A(t)\rangle \otimes |\psi_B(t)\rangle\right).$$

Example 9.2.3 (Decoherence and Pointer States). Consider a system S interacting with an environment E. Decoherence is the manifestation of this interaction. This interaction favors certain states, known as "pointer states," which are not affected by decoherence, regardless of the initial

state of the system. In fact, equation 9.2 suggests that the interaction will favor the eigenstates of the system since these states remain factorized over time, with the environment not acting on the system. However, the state of the environment evolves because the system interacts with the environment. For example, if a system composed of a quantum bit interacts with the environment, let $\{|0\rangle, |1\rangle\}$ be the pointer states of the system and $|0_E\rangle$ be the initial state of the environment. Suppose the time evolution is given by:

$$|0\rangle \otimes |0_E\rangle \to |0\rangle \otimes |1_E\rangle,$$

$$|1\rangle \otimes |0_E\rangle \to |0\rangle \otimes |2_E\rangle.$$

Suppose that after a time interval Δt, a transition occurs with probability p, meaning that after a time interval Δt:

$$|00_E\rangle \to \sqrt{1-p}\,|00_E\rangle + \sqrt{p}\,|01_E\rangle,$$
$$|10_E\rangle \to \sqrt{1-p}\,|10_E\rangle + \sqrt{p}\,|12_E\rangle.$$

If the system is in the state $|\psi\rangle = \lambda|0\rangle + \mu|1\rangle$ at time $t = 0$, then after a time Δt, it will be in the state:

$$|\psi\rangle = \lambda\sqrt{1-p}\,|00_E\rangle + \lambda\sqrt{p}\,|01_E\rangle + \mu\sqrt{1-p}\,|10_E\rangle + \mu\sqrt{p}\,|12_E\rangle.$$

The density matrix at the step Δt is given by:

$$\rho_S = \mathrm{Tr}_E(\rho) = \begin{pmatrix} |\lambda|^2 & \mu^*\lambda(1-p) \\ \lambda^*\mu(1-p) & |\mu|^2 \end{pmatrix}.$$

After n time steps of Δt:

$$\rho_S = \mathrm{Tr}_E(\rho) = \begin{pmatrix} |\lambda|^2 & \mu^*\lambda(1-p)^n \\ \lambda^*\mu(1-p)^n & |\mu|^2 \end{pmatrix},$$

so that

$$\lim_{t\to\infty} \rho_S = \begin{pmatrix} |\lambda|^2 & \mu^*\lambda e^{-\Gamma t} \\ \lambda^*\mu e^{-\Gamma t} & |\mu|^2 \end{pmatrix},$$

where $\Gamma = np$.

Chapter 10

Elements of Quantum Information

Computers are fundamentally machines based on physical processes. The physics of these systems is governed by the laws of quantum mechanics. One can thus consider every computer as being "quantum." In reality, this is not the case: their operations can be ideally described by elements of classical physics. For example, Alan Turing constructed a basic computer, the Turing machine, using mechanical components (and following purely classical considerations).

A genuinely quantum computer fully utilizes specifically quantum phenomena (such as entanglement) that have no classical equivalent.

During the 1970s, the issue of reversibility is addressed: a logical operation (such as XOR) is irreversible.

p	q	XOR
0	0	0
0	1	1
1	0	1
1	1	1

Table 10.1: Truth Table for XOR Operation

Indeed, it is impossible to determine from an output $XOR(p,q) = 1$ whether $(p,q) = (0,1)$ or $(p,q) = (1,0)$. Thus, this operation dissipates energy. In fact, there are 4 possible input combinations for 2 possible output combinations. Entropy, quantifying the unknown information about the system's state, is given, for N possible combinations, by:

$$S = k_B \ln N$$

Consider, for example, a system S consisting of a box containing a gas consisting of a single particle.

Figure 10.1: System composed of a box with gas (**a**) when this gas can fill the box, (**b**) when the box is split in 2 and the gas is restrained.

If we consider this system to be isolated, then from (**a**) to (**b**), the gas has lost half of its configurations, i.e., the particle has only half of the available positions. Assuming an isothermal process:

$$\delta S = -k_B \ln 2$$

$$\delta F = \delta U - \delta ST \text{ isothermal} \Rightarrow \delta U = 0$$

$$\delta U \Rightarrow \text{same velocity}$$

However, the entropy of an isolated system cannot decrease. If we have $\delta S = -k_B \ln 2$ for a XOR, it's because it's not isolated: it dissipates heat into a thermal bath, causing the entropy of the thermal bath to increase by $\delta S = k_B \ln 2$ (still assuming an isothermal process). Thus:

$$\Delta U_{\text{dissipated}} \geq k_B T \ln 2$$

In practice, we are still far from this limit. However, it's possible to completely overcome this by using reversible logic gates. That's why we consider quantum mechanics here. In an isolated system, the operations are given by the unitary time evolution:

$$\hat{U}(t, t') = e^{-\frac{i\hat{H}(t-t')}{\hbar}}$$

which is unitary and, therefore, reversible.

Feynman became interested in this problem in the early 1980s (see the book "Lectures on Computation"). He immediately recognized an opportunity in quantum mechanics.

Consider N classical particles with positions $(\mathbf{r}_1, \cdots, \mathbf{r}_N)$. The equations of motion are given by $\ddot{r}_j = F_j(r_1, \cdots, r_N)$ or

$$\begin{cases} \dot{r}_j = v_j \\ \dot{v}_j = F_j(r_1, \cdots, r_N) \end{cases}$$

resulting in $6N$ coupled differential equations. Simulating this system involves discretization: $dt \to \Delta t$ and $\Delta x_j = \Delta t F_j(r_1, \cdots, r_n)$. Typically, $F_j(r_1, \cdots, r_N) = \sum_{k \neq j} F(x_j, x_k)$. The algorithm thus requires two loops, one over the index j and another over the index k, leading to a number of operations in $\mathcal{O}(N^2)$ per Δt.

Now consider a quantum system of N particles characterized by the wave function $\Psi(r_1, \cdots, r_N, t)$ and the evolution equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

For the numerical simulation of this system, it's necessary to discretize time as well as space. Let's assume a spatial grid of M cells. For $3N$ coordinates, we have $(M)^{3N}$ elements. So, the matrix $\hat{H}$ has a size of $(M)^{3N} \times (M)^{3N}$. Matrix-vector multiplication is performed in $\mathcal{O}(N^2)$ operations, which results in a number of operations in $\mathcal{O}((M)^{6N})$, which means exponential complexity!

So, we go from a tractable algorithm (N^2) to an intractable one (const^N).

Feynman sees this limitation as an opportunity, through the following reflection: a classical computer takes time $T = \mathcal{O}(\Delta t \cdot \text{const}^N)$ to simulate this system, while nature takes time $T = \mathcal{O}(\Delta t)$! Nature can solve an intractable problem for classical computers with zero complexity.

If we could redefine all numerical problems in terms of $e^{-\frac{i\hat{H}t}{\hbar}}$, we would have access to a very powerful universal computer (even if we had to build a system that behaves according to the desired $\hat{H}$). Currently (in 2020), this has not yet been fully realized, but some specific algorithms have been discovered (Deutsch, Shor, Grover, etc.).

10.1 Mathematical Formulation of the Qubit

A quantum bit or "qubit" is a "two-level" quantum system. This simply means that the states are defined in a 2-dimensional Hilbert space.

We choose a canonical basis, which we call the "computational basis," denoted by $\{|0\rangle, |1\rangle\} \equiv \mathcal{H}_1$.

Notice the analogy between classical computing bits and qubits. However, qubits have a fundamental difference. While classical bits can take the values 0 or 1, qubits can take values

$$|\Psi\rangle = \alpha\,|0\rangle + \beta\,|1\rangle\,,\ \alpha,\ beta \in \mathbb{C}$$

with $|\alpha|^2 + |\beta|^2 = 1$. Then, we can construct multi-qubit states. For N qubits, the space is given by

$$\mathcal{H}_N = \underbrace{\mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_1}_{N \text{ times}}$$

For two qubits, for example, the space is then

$$\mathcal{H}_2 = \{|0\rangle \otimes |0\rangle,\ |0\rangle \otimes |1\rangle,\ |1\rangle \otimes |0\rangle,\ |1\rangle \otimes |1\rangle\} = \{|00\rangle,\ |01\rangle,\ |10\rangle,\ |11\rangle\}$$

and the state of these two qubits is given by

$$|\Psi\rangle = \alpha\,|00\rangle + \beta\,|01\rangle + \gamma\,|10\rangle + \delta\,|11\rangle$$

with $|\alpha|^2 + |\beta|^2 + |\gamma|^2 + |\delta|^2 = 1$

In practice, to realize a qubit, we look for a physical system that is completely characterized by two states (or by a system with two energy states sufficiently separated from all others, so that the influence of the others is negligible, an influence calculated according to perturbation theory). The two main candidates for this practical realization of a qubit are currently the electron's spin and the photon's polarization. We can also consider a pair of atomic levels, the collective state of a supercurrent in a superconductor.

10.2 Quantum Operation

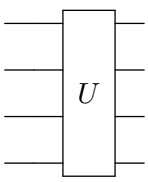
In the field of quantum information, systems are idealized: it is assumed that the only evolution is unitary, governed by the Hamiltonian

$$|\Psi(t)\rangle = \hat{U}(t,t')\,|\Psi(t')\rangle$$

$$\hat{U}(t,t') = e^{-i\frac{\hat{H}(t-t')}{\hbar}}$$

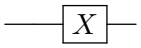
Certain phenomena are thus neglected, such as interaction with the environment and decoherence, for example.

For a system of N qubits, a quantum operation can be illustrated by a quantum circuit:



Each line represents the state of a qubit. This representation is due to the fact that a unitary operation U is completely defined (by linearity) by its action on the elements of the basis of

$\mathcal{H}_N$. Knowing how U acts on $|\alpha_1, \cdots, \alpha_N\rangle$, where $\alpha_i = 0, 1$, is enough to define U completely. For example, consider the NOT gate:



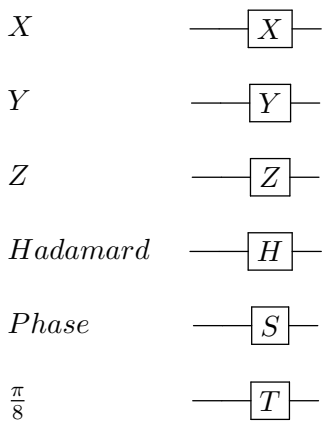
which can be rewritten in vector form with $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$:

$$X = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

(which is also the Pauli matrix σ_x). This gate maps $|0\rangle$ ($|1\rangle$) to $|1\rangle$ ($|0\rangle$). Its action on an arbitrary state $|\Psi\rangle$ follows from linearity.

10.3 Useful quantum gatesr

10.3.1 1 qubit



$$X = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$Y = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

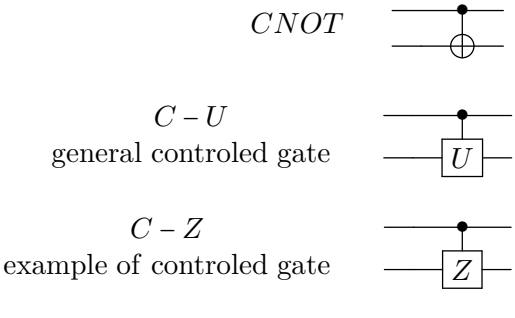
$$Z = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$H = \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

$$S = \begin{pmatrix} 1 & 0 \\ 0 & i \end{pmatrix}$$

$$T = \begin{pmatrix} 1 & 0 \\ 0 & e^{i\pi/4} \end{pmatrix} = e^{i\pi/8} \begin{pmatrix} e^{-i\pi/8} & 0 \\ 0 & e^{i\pi/8} \end{pmatrix}$$

10.3.2 2 qubits



$$C_{NOT} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

$$|c\rangle \otimes |x\rangle \to |c\rangle \otimes U^c |x\rangle$$

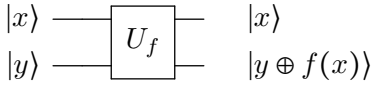
$$C - Z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

All quantum circuits can be constructed using sequences of H, S, T, and C_{NOT} gates; however, this takes exponential time. Some algorithms, on the other hand, do not require a complex architecture and are, therefore, very efficient.

However, there is still no quantum Turing machine: it is currently impossible to systematically express every algorithm in quantum terms to achieve efficiency gains.

10.4 Deutsch's Algorithm

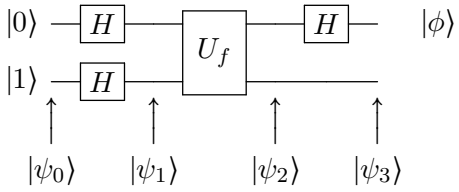
Consider a quantum gate U_f



where $|x\rangle$ and $|y\rangle$ represent one qubit each, $f(x)$ is a Boolean function, and $\oplus$ denotes modulo-2 addition.

We want to determine whether $f(x)$ is constant or balanced, meaning either $f(1) = f(0)$ or $f(1) \neq f(0)$, respectively. Classically, it is necessary to evaluate the function twice to determine this. Deutsch's algorithm allows us to know this characteristic in a single evaluation.

Consider the circuit:



Where H is the Hadamar gate, which sends $|0\rangle \to \frac{|0\rangle+|1\rangle}{\sqrt{2}}$, and $|1\rangle \to \frac{|0\rangle-|1\rangle}{\sqrt{2}}$, $|\psi_0\rangle$ the initial state, the $|\psi_1\rangle$, $|\psi_2\rangle$, $|\psi_3\rangle$ the intermediary states, and $|\phi\rangle$ the final state of the first registry. The final state of the second registry is not presented. let us detail the intermediary states. Firstly

$$|\psi_0\rangle = |0\rangle \otimes |1\rangle = |0,1\rangle \ ,$$

and

$$\begin{aligned} |\psi_1\rangle &= (H \otimes H)\,|\psi_0\rangle = (H \otimes H)\,|0\rangle \otimes |1\rangle \\ &= (H\,|0\rangle) \otimes (H\,|1\rangle) \\ &= \left(\frac{|0\rangle + |1\rangle}{\sqrt{2}}\right) \otimes \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right) , \end{aligned}$$

Before computing $|\psi_2\rangle = U_f\,|\psi_1\rangle$, we should note that

$$\begin{aligned} U_f\,|x\rangle \otimes \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right) &= |x\rangle \otimes \left(\frac{|f(x)\rangle - |1 \oplus f(x)\rangle}{\sqrt{2}}\right) \\ &= \begin{cases} |x\rangle \otimes \left(\dfrac{|0\rangle - |1\rangle}{\sqrt{2}}\right) & \text{if } f(x) = 0 \\ |x\rangle \otimes \left(\dfrac{|1\rangle - |0\rangle}{\sqrt{2}}\right) & \text{if } f(x) = 1 \end{cases} \\ &= |x\rangle \otimes (-1)^{f(x)} \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right) \\ &= (-1)^{f(x)}\,|x\rangle \otimes \left(\frac{|0\rangle - |1\rangle}{\sqrt{2}}\right) , \end{aligned}$$

where the last step follows from linearity of the tensor product and shows that the action of the operator on 2 qubits is essential to the algorithm.

From the following relation,

$$\begin{aligned}
|\psi_2\rangle &= U_f\,|\psi_1\rangle = U_f\left(\frac{|0\rangle+|1\rangle}{\sqrt{2}}\right)\otimes\left(\frac{|0\rangle-|1\rangle}{\sqrt{2}}\right)\\
&= \left(\frac{(-1)^{f(0)}\,|0\rangle+(-1)^{f(1)}\,|1\rangle}{\sqrt{2}}\right)\otimes\left(\frac{|0\rangle-|1\rangle}{\sqrt{2}}\right)\\
&= \begin{cases}(-1)^{f(0)}\left(\dfrac{|0\rangle+|1\rangle}{\sqrt{2}}\right)\otimes\left(\dfrac{|0\rangle-|1\rangle}{\sqrt{2}}\right) & \text{if } f(0)=f(1)\\[2ex] (-1)^{f(0)}\left(\dfrac{|0\rangle-|1\rangle}{\sqrt{2}}\right)\otimes\left(\dfrac{|0\rangle-|1\rangle}{\sqrt{2}}\right) & \text{if } f(0)\neq f(1)\,.\end{cases}
\end{aligned}$$

Which finally leads to

$$\begin{aligned}
|\psi_3\rangle &= (H\otimes\mathbf{1})\,|\psi_2\rangle\\
&= \begin{cases}(-1)^{f(0)}\,|0\rangle\otimes\left(\dfrac{|0\rangle-|1\rangle}{\sqrt{2}}\right) & \text{if } f(0)=f(1)\\[2ex] (-1)^{f(0)}\,|1\rangle\otimes\left(\dfrac{|0\rangle-|1\rangle}{\sqrt{2}}\right) & \text{if } f(0)\neq f(1)\end{cases}\\
&= (-1)^{f(0)}\,|f(0)\oplus f(1)\rangle\otimes\left(\frac{|0\rangle-|1\rangle}{\sqrt{2}}\right).
\end{aligned}$$

We only need then to execute a measure on the first qubit of an observable that is diagonal in the computational basis $\{|0\rangle,|1\rangle\}$. The result of such a measure will tell us with certainty if $f(x)$ is constant or balanced.

Chapter 11

EPR Paradox, Bell's Theorem, and Quantum State Interpretation

The absence of determinism in the quantum measurement process posed a major problem of interpretation in the decades following the birth of the theory.

According to a classical idea, the measurement process merely reveals a pre-existing value of a physical quantity. The doctor measuring blood pressure is simply discovering the value, which existed independently and was the cause of the patient's discomfort.

Without delving into the technical details of the measurement process (which, in principle, should be designed with minimal interaction with the system to avoid influencing it), it could be possible to establish the principle that the value of a physical quantity represents an "element of objective reality" if it can be measured with a probability of 1 through a measurement process. This value should, therefore, be pre-existing and independent of the measurement process. A complete quantum theory should then, in describing this phenomenon, predict this value with probability 1.

Unfortunately, orthodox quantum physics, as it is taught, does not meet these simple criteria. In particular, given an observable $\hat{A}$, a self-adjoint operator in the Hilbert space $\mathcal{H}$, with eigenvalues $\{a_n\}$, and eigenstates $|a_n\rangle$, the result of a measurement of $\hat{A}$ fulfills the above criteria only for a system already in a state $|a_n\rangle$, with eigenvalue a_n. However, for any arbitrary state $|\Psi\rangle$, the value obtained from the measurement of $\hat{A}$ is not pre-existing and cannot be predicted with certainty by the theory. In such a quantum state, the value of $\hat{A}$ is not an "element of objective reality." One might attempt to circumvent the problem by restricting the consideration to the $|a_n\rangle$ states alone. But this is not a solution because if two observables $\hat{A}$ and $\hat{B}$ have $[\hat{A}, \hat{B}] \neq 0$, then a system in an eigenstate of $\hat{A}$ is undetermined when measured by $\hat{B}$. If $\hat{A}$ is therefore an "element of objective reality," then $\hat{B}$ is not.

It could be argued that the measurement process in quantum physics generally has a negligible influence on the system, and therefore, it can never be reduced to the classical idea of measurement.

To address this question, Albert Einstein, Boris Podolsky, and Nathan Rosen published their famous article titled *Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?* in 1935. This is Einstein's most cited paper with over 12,000 citations on Google Scholar. The EPR argument aims to show that — under certain assumptions — orthodox quantum mechanics must be incomplete and, in particular, the results of measurements must preexist, contrary to the principles of orthodox quantum mechanics. The assumptions of the EPR paradox play a very important role. They are:

1. Exact correlations between measurements of two subsystems in a specific state (referred

to as an entangled state hereafter).

2. The impossibility, through a measurement performed on one subsystem, of influencing the state of another subsystem sufficiently far away (the locality assumption).

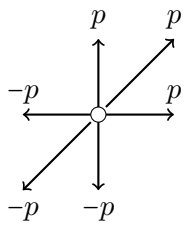
To illustrate the EPR paradox, an example of an entangled state corresponding to the first assumption must be introduced. Historically, the EPR paper introduced a state describing two particles, given by the wave function

$$\Psi(x_1, x_2) = \int_{-\infty}^{\infty} e^{\frac{2\pi i}{h}(x_1 - x_2 + x_0)p} dp = \hbar\delta(x_2 - x_1 + x_0)$$

This is a state for which the distance between the two particles is certain and given by x_0. The idea is to choose x_0 large enough so that two measurements performed on the two particles at a sufficiently short time interval cannot influence each other through an interaction. This state can also be expressed as

$$|\Psi(x_1, x_2)\rangle = \int_{-\infty}^{\infty} dp e^{\frac{2\pi i}{h}x_1 p} e^{\frac{-2\pi i}{h}(x_2 - x_0)p} = \int_{-\infty}^{\infty} dp e^{\frac{2\pi i}{h}x_0} |p\rangle_1 \otimes |-p\rangle_2$$

This expression can be interpreted as a linear superposition (with constant probability) of states where both particles propagate with equal and opposite momenta.



There exists a version of this example due to Bohr, simple and more modern, using the spin state of two spin-$\frac{1}{2}$ particles.

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(\uparrow \otimes \downarrow + \uparrow \otimes \downarrow)$$

Here, $\uparrow$ and $\downarrow$ are, for example, the eigenstates of $\hat{S}_z$. This is the singlet state, i.e., the eigenstate of $\hat{S}^2$ ($\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$) with eigenvalue $S = 0$. Note the analogy with the original EPR state: both are superpositions of states produced with opposite eigenvalues.

The state $|\Psi\rangle$ has another important characteristic. Let's apply a change of basis in the Hilbert space of each spin using a unitary matrix:

$$\hat{O} = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix} \quad \begin{matrix} \uparrow = \alpha \uparrow' + \beta \downarrow' \\ \downarrow = \gamma \uparrow' + \delta \downarrow' \end{matrix}$$

This change corresponds to transitioning from the basis of eigenstates of $\hat{S}_z$ to the basis of eigenstates of $\hat{n} \cdot \hat{S}$, where $\hat{n}$ is arbitrary. Replacing these expressions in $|\Psi\rangle$ and after some simple algebraic calculations, we find (with a negligible global phase factor):

$$|\Psi\rangle \equiv \frac{1}{\sqrt{2}}(\uparrow' \otimes \downarrow' - \downarrow' \otimes \uparrow')$$

where we used the property of the unitary matrix:

$$|\det U| = |\alpha\delta - \gamma\beta| = 1$$

So, the state has exactly the same form regardless of the chosen basis. This property is not required for the EPR argument, but it simplifies the task.

Let $|\Psi\rangle$ be a non-separable state, meaning it cannot be written as a tensor product of two states defined in the respective Hilbert spaces of the two isolated particles:

$$|\Psi\rangle \neq |\Psi_1\rangle \otimes |\Psi_2\rangle$$

The condition of non-separability is essentially at the core of the concept of quantum entanglement.

Another important characteristic is the correlation between measurements performed on the two subsystems. Imagine two distant particles. Two observers, Alice and Bob, each operate a Stern-Gerlach device, which includes a magnet generating a non-uniform magnetic field capable of deflecting opposite spin particles in opposite directions. The orientation of field B defines the spin orientation of the observable. This device allows Alice and Bob to measure the spin $\hat{S}_z$ of their respective particles.

Alice measures first. If she obtains $S_z = +\frac{\hbar}{2}$, then, according to orthodox quantum mechanics, she will have projected the system onto the projector

$$|\uparrow\rangle\langle\uparrow| \otimes I$$

The state will, therefore, be projected as

$$|\Psi\rangle \to |\uparrow\rangle \otimes |\downarrow\rangle$$

In this state, a measurement of $\hat{S}_z$ by Bob on the other particle will give $S_z = -\frac{\hbar}{2}$ with certainty. On the contrary, if Alice measures $S_z = -\frac{\hbar}{2}$, Bob will measure $S_z = +\frac{\hbar}{2}$ with certainty.

Imagine the experiment is repeated several times on the same state $|\Psi\rangle$. The results of Alice and Bob will be strictly random but always entirely correlated. This correlation exists independently of the axis along which Alice and Bob make their measurements. Indeed, we have seen that $|\Psi\rangle$ takes exactly the same form when written in terms of the eigenstates of $\hat{n}\cdot|\hat{S}\rangle$ with an arbitrary $|n\rangle$.

The EPR correlation is explained by orthodox quantum mechanics but also by a purely "realistic" hypothesis that assumes the values of S_{z_1} and S_{z_2} existed prior to the measurement.

Imagine a third actor, Charlie, who prepares pairs of beads - one white and one black - and then places each in a box, randomly sending one box to Bob and the other to Alice. Upon opening their boxes, they will find a white or black bead at random, but always of the opposite color to the other.

The EPR argument maintains that after Alice's measurement, the second assumption in the EPR paper and Bob's great distance ensure the impossibility of any influence from Alice's measurement on Bob's particle. According to EPR, the only possible explanation for the correlations is that Bob's result was pre-existing. The same argument applied to a measurement along an arbitrary axis $\hat{n}\cdot|\hat{S}\rangle$ concludes that the spin values of Bob's particle along the three axes $\hat{x}$, $\hat{y}$, and $\hat{z}$ are pre-existing simultaneously, which is prohibited by orthodox quantum mechanics because $[\hat{S}_j, \hat{S}_k] = i\hbar\epsilon_{ikl}\hat{S}_l$.

EPR's conclusion is that orthodox quantum mechanics is an incomplete theory, and the result of a measurement - which, according to this theory, is random - is, in reality, pre-existing, or, in other words, an "element of objective reality." With a single realization of the experiment, it is obviously impossible to know if the result was pre-existing or if it was created at the time of measurement, as per the idea of orthodox quantum mechanics. Therefore, EPR suggests that with each repetition of the experiment, ideally with the same state $|\Psi\rangle$, the true state containing the "elements of objective reality," i.e., the pre-existing values of the spins, is not the same but

rather characterized by a random component in these pre-existing values, which justifies the random outcome of the subsequent measurements by Alice and Bob. These additional variables are commonly referred to as "hidden variables."

EPR's conclusion is strengthened by another argument. Suppose Alice and Bob choose to measure along two different axes. If Alice measures $\hat{S}_z$ and obtains $+\frac{\hbar}{2}$, Bob's particle will be in the state $|\downarrow\rangle_z$. If, on the other hand, Alice measures along $\hat{S}_x$ and obtains $+\frac{\hbar}{2}$, Bob's particle will be in the state $|\downarrow\rangle_x = \frac{1}{\sqrt{2}}(|\uparrow\rangle_z - |\downarrow\rangle_z)$.

Since Bob is at a great distance from Alice, it is reasonable to assume that Alice's measurement did not influence Bob's particle's state. The two states $|\downarrow\rangle_x$ and $|\downarrow\rangle_z$ must, therefore, represent the same physical state. But this conclusion is prohibited by the orthodox interpretation of quantum mechanics since, in the first case, the value of $\hat{S}_z$ is not an "element of objective reality," whereas, in the second case, it is. Therefore, it is necessary to assume the existence of a hidden variable that determines the outcome of Bob's measurement of $\hat{S}_z$ in both cases.

The three decades following the EPR paper saw several attempts to provide a demonstration that the concept of hidden variables is incompatible with the predictions of quantum mechanics. Almost 30 years later, John Bell embarked on the most successful of these attempts.

The work preceding Bell's had produced "no-hidden-variables theorems" based on unjustified or incorrect assumptions. Bell was inspired by research undertaken by Bohm around 1952. Bohm had developed a theory that extended quantum mechanics by introducing a "pilot wave" - a form of hidden variables.

The Bohm theory is perfectly capable of replicating all the predictions of orthodox quantum mechanics while being a completely "realistic" theory. It thus stands as a counterexample to all the (false) theorems from previous years. However, the cost of this success is the abandonment of locality in the Bohm theory. John Bell comments on Bohm's work as follows:

> *In this theory, an explicit causal mechanism exists whereby the disposition of one piece of apparatus affects the results obtained with a distant piece. In fact, the EPR paradox is resolved in the way which Einstein would have liked least.*

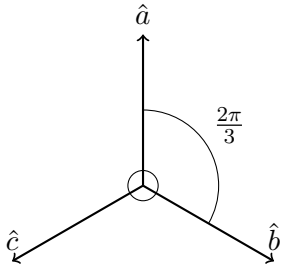
While EPR where convinced that a complete theory (using hidden variables) was emerging. according to them:

> *While we have thus shown that the wave function does not provide a complete description of the physical reality, we left open the question of whether or not such a description exists. We believe, however, that such a theory is possible.*

Bohm then shows that it is possible to realize this theory by introducing an instantaneous causal mechanism, thus abandoning the locality that Einstein held dear. Bell, in his 1966 article (written before the one published in 1965), poses the question of whether giving up locality is a necessary condition for realizing a theory that uses hidden variables and is compatible with orthodox quantum mechanics (and thus constructing a theory that contains only "elements of objective reality").

Suppose, on the other hand, that the measurement results are pre-existing. We call $Z^i_{\hat{n}} = \pm\frac{\hbar}{2}$ the value of the spin component along the axis $\hat{n}$ for particle i ($i = 1, 2$). These values will change from one repetition of the experiment to another. Therefore, we can treat them as random variables.

Consider three axes $\hat{a}$, $\hat{b}$, and $\hat{c}$, defined in the same plane and at an angle of $2\pi/3$ with respect to each other.



In this case, for each pair of axes:

$$P_{\pm} = \frac{1 + \cos(2\pi/3)}{2} = -\frac{1}{4}$$

For this realistic theory to reproduce this result, it is required that:

$$P(Z_{\alpha}^{1} \neq Z_{\beta}^{2}) = \frac{1}{4}$$

if $\alpha \neq \beta$ and $\alpha, \beta = \hat{a}, \hat{b}, \hat{c}$, and that:

$$Z_{\alpha}^{1} = -Z_{\alpha}^{2}$$

(EPR correlation)

Theorem 11.0.1. *If the above assumptions are met, then:*

$$P(Z_{a}^{1} \neq Z_{b}^{2}) + P(Z_{b}^{1} \neq Z_{c}^{2}) + P(Z_{c}^{1} \neq Z_{a}^{2}) \geq 1$$

Demo. Z_{a}^{1}, Z_{b}^{1}, Z_{c}^{1} cannot all be different, as they can only take two distinct values.

