Quantum mechanics II, Quantum mechanics II, Solutions 8 - Perturbation Theory II

TA : Achille Mauri, Behrang Tafreshi, Gabriel Pescia, Manuel Rudolph, Reyhaneh Aghaei Saem, Ricard Puig, Sacha Lerch, Samy Conus, Tyson Jones

Problem 1 : Degenerate Perturbation Theory for a 3-State System

We consider the following Hamiltonian acting on a spin 1 :

$$\hat{H} = -D\hat{S}_z^2 + \lambda B \hat{S}_x \tag{1}$$

This is a model that can be realistic in certain materials. The first term represents an anisotropy, and the second a magnetic field along the x direction. We propose to diagonalize this Hamiltonian by considering the term $\lambda B \hat{S}_x$ as a perturbation. Subsequently, we assume that B and D are non-zero.

1. Under what condition does the Hamiltonian commute with $\hat{S}_z$? In this case, give the eigenvalues and eigenvectors of $\hat{H}$.

   By definition of the angular momentum operators, the commutator of H with $\hat{S}_z$ yields

   $$[H, \hat{S}_z] = -D[\hat{S}_z^2, \hat{S}_z] + \lambda B[\hat{S}_x, \hat{S}_z] = -i\hbar\lambda B \hat{S}_y \tag{2}$$

   Assuming B is non-zero, $[H, \hat{S}_z] = 0$ only if $\lambda = 0$. In this case, the eigenstates of $\hat{S}_z$ are also eigenstates of H, and applying H to them gives their energy. We have $\hat{S}_z^2|m\rangle = \hbar m \hat{S}_z|m\rangle = \hbar^2 m^2|m\rangle$, hence the eigenstates and eigenenergies of H are :

   $$|0\rangle \equiv |m = 0\rangle : \quad E = 0 \tag{3}$$
   $$|\bar{1}\rangle \equiv |m = -1\rangle : \quad E = -D\hbar^2 \tag{4}$$
   $$|1\rangle \equiv |m = +1\rangle : \quad E = -D\hbar^2 \tag{5}$$

   The eigenenergy $-D\hbar^2$ is thus two-fold degenerate.

2. Subsequently, we consider $\lambda \neq 0$. Write down the matrix of the Hamiltonian in the basis of eigenstates of $\hat{S}_z$. Using second order perturbation theory, compute the energy correction for the state $|m = 0\rangle$. Calculate the correction to the associated eigenvector, to first order in perturbation theory.

   We write the Hamiltonian in the basis $\mathcal{B}_1 = \{|\bar{1}\rangle, |0\rangle, |1\rangle\}$. To determine the matrix of the operator $\hat{S}_x$, we use the formula $\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-)$ and (for a spin-s) :

   $$\hat{S}_\pm |s, m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)} |s, m \pm 1\rangle . \tag{6}$$

It is then easy to apply $\hat{S}_x$ on the basis states :

$$\hat{S}_x|\bar{1}\rangle = \frac{\hbar}{2}\sqrt{2}|0\rangle = \frac{\hbar}{\sqrt{2}}|0\rangle \tag{7}$$

$$\hat{S}_x|0\rangle = \frac{\hbar}{2}[\sqrt{2}|1\rangle + \sqrt{2}|\bar{1}\rangle] = \frac{\hbar}{\sqrt{2}}[|\bar{1}\rangle + |1\rangle] \tag{8}$$

$$\hat{S}_x|1\rangle = \frac{\hbar}{2}\sqrt{2}|0\rangle = \frac{\hbar}{\sqrt{2}}|0\rangle \tag{9}$$

The action of $\hat{S}_z^2$ is simply $\hat{S}_z^2|\bar{1}\rangle = \hbar^2|\bar{1}\rangle$, $\hat{S}_z^2|0\rangle = 0$, and $\hat{S}_z^2|1\rangle = \hbar^2|1\rangle$. The matrix of the Hamiltonian is then equal to

$$H = \begin{pmatrix} -D\hbar^2 & \lambda B\frac{\hbar}{\sqrt{2}} & 0 \\ \lambda B\frac{\hbar}{\sqrt{2}} & 0 & \lambda B\frac{\hbar}{\sqrt{2}} \\ 0 & \lambda B\frac{\hbar}{\sqrt{2}} & -D\hbar^2 \end{pmatrix} \tag{10}$$

