Chapter 6

Perturbation Theory

Say you have some system H of an n particle system and want to calculate its eigenspectrum (i.e. its eigenvalues and eigenstates) or the dynamics it induces. In certain cases this is easy - e.g., if the n particles are non-interacting or if we can apply physics intuition to transform into some other clever basis where diagonalizing the Hamiltonian is easy. But generally this is hard and we need to resort to approximation techniques.

Perturbation theory is an approach to handling complex Hamiltonians by breaking up the Hamiltonian into 'easier' terms that you know how to diagonalize and small corrections that we can treat as inducing perturbative corrections. Exactly, how to do this in practise depends on whether there is or isn't a time dependence, whether there is or isn't degeneracy in the eigenstates, as well as the available computational power. Let's start with the simple non-degenerative time-independent case.

6.1 Non-degenerate Time-Independent Perturbation Theory

Let's consider a physical problem governed by a Hamiltonian $\hat{H}$, which we decompose as

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \tag{6.1}$$

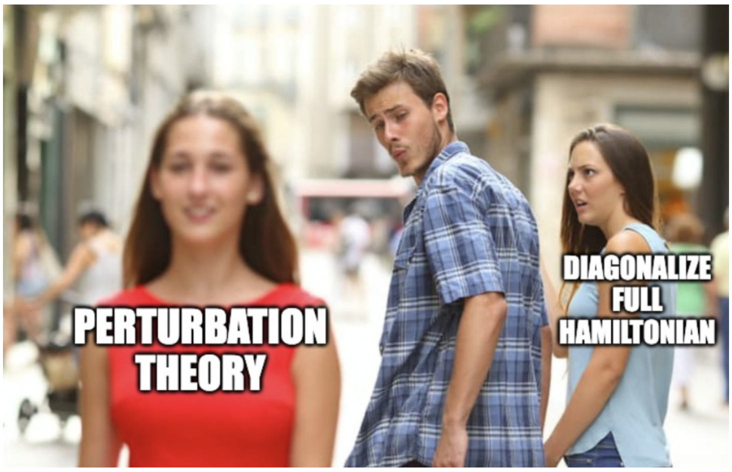

Figure 6.1: Caption

where $\hat{H}_0$ is a Hamiltonian with known eigenenergies and eigenstates (i.e. its the easy part) and $\lambda \in \mathbb{R}^+$ is a real positive parameter determining the strength of the additional term $\hat{V}$ which is treated as a *perturbation* of the system. We are interested in studying the limit of this problem where λ is small (i.e., the limit of small perturbations).

Let $|\phi_n\rangle$ denote the *known* eigenstates of $\hat{H}_0$ and ϵ_n the associated eigenenergies. The goal of this section is to establish techniques to determine the eigenenergies of the total Hamiltonian $\hat{H}$. For sufficiently small perturbations λ, 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 the limit of very small λ, the solution can be expanded in powers of λ:

$$|\psi_n\rangle = |\phi_n\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots \tag{6.2}$$

$$E_n = \epsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots. \tag{6.3}$$

And Schrödinger equation is written as:

$$\begin{aligned}\left(\hat{H}_0 + \lambda\hat{V}\right)&\left(|\phi_n\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots\right)\\ &= \left(\epsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots\right)\left(|\phi_n\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots\right).\end{aligned} \tag{6.4}$$

Our goal is to find explicit expressions for the perturbations to the eigenstates $|\psi_n^{(k)}\rangle$ and corrections to the eigenenergies $E_n^{(k)}$ for $k = 1, 2, ...$

The equation 6.4 must be satisfied at each order in λ. This allows us to iteratively identify the corrections $E_n^{(k)}$ and $|\psi_m^{(k)}\rangle$.

Zero-th Order. At order 0 we simply have the unperturbed eigenvalue problem:

$$\hat{H}_0 |\phi_n\rangle = \epsilon_n |\phi_n\rangle .$$

1st Order. At order 1 we have:

$$\hat{H}_0 |\psi_n^{(1)}\rangle + \hat{V} |\phi_n\rangle = \epsilon_n |\psi_n^{(1)}\rangle + E_n^{(1)} |\phi_n\rangle, . \tag{6.5}$$

To isolate the first order correction to the eigenenergy, $E_1^{(1)}$, we can bra through with $\langle\phi_n|$:

$$\langle\phi_n|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\phi_n|\hat{V}|\phi_n\rangle = \epsilon_n\langle\phi_n|\psi_n^{(1)}\rangle + E_n^{(1)} \underbrace{\langle\phi_n|\phi_n\rangle}_{=1} \tag{6.6}$$

$$\epsilon_n\langle\phi_n|\psi_n^{(1)}\rangle + \langle\phi_n|\hat{V}|\phi_n\rangle = \epsilon_n\langle\phi_n|\psi_n^{(1)}\rangle + E_n^{(1)} \tag{6.7}$$

where in the second line we have used $\hat{H}_0 |\phi_0\rangle = \epsilon_0 |\phi_0\rangle$. We therefore find that the first order correction to the energy of $\hat{H}_0$ due to $\hat{V}$ is given by:

$$E_n^{(1)} = \langle\phi_n|\hat{V}|\phi_n\rangle \tag{6.8}$$

and so the eigenenergies of H to 1st order are:

$$E_n = \epsilon_n + \lambda \langle\phi_n|\hat{V}|\phi_n\rangle + \mathcal{O}(\lambda^2) \tag{6.9}$$

What about the first order correction to the eigenstate? Our goal will be to write the correction in the basis of the original eigenstates:

$$|\psi_n^{(1)}\rangle = \sum_m \langle\phi_m|\psi_n^{(1)}\rangle|\phi_m\rangle\,. \tag{6.10}$$