In his landmark 1965 article, Bell successfully demonstrated this theorem. He claimed that a theory based on the assumptions of locality and "realism" necessarily implies quantitative constraints expressed as inequalities for measurement results. Orthodox quantum mechanics violates these inequalities!

Here, we provide a basic proof of the theorem, which relies on the EPR result. Later on, we will present a more general and self-contained proof.

We start from the singlet state:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

Suppose that Alice and Bob measure the components $\hat{n} \cdot \hat{\mathbf{S}}$ and $\hat{m} \cdot \hat{\mathbf{S}}$, respectively. Let θ be the angle between axes $\hat{n}$ and $\hat{m}$. It is observed (without proof, as an exercise for the reader) that the probability that Alice and Bob measure two opposite values (i.e., $+\frac{\hbar}{2}$ and $-\frac{\hbar}{2}$ or vice versa) is according to orthodox quantum mechanics:

$$P_{\pm} = \frac{1 + \cos\theta}{2} \quad \theta \in [0, \pi]$$

In each configuration of the possible values for these three variables, at least two of the three will be equal. The union of the sets of configurations in which at least two of the three variables are equal is therefore the set of all possible configurations.

$$\{Z_{a}^{1} = Z_{b}^{1}\} \cup \{Z_{b}^{1} = Z_{c}^{1}\} \cup \{Z_{c}^{1} = Z_{a}^{1}\} = \{Z_{a}^{1}, Z_{b}^{1}, Z_{c}^{1}\}$$

The sum of the three probabilities is thus:

$$P(Z_{a}^{1} = Z_{b}^{1}) + P(Z_{b}^{1} = Z_{c}^{1}) + P(Z_{c}^{1} = Z_{a}^{1}) \geq 1$$

Since $Z^1_\alpha = -Z^2_\alpha$, $\alpha = \hat{a}, \hat{b}, \hat{c}$, we have $P(Z^1_\alpha = Z^1_\beta) = P(Z^1_\alpha \neq Z^2_\beta)$, so:

$$P(Z^1_a \neq Z^2_b) + P(Z^1_b \neq Z^2_c) + P(Z^1_c \neq Z^2_a) \geq 1$$

□

According to the expression for $P_\pm = 1/4$, the value predicted by orthodox quantum mechanics for the same sum is:

$$P_\pm + P_\pm + P_\pm = 3/4 < 1$$

This is inconsistent with the previous result. This inequality is an example of what are called "Bell inequalities."

The EPR and Bell arguments can thus be summarized as follows.

EPR: If (1) we assume a principle of locality, and (2) we accept the correlations between measurements on the state $|\Psi\rangle$, we are forced to admit that the measurement outcomes preexist, meaning they are "elements of objective reality."

Bell: If we assume that the measurement values on $|\Psi\rangle$ (on different axes) all preexist, then we obtain an inequality that is incompatible with the predictions of orthodox quantum mechanics.

The conjunction of these two arguments, therefore, implies that the principle of locality is incompatible with the predictions of orthodox quantum mechanics. We must admit that a measurement has an instantaneous, distant effect.

11.1 Bell Inequalities: General Formulation

The argument used previously to deduce Bell's theorem is based on two fundamental assumptions.

1. The EPR argument: locality and correlations predicted by orthodox quantum mechanics imply the existence of hidden variables. In other words, "elements of objective reality" associated with the measured quantities.

2. The validity of the perfect correlations predicted by orthodox quantum mechanics for measurements on the singlet spin state.

Bell's theorem sparked intense discussions in the years that followed, particularly about the restrictive nature of these two assumptions.

Thus, Bell's theorem can be improved in two aspects: firstly, it does not rely on the EPR argument or on perfect correlations in the singlet spin state because they may not be realized in practice. These resulting minor deviations can bring orthodox quantum mechanics within the limits imposed by Bell.

To address these objections, Bell developed a generalized version of his theorem that (1) starts from independent assumptions, without using EPR, and that (2) establishes inequalities that depend on the value of certain correlations between observables continuously. Thus, it is possible to show that, to bring orthodox quantum mechanics within the limits imposed by the theorem, the measured values of the correlations should significantly differ from values predicted by orthodox quantum mechanics — differences that would be experimentally measurable.

This new version of Bell's theorem leads to the famous CHSH inequalities, tested by some of the earliest experiments.

Suppose we make a measurement on a system composed of two subsystems that interacted in the past (producing correlations) and are now very distant. The EPR state can be taken as an example.

α_1 and α_2 are the control parameters that determine the type of measurement made on subsystems 1 and 2, respectively. For example, in the EPR state, α_1 and α_2 represent the two axes along which Alice and Bob, respectively, choose to make their measurements.

Suppose α_1 and α_2 are chosen freely and randomly by Alice and Bob, immediately before the measurement, in a way that there is no way for Alice's choice of α_1 to influence Bob's choice of α_2.

Once α_1 and α_2 are chosen, measurements are performed, resulting in values A_1 and A_2, respectively. According to orthodox quantum mechanics, A_1 and A_2 exhibit a random behavior from one measurement to another, i.e., over multiple repetitions of the experiment under identical conditions (with constant values of α_1 and α_2. For each pair of chosen values of α_1 and α_2, the values A_1 and A_2 are subject to a probability distribution:

$$P_{\alpha_1,\alpha_2}(A_1, A_2)$$

which generally depends on α_1 and α_2.

It's important to note at this point that the assumption of pre-existing values has not been introduced yet. Nothing is assumed regarding the origin of the random nature of the results A_1 and A_2. These values may be partly pre-existing and partly derived from the measurement process.

In this sense, this initial assumption is very different from the assumption in the simplified version of Bell's theorem, in which pre-existing values are assumed from the beginning.

The concept of locality must be rigorously expressed. Simply factorizing the probability distribution as follows is not possible:

$$P_{\alpha_1,\alpha_2}(A_1, A_2) = P_{\alpha_1,\alpha_2}(A_1)P_{\alpha_1,\alpha_2}(A_2)$$

Indeed, the two subsystems may have interacted previously and thus contain correlations resulting from the initial preparation.

However, locality must imply a decorrelation of any random behavior in the outcomes of A_1 and A_2 once the "elements of objective reality" (and thus the values of hidden variables) are fixed. More precisely, let λ represent the set of (hidden) variables that determine the "elements of objective reality" in the measurements of A_1 and A_2. The value of λ changes from one experiment repetition to another, following the probability distribution $P(\lambda)$. Any correlation between the values of A_1 and A_2 should only be attributed to their dependence on λ. In other words:

$$P_{\alpha_1,\alpha_2}(A_1, A_2) = \int d\lambda P_{\alpha_1,\alpha_2}(A_1, A_2|\lambda)P(\lambda)$$

where $P_{\alpha_1,\alpha_2}(A_1, A_2|\lambda)$ is the conditional probability distribution given a specific value of λ.

According to our definition of locality, any remaining random character described by $P_{\alpha_1,\alpha_2}(A_1, A_2|\lambda)$ must be decorrelated. Therefore, locality implies:

$$P_{\alpha_1,\alpha_2}(A_1, A_2|\lambda) = P_{\alpha_1}(A_1|\lambda)P_{\alpha_2}(A_2|\lambda)$$

with the additional assumption that measurements depend locally on α_1 and α_2. For example, $P_{\alpha_1}(A_1|\lambda)$ cannot depend on α_2."

Since α_1 and α_2 are arbitrarily chosen by Alice and Bob, our analysis must also include the assumption that $P(\lambda)$ does not depend on α_1 and α_2. This is an additional assumption compared to the locality assumption, and it expresses the free will of Alice and Bob. This type of assumption is referred to as "non-conspiracy." Indeed, since λ is chosen by Nature, the possibility that this choice is determined by Alice and Bob should be considered an incredible conspiracy on the part of Nature, attempting to prevent any rational analysis.

Let's now define the correlation function $C(\alpha_1, \alpha_2)$ for the observables α_1 and α_2.

$$C(\alpha_1, \alpha_2) = E_{\alpha_1,\alpha_2}(A_1 \cdot A_2) = \int d\lambda E_{\alpha_1,\alpha_2}(A_1 \cdot A_2|\lambda)P(\lambda)$$

where $E_{\alpha_1,\alpha_2}(A_1 \cdot A_2)$ is the expectation value of the product $A_1 \cdot A_2$ for a given choice of α_1 and α_2. $E_{\alpha_1,\alpha_2}.(A_1 \cdot A_2|\lambda)$ represents the same quantity, conditioned on λ.

$$E_{\alpha_1,\alpha_2}(A_1 \cdot A_2) = \sum_{A_1,A_2} A_1 A_2 P_{\alpha_1,\alpha_2}(A_1, A_2)$$

$$E_{\alpha_1,\alpha_2}(A_1 \cdot A_2|\lambda) = \sum_{A_1,A_2} A_1 A_2 P_{alpha_1,alpha_2}(A_1, A_2|\lambda)$$

From these expressions, it is possible to prove the CHSH-Bell inequality.

Theorem 11.1.1. *Suppose that* ± 1 *are the only allowed values for* A_1 *and* A_2*. The hypothesis above imply*

$$|C(a,b) - C(a,c)| + \big|C(a,b) + C(a',c)\big| \leq 2$$

for all choices of parameters a, b, c, a'*.*

Demo. We have

$$E_{\alpha_1,\alpha_2}(A_1, A_2|\lambda) = E_{\alpha_1}(A_1|\lambda)E_{\alpha_2}(A_2|\lambda) \quad \forall \lambda, \alpha_1, , \alpha_2$$

from which

$$\begin{aligned} & |C(a,b) - C(a,c)| + |C(a,b) + C(a',c)| \\ \leq & \int \big[|E_a(A_1|\lambda)| \cdot |E_b(A_2|\lambda) - E_c(A_2|\lambda)| + |E_{a'}(A_1|\lambda)| \cdot |E_b(A_2|\lambda) + E_c(A_2|\lambda)|\big]P(\lambda)d\lambda \\ \leq & \int \big[|A_b(A_2|\lambda) - E_c(A_2|\lambda)| + |E_b(A_2|\lambda) + E_c(A_2|\lambda)|\big]P(\lambda)d\lambda \end{aligned}$$

where the first inequality is taken from

$$\Big|\int f(x)dx\Big| \leq \int |f(x)|\, dx$$

and the second one

$$|E_\alpha(A_1|\lambda)| \leq 1$$

The proof of the theorem follows from

Lemme 11.1.2. *for* $x, y \in \mathbb{R}$ *and* $x, y \in [-1, 1]$ *we have* $|x - y| + |x + y| \leq 2$

Demo.

$$\begin{aligned} \big(|x-y| + |x+y|\big)^2 &= 2x^2 + 2y^2 + 2|x^2 - y^2| \\ &= \begin{cases} 4x^2 & x^2 > y^2 \\ 4y^2 & x^2 < y^2 \end{cases} \\ &\leq 4 \end{aligned}$$

□

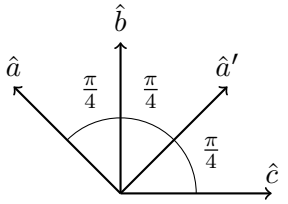
The CHSH-Bell inequality is thus proven. What does orthodox QM predict for $C(\alpha, \beta)$? Consider bell state

$$|\Psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle)$$

where $|\uparrow\rangle$ and $|\downarrow\rangle$ are the eigenstates of a spin component $\hat{u} \cdot \hat{\mathbf{S}}$, we can show (exercise) that orthodox QM says

$$C(\hat{a}, \hat{b}) = -\hat{a} \cdot \hat{b}$$

where $\hat{a}$ and $\hat{b}$ are the unitary vectors wrt which the spins are measured, and "$\cdot$" is the Euclidean scalar product. If we choose



we obtain the maximal violation of the inequality.

$$\begin{aligned} &|C(\hat{a}, \hat{b}) - C(\hat{a}, \hat{c})| + |C(\hat{a}', \hat{b}) + C(\hat{a}', \hat{c})| \\ &= \left|-\cos(\frac{\pi}{4}) + \cos(\frac{3\pi}{4})\right| + \left|-\cos(\frac{\pi}{3}) - \cos(\frac{\pi}{4})\right| \\ &= \left|-\frac{\sqrt{2}}{2} - \frac{\sqrt{2}}{2}\right| + \left|-\frac{\sqrt{2}}{2} - \frac{\sqrt{2}}{2}\right| = 2\sqrt{2} > 2 \end{aligned}$$

This new version of Bell's theorem, coming from only the locality hypothesis is also incompatible with orthodox QM.

Since the publication of this original proof, tens of experiments, have demonstrated this violation.

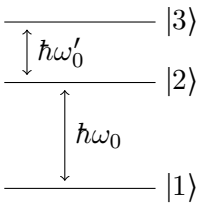
Appendix A

Exercises

A.1 2014 exam

Exercise 1 : 2 photon transition (1,5 points)

An atom is modeled by a 3-level system represented here, with $\omega_0 \neq \omega_0'$:



Starting from $t = 0$, this system is subjected to a perturbation $\hat{V}(t) = e^{i\omega t}\hat{v} + e^{-i\omega t}\hat{v}^\dagger$, where

$$\hat{v} = \hbar\Omega\,|1\rangle\langle 2| + \hbar\Omega'\,|2\rangle\langle 3|\,, \tag{A.1}$$

and $\Omega, \Omega' \in \mathbb{R}$ are angular frequencies introduced here to simplify the coupling amplitudes. This perturbation $\hat{V}(t)$ represents the action of a photon field with energy $\hbar\omega$.

1. Calculate the probability $P_{12}^{(1)}(\omega, t)$ for the transition from the state $|1\rangle$ to the state $|2\rangle$ at the first-order perturbation.
2. By examining the ratio $P_{12}^{(1)}(\omega, t)/P_{12}^{(1)}(\omega_0, t)$, show that at long times, the dependence of $P_{12}^{(1)}(\omega, t)$ on ω is sharply peaked around ω_0 (resonance).
3. Calculate $P_{13}^{(1)}(\omega, t)$, the probability of transition from $|1\rangle$ to $|3\rangle$ at the first order.
4. Show that the probability of transition between $|1\rangle$ and $|3\rangle$ at the second-order perturbation is $P_{13}^{(2)}(\omega, t) = |a_{13}^{(2)}(\omega, t)|^2$, where

$$a_{13}^{(2)}(\omega, t) = \frac{\Omega\Omega'}{\omega_0 - \omega}\left(\frac{e^{i(\omega_0+\omega_0'-2\omega)t} - 1}{\omega_0 + \omega_0' - 2\omega} - \frac{e^{i(\omega_0'-\omega)t} - 1}{\omega_0' - \omega}\right). \tag{A.2}$$

It can be shown (calculation not required) that this probability is written in the form

$$P_{13}^{(2)}(\omega, t) = \frac{4\Omega^2\Omega'^2}{\delta^2\delta'\Delta}\sin^2\left(\frac{\delta t}{2}\right) + \frac{4\Omega^2\Omega'^2}{\delta(\delta')^2\Delta}\sin^2\left(\frac{\delta' t}{2}\right) - \frac{4\Omega^2\Omega'^2}{\delta\delta'\Delta^2}\sin^2\left(\frac{\Delta t}{2}\right), \tag{A.3}$$

where $\delta = \omega_0 - \omega$, $\delta' = \omega_0' - \omega$, and $\Delta = \omega_0 + \omega_0' - 2\omega$. Qualitatively sketch the shape of $P_{13}^{(2)}(\omega, t)$ as a function of ω at long times. What about $P_{12}^{(2)}(\omega, t)$?

5. Deduce from the previous questions the schematic appearance of the absorption spectrum (as a function of ω, considering processes at the first and second orders) when the atom is initially in the ground state $|1\rangle$. Take the limit of long times. Indicate for each absorption line the process $|1\rangle \to |f\rangle$ involved, as well as the corresponding perturbation order.

6. How do you interpret the last of the three terms in equation (A.3)? What is the physical process involved? Does it imply conservation of energy?

Exercise 2 : Fine structure of an atom (2,0 points)

We are interested in the spin orbit coupling effect on the first levels of the hydrogen atom. With such a coupling, the hamiltonian is $\hat{H} = \hat{H}_0 + \hat{V}_{LS}$ where (with $g_e \simeq 2$)

$$\hat{H}_0 = \frac{\hat{\boldsymbol{p}}^2}{2m_e} + V(r), \qquad V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \qquad \hat{V}_{LS} = A(r)\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}, \qquad A(r) = \frac{g_e}{4m_e^2c^2}\frac{1}{r}\frac{dV}{dr}. \tag{A.4}$$

1. The total angular momentum $\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$ is defined, and we denote the eigenvalues of $\hat{\boldsymbol{J}}^2$, $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{S}}^2$, $\hat{J}_z$, $\hat{L}_z$, and $\hat{S}_z$ as $j(j+1)\hbar^2$, $l(l+1)\hbar^2$, $s(s+1)\hbar^2$, $m_j\hbar$, $m_l\hbar$, and $m_s\hbar$, respectively (reminder: the electron has a spin of $s = 1/2$). What are the possible values of j as a function of l? What are the corresponding values of m_j?

2. It is recalled that $\hat{\boldsymbol{L}}^2$, $\hat{L}_z$, $\hat{\boldsymbol{S}}^2$, and $\hat{S}_z$ commute with $\hat{H}_0$. Express $\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}$ in terms of $\hat{\boldsymbol{J}}^2$, $\hat{\boldsymbol{L}}^2$, and $\hat{\boldsymbol{S}}^2$. Calculate the commutators of $\hat{\boldsymbol{J}}^2$, $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{S}}^2$, $\hat{J}_z$, $\hat{L}_z$, and $\hat{S}_z$ with $\hat{H}$.

3. We are only interested in the bound states of hydrogen. The simultaneous eigenstates of $\hat{H}_0$, $\hat{\boldsymbol{J}}^2$, and $\hat{J}_z$, denoted as $\{|nlsjm_j\rangle\}$, arise from the combination of orbital angular momentum and spin. Are the states $\{|nlsjm_j\rangle\}$ eigenstates of $\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$? Are they eigenstates of $\hat{V}_{LS}$? Justify.

4. Consider $\hat{V}_{LS}$ as a perturbation to $\hat{H}_0$. Calculate the energy variation ΔE_{nlj} of the states $\{|nlsjm_j\rangle\}$ to first-order perturbation theory in terms of the mean values $\langle R_{nl}|A(r)|R_{nl}\rangle$, where R_{nl} are the radial wave functions of the bound states. What is the correction for the s states ($l = 0$)? For $l \geq 1$, simplify the expression for ΔE_{nlj} using the result from question 1. Explain how the spin-orbit interaction introduces the "fine" structure of the hydrogen atom.

5. In the context of our model, we focus on the 2P level ($n = 2$, $l = 1$): what are the possible values of j? Denote the associated levels of fine structure as $2P_j$. Calculate their energy shifts due to $\hat{V}_{LS}$, knowing that $\langle R_{21}|A(r)|R_{21}\rangle = \alpha^4 m_e c^2/(48\hbar^2)$, with $\alpha = e^2/(4\pi\epsilon_0\hbar c)$, the fine-structure constant. Numerical application: at a level of approximation that doesn't require a calculator, estimate the energy shifts and the magnitude of degeneracy lifting of the $2P_j$ levels in eV and MHz (reminder: $\hbar = 1.05 \times 10^{-34}$ J.s, $m_e = 9.11 \times 10^{-31}$ kg, $\epsilon_0 = 8.85 \times 10^{-12}$ F.m^{-1}).

Exercise 3 : Time evolution of a density matrix (1,5 points)

Consider a two spin $\frac{1}{2}$ system, with states defined in a 4d hilbert sapce with basis $\mathcal{B}$ made of vectors $|S_1^z\rangle \otimes |S_2^z\rangle = |S_1^z S_2^z\rangle$. Here $|S_j^z\rangle$ are the eigenstates of $\hat{S}_j^z$ $(j = 1, 2)$ with eigenvalues $\pm\frac{\hbar}{2}$. For simplicity, we will write $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ theses same states. Suppose that the time evolution is determined by the Hamiltonian

$$\hat{H} = g(\hat{S}_1^+ \otimes \hat{S}_2^- + \hat{S}_1^- \otimes \hat{S}_2^+), \tag{A.5}$$

where $\hat{S}_j^\pm = \hat{S}_j^x \pm i\hat{S}_j^y$.

1. Find a matrix for $\hat{H}$ in the $\mathcal{B}$ basis.
2. Find the eigenvalues and eigenstates of $\hat{H}$.
3. At $t = 0$, the system is in $|\Psi(0)\rangle = |\downarrow\uparrow\rangle$. Find state $|\Psi(t)\rangle$ at t. *Hint: use the eigenstates found above.*
4. write the density matrix $\rho(t)$ corresponding to the state $|\Psi(t)\rangle$, in basis $\{|\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\uparrow\uparrow\rangle\}$.
5. Compute the reduced density matrix $\rho_1(t)$ of the first spin by using the partial trace over the second spin.
6. Consider $\rho_1(t)$ at $t = 0$, and at $g\hbar t = \frac{\pi}{4}$. Discuss these 2 matrices underlying their nature (pure or mixed) and discuss the link with entanglement between the 2 spins.

A.2 2015 Exam

Exercise 4 : Sudden Displacement of Harmonic Oscillator (2 points)

Consider a one-dimensional harmonic oscillator characterized by the potential $\hat{V} = \frac{m\omega^2\hat{x}^2}{2}$ and, therefore, by the Hamiltonian $\hat{H}_0 = \hbar\omega(\hat{a}^\dagger\hat{a} + 1/2)$ (where m is the mass and ω is the angular frequency). An experimenter prepares the system in the first excited state $|1\rangle = \hat{a}^\dagger|0\rangle$, where $|0\rangle$ is the ground state of $\hat{H}_0$. At $t = 0$, the experimenter accidentally hits the table, causing the center of the oscillator to instantly move to a new position $x = b$.

1. Express the operator $\hat{V}(t)$ associated with the perturbation in terms of $\hat{a}$ and $\hat{a}^\dagger$, i.e., such that $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$.
2. Suppose the experimenter does not notice the displacement, and a very long time elapses. Calculate, in this limit and to the lowest order of perturbation in b, the probability per unit time $W_{1\to n}$ that the system makes a transition to an eigenstate $|n\rangle$ of $\hat{H}_0$ with $n \neq 1$.
3. Suppose, on the other hand, that after a time $T > 0$, the experimenter notices the displacement and instantly returns the oscillator to its initial position. Calculate, to the lowest order in b, the probability $P_{1\to n}$ that the system is in a state $|n\rangle$ with $n \neq 1$ for $t > T$.

   Suggestion: In this second part, if you don't remember the expression for the transition probability, it may be useful to directly apply the time evolution operator $\hat{U}_S(t, 0)$ (Schrödinger's viewpoint). In this case, remember that $\hat{U}_S(t, 0) = e^{-i\hat{H}_0 t/\hbar}\hat{U}_I(t, 0)$, where $U_I(t, 0)$ is the operator in the interaction viewpoint, given by $\hat{U}_I(t, 0) = T\exp\left[-\frac{i}{\hbar}\int_0^t \hat{V}_I(t')dt'\right)$, and $\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{V}e^{-i\hat{H}_0 t/\hbar}$.

Exercise 5 : Variational Principle for an Anharmonic Potential (1 point)

Consider a one-dimensional particle with mass m, subjected to a potential $V(x) = \alpha x^4$.

1. Up to a dimensionless factor, we can express the energy of the ground state as a product of powers of the constants that define the problem, i.e., $E_0 \propto \hbar^a m^b \alpha^c$. Find the values of a, b, and c using dimensional analysis alone.

2. Using the variational principle, determine an upper bound on the energy E_0 of the ground state. Use a Gaussian as a trial function: $\psi(x) = \exp\left(-\frac{x^2}{2\sigma^2}\right)$. Note that

$$\int_{-\infty}^{+\infty} e^{-y^2} dy = \sqrt{\pi}\,, \qquad \int_{-\infty}^{+\infty} y^2 e^{-y^2} dy = \frac{\sqrt{\pi}}{2}\,, \qquad \int_{-\infty}^{+\infty} y^4 e^{-y^2} dy = \frac{3}{4}\sqrt{\pi}\,.$$

Exercise 6 : Entanglement criteria (2 points)

A quantum system is composed of 2 subsystems and is defined in Hilbert space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$, where $\mathcal{H}_1$ and $\mathcal{H}_2$ are the space of both subsystems respectively. The state of such a subsystems is separable if we can express its density matrix as

$$\rho_s = \sum_k p_k \rho_k^{(1)} \otimes \rho_k^{(2)}\,, \tag{A.6}$$

with $\sum_k p_k = 1$, $p_k \geq 0$, and $\rho_k^{(1)}$ and $\rho_k^{(2)}$ being density matricies in spaces $\mathcal{H}_1$ and $\mathcal{H}_2$ respectively. A system that cannot be described by a matrix of this type (A.6), is a system with quantum entanglement.

Recall that a density matrix must obey the following properties: (i) $\mathrm{Tr}(\rho) = 1$; (ii) $\rho = \rho^\dagger$; (iii) Positive semi definiteness. $\langle\psi|\rho|\psi\rangle \geq 0$ for all $|\psi\rangle$ in their space of definition.

1. Show that, for such a separable state, the average value of an arbitrary observable A_1 of subsystem 1 does not depend on subsystem 2. In other words, it does not depend on $\rho_k^{(2)}$.

2. Three actors, named A, B, and C (or Alice, Bob, and Charlie), each has a quantum bit (a quantum system defined in a 2-dimensional Hilbert space with basis $\{|0\rangle, |1\rangle\}$). The system of the three quantum bits is in the state $|\psi_{GHZ}\rangle = \frac{1}{\sqrt{2}}(|000\rangle + |111\rangle)$ (here and throughout, in the notation $|ijk\ldots\rangle$, index i indicates the state of Alice's qubit, index j indicates Bob's qubit, etc.). Alice lives in another galaxy, and Bob and Charlie have no knowledge of the total state of the three quantum bits. Calculate the density matrix associated with the mixed state that describes the subsystem formed by the quantum bits of Bob and Charlie (in the basis $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$). Show that this matrix is of separable type.

Now, let's consider the operation of partial transposition (not to be confused with partial trace). Consider a density matrix ρ that describes the state of a system composed of two subsystems. Let $\{|i\rangle, |j\rangle, \ldots\}$ represent the states of the basis of the first subsystem, $\{|\mu\rangle, |\nu\rangle, \ldots\}$ represent the states of the basis of the second subsystem, and $\{|i\mu\rangle, |i\nu\rangle, |j\mu\rangle, |j\nu\rangle, \ldots\}$ represent the states of the basis of the total system. If the matrix ρ has matrix elements $\rho_{i\mu,j\nu} = \langle i\mu|\rho|j\nu\rangle$, then the matrix elements of the density matrix ρ^{T_P}, obtained by performing partial transposition with respect to the second subsystem, are defined as $(\rho^{T_P})_{i\mu,j\nu} = \langle i\nu|\rho|j\mu\rangle$. (Partial transposition with respect to the first subsystem is defined similarly).

3. Show that for a separable state of two subsystems, of the form (A.6), the partial transpose $\rho_s^{T_P}$ with respect to one of the two subsystems is still a valid density matrix. In other words, it still satisfies the three properties (i), (ii), and (iii) mentioned above.

   Remark: We will thus have demonstrated a necessary condition for a density matrix to be separable. Automatically, we will have a sufficient condition for a density matrix to be non-separable, i.e., entangled.

4. Four actors, named A, B, C, and D (or Alice, Bob, Charlie, and David), each have a quantum bit. The system of the four quantum bits is in the state $|\psi_S\rangle = \frac{1}{2}(|0000\rangle + |0011\rangle + |1100\rangle - |1111\rangle)$. As before, Alice lives in another galaxy. Calculate the density matrix associated with the mixed state that describes the subsystem formed by the quantum bits of Bob, Charlie, and David (in the basis $\{|000\rangle, |001\rangle, |010\rangle, \ldots, |111\rangle\}$). Demonstrate that the mixed state shared by Bob, Charlie, and David is an entangled state. In this regard, we will use the criterion just defined.

   Suggestion: study the eigenvalues of the partial transpose. Note: there are several ways to divide a system of three qubits into two subsystems. Remark: if no mistakes are made, diagonalizations should only be performed in 2-dimensional subspaces.

A.3 2016 Exam

Exercise 7 : 3 coupled harmonic oscillators (3 points)

Consider the system of three coupled harmonic oscillators, described by the Hamiltonian

$$\hat{H} = \sum_{j=1}^{3} \hbar\omega \hat{a}_j^\dagger \hat{a}_j - \sum_{j<k} J(\hat{a}_j^\dagger \hat{a}_k + \hat{a}_k^\dagger \hat{a}_j)\,, \tag{A.7}$$

where the second sum is taken over distinct pairs of indices (j,k), i.e., $(1,2)$, $(1,3)$, and $(2,3)$. We assume that the three oscillators are placed at the vertices of an equilateral triangle. Therefore, the system is invariant under the operations of the C_{3v} symmetry group. In particular, each operation of C_{3v} realizes a permutation of the three oscillators. The character table of C_{3v} is provided below. We denote states with a non-negative number of quanta on each oscillator as $|n_1, n_2, n_3\rangle$. These states form an orthonormal basis.

1. Show that the Hamiltonian commutes with the number operator, i.e., $[\hat{H}, \hat{N}] = 0$, where $\hat{N} = \sum_{j=1}^{3} \hat{a}_j^\dagger \hat{a}_j$. Explain what this implies for the eigenstates of $\hat{H}$.

2. Now consider the three states $|100\rangle$, $|010\rangle$, and $|001\rangle$. Using group representation theory and simple symmetry considerations, find the eigenvalues and eigenvectors of $\hat{H}$ in the subspace generated by these three vectors. In particular, explain the degeneracies imposed by symmetry.