Since the energy level $\epsilon_1 = 0$ is non-degenerate, for $\lambda = 0$, we can use non-degenerate perturbation theory. According to the course, the first-order correction is (Eq. 6.8)

$$E_1^{(1)} = B\langle 0|\hat{S}_x|0\rangle = 0 \tag{11}$$

At second order, in the Rayleigh-Schrödinger formalism (Eq. 6.22) :

$$E_1^{(2)} = \frac{|\langle\bar{1}|B\hat{S}_x|0\rangle|^2}{0 - (-D\hbar^2)} + \frac{|\langle 1|B\hat{S}_x|0\rangle|^2}{0 - (-D\hbar^2)} = B^2/D \tag{12}$$

Notice that in this calculation, λ does not appear. It is introduced in the energy correction (Eq. 6.3) :

$$E_1 = \underbrace{\epsilon_0}_{=0} + \lambda\underbrace{E_1^{(1)}}_{=0} + \lambda^2 E_1^{(2)} + \mathcal{O}(\lambda^3), \tag{13}$$

so

$$E_1 = \lambda^2 B^2/D + \mathcal{O}(\lambda^3) \tag{14}$$

The correction to the eigenvector to first order is given by (Eq. 6.13) :

$$\langle\bar{1}|\Psi_1^{(1)}\rangle = \frac{\langle\bar{1}|B\hat{S}_x|0\rangle}{D\hbar^2} = \frac{B}{\sqrt{2}D\hbar} \tag{15}$$

$$\langle 1|\Psi_1^{(1)}\rangle = \frac{\langle 1|B\hat{S}_x|0\rangle}{D\hbar^2} = \frac{B}{\sqrt{2}D\hbar} \tag{16}$$

Therefore, to first order in λ, the eigenvector associated with the energy $E_1 = \lambda^2 B^2/D$ is (Eq. 6.19) :

$$|\Psi_1\rangle = |0\rangle + \lambda\left(\langle\bar{1}|\Psi_1^{(1)}\rangle|\bar{1}\rangle + \langle 1|\Psi_1^{(1)}\rangle|1\rangle\right) + \mathcal{O}(\lambda^2)$$

Finally,

$$|\Psi_1\rangle = |0\rangle + \frac{1}{\sqrt{2}}\frac{B\lambda}{D\hbar}\left(|\bar{1}\rangle + |1\rangle\right) + \mathcal{O}(\lambda^2) \tag{17}$$

3. To calculate the effect of the perturbation on the other two states, it is necessary to use degenerate perturbation theory. What is the matrix of the operator $\hat{S}_x$ in the degenerate subspace ? Deduce that the first-order correction is zero.

According to degenerate perturbation theory, the first-order correction to the energy is given by the eigenvalues of the restriction $\tilde{V}$ of $V = \lambda B \hat{S}_x$ to the subspace $\{|\bar{1}\rangle, |1\rangle\}$ (Chapter 6.2). This matrix is written as :

$$\tilde{V} = \begin{pmatrix} \langle \bar{1}| V |\bar{1}\rangle & \langle \bar{1}| V |1\rangle \\ \langle 1| V |\bar{1}\rangle & \langle 1| V |1\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \tag{18}$$

Here, the eigenvalues of $\tilde{V}$ are 0, and therefore the first-order correction to the energy is zero.

> **Remarque**
> In the general case where the matrix $\tilde{V}$ has two different eigenvalues, it lifts the degeneracy and allows us to find the eigenvectors $\left|\Psi_{2,3}^{(0)}\right\rangle$ which will be the starting point for the perturbation expansion of the vectors $|\Psi_{2,3}\rangle$. Here, we are in the particular case where the degenerate subspace for H_0 is also degenerate for $\tilde{V}$. Therefore, we will need to go to the next order to find the desired eigenvectors.