3. Consider the subspace of dimension 6 generated by states $|n_1, n_2, n_3\rangle$ with $n_1 + n_2 + n_3 = 2$. Without explicitly calculating the eigenvalues and eigenvectors of $\hat{H}$ but only using representation theory, determine the number of distinct energy levels and their degeneracies characterizing the eigenstates of $\hat{H}$ in this subspace.

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	1	−1
$\Gamma^{(3)}$	2	−1	0

Table A.1: Character table for C_{3v}

Suggestion. To calculate the characters associated with the operations of C_{3v}, it is worth noting that you only need to know the diagonal elements of the corresponding matrices, and it is sufficient to perform this calculation once for each equivalence class of the group. Also, it is worth noting that, to solve this problem, the use of "projectors" onto the irreducible representations of the group is not necessary.

Exercise 8 : Entanglement entropy (2 points)

Consider a quantum system in a Hilbert space $\mathcal{H}_1$ of dimension 2, described by the following density matrix:

$$\hat{\rho} = \begin{pmatrix} x & 0 \\ 0 & 1-x \end{pmatrix} \qquad 0 \leq x \leq 1 \tag{A.8}$$

1. Calculate the von Neumann entropy of $\hat{\rho}$, defined as $S(\hat{\rho}) = -\mathrm{Tr}(\hat{\rho}\ln(\hat{\rho})) = S(x)$. Study the behavior of $S(x)$ within its domain. What is the value of S when $\hat{\rho}$ is a pure state? For what value of x does $S(x)$ reach a maximum, and what type of state does it correspond to?

Now, consider a system composed of two subsystems A and B, as seen in the previous section. The states of this system are defined in the Hilbert space $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_1$. We will now use the concept of Schmidt decomposition: it can be shown that it is always possible to find two orthonormal bases $\{|a_1\rangle, |a_2\rangle\}$ and $\{|b_1\rangle, |b_2\rangle\}$ in the Hilbert space $\mathcal{H}_1$, allowing an arbitrary pure state $|\psi\rangle \in \mathcal{H}$ to be written as:

$$|\psi\rangle = \sum_{j=1,2} \lambda_j |a_j\rangle \otimes |b_j\rangle, \quad \text{with } \lambda_j \in \mathbb{R},\ 0 \leq \lambda_j \leq 1,\ \text{and } \sum_{j=1,2} \lambda_j^2 = 1\,. \tag{A.9}$$

2. Using the Schmidt decomposition, calculate the reduced density matrices $\hat{\rho}_A = \mathrm{Tr}_B(|\psi\rangle\langle\psi|)$, and $\hat{\rho}_B = \mathrm{Tr}_A(|\psi\rangle\langle\psi|)$.

3. Calculate $S(\hat{\rho}_A)$ and $S(\hat{\rho}_B)$. What is the relationship between these two values? What is the value of $S(\hat{\rho}_A)$ if $|\psi\rangle$ is a separable state (i.e., non-entangled)? And if $|\psi\rangle$ is a state with maximum entanglement between the two subsystems?

4. Explain qualitatively (and briefly) why $S(\hat{\rho}_A)$ is called "entanglement entropy."

Exercise 9 : Hydrogen atom in cubic potential (1 point)

A hydrogen atom is subjected to a time-independent perturbation described by the potential

$$V(\mathbf{r}) = \frac{V_0}{a_B^3} xyz, \quad \text{where } V_0 > 0 \text{ and } a_B = \text{Bohr radius}\,. \tag{A.10}$$

1. Can $V(\mathbf{r})$ produce, at first-order perturbation, a finite correction to the eigenenergy of the atom's $1s$ level, i.e., the one with the principal quantum number $n = 1$?

2. Can $V(\mathbf{r})$ produce, at first-order perturbation, a finite correction to the eigenenergies of the four levels $(2s, 2p)$ of the atom, i.e., those with $n = 2$?

Suggestion. Write $V(\mathbf{r})$ in spherical coordinates. Use the operator $\hat{L}_z = -i\hbar\partial/\partial\phi$ to express $V(\mathbf{r})$ as a linear combination of spherical tensors.

A.4 2017 exam

Exercise 10 : 2-D perturbed harmonic oscillator (2 points)

A two-dimensional harmonic oscillator is described by the Hamiltonian $\hat{H}_0 = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2 = \hat{H}_x + \hat{H}_y$. Since it is a separable Hamiltonian, the eigenstates are tensor products of eigenstates of the two harmonic oscillators along x and y: $|n,m\rangle = |n\rangle\otimes|m\rangle = \frac{(\hat{a}_x^\dagger)^n}{\sqrt{n!}}|0\rangle\otimes\frac{(\hat{a}_y^\dagger)^m}{\sqrt{m!}}|0\rangle$, where $\hat{a}_x = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + i\frac{\hat{p}_x}{\sqrt{2m\hbar\omega}}$ and $\hat{a}_y = \sqrt{\frac{m\omega}{2\hbar}}\hat{y} + i\frac{\hat{p}_y}{\sqrt{2m\hbar\omega}}$. The corresponding eigenvalues of $\hat{H}_0$ are, up to an additive constant, given by $\hat{H}_0|n,m\rangle = \hbar\omega(n+m)|n,m\rangle$.

The oscillator is subjected to an external potential $V(\hat{x},\hat{y})$ that is invariant under the symmetry group of the square, denoted as D_4. The group elements consist of two C_4 rotations around the $\hat{z}$ axis (which is orthogonal to the square), a C_2 rotation around the $\hat{z}$ axis, two C_2' rotations around the $\hat{x}$ and $\hat{y}$ axes, and two C_2'' rotations around the two diagonals of the square. The total Hamiltonian is $\hat{H} = \hat{H}_0 + V(\hat{x},\hat{y})$.

It is noted that the operators $\hat{a}_x$ and $\hat{a}_y$, under the transformations of D_4, transform like the coordinates x and y, respectively.

1. Determine if the degeneracy of states $|1,0\rangle$ and $|0,1\rangle$ can be lifted by the perturbation $V(\hat{x},\hat{y})$.

2. Determine if the degeneracy of states $|2,0\rangle$, $|1,1\rangle$, and $|0,2\rangle$ can be lifted by the perturbation $V(\hat{x},\hat{y})$. If yes, specify the residual degeneracy. Suggestion: One of these three states alone generates a subspace invariant under the operations of D_4.

3. Determine if the degeneracy of states $|3,0\rangle$, $|2,1\rangle$, $|1,2\rangle$, and $|0,3\rangle$ can be lifted by the perturbation $V(\hat{x},\hat{y})$. If yes, specify the residual degeneracy.

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
$\Gamma^{(1)}$	1	1	1	1	1
$\Gamma^{(2)}$	1	1	1	−1	−1
$\Gamma^{(3)}$	1	−1	1	1	−1
$\Gamma^{(4)}$	1	−1	1	−1	1
$\Gamma^{(5)}$	2	0	−2	0	0

Table A.2: Character table of D_4 group

Suggestion: First, determine the explicit transformation laws of the operators $\hat{a}_x$ and $\hat{a}_y$ under the operations of D_4. This will directly yield the transformation laws of the states and, consequently, the representations of the group D_4 associated with them. It is also worth noting that, to solve this problem, the use of "projectors" onto the irreducible representations of the group is not essential.

Exercise 11 : Density matrix purification (2 points)

Consider a spin 1/2, which, in the basis $\{|+\rangle, |-\rangle\}$ of the eigenstates of $\hat{S}_z$, is in a mixed state described by the density matrix:

$$\rho_A = \frac{1}{8}\begin{pmatrix} 5 & \sqrt{3} \\ \sqrt{3} & 3 \end{pmatrix} \tag{A.11}$$

1. Verify that this matrix satisfies the three properties of density matrices. *Suggestion*: It will be useful to find the eigenvalues of matrix (1).

2. Now, consider a second spin 1/2. We have a system composed of two subsystems, A and B, given by the first and second spins, respectively. Find an explicit expression for a pure state $|\psi\rangle = \sum_{j,k=\pm} \alpha_{jk} |j,k\rangle$ such that $\rho_A = \mathrm{Tr}_B(|\psi\rangle\langle\psi|)$. *Suggestion*: It will be useful to first find the eigenvectors of the density matrix (1).

3. Is the state $|\psi\rangle$ thus found unique? If not, find a second state $|\psi'\rangle = \sum_{j,k=\pm} \beta_{jk} |j,k\rangle$ such that $\rho_A = \mathrm{Tr}_B(|\psi'\rangle\langle\psi'|)$.

Exercise 12 : Perturbed harmonic oscillator (2 points)

A harmonic oscillator is described (up to an additive constant) by the Hamiltonian $\hat{H}_0 = \hbar\omega\hat{a}^\dagger\hat{a}$. The eigenstates of $\hat{H}_0$ are denoted as $|n\rangle$, where $n = 0, 1, 2, \ldots$, and $\hat{H}_0|n\rangle = n\hbar\omega|n\rangle$. At time $t = 0$, a perturbation is switched on:

$$\hat{V}(t) = \begin{cases} 0 & t < 0 \\ \hat{V} & t \geq 0 \end{cases}$$

where $\hat{V} = \hbar\gamma(\hat{a}^2 + \hat{a}^{\dagger 2})$, $\gamma \in \mathbb{R}$, and $\gamma > 0$. We assume that at $t < 0$, the oscillator is in its ground state $|0\rangle$.

1. Express, at the first order of time-dependent perturbation theory, the probability $P_{0\to n}(t)$ that the oscillator, at $t > 0$, is in the state $|n\rangle$, with $n > 0$. For which states $|n\rangle$ does the probability $P_{0\to n}(t)$ have a finite value? What is the limit of $P_{0\to n}(t)$ as $t \to +\infty$?

We will now consider the system described by the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ and study its fundamental stationary state using the variational principle.

2. Use the variational assumption $|0'\rangle = |0\rangle + \alpha|2\rangle$, where $\alpha \in \mathbb{R}$ is the parameter to be varied (note that the state $|0'\rangle$ expressed this way is not normalized). Under the assumption that $\gamma \ll \omega$, calculate the state $|0'\rangle$ that minimizes the average energy value and express this average value to the lowest order in γ/ω.

3. Discuss the difference between the result found in point 2 and that obtained in point 1 in the limit $t \to +\infty$.

Suggestion: In the limit $\gamma \ll \omega$, one would expect that the difference between the states $|0\rangle$ and $|0'\rangle$ is small, and therefore the solution to the variational problem satisfies the condition $\alpha \ll 1$.

A.5 2018 Exam

Exercise 13 : 2-Site Ising Model with Transverse Field (2 points)

Consider a model of two interacting spins subjected to a transverse magnetic field. The system's Hamiltonian is given by

$$\hat{H} = -J\hat{\sigma}_1^{(z)} \otimes \hat{\sigma}_2^{(z)} - h\hat{\sigma}_1^{(x)} \otimes \hat{I}_2 - h\hat{I}_1 \otimes \hat{\sigma}_2^{(x)}\,, \tag{A.12}$$

where $\hat{\sigma}_j^{(z)}$ and $\hat{\sigma}_j^{(x)}$ are the Pauli matrices, $j = 1, 2$ for the first and second spin, respectively, with $J > 0$ and $h > 0$. Here, $\hat{I}_1$ and $\hat{I}_2$ represent the identity operator in the space of the first and second spins, respectively. We will consider the basis $\{|--\rangle, |+-\rangle, |-+\rangle, |++\rangle\}$ of the eigenstates of $\hat{\sigma}_1^{(z)}$ and $\hat{\sigma}_2^{(z)}$.

1. Explicitly write the matrix associated with $\hat{H}$ in this basis.
2. We consider the following variational assumption for the system's ground state:

$$|\psi_0(\alpha)\rangle = |--\rangle + \alpha\,|+-\rangle + \alpha\,|-+\rangle + |++\rangle\,, \tag{A.13}$$

   with $\alpha \in \mathbb{R}$. Note that the state $|\psi_0(\alpha)\rangle$ as expressed is not normalized. Using the variational principle, show that the value of α that minimizes the average energy is

$$\alpha_m = -\frac{J}{2h} + \sqrt{\frac{J^2}{(2h)^2} + 1}\,. \tag{A.14}$$

3. Calculate the average energy E_0 over the state $|\psi_0(\alpha)\rangle$ for $\alpha = \alpha_m$.
4. Demonstrate that the state found by the variational principle is indeed the exact ground state of the problem. Why can the exact ground state be described by the assumption $|\psi_0(\alpha)\rangle$, which contains only one variational parameter?

Exercise 14 : Entanglement Entropy in the Transverse Ising Model (2 points)

Consider the state of two spins:

$$|\psi_0(\alpha_m)\rangle = \frac{|--\rangle + \alpha_m\,|+-\rangle + \alpha_m\,|-+\rangle + |++\rangle}{\sqrt{2(\alpha_m^2 + 1)}}\,, \tag{A.15}$$

with α_m given previously. We will apply the concept of entanglement entropy, which provides a measure of the entanglement between the two spins. Entanglement entropy is defined as $S = -\mathrm{Tr}[\hat{\rho}_1 \ln(\hat{\rho}_1)]$, where $\hat{\rho}_1 = \mathrm{Tr}_2[\hat{\rho}]$ is the reduced density operator of the first spin, obtained by taking the partial trace of the density operator $\hat{\rho}$ associated with the state of the two spins.

1. Explicitly write the matrix associated with the density operator $\hat{\rho}$ in the basis $\{|--\rangle, |+-\rangle, |-+\rangle, |++\rangle\}$.
2. Calculate the matrix associated with $\hat{\rho}_1$.
3. Calculate S.
4. What is the value of S in the limit $J/h \to \infty$? And in the limit $J/h \to 0$? What conclusions can be drawn about the entanglement between the two spins in these two limits?

Exercise 15 : Vibrational Modes of a Triangular Molecule (2 points)

A molecule consists of three identical atoms arranged at the vertices of an equilateral triangle. We are interested in the normal vibrational modes of the molecule around the equilibrium

positions of the three atoms. The symmetry group of an equilateral triangle in $\mathbb{R}^3$ is D_{3h}, and its character table is provided below. We consider the $\hat{z}$ axis oriented perpendicular to the plane of the triangle. The operations of D_{3h} include the identity, two C_3 rotations around the $\hat{z}$ axis, three C_2 rotations around the three axes connecting each vertex to the midpoint of the opposite side, the mirror plane σ_h parallel to the triangle's plane, two improper rotations S_3 resulting from the C_3 rotations followed by σ_h, and three vertical mirrors σ_v on planes orthogonal to the triangle's plane.

Each atom can move independently in $\mathbb{R}^3$. Thus, the system has 9 independent degrees of freedom, which generate a representation Γ of dimension 9 for the group D_{3h}.

1. Calculate the characters of the representation Γ.
2. Determine the decomposition of Γ into a direct sum of irreducible representations of D_{3h}, $\Gamma = b_1\Gamma^{(1)} + \ldots + b_6\Gamma^{(6)}$.
3. In this decomposition, which irreducible representations are associated with the translation of the center of mass?
4. And which irreducible representations are associated with the rigid rotations of the molecule?
5. Which irreducible representations are associated with the proper vibrational modes of the molecule (i.e., other than the center of mass translation and rotations)? What is the degeneracy of the corresponding normal vibrational frequencies?

Suggestion: The representation Γ can be determined by taking the tensor product between the representation generated by a displacement vector and the representation associated with permutations of the three vertices generated by the group's operations.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
$\Gamma^{(1)}$	1	1	1	1	1	1		x^2+y^2, z^2
$\Gamma^{(2)}$	1	1	−1	1	1	−1	R_z	
$\Gamma^{(3)}$	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
$\Gamma^{(4)}$	1	1	1	−1	−1	−1		
$\Gamma^{(5)}$	1	1	−1	−1	−1	1	z	
$\Gamma^{(6)}$	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

Table A.3: Character table for the D_{3h} group

A.6 2019 Exam

Exercise 16 : Harmonic oscillator in an external field (15/50 points)

Consider an isotropic 2-D harmonic oscillator. The oscillator is subjected to an external potential $V(x, y)$ that is invariant under the symmetry transformations of a pentagon (group D_5, character table below). Therefore, the Hamiltonian is $H = H_0 + V(x, y)$, where

$$H_0 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2}m\omega^2(x^2+y^2)\,. \tag{A.16}$$

The eigenstates of H_0 will be denoted as $|n_x, n_y\rangle$, where n_x and n_y are the numbers of quanta in each direction of the oscillations. The corresponding eigenenergies are $E_N = N\hbar\omega$, with $N = n_x + n_y$.

Consider $V(x, y)$ as a time-independent perturbation.

1. Using group representation theory, determine if the energy degeneracy of states with $N = 1$ is lifted by $V(x, y)$ at the first-order perturbation. If so, how is it lifted?
2. Same question, for states with $N = 2$.
3. Same question, for states with $N = 3$.

It is recalled that the eigenstates of the 2-D harmonic oscillator can be constructed from those of the 1-D harmonic oscillator, which are

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right), \quad n = 0, 1, 2, \ldots$$

In particular, we have $H_1(x) = 2x$, $H_2(x) = 4x^2 - 2$, and $H_3(x) = 8x^3 - 12x$.

D_5	E	$2C_5$	$2(C_5)^2$	$5C_2'$			
A_1	1	1	1	1		x^2+y^2, z^2	
A_2	1	1	1	−1	z, R_z		z^3, $z(x^2+y^2)$
E_1	2	$2\cos\left(\frac{2\pi}{5}\right)$	$2\cos\left(\frac{4\pi}{5}\right)$	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
E_2	2	$2\cos\left(\frac{4\pi}{5}\right)$	$2\cos\left(\frac{2\pi}{5}\right)$	0		(x^2-y^2, xy)	$[xyz, z(x^2-y^2)]$ $[y(3x^2-y^2, x(x^2-3y^2)]$

Table A.4: Character table of the D_5 group

Exercise 17 : Entropy of a quantum system (15/50 points)

The state of a quantum system is described by a density operator $\hat{\rho}$. The Von Neumann entropy is defined as $S = -\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})$ (note that this involves the logarithm of an operator!). The entropy measures the extent to which the state is a statistical mixture.

1. What is the value of S for a pure state $\hat{\rho} = |\psi\rangle\langle\psi|$?
2. Show that if the density operator evolves in time according to the Von Neumann equation
$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}, \hat{\rho}],$$
the entropy $S(t)$ remains constant over time.
3. Now consider a spin 1/2 system. It is assumed that the interaction with the environment results in a time evolution governed by the equation
$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}, \hat{\rho}] - \frac{\gamma}{2}\left(\hat{n}^2\hat{\rho} + \hat{\rho}\hat{n}^2 - 2\hat{n}\hat{\rho}\hat{n}\right),$$
where $\hat{n} = (\mathbb{I} + \hat{\sigma}_z)/2$ and $\hat{H} = \omega\hat{\sigma}_z$. If at $t = 0$, in the basis $\{|\sigma_z = +1\rangle, |\sigma_z = -1\rangle\}$ of the eigenstates of $\hat{\sigma}_z$,
$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22} \end{pmatrix}$$
calculate the matrix $\rho(t)$ at time t.

4. For the same spin 1/2 system, it is now assumed that at $t = 0$, the system is in the pure state $|\psi\rangle = (|+1\rangle + |-1\rangle)/\sqrt{2}$. Calculate the entropy $S(t)$ as a function of time. What is the value of $S(t)$ in the limit $t \to \infty$?

Exercise 18 : Perturbed Harmonic Oscillator (20/50 points)

The motion of a particle with mass m in one dimension is governed by the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 e^{\lambda x^2},$$

with $\lambda > 0$. This problem can be considered as a perturbation of the harmonic oscillator, with $H = H_0 + V$ where

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$
$$V(x) = \frac{1}{2}m\omega^2 x^2\left(e^{\lambda x^2} - 1\right).$$

Recall that the wave function of the ground state of the harmonic oscillator is $\psi_0(x) = \left(\frac{\beta_0}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\beta_0 x^2}{2}}$ where $\beta_0 = \frac{m\omega}{\hbar}$. For the solution of this problem, we assume $\lambda \ll \beta, \beta_0$. Also, remember that for Gaussian integrals, we have $\int_{-\infty}^{+\infty} dx\, e^{-\beta x^2} = \sqrt{\pi/\beta}$ and $\int_{-\infty}^{+\infty} dx\, x^2 e^{-\beta x^2} = (1/2)\sqrt{\pi/\beta^3}$.

1. Calculate the energy of the ground state to first order in the perturbation $V(x)$.
2. Calculate the energy of the ground state, this time using the variational principle. Use the normalized trial wave function for the ground state

$$\psi(x) = \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\beta x^2}{2}},$$

with $\beta > 0$.

A.7 2015 Midterm

Exercise 19 : Confined Quantum Stark Effect (2.5 points) Consider an electron with mass m in a one-dimensional potential well of width L, with infinite barriers located at $x = \pm L/2$, described by the Hamiltonian $\hat{H}_0$. A constant electric field of intensity E is applied to the system, subjecting the electron to the Coulomb force $F = -eE$, resulting in a perturbation $\hat{V} = F\hat{x}$.

1. Schematically represent the total potential experienced by the electron for $F > 0$.
2. Provide the Hamiltonian $\hat{H}_0$. Recall the eigenenergies E_n and wave functions $\varphi_n(x)$ ($n = 1, 2, \ldots$) of the unperturbed electron, i.e., when $F = 0$, distinguishing between even and odd values of n.
3. In the case where $F \neq 0$, calculate the first-order energy correction $E_1^{(1)}$ of the ground state. What do you observe?

4. Deduce the first-order energy corrections of excited states $E_n^{(1)}$ with $n > 1$.

5. Now, calculate the second-order energy correction $E_1^{(2)}$ of the ground state (exploit the parity of wave functions). For the sums over intermediate states, restrict to only states $\varphi_1(x)$ and $\varphi_2(x)$, and indicate V_{21} as the matrix element of the perturbation, calculated between these two states.

6. Intuitively and qualitatively represent the shape of the wave function for the ground state in the total potential.

Exercise 20 : Interacting Particles in a Potential Well (2.5 points) Consider 2 indistinguishable particles (without spin) with mass m confined in a square one-dimensional potential well $V(x)$. Assume that the height of the barriers is such that only states associated with wave functions $\varphi_1(x)$ and $\varphi_2(x)$ are confined in the well. The Hamiltonian of the system is given by

$$\hat{H}^{(0)} = \hat{H}_1 + \hat{H}_2, \tag{A.17}$$

with

$$\hat{H}_1 = \frac{\hat{p}_1^2}{2m} + V(\hat{x}_1), \quad \hat{H}_2 = \frac{\hat{p}_2^2}{2m} + V(\hat{x}_2). \tag{A.18}$$

1. Suppose that the two-particle states are even under permutations. Determine a basis of two-particle states, considering 2 particles from φ_1 and φ_2.

2. Now, suppose that the particles can interact when they are precisely at the same location (contact interaction), which is represented by the perturbation $\hat{V}_{\text{int}} = V_0\delta(\hat{x}_1 - \hat{x}_2)$, where $\delta(\hat{x}_1 - \hat{x}_2)$ is the Dirac delta function. Calculate the first-order energy correction for each of the previously established two-particle states. Discuss the relative values and signs of these corrections.

3. Repeat the previous calculations in the case where the two-particle states are odd under permutations. Compare the results obtained with the symmetric case and draw conclusions.

Exercise 21 : Quantum Information (1 point)

Alice sends Bob a large number of qubits. These qubits are prepared as follows:

- Alice flips a coin.
- She uses an "instruction manual" (the same for all qubits) that states that if she gets "heads," Alice sends a qubit in the state $|\psi_p\rangle$, and if she gets "tails," she sends a qubit in the state $|\psi_f\rangle$.

Bob must understand which instruction manual Alice is using. At the beginning of the process, Alice chooses one of the three instruction manuals, A, B, C:

$$\begin{aligned}
A &: \quad |\psi_p\rangle = |0\rangle \qquad |\psi_f\rangle = |1\rangle \\
B &: \quad |\psi_p\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \qquad |\psi_f\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \\
C &: \quad |\psi_p\rangle = |0\rangle \qquad |\psi_f\rangle = \frac{1}{\sqrt{2}}(|0\rangle + i\,|1\rangle)
\end{aligned}$$

Is it possible for Bob to guess which instruction manual Alice is using? Why?

Suggestion: For each instruction manual, Alice is producing a statistical mixture of states. Establish the corresponding density matrix for each instruction manual.

A.8 2016 Midterm

Exercise 22 : Impurity in a crystal field (3 points)

Consider an atom with an electron in a state of the $3d$ orbital (i.e., with angular momentum $L = 2$, which means the orbital is fivefold degenerate). We will neglect the electron's spin. The atom is placed as an impurity in a crystal that is invariant under the symmetry operations of the T_d symmetry group (the symmetries of a tetrahedron). We can approximate the rest of the electrons in the atom and its nucleus as if they form a simple positively charged nucleus. Therefore, we associate one of the wave functions of the hydrogen atom with $n = 3$ and $L = 2$ with the electron in the $3d$ orbital. The electron is influenced by the electrostatic field produced by the surrounding crystal. The Hamiltonian of the system is thus $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ is the Hamiltonian that gives rise to the $3d$ levels of the atom in the absence of the crystal field, and $\hat{V}$ is the effect of the crystal field.

1. Using group representation theory and time-independent perturbation theory (degenerate case), determine how the degeneracy of the 5 $3d$ states is lifted. More precisely, determine (i) how many distinct energy eigenvalues will result from the perturbation, and (ii) how many times they are degenerate.

2. Consider electric dipole transitions between the degenerate levels that have been found. Determine the selection rules for these transitions.

3. The wave functions associated with $3d$-type states are even under spatial inversion. Discuss whether the transitions seen in the previous point are allowed by parity or not. Note that the T_d group does not include inversion among its elements.

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	Fcts linéaires	Fcts quadratiques
$\Gamma^{(1)}$	1	1	1	1	1		$x^2+y^2+z^2$
$\Gamma^{(2)}$	1	1	1	−1	−1		
$\Gamma^{(3)}$	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
$\Gamma^{(4)}$	3	0	−1	−1	1	(R_x, R_y, R_z)	
$\Gamma^{(5)}$	3	0	−1	1	−1	(x, y, z)	(yz, xz, xy)

Table A.5: Character table for the T_d group

Recall that

- For the group $SO(3)$, all rotations of the same angle α belong to the same equivalence class. To determine the character of a rotation by an angle α around any axis, you can simply calculate the character of a rotation by an angle α around the $\hat{z}$ axis, for which the matrices of the irreducible representations are diagonal and known.

- The operation σ_d in T_d is a mirror operation, thus a rotation by $\alpha = \pi$ followed by inversion. The operation S_4 in T_d is an improper rotation, hence a rotation by $\alpha = \pi/2$ followed by inversion.

- The wave functions of the $3d$ orbital are even under inversion. The matrix associated with inversion, for all representations generated by these states, is therefore the identity.

Exercise 23 : Perturbed 2-D Harmonic Oscillator (3 points)

We will consider the isotropic two-dimensional harmonic oscillator. The Hamiltonian is given by

$$\begin{aligned} \hat{H} &= \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{\hat{p}_y^2}{2m} + \frac{1}{2}m\omega^2\hat{y}^2 \\ &= \hat{H}_1(\hat{x}) + \hat{H}_1(\hat{y}) \end{aligned}$$

where

$$\hat{H}_1(\hat{x}) = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$$

is the Hamiltonian of the one-dimensional harmonic oscillator.

As it is a separable Hamiltonian, the eigenstates of $\hat{H}$ are $\psi_{nm}(x,y) = \phi_n(x)\phi_m(y)$, where $\phi_n(x)$ are the eigenstates of $\hat{H}_1(\hat{x})$ with eigenenergy $\epsilon_n = \hbar\omega(n+1/2)$ and $n = 0, 1, 2, \ldots$. Thus, we have $\hat{H}\psi_{nm} = E_{nm}\psi_{nm}$ with $E_{nm} = \epsilon_n + \epsilon_m$.

We introduce a small perturbation $\hat{V} = \lambda\hat{x}\hat{y}$.

1. What is the lowest order of perturbation for which there exists a non-zero correction to the energy E_{00} of the ground state of $\hat{H}+\hat{V}$? Provide a rigorous argument for your answer.

2. What is the lowest order of perturbation for which there exists a non-zero correction to the energies E_{01} and E_{10} of the first two excited states? Provide a rigorous argument for your answer. Calculate the new energies resulting from this order of perturbation. Calculate the eigenstates associated with the obtained energies. To what order in $\hat{V}$ do these new eigenstates differ from the initial states?

We recall that, for the one-dimensional harmonic oscillator, we have

$$\begin{aligned} \phi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2/2} \\ \phi_1(x) &= \sqrt{2\alpha}x\phi_0(x) \end{aligned}$$

with $\alpha = m\omega/\hbar$ and

$$\int_{-\infty}^{+\infty} dx e^{-x^2} = \sqrt{\pi}$$

A.9 2017 Midterm

Exercise 24 : Attractive 1-D Potential Always Has 1 Bound State (2 points)

Consider the problem of a particle in one dimension, defined by the Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}(x)$. The potential $\hat{V}(x)$ takes the form of a well, i.e., $\hat{V}(x) \leq 0 \ \ \forall x \in \mathbb{R}$, and $\hat{V}(x) \to 0$ as $|x| \to \infty$. Use the variational principle and the wave function $\langle x|\psi\rangle = \psi(x) = A\exp(-\lambda x^2)$, which depends on the variational parameter $\lambda > 0$, to show that there is always at least one bound eigenstate, i.e., with eigenenergy $E_0 < 0$. In particular,

1. Calculate the normalization factor A.
2. Calculate $\langle\psi|\hat{T}(x)|\psi\rangle = \langle\psi|\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)|\psi\rangle$.
3. We denote $I(\lambda) = \langle\psi|\hat{V}(x)|\psi\rangle$. So $\langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{T}(x)|\psi\rangle + I(\lambda)$. Explicitly write the condition that minimizes the expectation of energy $\langle\psi|\hat{H}|\psi\rangle$. Use the resulting relation to derive an expression for $I(\lambda)$. Use this result in the expression for $\langle\psi|\hat{H}|\psi\rangle$ and demonstrate that we always have $\langle\psi|\hat{H}|\psi\rangle < 0$.

Recall that $\int_{-\infty}^{+\infty} dx \exp(-x^2) = \sqrt{\pi}$. Use change of variables and integration by parts to derive all necessary integrals for the resolution of this exercise.

Exercise 25 : Symmetry of Second-Degree Polynomials in $\mathbb{R}^3$ (2 points)

Consider six functions $\psi_j(\mathbf{r})$, with $\mathbf{r} = (x, y, z) \in \mathbb{R}^3$ and $j = 1, 2, 3, 4, 5, 6$, defined as follows: $\psi_1 = x^2$, $\psi_2 = y^2$, $\psi_3 = z^2$, $\psi_4 = xy$, $\psi_5 = xz$, $\psi_6 = yz$. (Note: these functions are orthogonal but not normalized. Their norm can be neglected for the rest of this exercise). Under rotations in 3D space $\mathbb{R}^3$, these functions generate a representation D of $SO(3)$.

1. Calculate, for this space, the matrix associated with the rotation by an angle ϕ around the $\mathbf{z}$ axis.
2. Using the characters, prove that $D = D^{(0)} \oplus D^{(2)}$, where $D^{(l)}$ are the irreducible representations of $SO(3)$. For this, it will be helpful to calculate the characters $\chi^{(l)}(\phi)$ associated with the irreducible representations $D^{(l)}$. Recall that all rotations by the same angle ϕ around any axis belong to the same conjugacy class of the group $SO(3)$.
3. Determine the linear combination of $\psi_j(\mathbf{r})$ that generates the irreducible representation $D^{(0)}$.
4. Now, assume that the symmetry group is smaller than $SO(3)$ (for example, due to the introduction of a perturbation). In particular, suppose that the new symmetry group is C_{3v}. Determine the decomposition of D as a direct sum of irreducible representations of C_{3v}.

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	1	−1
$\Gamma^{(3)}$	2	−1	0

Exercise 26 : Harmonic Oscillator Subjected to a Pulsed Perturbation (2 points)

A harmonic oscillator, characterized by the Hamiltonian $\hat{H}_0 = \hbar\omega\hat{a}^\dagger\hat{a}$, is subjected to a perturbation in the form of a Gaussian pulse in time: $\hat{V}(t) = \mathcal{E}\hat{x}\exp(-t^2/\tau^2)$, where $\tau > 0$ measures the duration of the pulse, and $\hat{x} = \sqrt{\hbar/(2m\omega)}(\hat{a} + \hat{a}^\dagger)$. At $t \to -\infty$, the system is in the ground state $|0\rangle$ of $\hat{H}_0$.

1. Calculate, to the first order of perturbation in $\hat{V}$, the probability that the system is in the state $|1\rangle = \hat{a}^\dagger|0\rangle$ for $t \to +\infty$.
2. Discuss the limits $\omega t \to \infty$ and $\omega t \to 0$ of the probability you found. What is the probability in these two limits? For what physical reason? Determine the duration τ_m that maximizes the probability found in point 1.
3. What is the lowest order of perturbation in $\hat{V}$ required to have a finite probability of being in the state $|n\rangle$, with $n > 1$, for $t \to +\infty$?

A.10 2018 Midterm

Exercise 27 : Lifting Degeneracy in the Presence of an External Field (3 points)

Consider the 5-dimensional space with a basis of spherical harmonics $Y_l^m(\theta, \phi)$ where $l = 2$. This space defines the irreducible representation D_2 of the group $SO(3)$.

1. Write, in the given basis, the transformation matrix corresponding to a rotation by an angle α around the $\mathbf{z}$ axis.
2. Calculate the character $\chi(\alpha)$ of the representation D_2 for a rotation by an angle α around an arbitrary axis $\mathbf{n}$ and show that it is given by $\chi(\alpha) = \frac{\sin(l+1/2)\alpha}{\sin\alpha/2}$. Why does this result not depend on the axis $\mathbf{n}$?

Imagine an electron in an atom with angular momentum $L = 2$ (neglecting its spin degree of freedom), described by a state in the above-mentioned space. The corresponding energy level is necessarily 5-fold degenerate due to the $SO(3)$ symmetry. An external potential $V(\mathbf{r})$ is introduced, which is invariant under the symmetry group O_h of a cube (character table at the end of the statement). Note that an operation denoted by C_n is a rotation by an angle $2\pi/n$; an operation σ_h or σ_d is a mirror operation, equivalent to a C_2 rotation followed by inversion; an operation S_n is a rotation by $2\pi/n$ followed by a mirror operation with respect to the plane orthogonal to the rotation; E and i represent identity and inversion, respectively.

1. Calculate the characters of the representation D_2 associated with the operations of the O_h group.
2. With respect to the new symmetry group O_h, is the representation D_2 reducible? If yes, provide its decomposition into irreducible representations of the O_h group. What is the consequence on the degeneracy of the electron's energy levels?

Exercise 28 : Two Fermions in a Potential Well (3 points)

Consider two identical fermions with mass m and spin $s = 1/2$, subject to a potential well of width L with infinite barriers. The potential of the well is 0 inside.

To start, we assume that the two particles do not interact with each other.

1. Provide the wave function of the ground state of the two-particle system (including the spin part). What is the energy of the ground state?

2. What is the energy of the first excited level? What is its degeneracy? Write the wave functions of the states corresponding to this level.

3. What is the energy of the second excited level? What is its degeneracy? Write the wave functions of the states corresponding to this level.

Now, we assume that the two particles interact with each other through a potential $V(x_1, x_2) = V_0\delta(x_1 - x_2)$.

1. Provide the correction to the energy of the ground state, to the lowest order in V_0? (You can leave this expression in its integral form).

2. Provide the correction to the energy of the first excited level, to the lowest order in V_0? (You can leave this expression in its integral form). Is the degeneracy lifted? If so, what is the new degeneracy?

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear, rotations	quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

Figure A.1: Character table of the O_h group

A.11 2019 Midterm

Exercise 29 : Four Coupled Harmonic Oscillators (3 points)
Consider a system of four coupled harmonic oscillators described by the Hamiltonian

$$\hat{H} = \sum_{j=1}^{4} \hbar\omega \hat{a}_j^\dagger \hat{a}_j - \sum_{\langle j,k \rangle} J(\hat{a}_j^\dagger \hat{a}_k + \hat{a}_k^\dagger \hat{a}_j)\,, \tag{A.19}$$

where the second sum is performed over pairs of adjacent values (j, k), i.e., $(1, 2)$, $(2, 3)$, $(3, 4)$, and $(4, 1)$. It is assumed that the four oscillators are placed at the vertices of a square. The system is thus invariant under the operations of the symmetry group D_4. In particular, each

operation of D_4 performs a permutation of the four oscillators. The character table of D_4 is given below. The states $|n_1, n_2, n_3, n_4\rangle$ are indicated, representing states with a number $n_j \geq 0$ of quanta on each oscillator. These states form an orthonormal basis.

1. Show that the Hamiltonian commutes with the number operator, i.e., $[\hat{H}, \hat{N}] = 0$, where $\hat{N} = \sum_{j=1}^{4} \hat{a}_j^\dagger \hat{a}_j$. Explain what this implies for the eigenstates of $\hat{H}$.

2. Now consider the four states $|1000\rangle$, $|0100\rangle$, $|0010\rangle$, and $|0001\rangle$. Using group representation theory and simple symmetry considerations, find the eigenvalues and eigenvectors of $\hat{H}$ in the subspace generated by these four vectors. In particular, specify the degeneracies imposed by symmetry.

3. Consider the subspace of dimension 10 generated by states $|n_1, n_2, n_3, n_4\rangle$ with $n_1 + n_2 + n_3 + n_4 = 2$. Without explicitly calculating the eigenvalues and eigenvectors of $\hat{H}$ but solely using group representation theory, determine the number of distinct energy levels and their degeneracies characterizing the eigenstates of $\hat{H}$ in this subspace.

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	−1	1	1	−1
B_2	1	−1	1	−1	1
E	2	0	−2	0	0

Character table of the D_4 group. Rotations C_4 and C_2 are around the orthogonal axis of the square. The C_2' are around the medians. The C_2'' are around the diagonals.

Suggestion. To calculate the characters associated with the operations of D_4, it is worth noting that you only need to know the diagonal elements of the corresponding matrices, and you need to perform this calculation only once for each equivalence class of the group. It's also worth noticing that, to solve this problem, the use of "projectors" on the irreducible representations of the group is not necessary.

Exercise 30 : Variational Principle for Two Spin 1/2 Particles (3 points)
Consider a system composed of two spin 1/2 particles. These two spins interact with each other and an external field according to the Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{H}_{cl} + \hat{H}_{ext} \\ \hat{H}_{cl} &= \hat{\sigma}_1^{(z)} \hat{\sigma}_2^{(z)} \\ \hat{H}_{ext} &= h\left(\hat{\sigma}_1^{(x)} + \hat{\sigma}_2^{(x)}\right) \qquad h \geq 0 \end{aligned}$$

We will use the basis of the eigenstates of $\hat{\sigma}_1^{(z)}$ and $\hat{\sigma}_2^{(z)}$: $\{|\sigma_1, \sigma_2\rangle\}$, with $\sigma_1, \sigma_2 = \pm 1$. The Hamiltonian $\hat{H}_{cl}$ is diagonal in this basis, and its diagonal matrix elements can be denoted as $H_{cl}(\sigma_1, \sigma_2)$.
Consider the variational state

$$\begin{aligned} \psi(\sigma_1, \sigma_2) &= \langle \sigma_1, \sigma_2 | \psi \rangle \\ &= \exp\left(-\beta H_{cl}(\sigma_1, \sigma_2)\right) \qquad \beta \geq 0 \end{aligned}$$

1. Write the equations dictated by the variational principle for the ground state of the problem.
2. Solve these equations (graphically?) to find the value of β that minimizes the energy of the ground state.
3. Calculate the variational energy and the associated ground state in the limit $h \to 0$. How does this result compare with the exact result in this limit?

Appendix B

Solutions

B.1 2014 Exam

Exercise 1 : 2 Photon transition

1. The translation amplitude $a_{i\to f}(t)$ of a state $|i\rangle$ towards state $|f\rangle$ under the effect of a branched perturbation from $t_0 = 0$ to t is given by

$$a_{i\to f}(t) = \langle f|\hat{U}_I(t,0)|i\rangle, \tag{B.1}$$

with

$$\hat{U}_I(t,t_0) = \mathbb{1} + \sum_{n=1}^{+\infty}\left(\frac{-i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{V}_I(t_1)\hat{V}_I(t_2)\cdots\hat{V}_I(t_n) \tag{B.2}$$

$$\hat{V}_I(t) = e^{i\hat{H}_0 t/\hbar}\hat{V}(t)\, e^{-i\hat{H}_0 t/\hbar}. \tag{B.3}$$

At first perturbation order, the transition amplitude from $|1\rangle$ to $|2\rangle$ is written

$$a_{12}^{(1)}(t) = \frac{-i}{\hbar}\int_0^t dt_1 \langle 2|e^{i\hat{H}_0 t_1/\hbar}\hat{V}(t_1)e^{-i\hat{H}_0 t_1/\hbar}|1\rangle = \frac{-i}{\hbar}\int_0^t dt_1 e^{i(\omega_2-\omega_1)t_1}\langle 2|\hat{V}(t_1)|1\rangle, \tag{B.4}$$

where $\omega_i = E_i/\hbar$. Examining the form of $\hat{V}(t)$, we note that term $\hat{v}$ lowers between levels, while $\hat{v}^\dagger$ causes an increase. Notably, we have $\hat{V}(t)\,|1\rangle = \hbar\Omega e^{-i\omega t}\,|2\rangle$, from where

$$a_{12}^{(1)}(\omega,t) = -i\Omega\int_0^t dt_1 e^{i(\omega_0-\omega)t_1}, \qquad \omega_0 = \omega_2 - \omega_1. \tag{B.5}$$

For $\omega \neq \omega_0$, we get

$$a_{12}^{(1)}(\omega,t) = -i\Omega\frac{e^{i(\omega_0-\omega)t}-1}{i(\omega_0-\omega)} = \frac{-2i\Omega}{\omega_0-\omega}e^{i(\omega_0-\omega)t/2}\sin\frac{(\omega_0-\omega)t}{2}, \tag{B.6}$$

and for $\omega = \omega_0$, integration gives $a_{12}^{(1)}(\omega_0,t) = -i\Omega t$. Finally, we get for the transition probability

$$P_{12}^{(1)}(\omega,t) = |a_{12}^{(1)}(\omega,t)|^2 = \frac{4\Omega^2}{(\omega_0-\omega)^2}\sin^2\frac{(\omega_0-\omega)t}{2}, \tag{B.7}$$

with continuous extension in $\omega = \omega_0$ giving $P_{12}^{(1)}(\omega_0,t) = \Omega^2 t^2 = |a_{12}^{(1)}(\omega_0,t)|^2$.

2. We have

$$\frac{P_{12}^{(1)}(\omega,t)}{P_{12}^{(1)}(\omega_0,t)} = f_{1/t}(\omega_0-\omega), \qquad f_\alpha(x) = \mathrm{sinc}^2\left(\frac{x}{2\alpha}\right). \tag{B.8}$$

In other words, the ratio has the shape of a *sinc* whose value in $\omega_0 - \omega = x = 0$ is always 1 and whose pulsation, given by $\alpha = 1/t$, tends to zero in the limit $t \to \infty$. This shows that the function who at ω associates $P_{12}^{(1)}(\omega,t)$ is shrply peaked around the resonnance frequency ω_0 for long times.

3. Since $\langle 3|\hat{V}(t_1)|1\rangle = 0$ for all time t_1, we have

$$a_{13}^{(1)}(\omega,t) = \frac{-i}{\hbar}\int_0^t dt_1 e^{i(\omega_3-\omega_1)t_1}\langle 3|\hat{V}(t_1)|1\rangle = 0, \tag{B.9}$$

and the transition probability $P_{13}^{(1)}(\omega,t) = |a_{13}^{(1)}(\omega,t)|^2$ is thus zero. to obtain the first nonzero probability at transtion probability P_{13}, we need at least perturbation order 2.

4. The use of expressions (B.1) and (B.3) at second order, imply

$$a_{13}^{(2)}(\omega,t) = -\frac{1}{\hbar^2}\int_0^t dt_1 \int_0^{t_1} dt_2 \langle 3|e^{i\hat{H}_0 t_1/\hbar}\hat{V}(t_1)e^{-i\hat{H}_0(t_1-t_2)/\hbar}\hat{V}(t_2)e^{-i\hat{H}_0 t_2/\hbar}|1\rangle. \tag{B.10}$$

Since

$$\hat{V}(t_2)\,|1\rangle = \hbar\Omega e^{-i\omega t_2}\,|2\rangle \tag{B.11}$$

$$\hat{V}(t_1)\,|2\rangle = \hbar\Omega e^{i\omega t_1}\,|1\rangle + \hbar\Omega' e^{-i\omega t_1}\,|3\rangle, \tag{B.12}$$

We get

$$\begin{aligned} a_{13}^{(2)}(\omega,t) &= -\Omega\Omega'\int_0^t dt_1\int_0^{t_1} dt_2 e^{i\omega_3 t_1}e^{-i\omega t_1}e^{-i\omega_2(t_1-t_2)}e^{-i\omega t_2}e^{-i\omega_1 t_2} \\ &= -\Omega\Omega'\int_0^t dt_1 e^{i(\omega_0'-\omega)t_1}\int_0^{t_1} dt_2 e^{i(\omega_0-\omega)t_2}. \end{aligned} \tag{B.13}$$

For ω distinct from ω_0 and ω_0', integration gives

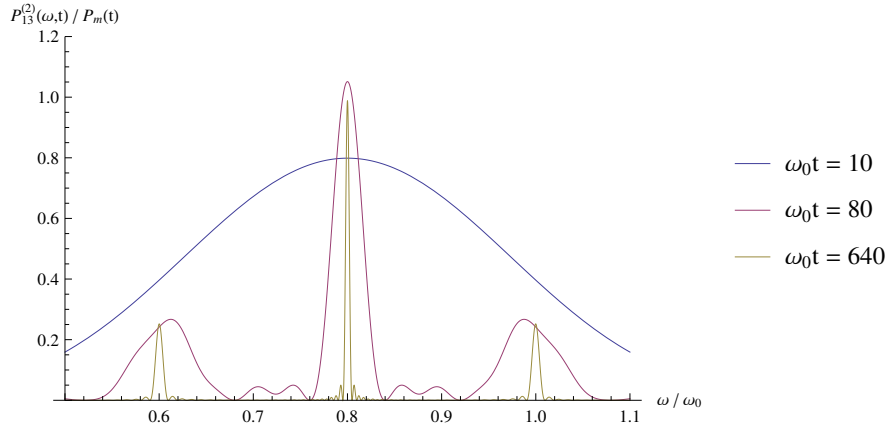
$$\begin{aligned} a_{13}^{(2)}(\omega,t) &= -\frac{\Omega\Omega'}{i(\omega_0-\omega)}\int_0^t dt_1 e^{i(\omega_0'-\omega)t_1}\left(e^{i(\omega_0-\omega)t_1}-1\right) \\ &= \frac{\Omega\Omega'}{\omega_0-\omega}\left(\frac{e^{i(\omega_0+\omega_0'-2\omega)t}-1}{\omega_0+\omega_0'-2\omega} - \frac{e^{i(\omega_0'-\omega)t}-1}{\omega_0'-\omega}\right), \end{aligned} \tag{B.14}$$

Which is the result we asked for.

To analyze the pulsation dependence of $P_{13}^{(2)}(\omega,t)$ at long time, we note that the formula given can be written

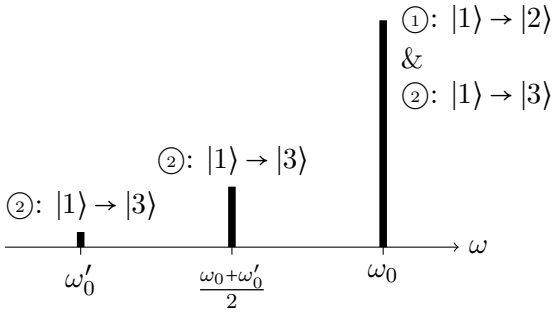
$$\begin{aligned} P_{13}^{(2)}(\omega,t) = {} & \frac{(\Omega\Omega')^2t^2}{(\omega_0'-\omega)(\omega_0+\omega_0'-2\omega)}f_{1/t}(\omega_0-\omega) + \frac{(\Omega\Omega')^2t^2}{(\omega_0-\omega)(\omega_0+\omega_0'-2\omega)}f_{1/t}(\omega_0'-\omega) \\ & - \frac{(\Omega\Omega')^2t^2}{(\omega_0-\omega)(\omega_0'-\omega)}f_{1/2t}\left(\frac{\omega_0+\omega_0'}{2}-\omega\right), \end{aligned} \tag{B.15}$$

That is to say, as the sum of 3 *sinc* square (filter function) centered in ω_0, ω_0' and $(\omega_0 + \omega_0')/2$, of typical respective width $1/t$, $1/t$ and $1/(2t)$, and of max value (at the origine) respectively $P_m/4$, $P_m/4$ and P_m, where $P_m = P_m(t) = 4\Omega^2\Omega'^2t^2/(\omega_0'-\omega_0)^2$. In the long time limit, we get a function of ω sharply peaked around the 3 resonance pulsations, with 3 well separated peaks at $t \gg 1/|\omega_0'-\omega_0|$. For $\omega_0' = 0.6\,\omega_0$, this figure shows the behavior:



To examine $P^{(2)}_{12}(\omega, t)$, we revisit the expressions (B.10) to (B.12) by replacing the *bra* corresponding to the final state $\langle 3|$ with $\langle 2|$, which results in $P^{(2)}_{12}(\omega, t) = 0$. Indeed, one cannot transition from $|1\rangle$ to $|2\rangle$ through a second-order process because each of the two applications of $\hat{V}$ either raises ($\hat{v}^\dagger$) or lowers ($\hat{v}$) the energy level; starting from $|1\rangle$, the probabilities lead to either $|1\rangle$ or $|3\rangle$ (in fact, a superposition of $|1\rangle$ and $|3\rangle$), but not to $|2\rangle$.

5. The absorption probability is given by $P_{abs}(\omega, t) = P_{12}(\omega, t) + P_{13}(\omega, t) \simeq P^{(1)}_{12}(\omega, t) + P^{(2)}_{13}(\omega, t)$ up to the second order of perturbation. By including the processes of the 1st (①) and the 2nd (②) order, we obtain the absorption line spectrum as follows:

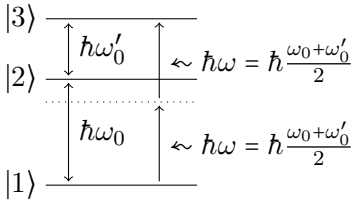


where the height of the lines symbolizes the absorption efficiency; the lines for second-order processes are smaller than those for first-order processes since, by assumption, we are in a perturbative regime, so Ω and Ω' are small, and $P_m(t)/P^{(1)}_{12}(\omega_0, t) = 4\Omega'^2/(\omega'_0 - \omega_0)^2 \ll 1$.

6. The last of the three terms in equation (3) of the statement corresponds to a resonance

$$2\hbar\omega = \hbar\omega_0 + \hbar\omega'_0 = E_3 - E_1 \tag{B.16}$$

in the excitation process of atoms $|1\rangle$ and $|3\rangle$. This resonance, therefore, corresponds to a situation where the energy of two photons exactly matches the energy difference between the initial and final states. This implies that it is a two-photon excitation process (two photons are absorbed in the electromagnetic field to excite the atom from $|1\rangle$ to $|3\rangle$), which aligns intuitively with it being a second-order process (in this interpretation, the operator $e^{-i\omega t}\hat{v}^\dagger$ corresponds to the absorption/annihilation of a photon and the simultaneous excitation of the atom, and it must be applied twice to go from $|1\rangle$ to $|3\rangle$). This two-photon process would have the following representation:



It can be seen that the two-photon process conserves energy "globally" since the combined energy of the two photons allows for the difference between the initial and final states to be bridged. Nevertheless, it can be observed that energy is not conserved in the "individual" underlying processes, namely, the absorption of a "first" photon that transitions the atom from $|1\rangle$ to $|2\rangle$, and then the absorption of a "second" photon that transitions the atom from $|2\rangle$ to $|3\rangle$.

Note 1 (not requested): In reality, the fact that the transfer from $|1\rangle$ to $|3\rangle$ is not sequential (coupling $|1\rangle \to |2\rangle$, waiting time of a similar duration, coupling $|2\rangle \to |3\rangle$) allows for the energy difference between the dashed line and the level E_2.

Note 2 (not requested): The first two terms of equation (3) in the statement (resonances at ω_0 and ω_0') correspond to processes that do not globally conserve energy ($2\hbar\omega_0 \neq E_3 - E_1$, $2\hbar\omega_0' \neq E_3 - E_1$); they result from the abrupt, step-like branching of the perturbation at $t = 0$. This type of branching does not have an "adiabatic" limit when tending to infinity, and, therefore, there is no energy conservation. For any other type of branching that has an adiabatic limit (for example, a linear ramp between 0 and t, with a given average amplitude over this interval, which becomes infinitely slow as $t \to +\infty$),these processes would become negligible in the limit of long times, and the peaks at ω_0 and ω_0' would disappear from the spectrum above. Nevertheless, it is observed that these terms, which violate the overall conservation of energy corresponding to a favored $|1\rangle \to |2\rangle \to |3\rangle$ transfer due to the resonant nature of $|1\rangle \to |2\rangle$ at the frequency ω_0 (even if $|2\rangle \to |3\rangle$ is not resonant at that time) or $|2\rangle \to |3\rangle$ at the frequency ω_0'.

Exercise 2 : Fine structure of an atom

1. The values of j range from $|l - s|$ to $l + s$. In other words, for $l = 0$, the only possible value is $j = 1/2$. For $l \geq$, there are two possible values: $j = l - 1/2$ and $j = l + 1/2$. Regardless of j, the corresponding values of m_j are $-j, -j+1, \ldots, j-1, j$.

2. The components of $\hat{\boldsymbol{L}}$ commute with those of $\hat{\boldsymbol{S}}$ (one acts on the spatial degree of freedom of the electron, the other on the spin degree of freedom), so $\hat{\boldsymbol{J}}^2 = (\hat{\boldsymbol{L}} + \hat{\boldsymbol{S}})^2 = \hat{\boldsymbol{L}}^2 + 2\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}} + \hat{\boldsymbol{S}}^2$. Hence,

$$\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}} = \frac{1}{2}\left(\hat{\boldsymbol{J}}^2 - \hat{\boldsymbol{L}}^2 - \hat{\boldsymbol{S}}^2\right). \tag{B.17}$$

To calculate the commutators with $\hat{H}$, it is first noticed that all components of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ commute with $\hat{H}_0$ and operators that depend only on r, such as $A(r)$. Therefore, for operators $\hat{O} = \hat{\boldsymbol{J}}^2, \hat{\boldsymbol{L}}^2, \hat{\boldsymbol{S}}^2, \hat{J}_z, \hat{L}_z, \hat{S}_z$, we have

$$[\hat{O}, \hat{H}] = [\hat{O}, \hat{H}_0] + [\hat{O}, A(r)\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = A(r)[\hat{O}, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] \tag{B.18}$$

It is then established that

$$[\hat{\boldsymbol{L}}^2, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{\boldsymbol{L}}^2, \hat{L}_x]\hat{S}_x + [\hat{\boldsymbol{L}}^2, \hat{L}_y]\hat{S}_y + [\hat{\boldsymbol{L}}^2, \hat{L}_z]\hat{S}_z = 0 \tag{B.19}$$

$$[\hat{\boldsymbol{S}}^2, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{\boldsymbol{S}}^2, \hat{S}_x]\hat{L}_x + [\hat{\boldsymbol{S}}^2, \hat{S}_y]\hat{L}_y + [\hat{\boldsymbol{S}}^2, \hat{S}_z]\hat{L}_z = 0 \tag{B.20}$$

$$[\hat{\boldsymbol{J}}^2, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{\boldsymbol{L}}^2, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] + [\hat{\boldsymbol{S}}^2, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] + 2[\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = 0 \tag{B.21}$$

and that

$$[\hat{L}_z, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{L}_z, \hat{L}_x]\hat{S}_x + [\hat{L}_z, \hat{L}_y]\hat{S}_y = i\hbar(\hat{L}_y\hat{S}_x - \hat{L}_x\hat{S}_y) \tag{B.22}$$

$$[\hat{S}_z, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{S}_z, \hat{S}_x]\hat{L}_x + [\hat{S}_z, \hat{S}_y]\hat{L}_y = i\hbar(\hat{L}_x\hat{S}_y - \hat{L}_y\hat{S}_x) \tag{B.23}$$

$$[\hat{J}_z, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = [\hat{L}_z, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] + [\hat{S}_z, \hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}] = 0. \tag{B.24}$$

We have thus shown that $\hat{\boldsymbol{S}}^2$, $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{J}}^2$, and $\hat{J}_z$ commute with the perturbation $A(r)\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$ and the complete Hamiltonian $\hat{H}$. However, the components (projections) of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ do not commute with $\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$ and $\hat{H}$ and, therefore, do not correspond to conserved quantities.

3. By assumption (by construction), the states $|nlsjm_j\rangle$ are eigenstates of $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{S}}^2$, and $\hat{\boldsymbol{J}}^2$ with the respective eigenvalues $\hbar^2 l(l+1)$, $\hbar^2 s(s+1)$, and $\hbar^2 j(j+1)$. Due to the identity (B.17), they are also eigenvectors of $\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$ (with eigenvalues $\frac{1}{2}\hbar^2[j(j+1) - l(l+1) - s(s+1)]$). The quantum number n indicates that $|nlsjm_j\rangle$ are solutions of the radial Schrödinger equation (depending only on l and r) for the hydrogen atom. These solutions are not eigenstates of the operator $A(r)$ (equivalent to a $1/r^3$ term), and therefore, $|nlsjm_j\rangle$ are not eigenstates of $\hat{V}_{LS} = A(r)\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$. From the above results, it follows that the matrix elements of $\hat{V}_{LS}$ are

$$\langle n'l'sj'm_{j'}|\hat{V}_{LS}|nlsjm\rangle = \langle R_{n'l}|A(r)|R_{nl}\rangle \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]\delta_{l,l'}\delta_{j,j'}\delta_{m_j,m_{j'}}, \tag{B.25}$$

where $|R_{nl}\rangle$, $n \geq l+1$, represents the radial wave functions of the usual hydrogen atom.

4. The eigenstates of $\hat{H}_0$ are degenerate since their energy depends only on n. We must employ degenerate perturbation theory. At the first order, the perturbation only mixes states within the same degenerate subspace n, and the energy corrections (energy shifts) are given by the eigenvalues of the matrix

$$M_n^{(1)} = \left(\langle nl'sj'm_j'|\hat{V}_{LS}|nlsjm_j\rangle\right)_{l'j'm_{j'},ljm_j}. \tag{B.26}$$

The considerations from the previous question, summarized in Eq. (B.25), show that this matrix is diagonal, with diagonal elements given by

$$\langle nlsjm_j|\hat{V}_{LS}|nlsjm\rangle = \langle R_{nl}|A(r)|R_{nl}\rangle \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]. \tag{B.27}$$

The eigenstates remain unchanged at the first order of perturbation, but the eigenenergies experience a shift $\Delta E = \Delta E_{nlj}$ given by these diagonal elements (the dependence on s is not indicated as $s = 1/2$ is fixed):

$$\Delta_{nlj} = \langle nlsjm_j|\hat{V}_{LS}|nlsjm\rangle. \tag{B.28}$$

(i) At first-order perturbation, due to degeneracy, everything happens as if the $|nlsjm\rangle$ states were eigenstates of $\hat{V}_{LS}$. For the s states ($l = 0$), only the case $j = 1/2 = s$ exists, and we have

$$\Delta E_{n0j} = \Delta E_{n\,0\,\frac{1}{2}} = 0. \tag{B.29}$$

For $l \geq 1$, we have $j = l + 1/2$ or $j = l - 1/2$, and the expression (B.27) yields

$$\Delta E_{n,\,l\geq 1,\,j} = \langle R_{nl}|A(r)|R_{nl}\rangle \frac{\hbar^2}{2} \times \begin{cases} l & \text{if } j = l + 1/2 \\ -(l+1) & \text{if } j = l - 1/2 \end{cases}. \tag{B.30}$$

The $\hat{\boldsymbol{L}}.\hat{\boldsymbol{S}}$ coupling partially lifts the degeneracy of each level n by creating, at the first-order perturbation, sub-levels whose energy depends on l (infinitely many values) and j (two values for each j value), but not on m_j. This division into sub-levels is called fine structure.