Problem 2 : **Hydrogen atom in an external magnetic field**

The Hamiltonian of a hydrogen atom under a weak uniform magnetic field directed along the z axis can be expressed as

$$H = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} - \frac{e^2}{|\mathbf{r}|} - \boldsymbol{\mu} \cdot \mathbf{B} \ . \tag{19}$$

Here $\boldsymbol{\mu} = 2\mu_e \mathbf{s}$, with μ_e the electron magnetic moment and $\mathbf{s}$ the electron spin. Using the radial gauge $\mathbf{A} = \frac{1}{2}(-By, Bx, 0) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, and neglecting, for small B, terms of order B^2, the Hamiltonian can then be rewritten as

$$\begin{aligned} H &= \frac{\mathbf{p}^2}{2m} - \frac{e^2}{|\mathbf{r}|} + \frac{e}{2m}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) - 2\mu_e \mathbf{s} \cdot \mathbf{B} \\ &= H_0 + \frac{e}{4m}(\mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) + (\mathbf{B} \times \mathbf{r}) \cdot \mathbf{p}) - 2\mu_e \mathbf{s} \cdot \mathbf{B} \\ &= H_0 + \frac{e\hbar}{2m}\mathbf{B} \cdot \mathbf{L} - 2\mu_e \mathbf{s} \cdot \mathbf{B} \end{aligned} \tag{20}$$

where $H_0 = H|_{\boldsymbol{B}=0}$.

Calculate the splitting of the hydrogen energy levels to first order in $\mathbf{B}$.

Hint. By rotational invariance, the spectrum cannot depend on the direction of the magnetic field. This invariance can be used to simplify the calculations.

The unperturbed Hamiltonian H_0 in this case is the Hamiltonian of the hydrogen atom, for which the spectrum and the eigenstates are exactly known. In order to calculate the splitting induced by the magnetic field, we need to use *degenerate* perturbation theory, because the spectrum of H_0 is degenerate : the energy level n has degeneracy $g_n = 2n^2$.

To find the energy eigenstates to zero order, we have to diagonalize for each degenerate level the matrix $\langle \alpha|V|\beta\rangle$, where $V = e\hbar(\mathbf{B} \cdot \mathbf{L})/(2m) - 2\mu_e(\mathbf{s} \cdot \mathbf{B})$ is the perturbation operator and $|\alpha\rangle$, $|\beta\rangle$ range over a complete set of states forming a basis of the degenerate level. For the hydrogen case,

the basis for the energy level n can be chosen in a standard way as the set of states $|n, \ell, M, s_z\rangle$ with $\ell = 0, .., n-1$, $M = -\ell, .., \ell$, $s_z = \pm 1/2$.

By rotational invariance we are free to choose the z axis in any direction we like, without affecting the final results. Here, the most natural choice is to choose the z axis in the direction of the external magnetic field $\mathbf{B}$. Thus, without any loss of generality, we can assume that the field is oriented along z and that the perturbation Hamiltonian is $e\hbar \ell_z/(2m) - 2\mu_e B s_z$. Then the problem simplifies considerably because the matrix to be diagonalized becomes :

$$\langle n, \ell', M', s_z'| \left(e\hbar \ell_z/(2m) - 2\mu_e B s_z\right) |n, \ell, M, s_z\rangle = B\delta_{\ell,\ell'}\delta_{MM'}\delta_{s_z s_z'} \left(e\hbar M/(2m) - 2\mu_e s_z\right) . \quad (21)$$

The matrix is already diagonal so no explicit diagonalization is necessary. From the diagonal elements we can read the energy corrections to first order in B, which are

$$E^{(1)} = B\left(e\hbar M/(2m) - 2\mu_e s_z\right) \simeq B\left(\frac{e\hbar M}{2m} + \frac{e\hbar}{m}s_z\right) = \frac{e\hbar B}{2m}\left(M + 2s_z\right) . \quad (22)$$

Problem 3 : **Perturbed two-dimensional harmonic oscillator**

Consider a two-dimensional harmonic oscillator governed by the Hamiltonian

$$H = H_0 + gH_1 , \qquad H_0 = \frac{1}{2m}(p_x^2 + p_y^2) + \frac{1}{2}m\omega^2(x^2 + y^2) , \qquad H_1 = x^2 y^2 . \quad (23)$$

The model, for example, can describe in an approximate way an optical phonon in a two dimensional lattice with square anisotropy.