(ii) For $l = 1$, the possible values of j are $j = 3/2$ and $j = 1/2$, denoted as $2\mathrm{P}_{1/2}$ and $2\mathrm{P}_{3/2}$, respectively. These levels are degenerate in the absence of $\hat{V}_{LS}$, and their shifts due to $\hat{V}_{LS}$ are

$$\Delta_{2,1,3/2} = +\frac{\hbar^2}{2}\langle R_{2,1}|A(r)|R_{2,1}\rangle = \frac{1}{96}\alpha^4 m_e c^2 \tag{B.31}$$

$$\Delta_{2,1,1/2} = -\hbar^2\langle R_{2,1}|A(r)|R_{2,1}\rangle = -\frac{1}{48}\alpha^4 m_e c^2. \tag{B.32}$$

Numerical application (with the oral indication that we will use $\alpha \simeq 1/137$ to simplify the calculations):

$$\frac{1}{96}\alpha^4 m_e c^2 = \frac{9.11 \cdot 3.00^2}{0.96 \cdot 1.37^4} 10^{-25} \simeq \frac{80}{\sqrt{2}^4} 10^{-25} = 2 \cdot 10^{-24}\,\mathrm{J}, \tag{B.33}$$

where we rounded down a bit. To convert results between units, we use $1\,\mathrm{J} = (1/1.60) \cdot 10^{19}\,\mathrm{eV}$ and Planck's constant $h = 2\pi\hbar = 6.63 \cdot 10^{-34}\,\mathrm{J.s}$, which allows us to express an energy E in terms of the corresponding frequency $\nu = E/h$. We can quickly find rough estimates:

$$\Delta_{2,1,3/2} \simeq 2 \cdot 10^{-24}\,\mathrm{J} \simeq 1 \cdot 10^{-5}\,\mathrm{eV} \simeq 3\,\mathrm{GHz} \times h \simeq 20\,\mathrm{GHz} \times \hbar \tag{B.34}$$

$$\Delta_{2,1,1/2} \simeq -4 \cdot 10^{-24}\,\mathrm{J} \simeq -2 \cdot 10^{-5}\,\mathrm{eV} \simeq -6\,\mathrm{GHz} \times h \simeq -40\,\mathrm{GHz} \times \hbar, \tag{B.35}$$

and a degeneracy lifting of the order of $3 \cdot 10^{-5}\,\mathrm{eV}$ (more precisely $4.55 \cdot 10^{-5}\,\mathrm{eV}$), or about ten GHz$\times h$ (more precisely $11.0\,\mathrm{GHz} \times h$).

(iii) There is still residual degeneracy of states with different m_j ($m_j = -j, -j+1, \ldots, j-1, j$) for each given level (n, l, j) of the fine structure. The fine level $2\mathrm{P}_{3/2}$ is four-fold degenerate ($m_j = -3/2, -1/2, 1/2, 3/2$), while the fine level $2\mathrm{P}_{1/2}$ is two-fold degenerate ($m_j = -1/2, 1/2$).

Exercise 3 : Time evolution of a density matrix

1. In basis $\mathcal{B} = \{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, The matrix $\hat{H}$ is given by

$$[H]_{\mathcal{B}} = g\hbar^2 \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{B.36}$$

2. The matrix of $\hat{H}$ is block diagonal. Its eigenvalues are 0 (twice degenerate) and $\pm g\hbar^2$ (the latter two are obtained by diagonalizing the central block). The corresponding eigenvectors are $|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle$ (for the eigenvalue 0), $v_+ = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$ (for $+g\hbar^2$), and $v_- = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ (for $-g\hbar^2$).

3. At $t = 0$, $|\Psi(0)\rangle = |\downarrow\uparrow\rangle = \frac{1}{\sqrt{2}}(v_+ - v_-)$, hence

$$|\Psi(t)\rangle = e^{-\frac{iHt}{\hbar}}|\Psi(0)\rangle = \frac{1}{\sqrt{2}}[e^{-ig\hbar t}v_+ - e^{ig\hbar t}v_-] = \cos(g\hbar t)|\downarrow\uparrow\rangle - i\sin(g\hbar t)|\uparrow\downarrow\rangle. \tag{B.37}$$

4. The density matrix is defined as $\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$. The matrix $\rho(t)$ in the basis $\mathcal{B}$ is given by

$$\rho(t) = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \sin^2(g\hbar t) & -\frac{1}{2}i\sin(2g\hbar t) & 0 \\ 0 & \frac{1}{2}i\sin(2g\hbar t) & \cos^2(g\hbar t) & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{B.38}$$

5. The reduced density matrix $\rho_1(t)$ obtained by taking the partial trace over the states of the second spin, and expressed in the basis $\{|\downarrow\rangle, |\uparrow\rangle\}$ of the first spin, is:

$$\rho_1(t) = \begin{pmatrix} \cos^2(g\hbar t) & 0 \\ 0 & \sin^2(g\hbar t) \end{pmatrix}. \tag{B.39}$$

6. We have

$$\rho_1(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \tag{B.40}$$

This matrix corresponds to a pure state. At time $t = \frac{\pi}{4g\hbar}$, the reduced density matrix becomes

$$\rho_1\left(\frac{\pi}{4g\hbar}\right) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}. \tag{B.41}$$

It corresponds in this case to a mixed state. This is due to the interaction between the 2 spins, modeled by $\hat{H}$, the 2 spin systems, initially in a separable state evolved, to find itself at $t = \frac{\pi}{4g\hbar}$ in an entangled state.

B.2 2015 Exam

Exercise 4 : Hamrmonic oscillator suddenly displaced(2 points)

1. After displacement, the system Hamiltonian becomes

$$\begin{aligned} \hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2(\hat{x} - b)^2 \\ &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \frac{1}{2}m\omega^2 b^2 - m\omega^2 b\hat{x} \\ &= \hat{H}_0 + \hat{V}(t) \end{aligned}$$

with $\hat{V}(t) = m\omega^2 b^2/2 - m\omega^2 b\hat{x}$, constant for $t > 0$. Furthermore, $\hat{x} = \sqrt{\hbar/2m\omega}\left(\hat{a}^\dagger + \hat{a}\right)$.

2. We can directly apply the Fermi golden rule for a constant perturbation $\hat{V}$, that is

$$W_{1\to n} = \frac{2\pi}{\hbar}\left|\langle n|\,\hat{V}\,|1\rangle\right|^2 \delta\left(E_n - E_1\right) \tag{B.42}$$

where the eigen energies are $E_n = \hbar\omega\left(n + 1/2\right)$. Note that if $n \neq 1$, then $\omega_n \neq \omega_1$ and thus (B.42) is identically zero.

3. The perturbation lasts for finite time T the fermi golden rule, useful in the approximation of a long perturbation, can no longer be applied. The transition probability at t is

$$\begin{aligned}
P_{1\to n} &= \left|\langle n \mid \psi\left(t\right)\rangle\right|^2 \\
&= \left|\langle n|\,\hat{U}_S\left(t,0\right)|1\rangle\right|^2 \\
&= \left|\langle n|\,e^{-i\hat{H}_0 t/\hbar}\hat{U}_I\left(t,0\right)|1\rangle\right|^2 \\
&= \left|\langle n|\,e^{-iE_n t/\hbar}\hat{U}_I\left(t,0\right)|1\rangle\right|^2 \\
&= \left|\langle n|\,\hat{U}_I\left(t,0\right)|1\rangle\right|^2
\end{aligned}$$

where indices S and I refer to the Schroedinger representation and interaction respectively. At first order in $\hat{V}$ we have

$$\begin{aligned}
\hat{U}_I\left(t,0\right) &= \mathbb{1} - \frac{i}{\hbar}\int_0^T dt'\hat{V}_I\left(t'\right) \\
&= \mathbb{1} - \frac{i}{\hbar}\int_0^T dt' e^{i\hat{H}_0 t'/\hbar}\hat{V}_I\left(t'\right)e^{-i\hat{H}_0 t'/\hbar}
\end{aligned}$$

The term in $\mathbb{1}$ does not contribute to the matrix element, as $\langle n|\,\mathbb{1}\,|1\rangle = 0$ and similarly for the term in b^2 in $\hat{V}$. We then have

$$\begin{aligned}
\langle n|\,\hat{U}_I\left(t,0\right)|1\rangle &= \langle n|\,e^{i\hat{H}_0 t'/\hbar}\hat{V}_I\left(t'\right)e^{-i\hat{H}_0 t'/\hbar}\,|1\rangle \\
&= -\frac{i}{\hbar}\int_0^T dt' e^{-i(E_1-E_n)t'/\hbar}\,\langle n|\,\hat{V}\,|1\rangle
\end{aligned}$$

We note that having $\hat{V} \propto \hat{a}^\dagger + \hat{a}$, the only states for which $n = 0$ and $n = 2$ will have a nonzero transition probability. We compute

$$\int_0^T dt' e^{-i(E_1-E_n)t'/\hbar} = -\frac{i\hbar}{E_1 - E_n}\left(e^{-i(E_1-E_n)t'/\hbar} - 1\right)$$

$$\langle n|\,\hat{V}\,|1\rangle = -m\omega^2 b\sqrt{\frac{\hbar}{2m\omega}}\,\langle n|\,\hat{a}^\dagger + \hat{a}\,|1\rangle$$

$$\langle 0|\,\hat{V}\,|1\rangle = -m\omega^2 b\sqrt{\frac{\hbar}{2m\omega}}$$

$$\langle 2|\,\hat{V}\,|1\rangle = -m\omega^2 b\sqrt{\frac{\hbar}{m\omega}}$$

and finally

$$\begin{aligned}
P_{1\to 0} &= \frac{2m\omega b^2}{\hbar}\sin^2\left(\frac{\omega T}{2}\right) \\
P_{1\to 2} &= 2P_{1\to 0}
\end{aligned}$$

Exercise 5 : Variational principle for an anharmonic potential (1 point)

1. Being given by $V(x) = \alpha x^4$ which has the dimension of an energy $[V] = [E]$, we can deduce

$$[\alpha] = [E][L]^{-4} \tag{B.43}$$

on the other hand $[\hbar] = [E][T]$, $[m] = [E][L]^{-2}[T]^2$ and $[E_0] = [E]$ so

$$([E][T])^a\left([E][L]^{-2}[T]^2\right)^b\left([E][L]^{-4}\right)^c = [E] \tag{B.44}$$

By identification we extract

$$\begin{aligned} a + b + c &= 1 \\ a + 2b &= 0 \\ -2b - 4c &= 0 \end{aligned}$$

Which we solve for exponents

$$a = \frac{4}{3}; \quad b = -\frac{2}{3}; \quad c = \frac{1}{3} \tag{B.45}$$

2. The system Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \hat{x}} + \alpha \hat{x}^4 \tag{B.46}$$

With the trial function

$$\psi_\sigma(x) = e^{-\frac{x^2}{2\sigma^2}} \tag{B.47}$$

non other than a gaussian of standard deviation σ, we will have to normalize energy by

$$\langle \psi_\sigma \mid \psi_\sigma \rangle = \int_{-\infty}^{+\infty} \psi_\sigma^2(x)\, dx = \sigma\sqrt{\pi} \tag{B.48}$$

The energy of the system in state $|\psi_\sigma\rangle$ is

$$\langle \psi_\sigma | \hat{H} | \psi_\sigma \rangle = -\frac{\hbar^2}{2m} \langle \psi_\sigma | \frac{\partial^2}{\partial \hat{x}} | \psi_\sigma \rangle + \alpha \langle \psi_\sigma | \hat{x}^4 | \psi_\sigma \rangle \tag{B.49}$$

with

$$\begin{aligned} \langle \psi_\sigma | \frac{\partial^2}{\partial \hat{x}} | \psi_\sigma \rangle &= -\frac{\sqrt{\pi}}{2\sigma} \\ \langle \psi_\sigma | \hat{x}^4 | \psi_\sigma \rangle &= \frac{3}{4}\sigma^5\sqrt{\pi} \end{aligned}$$

We find normalized energy

$$E_\sigma = \frac{\langle \psi_\sigma | \hat{H} | \psi_\sigma \rangle}{\langle \psi_\sigma \mid \psi_\sigma \rangle} = \frac{\hbar^2}{4m\sigma^2} + \frac{3}{4}\alpha\sigma^4 \tag{B.50}$$

We now look to minimize this energy in relation to σ by solving

$$\frac{\partial E_\sigma}{\partial \sigma} = 0 \tag{B.51}$$

To find

$$\sigma_{\text{var}} = \left(\frac{\hbar^2}{6m\alpha}\right)^{1/6}$$
$$E_{\text{var}} = \frac{3\times 6^{1/3}}{8}\left(\frac{\hbar^4\alpha}{m^2}\right)^{1/3}$$

compatible with the dimensional analysis of question 1.

Exercise 6 : Entanglement criteria(2 points)

1. Consider operator $A : \hat{H}_1 \mapsto \hat{H}_1$. In the global hilbert space $\hat{H}$, this operator becomes $\hat{A} = \hat{A}_1 \otimes \mathbb{1}_2$. We thus have

$$\begin{aligned}\left\langle \hat{A}\right\rangle &= \text{Tr}\left(\hat{A}\hat{\rho}\right)\\ &= \sum_k p_k \text{Tr}\left(\hat{A}\hat{\rho}_k^{(1)}\otimes\hat{\rho}_k^{(2)}\right)\\ &= \sum_k p_k \text{Tr}\left(\hat{A}_1\hat{\rho}_k^{(1)}\right)\text{Tr}\left(\hat{\rho}_k^{(2)}\right)\\ &= \sum_k p_k \text{Tr}\left(\hat{A}_1\hat{\rho}_k^{(1)}\right)\end{aligned}$$

since $\text{Tr}\left(\hat{\rho}_k^{(2)}\right) = 1$ for a density matrix. We have thus shown that $\left\langle \hat{A}\right\rangle$ is independant of $\hat{\rho}_k^{(2)}$

2. The density matrix at pure states $|\psi_{\text{GHZ}}\rangle$ is built as

$$\begin{aligned}\hat{\rho}_0 &= |\psi_{\text{GHZ}}\rangle\langle\psi_{\text{GHZ}}|\\ &= \frac{1}{2}\left(|000\rangle + |111\rangle\right)\left(\langle 000| + \langle 111|\right)\end{aligned}$$

The density matrix for subsystems B and C is given by the partial traces of $\hat{\rho}_0$ on the Alice system

$$\begin{aligned}\hat{\rho} &= \langle 0_A|\hat{\rho}_0|0_A\rangle + \langle 1_A|\hat{\rho}_0|1_A\rangle\\ &= \frac{1}{2}\left(|00\rangle\langle 00| + |11\rangle\langle 11|\right)\\ &= \frac{1}{2}\begin{pmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&1\end{pmatrix}\\ &= \frac{1}{2}\left(\hat{\rho}_0^{(1)}\otimes\hat{\rho}_0^{(2)} + \hat{\rho}_1^{(1)}\otimes\hat{\rho}_1^{(2)}\right)\end{aligned}$$

where $\hat{\rho}_0^{(j)} = |0\rangle\langle 0|$ and $\hat{\rho}_1^{(j)} = |1\rangle\langle 1|$.

3. For a separable density matrix $\hat{\rho}_S$, the definition of partial transposition is simply given by

$$\hat{\rho}_S^{T_B} = \sum_k \hat{\rho}_k^{(1)}\otimes\left(\hat{\rho}_k^{(2)}\right)^T \tag{B.52}$$

but the $\hat{\rho}_k^{(2)}$ are valid density matrices, that is:

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{\rho}_k^{(2)}\right)^T = \mathrm{Tr}\left(\hat{\rho}_k^{(2)}\right) = 1 \\
&\left(\left(\hat{\rho}_k^{(2)}\right)^T\right)^\dagger = \left(\hat{\rho}_k^{(2)}\right)^T \\
&\left(\hat{\rho}_k^{(2)}\right)^T \text{ and } \hat{\rho}_k^{(2)} \text{ have the same eigenvalues}
\end{aligned}$$

thus $\hat{\rho}_S^{T_B}$ is still a separable density matrix .

4. Like before, the pure state of A, B, C and D is described by $\hat{\rho}_0 = |\psi_S\rangle\langle\psi_S|$. We compute the partial trace relative to A

$$\begin{aligned}
\hat{\rho} &= \langle 0_A|\hat{\rho}_0|0_A\rangle + \langle 1_A|\hat{\rho}_0|1_A\rangle \\
&= \frac{1}{4}\left(|000\rangle\langle 000| + |000\rangle\langle 011| + |011\rangle\langle 000| + |011\rangle\langle 011|\right) \\
&+\frac{1}{4}\left(|100\rangle\langle 100| - |100\rangle\langle 111| - |111\rangle\langle 100| + |111\rangle\langle 011|\right) \\
&= \frac{1}{4}\begin{pmatrix}
1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -1 & 0 & 0 & 1
\end{pmatrix}
\end{aligned}$$

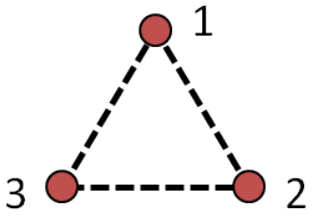
To show that it is a mixed state, we compute the partial transpose relative to C. We see that $\hat{\rho}^{T_C}_{000,011} = \hat{\rho}_{001,010}$ and $\hat{\rho}^{T_C}_{001,010} = \hat{\rho}_{000,011}$ and same for the 2^e diagonal blocks. Thus

$$\hat{\rho}^{T_C} = \frac{1}{4}\begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix} \tag{B.53}$$

We can easily calculate the eigenvalues of this block-diagonal structure. For both blocks, the secular equation is $\lambda^2 - 1 = 0$, which gives 2 pairs of eigenvalues $\lambda = \pm 1$. The matrix $\hat{\rho}^{T_C}$ thus has 2 negative eigenvalues, and therefore, it is not a valid density matrix. According to the condition established earlier, we are in a case of a non-separable state and hence, entangled.

B.3 2016 Exam

Exercise 7 : 3 coupled harmonic oscillators



(i) The first term in $\hat{H}$ corresponds to $\hbar\omega\hat{N}$ and thus commutes with $\hat{N}$. For the second term, it's sufficient to observe that this term does not change the total number of quanta since each term of the form $\hat{a}_j^\dagger\hat{a}_k$ destroys one quantum and creates another (or gives zero if $n_k = 0$). Therefore, the total number of quanta is conserved, and the term must commute with $\hat{N}$. For an explicit proof, let's calculate:

$$\begin{aligned}[\hat{a}_j^\dagger\hat{a}_k, \hat{a}_l^\dagger\hat{a}_l] &= \hat{a}_j^\dagger[\hat{a}_k, \hat{a}_l^\dagger\hat{a}_l] + [\hat{a}_j^\dagger, \hat{a}_l^\dagger\hat{a}_l]\hat{a}_k \\ &= \hat{a}_j^\dagger[\hat{a}_k, \hat{a}_l^\dagger]\hat{a}_l + \hat{a}_l^\dagger[\hat{a}_j^\dagger, \hat{a}_l]\hat{a}_k \\ &= \hat{a}_j^\dagger\hat{a}_l\delta_{kl} - \hat{a}_l^\dagger\hat{a}_k\delta_{jl}\,.\end{aligned}$$

where we have used $[\hat{a}_j, \hat{a}_k^\dagger] = \delta_{jk}$ and $[\hat{a}_j, \hat{a}_k] = 0$. We notice that $\sum_{j<k}(\hat{a}_j^\dagger\hat{a}_k + \hat{a}_k^\dagger\hat{a}_j) = \sum_{j\neq k}\hat{a}_j^\dagger\hat{a}_k$, from which we have:

$$\begin{aligned}[\hat{N}, \sum_{j<k}(\hat{a}_j^\dagger\hat{a}_k + \hat{a}_k^\dagger\hat{a}_j)] &\propto \sum_l\sum_{j\neq k}[\hat{a}_j^\dagger\hat{a}_k, \hat{a}_l^\dagger\hat{a}_l] \\ &= \sum_l\sum_{j\neq k}[\hat{a}_j^\dagger\hat{a}_l\delta_{kl} - \hat{a}_l^\dagger\hat{a}_k\delta_{jl}) \\ &= \sum_{j\neq k}(\hat{a}_j^\dagger\hat{a}_k - \hat{a}_j^\dagger\hat{a}_k) = 0\,.\end{aligned}$$

If $[\hat{N}, \hat{H}] = 0$, we can diagonalize both operators in the same basis. Consequently, $\hat{H}$ takes a block-diagonal form, where each block is defined in a subspace generated by vectors $\{|n_1, n_2, n_3\rangle\}$ with $n_1 + n_2 + n_3 = N$ and a fixed N.

(ii) As stated in point 1, we can find 3 eigenstates of $\hat{H}$ by diagonalizing it in this subspace. Thus, we have restricted the problem to a 3-dimensional space. Now, let's calculate the representation Γ of C_{3v} associated with this subspace. It is known from the problem statement that $\Gamma(g)$, for $g \in C_{3v}$, is a permutation. To find the characters, it's sufficient to determine a matrix per class of equivalence of C_{3v}.

- For E, we immediately have $\chi(E) = 3$.
- For C_3, it permutes $1 \to 2$, $2 \to 3$, and $3 \to 1$, which gives us the matrix

$$\Gamma(C_3) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \tag{B.54}$$

  so $\chi(C_3) = 0$.
- For σ_v across the plane passing through 1, it has $1 \to 1$, $3 \to 2$, and $2 \to 3$, which means $\chi(\sigma_v) = 1$.

Even without using the formula, we can see that $\chi(g) = \chi^{(1)}(g) + \chi^{(3)}(g)$, and therefore $\Gamma = \Gamma_1 \oplus \Gamma_3$. The eigenstates will have degeneracies of 1 and 2. The eigenstate

associated with Γ_1 is the totally symmetric state, so it must be

$$|\psi_1\rangle = \frac{1}{\sqrt{3}}\left(|100\rangle + |010\rangle + |001\rangle\right) \tag{B.55}$$

We can immediately verify that $\hat{H}|\psi_1\rangle = E_1|\psi_1\rangle$ with $E_1 = \hbar\omega - 2J$. We can now write two states orthogonal to $|\psi_1\rangle$, for example

$$|\psi_{2,3}\rangle = \frac{1}{\sqrt{3}}\left(|100\rangle + \alpha|010\rangle + \beta|001\rangle\right) \tag{B.56}$$

with $|\alpha|^2 + |\beta|^2 = 1$. Orthogonality with $|\psi 1\rangle$ implies $\alpha + \beta + 1 = 0$. These two conditions are satisfied by the cube roots of unity, and then

$$\alpha = e^{\pm 2i\frac{\pi}{3}}$$
$$\beta = e^{\mp 2i\frac{\pi}{3}}$$

We can verify that these are eigenstates of $\hat{H}$; indeed, $\hat{H}|\psi_{2,3}\rangle = E_{2,3}|\psi_{2,3}\rangle$ with $E_{2,3} = \hbar\omega + J$.

(iii) The six states are $|200\rangle, |020\rangle, |002\rangle, |110\rangle, |101\rangle, |011\rangle$. Let's calculate, as before, the characters of the representation Γ of dimension six defined in this subspace. For the identity, it's straightforward, $\chi(E) = 6$. Since C_3 maps each state to a different state, $\chi(C_3) = 0$. For the same σ_v as before, we have:

$$|020\rangle \longleftrightarrow |002\rangle \qquad\qquad |110\rangle \longleftrightarrow |101\rangle \tag{B.57}$$

but $|200\rangle$ and $|011\rangle$ stay in their place. So, the matrix will have two "1" values on the diagonal, and $\chi(\sigma_v) = 2$. Again, without necessarily using the formula, $\chi(g) = 2\chi^{(1)}(g) + 2\chi^{(3)}(g)$, so:

$$\Gamma = 2\Gamma_1 \oplus 2\Gamma_3 \tag{B.58}$$

There will be four distinct energy levels, two of which are non-degenerate, and two others are doubly degenerate.

Exercise 8 : Entanglement Entropy

(i) For a diagonal matrix, we have:

$$\ln(\hat{\rho}) = \begin{pmatrix} \ln(x) & 0 \\ 0 & \ln(1-x) \end{pmatrix} \tag{B.59}$$

and then

$$\begin{aligned} S(x) &= \mathrm{Tr}\left[\begin{pmatrix} x & 0 \\ 0 & 1-x \end{pmatrix}\begin{pmatrix} \ln(x) & 0 \\ 0 & \ln(1-x) \end{pmatrix}\right] \\ &= -\left[x\ln(x) + (1-x)\ln(1-x)\right] \end{aligned}$$

We can use the identity $\lim_{x\to 0} x\ln(x) = \lim_{x\to-\infty} ye^{y} = 0$ to conclude that $S(0) = S(1) = 0$. Now, let's calculate the derivative of S with respect to x, which we can easily find:

$$\frac{\mathrm{d}S(x)}{\mathrm{d}x} = \frac{\ln(1-x)}{x} \tag{B.60}$$

Then:

- For $x = 0.5$, $(1-x)/x = 1$, and $S'(x) = 0$
- For $x < 0.5$, $(1-x)/x > 1$, and $S'(x) > 0$
- For $x > 0.5$, $(1-x)/x < 1$, and $S'(x) < 0$

So, necessarily, $S(x)$ reaches a maximum at $x = 0.5$, and $S(0.5) = \ln(2)$. By making the variable change $1-x \to y$, we can also deduce that $S(x)$ is symmetric with respect to $x = 0.5$.

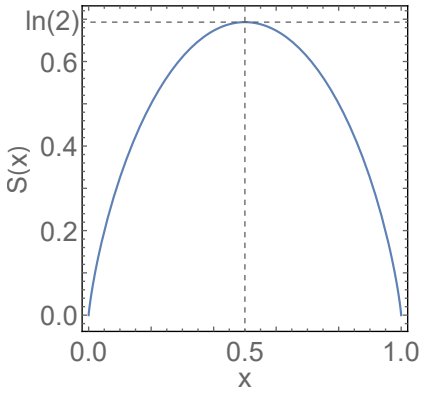


Figure B.1: Variation of entropy as a function of the parameter x

For a pure state, we need to verify $\mathrm{Tr}(\hat{\rho}^2) = x^2 + (1-x)^2 = 1$, which is achieved for $x = 0$ or $x = 1$, and thus, $S_{\mathrm{pure}}(x) = S(0) = S(1) = 0$. The case $S(0.5) = \ln(2) = S_{\mathrm{max}}$ corresponds to a completely mixed state associated with maximum entropy. So, we can interpret $S(x)$ as a measure of the degree of mixing for a given state.

(ii) Using the Schmidt decomposition, we have:

$$\hat{\rho}_A = \mathrm{Tr}_B\left(|\psi\rangle\langle\psi|\right) \tag{B.61}$$
$$= \sum_j \langle b_j|\psi\rangle\langle\psi|\psi\rangle \tag{B.62}$$
$$= \sum_{j,k} \lambda_k^2 |a_k\rangle\langle b_j|b_k\rangle\langle b_k|b_j\rangle\langle a_k| \tag{B.63}$$
$$= \sum_j \lambda_j^2 |a_j\rangle\langle a_j| \tag{B.64}$$
$$\hat{\rho}_B = \sum_j \lambda_j^2 |b_j\rangle\langle b_j| \tag{B.65}$$

(iii) In their respective bases, we have:

$$\hat{\rho}_A = \begin{pmatrix} \lambda_1^2 & 0 \\ 0 & \lambda_2^2 \end{pmatrix} = \hat{\rho}_B \tag{B.66}$$

Therefore, necessarily, $S(\hat{\rho}_A) = S(\hat{\rho}_B)$ since S, involving a trace, does not depend on the basis. We have $S(\hat{\rho}_A) = S(\lambda_1^2)$, which is the function studied in point 1, as $\lambda_2^2 = 1 - \lambda_1^2$ by definition.

- If $|\psi\rangle$ is separable, we can write $|\psi\rangle = |a\rangle \otimes |b\rangle$, which corresponds to $\lambda_1 = 1$ and $\lambda_2 = 0$, so $S(\hat{\rho}_A) = S(\hat{\rho}_B) = 0$. * If $|\psi\rangle$ is maximally entangled, then there exist 2 bases for which $|\psi\rangle = (|a_1\rangle \otimes |b_1\rangle + |a_2\rangle \otimes |b_2\rangle)/2$, and thus, $S(\hat{\rho}_A) = S(\hat{\rho}_B) = \ln(2) = S_{\max}$.

(iv) Given the shape of $S(x)$ and the results of points 2 and 3, we can propose that $S(\hat{\rho}_A) = S(\hat{\rho}_B)$ is a continuous measure of the entanglement present in $|\psi\rangle$. By measuring the entropy of one of the 2 subsystems, we can deduce the degree of entanglement between A and B wherein the terminology *entanglement entropy*.

Exercise 9 : Hydrogen Atom in a Cubic Potential We can express the potential in spherical coordinates as follows:

$$V(\mathbf{r}) = r^3 \sin^2(\theta)\cos(\theta)\cos(\phi)\sin(\phi) \tag{B.67}$$

$$= \frac{1}{2} r^3 \sin^2(\theta)\cos(\theta)\sin(2\phi) \tag{B.68}$$

$$= \frac{1}{4i} r^3 \sin^2(\theta)\cos(\theta)\left(\exp 2i\phi - \exp -2i\phi\right) \tag{B.69}$$

Now, let's express the potential as a sum of spherical tensors:

$$V = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} c_{k,q} T_q^{(k)} \tag{B.70}$$

We know that the relation $\left[L_z, T_q^{(k)}\right]|n,l,m\rangle = \hbar q T_q^{(k)}|n,l,m\rangle$ is valid for any state $|n,l,m\rangle$. In particular, if we evaluate it for $|n,l,0\rangle$, we obtain that $L_z T_q^{(k)} = \hbar q T_q^{(k)}$. Let's evaluate $L_z V$:

$$L_z V = -i\hbar \frac{\partial}{\partial \phi}\left(\frac{1}{4i} r^3 \sin^2(\theta)\cos(\theta)\left(\exp 2i\phi - \exp -2i\phi\right)\right) \tag{B.71}$$

$$= -\frac{\hbar}{4} r^3 \sin^2(\theta)\cos(\theta)\frac{\partial}{\partial \phi}\left(\exp 2i\phi - \exp -2i\phi\right) \tag{B.72}$$

$$= -\frac{\hbar}{4} r^3 \sin^2(\theta)\cos(\theta) 2\left(2\exp 2i\phi - (-2)\exp -2i\phi\right) \tag{B.73}$$

$$= 2\hbar c_{k,2} T_2^{(k)} - 2\hbar c_{k,-2} T_{-2}^{(k)} \tag{B.74}$$

where we defined the coefficients $c_{k,\pm 2} = \mp \frac{1}{4} r^3 \sin^2(\theta)\cos(\theta)$. We see that V is a linear combination of spherical tensors with $q = \pm 2$. The value of k is not important for this problem, but we know that $k \geq 2$.

According to the Wigner-Eckart theorem, only the matrix elements $\langle n', l', m'| V |n,l,m\rangle$ with $\Delta m = m' - m = q = \pm 2$ can be nonzero.

(i) For the state $|1s\rangle = |1,1,0\rangle$, the perturbation will be zero because $\Delta m = 0$.

(ii) For the four states $2s$ and $2p$, we need to apply degenerate perturbation theory. We need to calculate the matrix in the subspace generated by $|2,1,0\rangle$, $|2,2,-1\rangle$, $|2,2,0\rangle$, and $|2,2,1\rangle$. However, the same argument tells us that the only non-zero matrix elements are those between the states $|2,2,-1\rangle$ and $|2,2,1\rangle$ because these are the only cases where $\Delta m = \pm 2$. However, these elements are zero due to parity. In fact, both V and $\phi(\mathbf{r}) = \langle \mathbf{r}|\, 2,2,\pm 1\rangle$ are odd. So here too, the energy correction is zero.

Note that the parity argument also applies to the first case. However, relying solely on this argument might lead to the erroneous conclusion that a transition is possible between the states $|2,1,0\rangle$ and $|2,2,m\rangle$, which have different parities.

B.4 2017 exam

Exercise 10 : 2-D perturbed harmonic oscillator Since operators $\hat{a}_x$ and $\hat{a}_y$ transform, under operators of D_4, like x and y, we will start by figuring out the transformation laws for x and y. For the character computation, we only need to study one operation per conjugacy class

	x	y
E	x	y
C_4	y	$-x$
C_2	$-x$	$-y$
C_2'	$-x$	y
C_2''	y	x

Table B.1: The x and y transformation as funciton of elements of group D_4.

Associated 2×2 matrices

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{B.75}$$

And the character of each matrix is given by

$$\chi = 2, 0, -2, 0, 0, \tag{B.76}$$

Respectively. We immediately see that this coincides with the character of irreducible representation Γ_5 of dimension 2.

1. Since $\hat{a}_x$ and $\hat{a}_y$ transform like x and y, $|1,0\rangle = \hat{a}_x |0,0\rangle$ and $|0,1\rangle = \hat{a}_y |0,0\rangle$ also transform like x and y. These two states thus generate the irreducible representation Γ_5 of the symmetry group of the Hamiltonian.

   The degeneracy is therefore necessary and cannot be removed by the perturbation $V(x,y)$.

2. We proceed in the same manner and determine the transformation laws of x^2, xy, and y^2, which will also be those of $|2,0\rangle$, $|1,1\rangle$, and $|0,2\rangle$.

   We observe from exercise 1.1. that the state $|1,1\rangle$ transforms like xy and generates on its own an invariant subspace:

	E	C_4	C_2	C_2'	C_2''
xy	xy	$-xy$	xy	$-xy$	xy

Table B.2: xy transformation as function of the elements of group D_4.

The characters are given by

$$\chi = 1, -1, 1, -1, 1, \tag{B.77}$$

thus this state generates Γ_4.

The other 2 states act like x^2 and y^2 :

	E	C_4	C_2	C_2'	C_2''
x^2	x^2	y^2	x^2	x^2	y^2
y^2	y^2	x^2	y^2	y^2	x^2

Table B.3: The transformation of x^2 and y^2 as function of groupe elements D_4.

We can deduce the character

$$\chi = 2, 0, 2, 2, 0. \tag{B.78}$$

Without even applying the formula for decomposition, we see that this character corresponds to the one of $\Gamma_1 \oplus \Gamma_3$.

We conclude that the 3-dimensional space generated by $|2,0\rangle$, $|1,1\rangle$, and $|0,2\rangle$ decomposes into three invariant subspaces corresponding to $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4$.

Hence, there is no necessary degeneracy, and in general, the degeneracy will be lifted by $V(x,y)$.

3. Similar to the previous exercise, we easily observe that $\{|3,0\rangle, |0,3\rangle\}$ and $\{|2,1\rangle, |1,2\rangle\}$ are two invariant subspaces (x^3 can transform to $\pm x^3$ or $\pm y^3$ but not to x^2y or xy^2, and vice-versa). They generate two 2-dimensional representations, Γ and Γ'.

Thus, we obtain

	E	C_4	C_2	C_2'	C_2''
x^3	x^3	y^3	$-x^3$	$-x^3$	y^3
y^3	y^3	$-x^3$	$-y^3$	y^3	x^3
x^2y	x^2y	$-y^2x$	$-x^2y$	x^2y	y^2x
y^2x	y^2x	x^2y	$-y^2x$	$-y^2x$	x^2y

Table B.4: Transformation of x^3, y^3, x^2y, y^2x as function of elements of group D_4.

The characters associated with the two representations Γ and Γ' are

$$\chi(\Gamma) = 2,0,-2,0,0 \qquad \Longrightarrow \Gamma_5 \chi(\Gamma') = 2,0,-2,0,0 \qquad \Longrightarrow \Gamma_5 \tag{B.79}$$

The 4-dimensional space therefore decomposes into two irreducible subspaces associated with $\Gamma_5 \oplus \Gamma_5$.

The perturbation will thus partially lift the degeneracy, and two energy levels doubly degenerate will result from the perturbation $V(x,y)$.

Exercise 11 : Purification of density matrix

1. We must check that

   (i) $\mathrm{Tr}(\rho_A) = 1$,

   (ii) $\rho_A = \rho_A^\dagger$,

   (iii) ρ_A is positive.

   Verifying these 3 conditions :

   (i) $\mathrm{Tr}(\rho_A) = \frac{1}{8}(5+3) = 1$

   (ii) Being symmetric, we have $\rho_A = \rho_A^\dagger$.

   (iii) The matrix is positive if all eigenvalues are ≥ 0.
   We find that

$$\begin{aligned} & (5-x)(3-x) - 3 = 0 \\ \Rightarrow \quad & x^2 - 8x + 12 = 0 \\ \Rightarrow \quad & x = 4 \pm \sqrt{16-12} \\ & = 2,6 \end{aligned} \tag{B.80}$$

Thus

$$\rho_A = \begin{pmatrix} \frac{2}{8} & 0 \\ 0 & \frac{6}{8} \end{pmatrix} \tag{B.81}$$

is positive

2. Generally a density matrix can be expressed diagonally by
$\rho_A = \sum_j p_j |j\rangle\langle j|$, where $\{|j\rangle\}$ form a basis. We can always define a second subsystem B identical, with same basis $\{|k\rangle\}$.
By construction, a pure state always has property $\rho_A = \mathrm{Tr}_B(|\psi\rangle\langle\psi|)$ es

$$|\psi\rangle = \sum_j \sqrt{p_j}\,|j\rangle \otimes |j\rangle\,. \tag{B.82}$$

Indeed,

$$\begin{aligned} \mathrm{Tr}_B(|\psi\rangle\langle\psi|) &= \sum_l \langle l| \left(\sum_{j,k} \sqrt{p_j p_k} \Big(|j\rangle \otimes |j\rangle \Big) \Big(\langle k| \otimes \langle k| \Big) \right) |k\rangle \\ &= \sum_{l,j,k} \sqrt{p_j p_k}\, |j\rangle\langle k|\, \langle l|j\rangle\langle k|l\rangle \\ &= \sum_{l,j,k} \sqrt{p_j p_k}\, |j\rangle\langle k|\, \delta_{lj}\delta_{kl} \\ &= \sum_l p_l\, |l\rangle\langle l| \end{aligned} \tag{B.83}$$

□

In our case, we will find the pure states of ρ_A :

- 6th eigenvalue :

$$\begin{pmatrix} \zeta & \sqrt{3} \\ \sqrt{3} & \zeta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 6 \begin{pmatrix} x \\ y \end{pmatrix} \tag{B.84}$$

$$\begin{aligned} &\Rightarrow \quad \zeta x + \sqrt{3} y = 6x \\ &\Rightarrow \quad x = \sqrt{3} y \end{aligned} \tag{B.85}$$

$$\text{Norm}: \; 3y^2 + y^2 = 1 \quad \Rightarrow \quad \begin{cases} y = \frac{1}{2} \\ x = \frac{\sqrt{3}}{2} \end{cases}$$

- second eigenvalue :

$$\begin{pmatrix} \zeta & \sqrt{3} \\ \sqrt{3} & \zeta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = 2 \begin{pmatrix} x \\ y \end{pmatrix} \tag{B.86}$$

$$\begin{aligned} &\Rightarrow \quad \zeta x + \sqrt{3} y = 2x \\ &\Rightarrow \quad y = -\sqrt{3} x \end{aligned} \tag{B.87}$$

$$\text{Norm}: \; x^2 + 3x^2 = 1 \quad \Rightarrow \quad \begin{cases} x = \frac{1}{2} \\ y = -\frac{\sqrt{3}}{2} \end{cases}$$

The state in question is thus

$$|\psi\rangle = \sqrt{\frac{3}{4}}\,|\varphi_1\rangle \otimes |\varphi_1\rangle + \sqrt{\frac{1}{4}}\,|\varphi_2\rangle \otimes |\varphi_2\rangle\,, \tag{B.88}$$

In which

$$\begin{aligned} |\varphi_1\rangle &= \frac{\sqrt{3}}{2}|+\rangle + \frac{1}{2}|-\rangle, \\ |\varphi_2\rangle &= \frac{1}{2}|+\rangle - \frac{\sqrt{3}}{2}|-\rangle. \end{aligned} \tag{B.89}$$

Finally, we obtain

$$\begin{aligned} |\psi\rangle =& \frac{\sqrt{3}}{2}\left(\frac{\sqrt{3}}{2}|+\rangle + \frac{1}{2}|-\rangle\right) \otimes \left(\frac{\sqrt{3}}{2}|+\rangle + \frac{1}{2}|-\rangle\right) \\ &+ \frac{1}{2}\left(\frac{1}{2}|+\rangle - \frac{\sqrt{3}}{2}|-\rangle\right) \otimes \left(\frac{1}{2}|+\rangle - \frac{\sqrt{3}}{2}|-\rangle\right) \\ =& \frac{1}{8}\left[(3\sqrt{3}+1)|++\rangle + (3-\sqrt{3})|+-\rangle + (3-\sqrt{3})|-+\rangle + (3+\sqrt{3})|--\rangle\right]. \end{aligned} \tag{B.90}$$

3. This state is not unique. See form example that

$$|\psi'\rangle = \sqrt{\frac{3}{4}}|\varphi_1\rangle \otimes |\varphi_2\rangle + \sqrt{\frac{1}{4}}|\varphi_2\rangle \otimes |\varphi_1\rangle \tag{B.91}$$

gives the same matrix if we take partial trace relative to B :

$$\begin{aligned} |\psi'\rangle =& \frac{\sqrt{3}}{2}\left(\frac{\sqrt{3}}{2}|+\rangle + \frac{1}{2}|-\rangle\right) \otimes \left(\frac{1}{2}|+\rangle - \frac{\sqrt{3}}{2}|-\rangle\right) \\ &+ \frac{1}{2}\left(\frac{1}{2}|+\rangle - \frac{\sqrt{3}}{2}|-\rangle\right) \otimes \left(\frac{\sqrt{3}}{2}|+\rangle + \frac{1}{2}|-\rangle\right) \\ =& \frac{1}{8}\left[(3\sqrt{3}+1)|++\rangle - (3\sqrt{3}-1)|+-\rangle + (\sqrt{3}-3)|-+\rangle + (3+\sqrt{3})|--\rangle\right]. \end{aligned} \tag{B.92}$$

Exercise 12 : Perturbed Harmonic Oscillator

1. We can directly use the formula seen in the course for a constant perturbation V that is turned on at $t = 0$:

$$P_{0\to n} = \frac{4|\langle n|\hat{V}|0\rangle|^2}{\hbar^2 n^2 \omega^2} \sin^2\left(\frac{n\omega t}{2}\right). \tag{B.93}$$

Since $V = \hbar\gamma(\hat{a}^2 + \hat{a}^{\dagger 2})$, it is impossible to create two quanta from the state $|0\rangle$. So, the only possible final state at the 1st order of perturbation is the state $n = 2$.

In the limit $t \to +\infty$, we have

$$\begin{aligned} P_{0\to 2} =& \frac{2\pi}{\hbar} t\delta(2\hbar\omega - 0)|\langle 2|\hat{V}|0\rangle|^2 \\ =& 0. \qquad \text{due to the Dirac delta} \end{aligned} \tag{B.94}$$

Therefore, in this limit, the 1st order theory predicts that the system will be in the ground state of $\hat{H}_0$, $|0\rangle$.

2. In part 1, we have seen that the only state directly connected to $|0\rangle$ by $\hat{V}$ is $|2\rangle$.

   Since the variational principle is based on the calculation of the matrix element $\langle 0'|\left(\hat{H}_0+\hat{V}\right)|0'\rangle$, we only need to include the state $|2\rangle$ in the variational ansatz:

$$|0'\rangle = |0\rangle + \alpha\,|2\rangle\,. \tag{B.95}$$

   This state is not normalized, which needs to be taken into account later. We will minimize the expression of the energy:

$$E(\alpha) = \frac{\langle 0'|\left(\hat{H}_0+\hat{V}\right)|0'\rangle}{\langle 0'|0'\rangle}. \tag{B.96}$$

$$\begin{aligned}\hat{H}_0\,|0'\rangle =& \hat{H}_0\,|0\rangle + \alpha\hat{H}_0\,|2\rangle \\ =& 2\hbar\omega\alpha\,|2\rangle\,,\end{aligned} \tag{B.97}$$

$$\begin{aligned}\hat{V}\,|0'\rangle =& \hbar\gamma(\hat{a}^2+\hat{a}^{\dagger 2})(|0\rangle+\alpha\,|2\rangle) \\ =& \sqrt{2}\hbar\gamma\alpha\,|0\rangle + \sqrt{2}\hbar\gamma\,|2\rangle + \sqrt{12}\hbar\gamma\alpha\,|4\rangle\,.\end{aligned} \tag{B.98}$$

   The last component is proportional to $|4\rangle$ and does not play any role in the matrix element and can be neglected.

$$\begin{aligned}E(\alpha) =& \frac{\sqrt{2}\hbar\gamma\alpha + \sqrt{2}\hbar\gamma\alpha + 2\hbar\omega\alpha^2}{1+\alpha^2} \\ =& \frac{2\sqrt{2}\hbar\gamma\alpha + 2\hbar\omega\alpha^2}{1+\alpha^2}.\end{aligned} \tag{B.99}$$

   Let us look for extremal values

$$\begin{aligned}\frac{dE}{d\alpha} =& \frac{2\sqrt{2}\hbar\gamma + 4\hbar\omega\alpha}{1+\alpha^2} - \frac{2\alpha(2\sqrt{2}\hbar\gamma\alpha + 2\hbar\omega\alpha^2)}{(1+\alpha^2)^2} \\ =& \frac{-2\sqrt{2}\hbar\gamma\alpha^2 + 4\hbar\omega\alpha + 2\sqrt{2}\hbar\gamma}{(1+\alpha^2)^2}.\end{aligned} \tag{B.100}$$

   The condition $\frac{dE}{d\alpha} = 0$ can be translated by:

$$\begin{aligned}& \sqrt{2}\gamma\alpha^2 - 2\omega\alpha - \sqrt{2}\gamma = 0 \\ \Rightarrow\quad & \alpha^2 - \sqrt{2}\frac{\omega}{\gamma}\alpha - 1 = 0 \\ \Rightarrow\quad & \alpha = \frac{\omega}{\sqrt{2}\gamma} \pm \sqrt{\frac{\omega^2}{2\gamma^2}+1}.\end{aligned} \tag{B.101}$$

   In the limit $\gamma \ll \omega$,

$$\begin{aligned}\alpha &= \frac{\omega}{\sqrt{2}\gamma} \pm \frac{\omega}{\sqrt{2}\gamma}\sqrt{1+\frac{2\gamma^2}{\omega^2}} \\ &\simeq \frac{\omega}{\sqrt{2}\gamma} \pm \frac{\omega}{\sqrt{2}\gamma}\left(1+\frac{\gamma^2}{\omega^2}\right) \\ &= \begin{cases} \sqrt{2}\frac{\omega}{\gamma} + \frac{\gamma}{\sqrt{2}\omega}. \\ -\frac{1}{\sqrt{2}}\frac{\gamma}{\omega} \end{cases}\end{aligned} \tag{B.102}$$

Following the suggestion, it is clear that the solution that minimizes $E(\alpha)$ is $\alpha \simeq -\frac{1}{\sqrt{2}}\frac{\gamma}{\omega}$, so $|0'\rangle = |0\rangle - \frac{1}{\sqrt{2}}\frac{\gamma}{\omega}|2\rangle$, and

$$E(-\frac{1}{\sqrt{2}}\frac{\gamma}{\omega}) = -\hbar\frac{\gamma^2}{\omega} + \mathcal{O}\left(\frac{\gamma^4}{\omega^3}\right). \tag{B.103}$$

We can neglect the denominator since $\frac{1}{1+\alpha^2} \simeq 1-\alpha^2$, ad the term in α^2 will dominate the correction in order superior to α.

We find that $\min(E(\alpha)) < 0$, which is the unperturbed energy.

3. The variational approach provides an approximate result that includes all orders of perturbation in $\hat{V}$. Thus, we observe that $|0'\rangle \neq |0\rangle$.

   In the first point, we described the exam same physical situation in the limit $t \to +\infty$, but the theory at 1st order predicts that the fundamental states stays that of $\hat{H}_0$, that is $|0\rangle$.

B.5 2018 exam

Exercise 13 : 2 sites sing model with transverse field

1. We have
$$\hat{H} = -J\hat{\sigma}_1^z\hat{\sigma}_2^z - h\hat{\sigma}_1^x - h\hat{\sigma}_2^x$$
Expressed in basis $\{|--\rangle, |+-\rangle, |-+\rangle, |++\rangle\}$, we get
$$\hat{H} = -J\begin{pmatrix}-1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&-1\end{pmatrix} - h\begin{pmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{pmatrix} - h\begin{pmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{pmatrix} = \begin{pmatrix}-J&-h&-h&0\\-h&J&0&-h\\-h&0&J&-h\\0&-h&-h&-J\end{pmatrix}$$

2. With ansatz
$$|\Psi_0\rangle = |--\rangle + \alpha|+-\rangle + \alpha|-+\rangle + |++\rangle, \quad \alpha \in \mathbb{R}$$
we get
$$\langle\Psi_0|\hat{H}|\Psi_0\rangle = \begin{pmatrix}1&\alpha&\alpha&1\end{pmatrix}H\begin{pmatrix}1\\\alpha\\\alpha\\1\end{pmatrix} = \begin{pmatrix}1&\alpha&\alpha&1\end{pmatrix}\begin{pmatrix}-J-2h\alpha\\J\alpha-2h\\J\alpha-2h\\-J-2h\alpha\end{pmatrix} = 2(-J-2h\alpha)+2(J\alpha^2-2h\alpha)$$

and

$$\langle\Psi_0|\Psi_0\rangle = 2(1+\alpha^2)$$

thus

$$E(\alpha) = \frac{\langle\Psi_0|\,\hat{H}\,|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle} = \frac{J\alpha^2 - 4h\alpha - J}{1+\alpha^2}$$

we derive

$$\frac{dE(\alpha)}{d\alpha} = \frac{2J\alpha - 4h}{1+\alpha^2} - \frac{2\alpha(J\alpha^2 - 4h\alpha - J)}{(1+\alpha^2)^2} = \frac{4h\alpha^2 + 4J\alpha - 4h}{(1+\alpha^2)^2}$$

We then have

$$\frac{dE}{d\alpha} = 0 \Rightarrow h\alpha^2 + J\alpha - h = 0$$

deducing α:

$$\alpha = \frac{-J \pm \sqrt{J^2 + (sh)^2}}{2h} = -\beta \pm \sqrt{\beta^2+1}$$

with $\beta = \frac{J}{2h}$.

We then compute α^2

$$\alpha^2 = \beta^2 \mp 2\beta\sqrt{\beta^2+1} + \beta^2 + 1 = 2\beta^2 \mp 2\beta\sqrt{\beta^2+1} + 1$$

replacing the new expression in $E(\alpha)$

$$E(\alpha) = \frac{2J\beta^2 \mp 2J\beta\sqrt{\beta^2+1} + J + 4h\beta \mp 4h\sqrt{\beta^2+1} - J}{2(\beta^2 \mp \beta\sqrt{\beta^2+1} + 1)} = \frac{2J\beta(\beta \mp \sqrt{\beta^2+1}) + 4h(\beta \mp \sqrt{\beta^2+1})}{2\sqrt{\beta^2+1}(\sqrt{\beta^2+1} \mp \beta)}$$

For "-", we have

$$E(\alpha) = -\frac{J\beta + 2h}{\sqrt{\beta^2+1}}$$

and for "+"

$$E(\alpha) = \frac{J\beta + 2h}{\sqrt{\beta^2+1}}$$

Since $J, h > 0$, the fundamental state corresponds to $\alpha = -\beta + \sqrt{\beta^2+1}$.

3. We have

$$E(\alpha) = -\frac{(\frac{J^2}{2h} + 2h)}{\sqrt{\frac{J^2}{(2h)^2} + 1}} = -\frac{J^2 + 4h^2}{\sqrt{J^2 + 4h^2}} = -\sqrt{J^2 + 4h^2} = E_0$$

4. The exact fundamental state is given by

$$\begin{pmatrix} -J & -h & -h & 0 \\ -h & J & 0 & -h \\ -h & 0 & J & -h \\ 0 & -h & -h & -J \end{pmatrix} \begin{pmatrix} 1 \\ \alpha_m \\ \alpha_m \\ 1 \end{pmatrix} = \begin{pmatrix} -J - 2h\alpha_m \\ J\alpha_m - 2h \\ J\alpha_m - 2h \\ -J - 2h\alpha_m \end{pmatrix}$$

We can then compute

$$\begin{aligned} -J - 2h\alpha_m &= -J - 2h(-\frac{J}{2h} + \sqrt{\frac{J^2}{(2h)^2} + 1} \\ &= -J + J - \sqrt{J^2 + (2h)^2} \\ &= -\sqrt{J^2 + (2h)^2} = E_0 \end{aligned}$$

and

$$\begin{aligned} J\alpha_m - 2h &= -\frac{J^2}{2h} + \frac{J}{2h}\sqrt{J^2+(2h)^2} - 2h \\ &= \frac{-J^2 + J\sqrt{J^2+(2h)^2} - 2h}{2h} \\ &= -\frac{J^2+(2h)^2 - J\sqrt{J^2+(2h)^2}}{2h} \\ &= -\sqrt{J^2+(2h)^2}\left(\frac{-J+\sqrt{J^2+(2h)^2}}{2h}\right) = E_0\alpha_m \end{aligned}$$

Thus $\hat{H}\,|\Psi_0\rangle = E_0\,|\Psi_0\rangle$. For the most general state,

$$a\,|--\rangle + b\,|-+\rangle + c\,|+-\rangle + d\,|++\rangle$$

IIt is evident that we must have $b = c$ and $a = d$ since $\hat{H}$ is even under exchange $1 \Leftrightarrow 2$. A coefficient is found by normalization, and all that is left is one free parameter.

Exercise 14 : Entanglement entropy in the transverse Ising model

Going from

$$|\psi_0(\alpha_m)\rangle = \frac{|--\rangle + \alpha_m\,|+-\rangle + \alpha_m\,|-+\rangle + |++\rangle}{\sqrt{2(\alpha_m^2+1)}},$$

and

$$S = \mathrm{Tr}(\hat{\rho}_1(\ln\hat{\rho}_1)) \qquad\qquad \hat{\rho}_1 = \mathrm{Tr}_2(\hat{\rho})$$

1. we know that

$$|\psi_0\rangle = \frac{1}{N}\begin{pmatrix}1\\ \alpha\\ \alpha\\ 1\end{pmatrix}$$

So

$$|\psi_0\rangle\langle\psi_0| = \frac{1}{N^2}\begin{pmatrix}1 & \alpha & \alpha & 1\\ \alpha & \alpha^2 & \alpha^2 & \alpha\\ \alpha & \alpha^2 & \alpha^2 & \alpha\\ 1 & \alpha & \alpha & 1\end{pmatrix}$$

2. We calculate

$$\begin{aligned} \hat{\rho}_1 &= \langle -_2|\,\hat{\rho}\,|-_2\rangle + \langle +_2|\,\hat{\rho}\,|+_2\rangle \\ &= \frac{1}{N^2}\begin{pmatrix}1 & \alpha\\ \alpha & \alpha^2\end{pmatrix} + \frac{1}{N^2}\begin{pmatrix}\alpha^2 & \alpha\\ \alpha & 1\end{pmatrix} = \frac{1}{2(\alpha^2+1)}\begin{pmatrix}1+\alpha^2 & 2\alpha\\ 2\alpha & 1+\alpha^2\end{pmatrix} \\ &= \begin{pmatrix}\frac{1}{2} & \frac{\alpha}{1+\alpha^2}\\ \frac{\alpha}{1+\alpha^2} & \frac{1}{2}\end{pmatrix} \end{aligned}$$

3. We now have

$$S = \mathrm{Tr}[\hat{\rho}_1\ln(\hat{\rho}_1)]$$

if $\hat{\rho}_1 \sum_j p_j |j\rangle\langle j|$, then $S = \sum_j \eta_j \ln \eta_j$. We can calculate the eigenvalues:

$$(\frac{1}{2} - \eta)^2 - \frac{\alpha^2}{(1+\alpha^2)^2} = 0$$

$$\frac{1}{2} - \eta = \pm \frac{\alpha}{1+\alpha^2}$$

So

$$\eta = \frac{1}{2} \mp \frac{\alpha}{1+\alpha^2}$$

which we write

$$\eta_1 = \frac{(\alpha+1)^2}{2(1+\alpha^2)} \eta_2 = \frac{(\alpha-1)^2}{2(1+\alpha^2)}$$

We thus have

$$\ln \eta_1 = 2\ln[\alpha+1] - \ln[2(1+\alpha^2)]$$
$$\ln \eta_2 = 2\ln[\alpha-1] - \ln[2(1+\alpha^2)]$$

We can then calculate S:

$$S = \frac{(\alpha+1)^2}{1+\alpha^2} \ln[\alpha+1] - \frac{(\alpha+1)^2}{2(1+\alpha^2)} \ln[2(1+\alpha^2)] + \frac{(\alpha-1)^2}{1+\alpha^2} \ln[\alpha-1] - \frac{(\alpha-1)^2}{2(1+\alpha^2)} \ln[2(1+\alpha^2)]$$

4. we wrote

$$\alpha = -\frac{J}{2h} + \sqrt{\frac{J^2}{4h^2} + 1}$$

a $\frac{J}{h} \to \infty$

$$\alpha \to 0 \Rightarrow \eta_1 = \frac{1}{2},\ \eta_2 = \frac{1}{2}$$

$$S = \frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} = -\ln 2$$

b $\frac{J}{h} \to 0$ we have $\sqrt{1+x^2} \approx 1 + \frac{x^2}{2} + \cdots$ and $\alpha \to 1$

$$\eta_1 = 1,\ \eta_2 = 0 \Rightarrow S = 0$$

When the interaction tends to infinity, the system is entirely entangled. When the interaction is null, the state becomes separable.