1. Consider the unperturbed Hamiltonian H_0, which describes a two-dimensional harmonic oscillator. Describe the spectrum of H_0, expressing the eigenstates and the corresponding energies.

2. Study how the ground state, the first excited level, and the second excited level of the unpertubed Hamiltonian are modified by H_1, using perturbation theory to first order in g.

1. The unperturbed Hamiltonian is the sum of two independent harmonic oscillators in the x and the y directions. Thus the energy eigenstates can be expressed as $|n_x, n_y\rangle$, where n_x, n_y are the excitation numbers of the two oscillators. The corresponding energies are $E(n_x, n_y) = \hbar\omega(2 \times \frac{1}{2} + n_x + n_y) = \hbar\omega(1 + n_x + n_y)$. The degeneracy of the n-th excited level is $n+1$, since there are $n+1$ different ways of dividing n excitations between the x and the y coordinates. In particular, the ground state is nondegenerate, and corresponds to the state $|0, 0\rangle$. The first excited state has degeneracy 2. A basis for the states in the first level is $|1, 0\rangle$, $|0, 1\rangle$. The second excited state has degeneracy 3, and the basis states can be chosen as $|2, 0\rangle$, $|1, 1\rangle$, $|0, 2\rangle$.

2. To study the interaction in perturbation theory it is convenient to represent the coordinates in terms of creation and annihilation operators, introducing :

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_x + a_x^\dagger) , \qquad y = \sqrt{\frac{\hbar}{2m\omega}}(a_y + a_y^\dagger). \quad (24)$$

The perturbation is thus

$$V = \frac{g\hbar^2}{4m^2\omega^2}(a_x + a_x^\dagger)^2(a_y + a_y^\dagger)^2 . \quad (25)$$

4

For the ground state, which is nondegenerate, we can use the formulas of non-degenerate perturbation theory. The energy at first order in g is

$$
\begin{aligned}
E_1 &= \hbar\omega + \frac{g\hbar^2}{4m^2\omega^2}\langle 0,0|(a_x + a_x^\dagger)^2(a_y + a_y^\dagger)^2|0,0\rangle \\
&= \hbar\omega + \frac{g\hbar^2}{4m^2\omega^2}\langle 0,0|a_x a_x^\dagger a_y a_y^\dagger|0,0\rangle \\
&= \hbar\omega + \frac{g\hbar^2}{4m^2\omega^2} \ .
\end{aligned}
\tag{26}
$$

In the calculation, we used that $a|0\rangle = 0$ and $\langle 0|a^\dagger = 0$.

Consider now the first excited level. Since the level is two-fold degenerate, we have in principle to diagonalize the matrix

$$
\begin{vmatrix} \langle 1,0|V|1,0\rangle & \langle 1,0|V|0,1\rangle \\ \langle 0,1|V|1,0\rangle & \langle 0,1|V|0,1\rangle \end{vmatrix} \ .
\tag{27}
$$

However, it can be seen that the off-diagonal matrix elements are zero. In fact, the perturbation V has matrix elements only between states for which the number of excitations in the x direction remain equal or change by ± 2. (The same is true for the number of excitations in the y direction).