Exercise 15 : Vibration modes of a triangular molecule

In the symmetry group D_{3h}, we have the following elements:

- Identity
- Both C_3 rotations around $\hat{z}$
- All 3 C_2 rotations around the 3-axis linking the vertex to the center of the opposite edges.
- The mirror σ_h

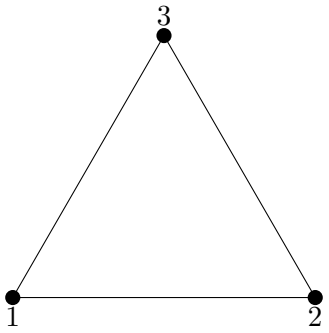
- S_3: C_3 and σ_h
- σ_v

Each atom can move in $\mathbb{R}^3$, we thus have $\dim(\Gamma) = 9$

1. Let us calculate the characters of Γ We start by determining the representation associated to the permutation of the 3 vertex, Γ_v:
   - $\Gamma_v(e) = \mathbb{1}_3 \Rightarrow \chi_v(e) = 3$ avec

     $$1 : \begin{pmatrix}1\\0\\0\end{pmatrix} \qquad 2 : \begin{pmatrix}0\\1\\0\end{pmatrix} \qquad 3 : \begin{pmatrix}0\\0\\1\end{pmatrix}$$

     for the triangle

   - Rotations C_3

     $$\left.\begin{aligned}\Gamma_v(C_3) &= \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\\ \Gamma_v(C_3^{-1}) &= \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}\end{aligned}\right\} \chi_v(C_3) = 0$$

   - Rotations C_2

     $$\left.\begin{aligned}\Gamma_v(C_2^{(1)}) &= \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\\ \Gamma_v(C_2^{(2)}) &= \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\\ \Gamma_v(C_2^{(3)}) &= \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\end{aligned}\right\} \chi_v(C_2) = 1$$

   - Mirror σ_h: $\Gamma_v(\sigma_h) = \mathbb{1}_3 \Rightarrow \chi_v(\sigma_h) = 3$
   - Improper rotations S_3.

     $$\Gamma_v(\sigma_h)\Gamma_v(C_3) = \mathbb{1}\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} = \Gamma_\sigma(C_3) \Rightarrow \chi_v(S_3) = \chi_v(C_3) = 0$$

- σ_v: $\Gamma_v(\sigma_2^{(i)}) = \Gamma_v(C_2^{(i)}) \Rightarrow \chi_v(\sigma_2^{(i)}) = \chi_v(C_2^{(i)})$

And determine the representations generated by displacement vector $\mathbf{r} = (x, y, z)$.

- $\Gamma_r(e) = \mathbb{1}_S$
- Rotations C_3

$$\Gamma_r(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \chi_r(C_3) = 0$$

$$\Gamma_r(C_3^{-1}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- Rotations C_2

$$\Gamma_r(C_2^{(1)}) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

- Mirror σ_h

$$\Gamma_r(\sigma_h) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

- S_3:

$$\Gamma_r(S_3) = \Gamma_r(\sigma_h), \Gamma_r(C_3) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

- $\Gamma_r(\sigma_v^{(1)}) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$

$\Gamma = \Gamma_r \otimes \Gamma_v$

$$\begin{aligned} \mathrm{Tr}(\Gamma_r \otimes \Gamma_v) &= \sum_{i_v} \sum_{i_r} \langle i_r | \otimes \langle i_v | \Gamma_r \otimes \Gamma_v | i_r \rangle \otimes | i_v \rangle \\ &= \sum_{i_r} \langle i_r | \Gamma_r | i_r \rangle \sum_{i_v} \langle I_v | \Gamma_v | i_v \rangle = \mathrm{Tr}(\Gamma_r) \cdot \mathrm{Tr}(\Gamma_v) \end{aligned}$$

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_v	3	0	1	3	0	1
Γ_r	3	0	−1	1	−2	1
Γ	9	0	−1	3	0	1

2. We can then determine the decomposition of Γ in irreducible representations.

$$\Gamma = b_1\Gamma^{(1)} + b_2\Gamma^{(2)} + b_3\Gamma^{(3)} + b_4\Gamma^{(4)} + b_5\Gamma^{(5)} + b_6\Gamma^{(6)}$$

center of mass translation: $\Gamma^{(3)}$, $\Gamma^{(5)}$.

	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	9	0	−1	3	0	1
$\ominus\Gamma^{(1)}$	8	−1	−2	2	−1	0
$\ominus\Gamma^{(3)}$	6	0	−2	0	0	0
$\ominus\Gamma^{(5)}$	5	−1	−1	1	1	−1
$\ominus\Gamma^{(6)}$	3	0	−1	3	0	−1
$\Gamma^{(3)} + \Gamma^{(2)}$	3	0	−1	3	0	−1

we then get

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus 2\Gamma^{(3)} \oplus \Gamma^{(5)} \oplus \Gamma^{(6)}$$

Alternatively, we can use equation

$$b_a = \frac{1}{N} \sum_{\mu}^{N_c} n_\mu \chi_a^*(C_\mu)\chi(C_\mu)$$

with $N = 12$, and find

$$b_1 = 1 \quad b_2 = 1 \quad b_3 = 2 \quad b_4 = 0 \quad b_5 = 1 \quad b_6 = 1$$

3. The basis functions associated with the center of mass are $\mathbf{r} = (x, y, z)$. We can see from the table that the corresponding representations are $\Gamma^{(3)}$ and $\Gamma^{(5)}$.

4. Rigid rotations transform like the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, i.e., under rotations R_x, R_y, R_z. Thus, the associated representations are $\Gamma^{(2)}$ and $\Gamma^{(6)}$.

5. $\Gamma^{(1)}$ and $\Gamma^{(3)}$ remain. Therefore, there exists a non-degenerate mode associated with $\Gamma^{(1)}$ and two degenerate modes associated with $\Gamma^{(3)}$.

B.6 2019 Exam

Exercise 16 : Harmonic oscillator in external field (15/50 points)

1. The states with $N = 1$ are $|a\rangle = |0, 1\rangle$ and $|b\rangle = |1, 0\rangle$. Therefore, the question is whether the two-dimensional space generated by these states corresponds to an irreducible representation of dimension 2 of D_4 or to two irreducible representations of dimension 1. We have

$$\langle x|a\rangle = \phi_0(x)\phi_1(y)$$
$$\langle x|b\rangle = \phi_1(x)\phi_0(y)$$

with

$$\phi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}} \left(X - \frac{\partial}{\partial X}\right)^n (\exp\left(-\frac{X^2}{2}\right))$$

where $X = \sqrt{\frac{m\omega}{\hbar}}x$. So

$$\begin{aligned}
\phi_0(x) &= \left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega x^2}{2\hbar}\right) = C_0 \exp\left(-\frac{m\omega x^2}{2\hbar}\right) \\
\phi_1(x) &= \frac{1}{\sqrt{2}}\left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}}\left(X - \frac{\partial}{\partial X}\right)\left(\exp\left(-\frac{X^2}{2}\right)\right) = C_1(Xe^{-\frac{X^2}{2}} + Xe^{-\frac{X^2}{2}}) \\
&= \left(\frac{mw}{\pi\hbar}\right)^{\frac{1}{4}}\left(\frac{2mw}{\hbar}\right)^{\frac{1}{2}} xe^{-\frac{m\omega x^2}{2\hbar}} \\
\Rightarrow \phi_0(x)\phi_1(y) &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\sqrt{\frac{2m\omega}{\hbar}} ye^{-\frac{m\omega}{2\hbar}(x^2+y^2)} \\
\phi_1(x)\phi_0(y) &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\sqrt{\frac{2m\omega}{\hbar}} xe^{-\frac{m\omega}{2\hbar}(x^2+y^2)}
\end{aligned}$$

Yet $(x^2 + y^2)$ is D_5 invariant. Furthermore, (x, y) transforms under E_1, which is a representation of dimension 2. Degeneracy is thus not lifted.

Alternative method Representation on (x, y)

- Representation on $\{(1, 0), (0, 1)\}$

$$\begin{aligned}
\Gamma_2(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
\Gamma_2(C_5) &= \begin{pmatrix} \cos(2\pi/5 =) & -\sin(2\pi/5) \\ \sin(2\pi/5) & \cos(2\pi/5) \end{pmatrix} \\
\Gamma(C_5^{-1}) &= \begin{pmatrix} \cos(2\pi/5) & \sin(2\pi/5) \\ -\sin(2\pi/5) & \cos(2\pi/5) \end{pmatrix} \\
\Gamma_2(C_5^2) &= \begin{pmatrix} \cos(4\pi/5) & -\sin(4\pi/5) \\ \sin(4\pi/5) & \cos(4\pi/5) \end{pmatrix} \\
\Gamma_2(C_2') &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}
\end{aligned}$$

- $\Rightarrow$ Representation on $\psi(x, y)$:

$$\begin{aligned}
\Gamma_f(E)\psi(x,y) &= \psi(\Gamma_2(E^{-1})\begin{pmatrix} x \\ y \end{pmatrix}) = \psi(x,y) \\
\Gamma_f(C_5)\psi(x,y) &= \psi(\Gamma_2(C_5^{-1})\begin{pmatrix} x \\ y \end{pmatrix}) = \psi(x\cos\alpha + y\sin\alpha, -x\sin\alpha + y\cos\alpha) \\
\Gamma_f(C_5)\psi(x,y) &= \psi(x\cos(2\alpha) + y\sin(2\alpha), -\alpha\sin(2\alpha + y\cos(2\alpha)) \\
\Gamma_f(C_2')\psi(x,y) &= \psi(-x,y)
\end{aligned}$$

with $\alpha = 2\pi/5$.

- In bais $\{|10\rangle, |01\rangle\} \propto \{xe^{-\beta(x^2+y^2)}, ye^{-\beta(x^2+y^2)}\}$.

$$\Gamma_f(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$
$$\Gamma_f(C_5) = \begin{pmatrix} \cos(\alpha) & * \\ * & \cos(\alpha) \end{pmatrix} \to 2\cos\alpha$$
$$\Gamma_f(C_5^2) = \begin{pmatrix} \cos(2\alpha) & * \\ * & \cos(2\alpha) \end{pmatrix} \to 2\cos(2\alpha)$$
$$\to \Gamma_f = E_1$$

2. For $N = 2$, we have $\{|02\rangle, |11\rangle, |20\rangle\}$ and

$$\left(X - \frac{\partial}{\partial X}\right)\left(2X\exp\left(-\frac{X^2}{2}\right)\right) = \left(2X^2\exp\left(-\frac{-X^2}{2}\right) - \left[2\exp\left(-\frac{-X^2}{2}\right) + 2X(-X)\exp\left(-\frac{X^2}{2}\right)\right]\right)$$
$$= \left(4X^2\exp\left(-\frac{X^2}{2}\right) - 2\exp\left(-\frac{X^2}{2}\right)\right)$$
$$\Rightarrow \phi_2(x) = \frac{1}{2\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(4\frac{m\omega x^2}{\hbar} - 2\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$
$$= \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(2\frac{m\omega x^2}{\hbar} - 1\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

So we have

$$|02\rangle : \phi_0(x)\phi_2(y) = \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\left(\frac{2m\omega}{\hbar}y^2 - 1\right)\exp\left(-\frac{m\omega}{2\hbar}(x^2+y^2)\right)$$
$$|11\rangle : \phi_1(x)\phi_1(y) = \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{2}} xy\exp\left(-\frac{m\omega}{2\hbar}(x^2+y^2)\right)$$
$$|20\rangle : \phi_2(x)\phi_0(y) = \frac{1}{\sqrt{2}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}}\left(\frac{2m\omega}{\hbar}x^2 - 1\right)\exp\left(-\frac{m\omega}{2\hbar}(x^2+y^2)\right)$$

Since $x^2 + y^2$ transforms under $A_4 \Rightarrow |20\rangle + |02\rangle$ is distinct from $|11\rangle$ and $|20\rangle - |02\rangle$. $(x^2 - y^2, xy)$ transform together under E_2. The degeneracy is only partially lifted; $\{|11\rangle, |20\rangle - |02\rangle\}$ belong to the same representation, which has 1 non-degenerate state and 2 degenerate states.

Alternative method N.B: This time the functions $\{(\mu x^2 - 1)e^{-\beta(x^2+y^2)}, xye^{-\beta(x^2+y^2)}, (\mu y^2 - 1)e^{-\beta(x^2+y^2)}\}$ are not orthogonal. Therefore, we need to start by choosing an appropriate basis. For example:

$$\{(x^2+y^2)e^{-\beta(x^2+y^2)}, xye^{-\beta(x^2+y^2)}, (x^2-y^2)e^{-\beta(x^2+y^2)}\}$$

Indeed,

$$(x^2+y^2)(x^2-y^2) = x^4 - y^4$$
$$\Rightarrow \int dxdy(x^2+y^2)e^{-\beta(x^2+y^2)}(x^2-y^2)e^{-\beta(x^2+y^2)} = 0$$

In this basis...

$$\Gamma_f(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma_f(C_5) = \begin{pmatrix} 1 & * & * \\ * & 2\cos(\alpha) & * \\ * & * & 2\cos(\alpha) \end{pmatrix}$$

$$\Gamma_f(C_5^2) = \begin{pmatrix} 1 & * & * \\ * & \cos(\alpha) & * \\ * & * & \cos(\alpha) \end{pmatrix}$$

$$\Gamma_f(C_2') = \begin{pmatrix} 1 & * & * \\ * & -1 & * \\ * & * & 1 \end{pmatrix}$$

knowing that

$$\begin{aligned} xy &\to (\cos^2(\alpha) - \sin^2(\alpha))xy = cos(2\alpha)xy \\ x^2 - y^2 &\to (\cos^2(\alpha) - \sin^2(\alpha))(x^2 - y^2) \\ xy &\to (\cos^2(2\alpha) - \sin^2(2\alpha))xy = \cos(4\alpha)xy \end{aligned}$$

3. For states with $N = 3$, we have $\{|03\rangle, |12\rangle, |21\rangle, |30\rangle\}$ and

$$\begin{aligned} &\left(X - \frac{\partial}{\partial X}\right)\left(\left(4X^2 - 2\right)\exp\left(-\frac{X^2}{2}\right)\right) \\ &= \left[\left(4X^3 - 2X\right)\exp\left(-\frac{X^2}{2}\right) - \left\{8X\exp\left(-\frac{X^2}{2}\right) - \left(4X^2 - 2\right)X\exp\left(-\frac{X^2}{2}\right)\right\}\right] \\ &= \left(8X^3 - 4X - 8X\right)\exp\left(-\frac{X^2}{2}\right) = 4\left(2X^3 - 3X\right)\exp\left(-\frac{X^2}{2}\right) \end{aligned}$$

$$\Rightarrow \phi_3(x) = \frac{1}{\sqrt{3}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(2\left(\frac{m\omega}{\hbar}\right)^{\frac{3}{2}}x^3 - 3\sqrt{\frac{m\omega}{\hbar}}x\right)\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

So

$$\begin{aligned} |03\rangle &= \phi_0(x)\phi_3(y) = \frac{1}{\sqrt{3}}\left(\frac{m\omega}{\pi\hbar}\right)y(2\frac{m\omega}{\hbar}y^2 - 3)\exp\left(-\frac{m\omega}{2\hbar}(x^2 + y^2)\right) \\ |12\rangle &= \phi_1(x)\phi_2(y) = \left(\frac{m\omega}{\pi\hbar}\right)x(2\frac{m\omega}{\hbar}y^2 - 1)\exp\left(-\frac{m\omega}{2\hbar}(x^2 + y^2)\right) \\ |21\rangle &= \phi_2(x)\phi_1(y) = \left(\frac{m\omega}{\pi\hbar}\right)y(2\frac{m\omega}{\hbar}x^2 - 1)\exp\left(-\frac{m\omega}{2\hbar}(x^2 + y^2)\right) \\ |30\rangle &= \phi_0(x)\phi_3(y) = \frac{1}{\sqrt{3}}\left(\frac{m\omega}{\pi\hbar}\right)y(2\frac{m\omega}{\hbar}y^2 - 3)\exp\left(-\frac{m\omega}{2\hbar}(x^2 + y^2)\right) \end{aligned}$$

At first perturbation order:

$$\begin{aligned} \frac{3}{\sqrt{3}}|21\rangle - |03\rangle &\propto y(3x^2 - y^2) \\ -\frac{3}{\sqrt{3}}|12\rangle + |30\rangle &\propto x(x^2 - 3y^2) \\ \Rightarrow \left\{\frac{1}{2}\left(\frac{3}{\sqrt{3}}|21\rangle - |03\rangle\right), \frac{1}{2}\left(\frac{3}{\sqrt{3}}|12\rangle + |30\rangle\right)\right\} & \end{aligned}$$

transforms under E_2 and are degenerate. then, orthogonal vectors are:

$$\begin{aligned}\frac{1}{2}\left(|21\rangle + \frac{3}{\sqrt{3}}|03\rangle\right) &\propto y\left(\frac{2m\omega}{\hbar}x^2 - 1\right) + y\left(2\frac{m\omega}{\hbar}y^2 - 3\right)\\ &= y\left(\frac{2m\omega}{\hbar}(x^2+y^2) - 4\right)\\ \frac{1}{2}\left(|12\rangle\frac{3}{\sqrt{3}}|30\rangle\right) &\propto x\left(\frac{2m\omega}{\hbar}(y^2+x^2) - 4\right)\end{aligned}$$

But, $\{x(x^2y^2), y(x^2+y^2)\}$ and $\{x, y\}$ transform under E_1. So both states are degenerate. The degeneracy is thus partially lifted towards 2 pairs of states.

lternative method Again, we start by choosing an orthogonal basis without which we couldn't take the trace. We have:

$$\{\mu y^3 - 3y, \mu x y^2 - x, \mu y x^2 - y, \mu x^3 - 3x\}$$

which is not orthongonal, so we choose

$$\{y(3x^2 - y^2), x(x^2 - 3y^2), y(\mu(x^2+y^2) - 4), x(\mu(y^2+x^2) - 4)\}$$

Then:

$$\Gamma_f(E) = \begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 1\end{pmatrix}$$

$$\Gamma_f(C_5) = \begin{pmatrix}\cos(2\alpha) & * & * & *\\ * & \cos(2\alpha) & * & *\\ * & * & \cos(\alpha) & *\\ * & * & * & \cos(\alpha)\end{pmatrix}$$

$$\Gamma_f(C_5^2) = \begin{pmatrix}\cos(\alpha) & * & * & *\\ * & \cos(\alpha) & * & *\\ * & * & \cos(2\alpha) & *\\ * & * & * & \cos(2\alpha)\end{pmatrix}$$

We then get

$$\Gamma_j = E_1 \oplus E_2$$

degeneracy is partially lifted.

Exercise 17 : Entropy of a quantum system (15/50 points)

1. We have

$$S = -\operatorname{Tr}[\hat{\rho}\ln\hat{\rho}]$$

if $\hat{\rho} = \sum_j n_j |j\rangle\langle j|$ then

$$S = -\sum_j n_j \ln n_j$$

and

$$\hat{\rho} = |\psi\rangle\langle\psi| \Rightarrow n = 1$$

and so

$$S = -1 \ln 1 = 0$$

2. we calculate

$$\frac{dS}{dt} = -\operatorname{Tr}\left[\frac{dS}{dt}\ln\hat{\rho} + \hat{\rho}\cdot\hat{\rho}^{-1}\cdot\frac{dS}{dt}\right] = -\operatorname{Tr}\left[-i[H,S]\ln\hat{\rho} - i[H,\hat{\rho}]\right]$$

but $\operatorname{Tr}[-[H,\hat{\rho}]] = 0$

$$= i\cdot\operatorname{Tr}[H\hat{\rho}\ln\hat{\rho}] - i\operatorname{Tr}[\hat{\rho}H\ln\hat{\rho}] = i\operatorname{Tr}[H\hat{\rho}\ln\hat{\rho}] - i\operatorname{Tr}[H\ln\hat{\rho}\hat{\rho}] = 0$$

where equality is due to the cyclic property of the trace.

3. In matrix form we have

$$\hat{H} = \begin{pmatrix}\omega & 0\\ 0 & -\omega\end{pmatrix}\hat{n} = \begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}$$

we substitute in the equation to obtain

$$\frac{d\hat{\rho}}{dt} = \begin{pmatrix}0 & -(\gamma/2+2i\omega)\rho_{12}\\ -(\gamma/2-2i\omega)\rho_{12}^{*} & 0\end{pmatrix}$$

solving the differential equation we get

$$\hat{\rho}(t) = \begin{pmatrix}\rho_{11} & \rho_{12}e^{-t(\gamma/2+2i\omega)}\\ \rho_{12}^{*}e^{-t(\gamma/2-2i\omega)} & \rho_{22}\end{pmatrix}$$

4. For $S = -\sum_j n_j \ln n_j$ we can diagonalize $\hat{\rho}(t)$

$$\hat{\rho}(t) = \frac{1}{2}\begin{pmatrix}\Sigma+\Omega & 0\\ 0 & \Sigma-\Omega\end{pmatrix}$$
$$\Sigma = \rho_{11}+\rho_{22}$$
$$\Omega = \sqrt{(\rho_{11}-\rho_{22})^2 + 4|\rho_{12}|^2\cdot e^{-\gamma t}}$$

for

$$\hat{\rho}(0) = |\psi\rangle\langle\psi| = \frac{1}{2}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}$$

we have

$$\hat{\rho}(t) = \begin{pmatrix}1+e^{-\gamma/2\cdot t} & 0\\ 0 & 1-e^{-\gamma/2\cdot t}\end{pmatrix}$$

then

$$S(t) = -\frac{1}{2}(1+e^{-\gamma/2\cdot t})\ln\left[\frac{1}{2}(1+e^{-\gamma/2\cdot t}\right] - -\frac{1}{2}(1-e^{-\gamma/2\cdot t})\ln\left[\frac{1}{2}(1-e^{-\gamma/2\cdot t}\right]$$

for $t\to\infty$,

$$\hat{\rho}(\infty) = \begin{pmatrix}\frac{1}{2} & 0\\ 0 & \frac{1}{2}\end{pmatrix}$$
$$S(\infty) = -\frac{1}{2}\ln\frac{1}{2} - \frac{1}{2}\ln\frac{1}{2} = \ln 2$$

Exercise 18 : Perturbed harmonic oscillator (20/50 points)

1. Hamiltonian is
$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 e^{\lambda x^2}$$
with $\lambda > 0$. We can write this hamiltonian like that of a harmonic oscillator with a perturbation.
$$H = H_0 + V(x)$$
$$H_0 = = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$
$$V(x) = \frac{1}{2}m\omega^2 x^2(e^{\lambda x^2} - 1)$$
The fundamental state of the harmonic oscillator is
$$\psi(x) = \left(\frac{\beta}{\hbar}\right)^{\frac{1}{4}} e^{-\beta\frac{x^2}{2}}$$
with $\beta = \frac{m\omega}{\hbar}$, with eigenenergy $E_0 = \frac{\hbar\omega}{2}$.

2. At 1^st order, perturbation theory gives:
$$E = E_0 + \Delta E,\ \Delta E = \langle\psi| V |\psi\rangle$$
$$\langle\psi| V |\psi\rangle = \sqrt{\frac{\beta}{\hbar}}\frac{1}{2}m\omega^2 \int_{-\infty}^{\infty} dx x^2(e^{\lambda x^2} - 1)e^{-\beta x^2}$$
but $\int_{-\infty}^{\infty} dx e^{-\beta x^2} = \sqrt{\frac{\pi}{\beta}}$ and so
$$\frac{d}{d\beta}\int_{-\infty}^{\infty} dx e^{-\beta x^2} = -\int_{-\infty}^{\infty} dx x^2 e^{-\beta x^2} = \frac{d}{d\beta}\sqrt{\frac{\pi}{\beta}} = \frac{\sqrt{\pi}}{2\beta^{3/2}}$$
so
$$\int_{-\infty}^{\infty} dx x^2 e^{-\beta x^2} = \frac{\sqrt{\pi}}{2\beta^{3/2}}$$
Then
$$\langle\psi| V |\psi\rangle = \sqrt{\frac{\beta}{\pi}}\frac{1}{2}m\omega^2\frac{\sqrt{\pi}}{2}\left[\frac{1}{(\beta-\lambda)^{3/2}} - \frac{1}{\beta^{3/2}}\right] = \frac{m\omega^2}{4}\left[\sqrt{\frac{\beta}{(\beta-\lambda)^3}} - \frac{1}{\beta}\right] = \frac{m\omega^2}{4}\sqrt{\frac{\beta}{(\beta-\lambda)^3}} - \frac{\hbar\omega}{4}$$
We use now $\lambda \ll \beta$ in the series expansion.
$$\sqrt{\frac{\beta}{(\beta-\lambda)^3}} = \frac{1}{\beta}\sqrt{\left(1-\frac{\lambda}{\beta}\right)^{-3}} \approx \frac{1}{\beta}\sqrt{1+\frac{3\lambda}{\beta}} = \frac{1}{\beta}\left(1+\frac{3\lambda}{2\beta}\right)$$
so
$$\langle\psi| V |\psi\rangle = \frac{m\omega^2}{4}\sqrt{\frac{\beta}{(\beta-\lambda)^3}} - \frac{\hbar\omega}{4} \approx \frac{\hbar\omega}{4}\left(1+\frac{3\hbar\lambda}{2m\omega}\right) - \frac{\hbar\omega}{4} = \frac{3\hbar^2\lambda}{8m}$$
and
$$E = E = \Delta V = \frac{\hbar\omega}{2} + \frac{3\hbar^2\lambda}{8m}$$

3. Variational theory: β is the variational parameter, suppose $\lambda \ll \beta$ and $\lambda \ll \frac{m\omega}{\hbar}$. We already know $\langle\psi| V |\psi\rangle$ as function of β. Calculate the average kinetic energy on sur $\psi(x)$.

$$\begin{aligned}
\frac{d\psi}{dx} &= \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} \left(-\beta x e^{-\beta x^2/2}\right) \\
\frac{d^2\psi}{dx^2} &= \left(\frac{\beta}{\pi}\right)^{\frac{1}{4}} \left(\beta^2 x^2 - \beta\right) e^{-\beta x^2/2} \\
\langle\psi| T |\psi\rangle &= -\frac{\hbar^2}{2m}\sqrt{\frac{\beta}{\pi}}\beta \int_{-\infty}^{\infty} dx(\beta x^2 - 1)e^{-\beta x^2} \\
&= -\frac{\hbar^2}{2m}\left(\sqrt{\frac{\beta}{\pi}}\beta^2 \int_{\infty}^{\infty} dx x^2 e^{-\beta x^2} - \beta\right) \\
&= -\frac{\hbar^2}{2m}\left(\sqrt{\frac{\beta}{\pi}}\beta^2 \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}} - \beta\right) \\
&= -\frac{\hbar}{2m}\left(-\frac{\beta}{2}\right) = \frac{\hbar^2\beta}{4m}
\end{aligned}$$

and

$$\begin{aligned}
E(\beta) &= \frac{\hbar^2}{4m}\beta + \frac{m\omega^2}{4}\sqrt{\frac{\beta}{(\beta-\lambda)^3}} \\
&\approx \frac{\hbar^2}{4m}\beta + \frac{m\omega^2}{4}\frac{1}{\beta}\left(1 + \frac{3\lambda}{2\beta}\right) \\
\frac{dE(\beta)}{d\beta} &= \frac{\hbar^2}{4m} - \frac{m\omega^2}{4}\frac{1}{\beta} - \frac{3m\omega^2}{4}\frac{\lambda}{\beta^3} \\
&= \frac{\hbar^2}{4m} - \frac{m\omega^2}{4\beta^2}\left(1 + \frac{3\lambda}{\beta}\right) \\
\frac{dE}{d\beta} = 0 &\Rightarrow \frac{\hbar^2\beta^2}{m\omega^2} = \left(1 + \frac{3\lambda}{\beta}\right) \\
\frac{\hbar\beta}{m\omega} &= \sqrt{1 + \frac{3\lambda}{\beta}} \approx 1 + \frac{3\lambda}{2\beta} \\
\frac{\hbar}{m\omega}\beta^2 &= \beta - \frac{3\lambda}{2} = 0 \\
\beta &= \frac{1 \pm \sqrt{1 + \frac{6\hbar\lambda}{m\omega}}}{\frac{2\hbar}{m\omega}}
\end{aligned}$$

Only the solution with "+" is valid, as $\beta > 0$

$$\begin{aligned}
\beta =\approx & \frac{m\omega}{2\hbar} + \frac{m\omega}{2\hbar}\left(1 + \frac{3\hbar\lambda}{m\omega}\right) = \frac{m\omega}{\hbar} + \frac{3\lambda}{2} \\
E(\beta) = & \frac{\hbar\omega}{4} + \frac{3\hbar^2}{8m}\lambda + \frac{m\omega^2}{4}\frac{1}{\frac{m\omega}{\hbar} + \frac{3\lambda}{2}}\left(1 + \frac{3\lambda}{2\frac{m\omega}{\hbar}}\right) \\
= & \frac{\hbar\omega}{4} + \frac{3\hbar^2\lambda}{8m} + \frac{\hbar\omega}{4}\frac{1}{1 + \frac{3\hbar\lambda}{2m\omega}}\left(1 + \frac{3\hbar\lambda}{2m\omega}\right) \\
\approx & \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4}\left(1 - \frac{3\hbar\lambda}{2m\omega}\right)\left(1 + \frac{3\hbar\lambda}{2m\omega}\right) + \frac{3\hbar^2\lambda}{8m} \\
= & \frac{\hbar\omega}{2} + \frac{3\hbar^2\lambda}{8m} - \frac{9\hbar^4\lambda^2}{16m^2\omega}
\end{aligned}$$

which is a little better than the perturbation at first order.

B.7 2015 Midterm

Exercise 19 : Confined quantum stark effect (2.5 points)

1. The total potential is an infinit barrier with an inclined bottom with positive gradient $F = -eE$ $(E < 0)$.

2. The Hamiltonian of the perturbed system is:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}) + F\hat{x} \tag{B.104}$$

In the case where $F = 0$ the eigenenergies of the confined electron are

$$E_n = n^2\frac{\pi^2\hbar^2}{2mL^2}, n > 0 \tag{B.105}$$

and the corresponding wavefunctions are

$$\begin{aligned}
\varphi_n(x) &= \sqrt{\frac{2}{L}}\cos\left(\frac{n\pi}{L}x\right), \text{ if } n \text{ is odd} \\
\varphi_n(x) &= \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right), \text{ if } n \text{ is even}
\end{aligned}$$

3. In the case where $F \neq 0$, the energy correction to the fundamental state is the average value on the non perturbed states

$$E_1^{(1)} = \int_{-L/2}^{+L/2} \varphi_1^*(x)\, Fx\varphi_1(x)\, dx = \frac{2F}{L}\int_{-L/2}^{+L/2} x\cos^2\left(\frac{\pi}{L}x\right)dx \tag{B.106}$$

Directly noting that $x \mapsto x\cos^2(x)$ is odd or by integrating by parts, we find $E_1^{(1)} = 0$.