As a result, we only need to calculate the diagonal matrix elements. In addition, the two diagonal elements are equal to each other : $\langle 1,0|V|1,0\rangle = \langle 0,1|V|0,1\rangle$. As a result, the two-fold degeneracy of the energy level is *not* lifted at first order in perturbation theory. The level remains degenerate and acquires an energy shift at first order equal to :

$$
\begin{aligned}
E_2 &= 2\hbar\omega + \langle 1,0|V|1,0\rangle \\
&= 2\hbar\omega + \frac{g\hbar^2}{4m^2\omega^2}\langle 1,0|(a_x + a_x^\dagger)^2(a_y + a_y^\dagger)^2|1,0\rangle \\
&= 2\hbar\omega + \frac{g\hbar^2}{4m^2\omega^2}\langle 1,0|(a_x a_x^\dagger + a_x^\dagger a_x)|1,0\rangle \\
&= 2\hbar\omega + \frac{3g\hbar^2}{4m^2\omega^2} \ .
\end{aligned}
\tag{28}
$$

Consider now the second excited level, for which the unperturbed energy is $E_3^{(0)} = 3\hbar\omega$. The level is three-fold degenerate, with basis states $|2,0\rangle$, $|1,1\rangle$, $|0,2\rangle$, so we need to diagonalize the 3×3 matrix

$$
\begin{vmatrix} \langle 2,0|V|2,0\rangle & \langle 2,0|V|1,1\rangle & \langle 2,0|V|0,2\rangle \\ \langle 1,1|V|2,0\rangle & \langle 1,1|V|1,1\rangle & \langle 1,1|V|0,2\rangle \\ \langle 0,2|V|2,0\rangle & \langle 0,2|V|1,1\rangle & \langle 0,2|V|0,2\rangle \end{vmatrix} \ .
\tag{29}
$$

Since the perturbation changes the number of excitations n_x, n_y by even numbers, the state $|1,1\rangle$ does not mix with $|2,0\rangle$, $|0,2\rangle$.

By explicit calculation, the nonzero elements of the matrix are :

$$
\begin{aligned}
\langle 2,0|V|2,0\rangle &= \langle 0,2|V|0,2\rangle = \frac{g\hbar^2}{4m^2\omega^2}\langle 2,0|(a_x a_x^\dagger + a_x^\dagger a_x)|2,0\rangle \\
&= \frac{g\hbar^2}{4m^2\omega^2}\langle 2,0|(1 + 2a_x^\dagger a_x)|2,0\rangle = \frac{g\hbar^2}{4m^2\omega^2}\langle 2,0|(1 + 2n_x)|2,0\rangle = \frac{5g\hbar^2}{4m^2\omega^2} \ ,
\end{aligned}
\tag{30}
$$

$$
\langle 1,1|V|1,1\rangle = \frac{g\hbar^2}{4m^2\omega^2}\langle 1,1|(2n_x + 1)(2n_y + 1)|1,1\rangle = \frac{9g\hbar^2}{4m^2\omega^2} \ ,
\tag{31}
$$

and the off-diagonal elements

$$\begin{aligned}\langle 0,2|V|2,0\rangle &= \frac{g\hbar^2}{4m^2\omega^2}\langle 0,2|(a_x+a_x^\dagger)^2(a_y+a_y^\dagger)^2|2,0\rangle \\ &= \frac{g\hbar^2}{4m^2\omega^2}\langle 0,2|a_x^2 a_y^{\dagger 2}|2,0\rangle = \frac{(\sqrt{2})^2 g\hbar^2}{4m^2\omega^2} = \frac{g\hbar^2}{2m^2\omega^2}\ .\end{aligned}\tag{32}$$

In the calculation we used the relations $a|n\rangle = \sqrt{n}|n-1\rangle\ a^\dagger|n\rangle = \sqrt{n+1}|n\rangle$ for the creation/annihilation operators.

To find the energy corrections, we need therefore to diagonalize the matrix

$$\frac{g\hbar^2}{4m^2\omega^2}\begin{vmatrix}5 & 0 & 2\\ 0 & 9 & 0\\ 2 & 0 & 5\end{vmatrix}\tag{33}$$

The eigenvalues are $(5\pm 2)g\hbar^2/(4m^2\omega^2)$ and $9g\hbar^2/(4m^2\omega^2)$ and the corresponding eigenvector, which determine the zero order wavefunctions in perturbation theory are $(|2,0\rangle \pm |0,2\rangle)/\sqrt{2}$, $|1,1\rangle$.