4. The energy corrections for the first 2 excited states are given by

$$E_2^{(1)} = \frac{2F}{L}\int_{-L/2}^{+L/2} x\sin^2\left(\frac{2\pi}{L}x\right)dx$$
$$E_3^{(1)} = \frac{2F}{L}\int_{-L/2}^{+L/2} x\cos^2\left(\frac{3\pi}{L}x\right)dx$$

and involve odd integrands, which is the case for any n, hence we simply have $E_n^{(1)} = 0$ for all n.

5. The energy correction $E_1^{(2)}$ for the ground state at order 2 involves non-zero matrix elements

$$V_{1j} = \frac{2F}{L}\int_{-L/2}^{+L/2} x\sin\left(\frac{j\pi}{L}x\right)\cos\left(\frac{\pi}{L}x\right)dx$$

only if j is even. Indeed, in cases where j is odd, the elements are zero due to parity. If we only consider the coupling with the first excited level, i.e., $j = 2$, the correction to the ground state is simply

$$E_1^{(2)} = -\frac{V_{21}^* V_{21}}{E_2 - E_1} \tag{B.107}$$

with

$$V_{21} = \frac{16}{9\pi^2}FL \tag{B.108}$$

using the identity $\sin(x)\cos(x) = \sin(2x)/2$ and integrating by parts $x\sin(2x)$. Thus, finally,

$$E_1^{(2)} = -\frac{256}{243\pi^4}\frac{F^2L^2}{E_1} \tag{B.109}$$

6. The wave function of the ground state becomes asymmetric and localizes where the total potential is weakest.

Exercise 20 : Particles interacting in a potential (2.5 points)

1. The 3 possible states are

$$\psi_1(x_1, x_2) = \varphi_1(x_1)\varphi_1(x_2)$$
$$\psi_2(x_1, x_2) = \left[\varphi_1(x_1)\varphi_2(x_2) + \varphi_1(x_2)\varphi_2(x_1)\right]/\sqrt{2}$$
$$\psi_3(x_1, x_2) = \varphi_2(x_1)\varphi_2(x_2)$$

2. 1st order corrections on the energies are

$$\Delta E_j^{(1)} = \langle\psi_j|\,\hat{V}_{\text{int}}\,|\psi_j\rangle \tag{B.110}$$

Using the definition of the delta function

$$\Delta E_1^{(1)} = V_0 \int \psi_1^4(x_1)\, dx_1$$
$$\Delta E_2^{(1)} = \frac{V_0}{2} \int \psi_1^2(x_1)\, \psi_2^2(x_1)\, dx_1$$
$$\Delta E_3^{(1)} = V_0 \int \psi_2^4(x_1)\, dx_1$$

3. ONly one possible state in that case

$$\psi_1(x_1, x_2) = \left[\varphi_1(x_1)\,\varphi_2(x_2) - \varphi_1(x_2)\,\varphi_2(x_1)\right]/\sqrt{2} \tag{B.111}$$

In this case the energy correction

$$\Delta E_1^{(1)} = V_0 \int \left[\varphi_1^2(x_1)\,\varphi_2^2(x_1) - \varphi_1^2(x_1)\,\varphi_2^2(x_1)\right] dx_1 = 0 \tag{B.112}$$

is zero. This is predictable as long as the potentials act when particles are at the same position, impossible when the wavefunction is odd.

Exercise 21 : Quantum information (1 point)

To determine if the operating modes can be distinguished, it is necessary to find an observable quantity that, when measured, yields different average values for the various operating modes. A necessary condition for being able to distinguish two operating modes is that the associated density matrices are different. Indeed, if the two density matrices coincide (in the same basis), then the measurement of any observable will yield the same average values in both cases. Let's calculate $\hat{\rho}_A$, $\hat{\rho}_B$, and $\hat{\rho}_C$.

$$\begin{aligned}\hat{\rho}_A &= \frac{1}{2}\left(|\psi_p\rangle\langle\psi_p| + |\psi_f\rangle\langle\psi_f|\right)\\ &= \frac{1}{2}\left(|0\rangle\langle 0| + |1\rangle\langle 1|\right)\end{aligned}$$

$$\rho_A = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{aligned}\hat{\rho}_B &= \frac{1}{2}\left(|\psi_p\rangle\langle\psi_p| + |\psi_f\rangle\langle\psi_f|\right)\\ &= \frac{1}{4}\left(|0\rangle\langle 0| + |1\rangle\langle 1| + |0\rangle\langle 1| + |1\rangle\langle 0|\right.\\ &+ \left.|0\rangle\langle 0| + |1\rangle\langle 1| - |0\rangle\langle 1| - |1\rangle\langle 0|\right)\\ &= \frac{1}{2}\left(|0\rangle\langle 0| + |1\rangle\langle 1|\right)\end{aligned}$$

$$\rho_B = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\begin{aligned}\hat{\rho}_C &= \frac{1}{2}\left(|\psi_p\rangle\langle\psi_p| + |\psi_f\rangle\langle\psi_f|\right)\\ &= \frac{1}{2}\left(|0\rangle\langle 0| + \frac{1}{2}\left(|0\rangle + i|1\rangle\right)\left(\langle 0| - i\langle 1|\right)\right)\\ &= \frac{3}{4}|0\rangle\langle 0| + \frac{1}{4}|1\rangle\langle 1| - \frac{i}{4}|0\rangle\langle 1| + \frac{i}{4}|1\rangle\langle 0|\end{aligned}$$

$$\rho_C = \frac{1}{4}\begin{pmatrix} 3 & -i \\ i & 1 \end{pmatrix}$$

It is therefore impossible for Bob to distinguish A from B. He can, however, distinguish C from A and B. To show this, it suffices to find the eigenvalues of ρ_c. The simple solution to the eigenvalue problem gives $p_C = (2 \pm \sqrt{2})/4 \simeq 0.854,\ 0.146$. Bob only needs to choose an observable quantity that has the form

$$O_C = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

in the basis that diagonalizes ρ_C. Measuring such an observable on the mixture C will yield -1 about 85.4% of the time and $+1$ about 14.6% of the time. For the instructions A and B, the measurement of O_C will always have an average value of zero.

B.8 2016 midterm

Exercise 22 : Impurity in a crystalline field (3 points) Degenerate perturbation theory tells us that the first-order correction in $\hat{V}$ is given by the diagonalization of the matrix:

$$M^{(1)} = \langle 3, 2, m|\, \hat{V}\, |3, 2, m'\rangle \tag{B.113}$$

where $|3, 2, m\rangle$ are the states of the $3d$ orbital. We can deduce the eigenvalues using group theory. We know that $\hat{V}$ is invariant under all operations of T_d, in other words, $[\hat{D}(g), \hat{V}] = 0, , \forall g \in T_d$. If we decompose the subspace defined by the five states $|3, 2, m\rangle$ into a direct sum of irreducible invariant subspaces of T_d, we will have simplified the search for eigenvalues. Moreover, if each $\Gamma^{(n)}$ from T_d present in this decomposition appears with multiplicity one, we will have directly diagonalized the problem.

1. The $3d$ states generate an irreducible representation $D^{(2)}$ of SO(3). This five-dimensional representation is reducible under the T_d group. Let's calculate the character of $D^{(2)}$ for the operations of T_d. Recall that all rotations by the same angle belong to the same equivalence class. Therefore, we can always consider rotations around the $\hat{z}$ axis, for which the matrices $D^{(2)}(\alpha, \hat{z})$ are diagonal:

$$D^{(2)}(\alpha, \hat{z}) = \begin{pmatrix} \exp i2\alpha & & & & \\ & \exp i\alpha & & & \\ & & 1 & & \\ & & & \exp -i\alpha & \\ & & & & \exp -i2\alpha \end{pmatrix} \tag{B.114}$$

   Thus, the trace of $D^{(2)}(\alpha, \hat{z})$ gives:

$$\mathrm{Tr}(D^{(2)}(\alpha, \hat{z})) = 2\cos(2\alpha) + 2\cos(\alpha) + 1 \tag{B.115}$$

Therefore, the character of C_2 is:

$$\chi(C_2) = \mathrm{Tr}(D^{(2)}(\pi, \hat{z})) = 1 \tag{B.116}$$

For C_3, we have:

$$\chi(C_3) = \mathrm{Tr}(D^{(2)}(2\pi/3, \hat{z})) = -1 \tag{B.117}$$

And for C_4:

$$\chi(C_4) = \mathrm{Tr}(D^{(2)}(\pi/2, \hat{z})) = -1 \tag{B.118}$$

Since the $3d$ orbitals are even under inversion, the matrix associated with inversion is the identity, and therefore:

$$\chi(\sigma_d) = \chi(\mathrm{Inv} \cdot C_2) = \chi(C_2) = 1 \tag{B.119}$$

$$\chi(S_4) = \chi(\mathrm{Inv} \cdot C_4) = \chi(C_4) = -1 \tag{B.120}$$

The character table of $D^{(2)}$ under the operations of T_d is:

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$D^{(2)}$	5	−1	1	1	−1

(B.121)

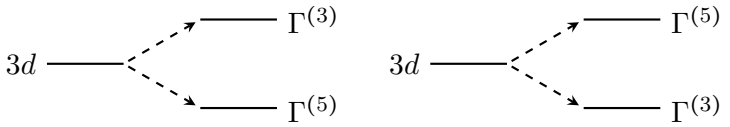
Without even using the formula for decomposition, we can see, with the help of the character table of T_d, that:

$$\chi(D^{(2)}) = \chi(\Gamma^{(3)}) + \chi(\Gamma^{(5)}) \tag{B.122}$$

And therefore:

$$D^{(2)} = \Gamma^{(3)} \oplus \Gamma^{(5)} \tag{B.123}$$

As the multiplicities are one, we are sure that the matrix $\hat{V}$ will be diagonal in the base that corresponds to this decomposition, and the subspaces associated with $\Gamma^{(3)}$ and $\Gamma^{(5)}$ will be degenerate. Thus, the $3d$ levels split into two levels with degeneracy two and three, respectively. Group theory does not tell us which level has the lowest energy. We have two possibilities :



2. The dipole operator is proportional to $\mathbf{r} = (x, y, z)$. According to the character table, we see that (x, y, z) generates the irreducible representation $\Gamma^{(5)}$ of T_d. There is only one transition to examine, that between the two degenerate levels that we have just found. We must determine the selection rules for a matrix element of the form:

$$\left\langle \Gamma^{(3)} \middle| \Gamma^{(5)} \middle| \Gamma^{(5)} \right\rangle \tag{B.124}$$

We can decompose $\Gamma^{(3)} \otimes \Gamma^{(5)}$ into a direct sum and check if $\Gamma^{(5)}$ appears.

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$\Gamma^{(3)} \otimes \Gamma^{(5)}$	6	0	−2	0	0

(B.125)

Again, without performing any calculation, we notice that $\chi(\Gamma^{(3)} \otimes \Gamma^{(5)}) = \chi(\Gamma^{(4)}) + \chi(\Gamma^{(5)})$, and thus $\Gamma^{(3)} \otimes \Gamma^{(5)} = \Gamma^{(4)} \oplus \Gamma^{(5)}$. Since both $\left\langle \Gamma^{(3)} \middle| \Gamma^{(5)} \right.$ and $\left| \Gamma^{(5)} \right\rangle$ involve the same irreducible representation, the transition is allowed.

Exercise 23 : Perturbed Harmonic Oscillator in 2-D (3 points)

1. Let's start by calculating the first-order energy correction $\Delta E^{(1)}$ by evaluating the perturbation $\hat{V}$ on the non-perturbed eigenstate $|\psi_{00}\rangle$:

$$\Delta E^{(1)} = \langle\psi_{00}|\hat{V}|\psi_{00}\rangle \tag{B.126}$$
$$= \int dxdy\phi_0^2(x)\,\phi_0^2(y)\,\lambda xy \tag{B.127}$$
$$\tag{B.128}$$
$$= \lambda\left[\int dx\phi_0^2(x)\,x\right]^2 \tag{B.129}$$

Since ϕ_0 is an even function, the integrand in (B.129) is an odd function, so $\Delta E^{(1)} = 0$. The second-order correction is given by:

$$\Delta E^{(2)} = \sum_{m,n} \frac{\langle\psi_{00}|\hat{V}|\psi_{mn}\rangle\langle\psi_{mn}|\hat{V}|\psi_{00}\rangle}{E_{00} - E_{mn}} \tag{B.130}$$

It can be noticed that at least the term associated with $m, n = 1$ contributes a non-zero term since:

$$\langle\psi_{11}|\hat{V}|\psi_{00}\rangle = \langle\psi_{00}|\hat{V}|\psi_{11}\rangle = \lambda\left[\int dx\phi_1(x)\,\phi_0(x)\,x\right]^2 \tag{B.131}$$

involves an even integrand. It can be shown that this term is, in fact, the only one contributing to the correction. Indeed, since $\hat{x} \propto \hat{a}^\dagger + \hat{a}$, non-zero matrix elements cannot occur for $m, n > 1$.

2. The states $|\psi_{10}\rangle$ and $|\psi_{01}\rangle$ are degenerate with an energy of $E_{10} = E_{01} = \epsilon_1 + \epsilon_0$. We must develop an appropriate perturbation theory. Due to parity, we immediately have $\langle\psi_{11}|\hat{V}|\psi_{00}\rangle = \langle\psi_{00}|\hat{V}|\psi_{11}\rangle = 0$. On the other hand, we have:

$$\begin{aligned}\langle\psi_{10}|\hat{V}|\psi_{01}\rangle &= \lambda\int dxdy\phi_1^2(x)\,\phi_0^2(y)\,xy \\ &= \lambda\int dx\sqrt{2\alpha}x^2\sqrt{\frac{\alpha}{\pi}}e^{-\alpha x^2}\int dy\sqrt{2\alpha}y^2\sqrt{\frac{\alpha}{\pi}}e^{-\alpha y^2} \\ &= \frac{2\lambda}{\pi}\left[\int dx\alpha x^2 e^{-\alpha x^2}\right]^2\end{aligned}$$

Let $\sqrt{\alpha}x := z$, then $dx = dz/\sqrt{\alpha}$, and we must now integrate

$$\int dx\alpha x^2 e^{-\alpha x^2} = \frac{1}{\sqrt{\alpha}}\int dz z^2 e^{-z^2} \tag{B.132}$$

by parts to finally find

$$\langle\psi_{10}|\hat{V}|\psi_{01}\rangle = \langle\psi_{01}|\hat{V}|\psi_{10}\rangle = \frac{\lambda}{2\alpha} \tag{B.133}$$

Thus, we have the perturbation matrix:

$$\hat{M}^{(1)} = \begin{pmatrix} \langle\psi_{10}|\hat{V}|\psi_{10}\rangle & \langle\psi_{10}|\hat{V}|\psi_{01}\rangle \\ \langle\psi_{01}|\hat{V}|\psi_{10}\rangle & \langle\psi_{01}|\hat{V}|\psi_{01}\rangle \end{pmatrix} = \begin{pmatrix} 0 & \lambda/2\alpha \\ \lambda/2\alpha & 0 \end{pmatrix} \tag{B.134}$$

Its eigenstates are

$$|\psi_\pm\rangle = \frac{|\psi_{10}\rangle \pm |\psi_{01}\rangle}{\sqrt{2}} \tag{B.135}$$

and eigenvalues

$$\Delta E_{\pm} = \pm\frac{\lambda}{2\alpha} \tag{B.136}$$

giving energy corrections. These perturbative correctiosn are of order 0 in $\hat{V}$ as expected in degenerate pertubration theory.

B.9 2017 Midterm

Exercise 24 : Attrictive 1-D potential always has a bound state (2 points)

1. we have

$$\int_{-\infty}^{\infty} dx\psi^2(x) = 1$$

$$\int_{-\infty}^{\infty} dx A^2 e^{-2\lambda x^2} = 1$$

using $-2\lambda x^2 = -y^2$

$$x = \frac{y}{\sqrt{2\lambda}}$$

$$dx = \frac{dy}{\sqrt{2\lambda}}$$

then

$$\begin{aligned}\int_{-\infty}^{\infty} dx A^2 e^{-2\lambda x^2} &= \int_{-\infty}^{\infty} \frac{dy}{\sqrt{s\lambda}} A^2 e^{-y^2} \\ &= A^2\sqrt{\frac{\pi}{2\lambda}} = 1 \\ &\Rightarrow A = \left(\frac{2\lambda}{\pi}\right)^{\frac{1}{4}}\end{aligned}$$

2. here, we calculate

$$\langle\psi|\hat{T}(x)|T\rangle = \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty} dx e^{-\lambda^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)e^{-\lambda x^2}$$

$$\begin{aligned}\frac{d^2}{dx^2}e^{-\lambda x^2} &= \frac{d}{dx}\left(-2\lambda x e^{-\lambda x^2}\right) \\ &= -2\lambda e^{-\lambda x^2} + 4\lambda^2 x^2 e^{-\lambda x^2}\end{aligned}$$

$$\langle\psi|\hat{T}|\psi\rangle = -\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty} dx 2\lambda\frac{\hbar^2}{2m}e^{-2\lambda x^2} + \sqrt{\frac{2\lambda}{\pi}}4\lambda^2\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} dx x^2 e^{-2\lambda x^2}$$

Integrating by parts

$$\begin{aligned}\int_{-\infty}^{\infty} dx x^2 e^{-2\lambda x^2} &= x\frac{e^{-2\lambda x^2}}{-4\lambda}\Bigg|_{-\infty}^{\infty} + \frac{1}{4\lambda}\int_{-\infty}^{\infty} dx e^{-2\lambda x^2} \\ &= \frac{1}{4\lambda}\sqrt{\frac{\pi}{2\lambda}}\end{aligned}$$

Finally

$$\begin{aligned}\langle\psi|\,\hat{T}\,|\psi\rangle &= \sqrt{\frac{2\lambda}{\pi}}\frac{\hbar^2}{2m}\left(-2\lambda\sqrt{\frac{\pi}{2\lambda}}+\lambda\sqrt{\frac{\pi}{2\lambda}}\right)\\ &= \frac{\hbar^2}{2m}\lambda\end{aligned}$$

3. We have

$$\begin{aligned}I(\lambda) &= \langle\psi|\,\tilde{V}(x)\,|\psi\rangle\\ &= \sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)e^{-2\lambda x^2}\\ &= \frac{\hbar^2}{2m}\lambda + I(\lambda)\end{aligned}$$

Calculating $\dfrac{dI}{d\lambda}$:

$$\begin{aligned}\frac{dI(\lambda)}{d\lambda} &= \frac{1}{2\sqrt{\lambda}}\sqrt{\frac{2}{\pi}}\int_{-\infty}^{\infty}dxV(x)e^{-2\lambda x^2}+\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)(-2x^2)e^{-2\lambda x^2}\\ &= \frac{I(\lambda)}{2\lambda}+\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)(-2x^2)e^{-2\lambda x^2}\end{aligned}$$

THe condition minimizing energy is simply given by

$$\frac{d\,\langle\psi|\,\hat{H}\,|\psi\rangle}{d\lambda} = 0$$

so

$$\frac{\hbar^2}{2m}+\frac{dI(\lambda)}{d\lambda} = 0$$

and

$$\frac{\hbar^2}{2m}+\frac{I(\lambda)}{2\lambda}+\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)(-2x^2)e^{-2\lambda x^2}$$

and we can deduce an expression for $I(\lambda)$ as asked

$$I(\lambda) = 2\lambda\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)2x^2e^{-2\lambda x^2}-2\lambda\frac{\hbar^2}{2m}$$

One can understand this expression as if we had inverted the relation $\lambda = \lambda(I)$ with I becoming the new variational parameter. In this case, the expression below is an implicit equation for $\lambda(I)$. Let's replace $I(\lambda)$ in $\langle\psi|\,\hat{H}\,|\psi\rangle$:

$$\begin{aligned}\langle\psi|\,\hat{H}\,|\psi\rangle &= \frac{\hbar^2}{2m}\lambda + I(\lambda)\\ &= -\frac{\hbar^2}{2m}+2\lambda\sqrt{\frac{2\lambda}{\pi}}\int_{-\infty}^{\infty}dxV(x)2x^2e^{-2\lambda x^2}\end{aligned}$$

Since $V(x) \leq 0$ and $\lambda > 0$, this expression is strictly less than zero. According to the variational principle, the true ground state will have $E_0 \leq \langle\psi|\,\hat{H}|\psi\rangle_\lambda < 0$ □

Exercise 25 : Second order polynomial symmetry in $\mathbb{R}^3$ (2 points)
Recall that $D(R)\psi(\mathbf{r}) = \psi(R^{-1}\mathbf{r})$.

1. For a rotation around axis $\hat{z}$, we have

$$x \to x\cos\phi + y\sin\phi$$
$$y \to x\sin\phi + y\cos\phi$$

So:

$$x^2 \to x^2\cos^2\phi + y^2\sin^2\phi + 2xy\cos\phi\sin\phi$$
$$y^2 \to x^2\sin^2\phi + y^2\cos^2\phi - 2xy\cos\phi\sin\phi$$
$$z^2 \to z^2$$
$$xy \to -x^2\cos\phi\sin\phi + xy(\cos^2\phi - \sin^2\phi) + y^2\cos\phi\sin\phi$$
$$xz \to xz\cos\phi + yz\sin\phi$$
$$yz \to -xz\sin\phi + yz\cos\phi$$

The matrix is then

$$D(\hat{z},\phi) = \begin{pmatrix} c^2 & s^2 & 0 & -cs & 0 & 0 & \\ s^2 & c^2 & 0 & cs & 0 & 0 & \\ 0 & 0 & 1 & 0 & & 0 & 0 \\ 2cs & -2cs & 0 & c^2-s^2 & 0 & 0 & \\ 0 & 0 & & 0 & 0 & c & s \\ 0 & 0 & 0 & 0 & 0 & -s & c \end{pmatrix}$$

where $c = \cos\phi$ and $s = \sin\phi$. It is not unitary since ψ_j are not normalized.

2. We first need to calculate the characters associated with D. Since the character of $D(\hat{n},\phi)$ only depends on ϕ (For teh same ϕ all $D(\hat{n},\phi)$ are in the same class).

We can use the matrix obtained in 1. For $\hat{n} = \hat{z}$.

$$\begin{aligned}\chi(\phi) &= 3\cos^2\phi - \sin^2\phi + 2\cos\phi + 1 \\ &= 2\cos^2\phi - 2\sin^2\phi + 1 + 2\cos\phi + 1 \\ &= 2\cos 2\phi + 2\cos\phi + 2\end{aligned}$$

We now need to calculate the characters of the irreducible representations $D^{(l)}$ of $SO(3)$.
recall that:

$$D^{(l)}(\hat{n},\phi) = e^{-i\phi\hat{n}\cdot\mathbf{L}/\hbar}$$

We can continue using $\hat{n} = \hat{z}$. For this choice, recall that

$$D^{(l)}(\hat{z},\phi) = e^{-i\phi\mathbf{L}_z/\hbar}$$

which is diagonal in basis $\{|l,m\rangle\}$ of eingestates for the kinetic moment.

$$D^{(l)}(\hat{z},\phi) = \begin{pmatrix} e^{il\phi} & 0 & 0 & \cdots & 0 \\ 0 & e^{i(l-1)\phi} & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & & \ddots & \vdots \\ 0 & 0 & \cdots & \cdots & e^{-il\phi} \end{pmatrix}$$

and

$$\begin{aligned}\chi^{(l)}(\phi) &= (e^{il\phi} + e^{-il\phi}) + (e^{i(l-1)\phi} + e^{-i(l-1)\phi}) + \cdots + 1 \\ &= 2\cos(l\phi) + 2\cos(l(-1)\phi) + \cdots + 1\end{aligned}$$

We immediately recognize

$$\chi(\phi) = \chi^{(0)}(\phi) + \chi^{(2)}(\phi)$$

showing

$$D = D^{(0)} \oplus D^{(2)}$$

3. A linear combination that is invariant under all arbitrary rotation is

$$p(r) = x^2 + y^2 + z^2$$

Since $D^{(0)}$ intervenes only once in the decomposition of D, this function is the one we were looking for.

4. Going again from the matrix calculated in point 1 to calculate the characters linked to the 3 classes of C_{3v}:

$$\chi(\phi) = 2\cos(2\phi) + 2\cos\phi + 2$$

so

$$\begin{aligned}\chi(E) &= 6 \\ \chi(C_3) &= \chi\left(\phi = \frac{2\pi}{3}\right) \\ &= 2\cos\left(\frac{4\pi}{3}\right) + 2\cos\left(\frac{2\pi}{3}\right) + 2 \\ &= 2\left(-\frac{1}{2}\right) + 2\left(\frac{-1}{2}\right) + 2 = 0\end{aligned}$$

The σ_v operation is an improper rotation and we can no longer use the expressing above for $\chi(\phi)$. Note that, out of the 3 operations, σ_v is the one that corresponds to the transformation

$$\begin{aligned}x &\to -x \\ y &\to y \\ z &\to z\end{aligned}$$

For this transformation, we have

$$\begin{aligned}x^2 &\to x^2 \\ y^2 &\to y^2 \\ z^2 &\to z^2 \\ xy &\to -xy \\ xz &\to -xz \\ yz &\to yz\end{aligned}$$

So

$$\chi(\sigma_v) = 1 + 1 + 1 - 1 - 1 + 1 = 2$$

Finally

$$\chi : 6, 0, 2$$

an, without using the equation for the decomposition using characters, we easily see that

$$\chi = 2\chi_2 + 2\chi_3$$

So

$$D = 2\Gamma_1 \oplus 2\Gamma_3$$

Exercise 26 : harmonic oscillator under a pulsed perturbation (2 points)

1. The temporal evolution operator from the interaction point of view, at 1^s order in $\hat{V}$ is

$$\begin{aligned}\hat{U}_I(t, t_0) &= \hat{I} - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 \hat{V}_I(t_1) \\ &= \hat{I} - \frac{i}{\hbar}\int_{t_0}^{t} dt_1 e^{i\hat{H}_0(t_1-t_0)/\hbar}\hat{V}(t_1)e^{-i\hat{H}_0(t_1-t_0)/\hbar}\end{aligned}$$

The probability we are looking for is then

$$\begin{aligned}P_{0\to1} &= \left|\langle 1|\, \hat{U}_I(t, t_0)\, |0\rangle\right|^2 \\ &= \frac{\epsilon^2}{\hbar^2} - \frac{\hbar}{2m\omega}\left|\int_{t_0}^{t} dt_1 \exp\left(i\frac{E_1 - E_0}{\hbar}(t_1 - t_0)\right)\exp\left(-\frac{t_1^2}{\tau^2}\right)\langle 1|\, (\hat{a} + \hat{a}^\dagger)\, |0\rangle\right|^2\end{aligned}$$

where we have used $\langle 1|\, \tilde{I}\, |0\rangle = 0$.

accepting that $t_0 \to -\infty$ and neglecting the phase $\exp\left(i\frac{(E_1 - E_=)}{\hbar}t_0\right)$ in the integral, which will give 1, after the square module.

$$P_{0\to1} = \frac{\epsilon^2}{2m\hbar\omega}\left|\int_{-\infty}^{\infty} dt e^{i\omega t}e^{-t^2/\tau^2}\right|^2$$

where we have taken $t \to +\infty$, $E_1 - E_0 = \hbar\omega$ and $\hat{a}^\dagger\, |0\rangle = |1\rangle$.
We must now calculate the integral

$$\int_{-\infty}^{\infty} \exp\left(-\left(\frac{t^2}{\tau^2} - i\omega t\right)\right)$$

Completing the square:

$$\begin{aligned}\frac{t^2}{\tau^2} - i\omega t &= t^2 - i\omega t - \frac{\omega^2\tau^2}{4} + \frac{\omega^2\tau^2}{4} \\ &= \left(\frac{t}{\tau} - i\frac{\omega\tau}{2}\right)^2 + \frac{\omega^2\tau^2}{4}\end{aligned}$$

$$\int_{-\infty}^{\infty} \exp\left(-\left(\frac{t^2}{\tau^2} - i\omega t\right)\right) = \int_{-\infty}^{\infty} dt \exp\left(-\frac{\omega^2\tau^2}{4}\right)\exp\left(-\left(\frac{t}{\tau} - i\frac{\omega\tau}{2}\right)^2\right)$$

Changing variables gives

$$\frac{t}{\tau} - i\frac{\omega\tau}{2} = x$$
$$\tau\left(x + i\frac{\omega\tau}{2}\right) = t$$
$$\tau dx = dt$$
$$\int_{-\infty}^{\infty} \exp\left(-\left(\frac{t}{\tau} - i\frac{\omega\tau}{2}\right)2\right) = \int_{-\infty}^{\infty} dx\tau e^{-x^2} = \tau\sqrt{\pi}$$

So

$$P_{0\to1} = \frac{\epsilon^2\pi\tau^2}{2m\hbar\omega}\exp\left(-\frac{\omega^2\tau^2}{2}\right)$$

2. In the limit $\omega\tau \to 0$, we have $P_{0\to1} = 0$, and similarly in the limit $\omega\tau \to \infty$

   In the first case, the perturbation acts on a very short timeframe keeping the same amplitude, making the energy go to zero. In the second case, the perturbation becomes quasi-stationary and we cannot change the energy of the system.

   The duration τ_m that maximizes $P_{0\to1}$ is given by

$$2\tau\exp\left(-\frac{\omega^2\tau^2}{2}\right) - \omega^2\tau^3\exp\left(-\frac{\omega^2\tau^2}{2}\right) = 0$$

$$\frac{dP_{0\to1}}{d\tau} = 0 \qquad \omega^2\tau^2 = 2 \qquad \tau_m = \frac{\sqrt{2}}{\omega}$$

3. To go from $|0\rangle$ to $|n\rangle$, one must apply n times $\hat{a}^\dagger$. This is only possible at perturbation order n, since $\hat{V}_I^n \propto (\hat{a}^\dagger + \hat{a})^n$ and so the perturbation has at least once $(\hat{a}^\dagger)^n$.

B.10 2018 Midterm

Exercise 27 : Degeneracy lifting in the presence of a field(3 points)
No correction

Exercise 28 : Two fermions in a potential well(3 points)
No correction

B.11 2019 Midterm

Exercise 29 : Four coupled Harmonic oscillators(3 points)

No correction

Exercise 30 : variational principle for two 1/2 spins (3 points)
No correction

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