Thus we need to compute the overlaps $\langle\phi_m|\psi_n^{(1)}\rangle$. To do this we start with Eq. (6.5) but instead bra through with $\langle\phi_m|$. This gives

$$\langle\phi_m|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\phi_m|\hat{V}|\phi_n\rangle = \epsilon_n\langle\phi_m|\psi_n^{(1)}\rangle + E_n^{(1)}\underbrace{\langle\phi_m|\phi_n\rangle}_{=0} \tag{6.11}$$

$$\epsilon_m\langle\phi_m|\psi_n^{(1)}\rangle + \langle\phi_m|\hat{V}|\phi_n\rangle = \epsilon_n\langle\phi_m|\psi_n^{(1)}\rangle \tag{6.12}$$

which can be rearranged to give:

$$\langle\phi_m|\psi_n^{(1)}\rangle = \frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}\,. \tag{6.13}$$

This looks promising but what is going on for $m = n$? To understand this remember that $\{|\psi_n\rangle\}$ are the eigenbasis of $\hat{H}$ and so form a normalised eigenbasis with

$$\langle\psi_n|\psi_{n'}\rangle = \delta_{n,n'}\,. \tag{6.14}$$

For $m = n$ this constraint can be rewritten to first order in λ as

$$1 = \langle\psi_n|\psi_n\rangle = \langle\phi_n|\phi_n\rangle + \lambda(\langle\phi_n|\psi_n^{(1)}\rangle + \langle\psi_n^{(1)}|\phi_n\rangle) + \mathcal{O}(\lambda^2)\,. \tag{6.15}$$

As λ is positive we therefore have that:

$$\langle\phi_n|\psi_n^{(1)}\rangle + \langle\psi_n^{(1)}|\phi_n\rangle = 2\mathfrak{Re}(\langle\psi_n^{(1)}|\phi_n\rangle) = 0\,. \tag{6.16}$$

We are free to choose the global (unphysical) phase of the original eigenstates $|\phi_n\rangle$ such that $\langle\psi_n^{(1)}|\phi_n\rangle$ is purely real. Thus we end up with

$$\langle\phi_n|\psi_n^{(1)}\rangle = \langle\psi_n^{(1)}|\phi_n\rangle = 0\,. \tag{6.17}$$

Putting this all together we have that

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n}\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}|\phi_m\rangle \tag{6.18}$$

and so the eigenstates of $\hat{H}$ to 1st order are:

$$|\psi_n\rangle = |\phi_n\rangle + \lambda|\psi_n^{(1)}\rangle + \mathcal{O}(\lambda^2) = |\phi_n\rangle + \lambda\sum_{m\neq n}\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}|\phi_m\rangle + \mathcal{O}(\lambda^2)\,. \tag{6.19}$$

2nd Order. At order 2 we have:

$$\hat{H}_0\,|\psi_n^{(2)}\rangle + \hat{V}\,|\psi_n^{(1)}\rangle = \epsilon_n\,|\psi_n^{(2)}\rangle + E_n^{(1)}\,|\psi_n^{(1)}\rangle + E_n^{(2)}\,|\phi_n\rangle\,. \tag{6.20}$$

To get the second order energy correction we can again bra through with $\langle\phi_n|$ which gives:

$$\epsilon_n\langle\phi_n|\psi_n^{(2)}\rangle + \langle\phi_n|\hat{V}\,|\psi_n^{(1)}\rangle = \epsilon_n\langle\phi_n|\psi_n^{(2)}\rangle + E_n^{(1)}\langle\phi_n|\psi_n^{(1)}\rangle + E_n^{(2)}\,. \tag{6.21}$$

On cancelling terms, recalling that $\langle\phi_n|\psi_n^{(1)}\rangle = 0$ and substituting in Eq. (6.18), this gives:

$$E_n^{(2)} = \langle\phi_n|\hat{V}|\psi_n^{(1)}\rangle = \sum_{m\neq n}\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}\langle\phi_n|\hat{V}|\phi_m\rangle = \sum_{m\neq n}\frac{|\langle\phi_m|\hat{V}|\phi_n\rangle|^2}{\epsilon_n - \epsilon_m}\,. \tag{6.22}$$

For the second order correction to the eigenstate things start to become messy but you can keep on iterating this procedure to obtain an explicit expression for the eigenstates to second order. You'll be pleased to know I won't make you do this in this course.

Comment 1. The above calculation implicitly assumed that the energy levels are non-degenerate. If you have degenerate eigenvalues (i.e. two different eigenstates with the same energy) then the denominator in Eq. (6.18) blows up. We will come back to how to deal with this case later in this section.

Comment 2. For this approximation to be valid we need the second order correction to be small compared to the first order correction. How can we check this? To derive one way of checking let Δ be the energy difference between ϵ_n and the nearest energy level i.e. $\Delta = \min_m |\epsilon_n - \epsilon_m|$. Then we can write:

$$\begin{aligned} \left|E_n^{(2)}\right| &= \Big|\sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2}{(\epsilon_n - \epsilon_m)}\Big| \\ &\leq \sum_{m\neq n} \frac{\left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2}{|\epsilon_n - \epsilon_m|} \\ &\leq \frac{1}{\Delta}\sum_{m\neq n} \left|\langle\phi_m|\hat{V}|\phi_n\rangle\right|^2 \\ &= \frac{1}{\Delta}\left(\sum_m \langle\phi_n|\hat{V}|\phi_m\rangle\langle\phi_m|\hat{V}|\phi_n\rangle - \left|\langle\phi_n|\hat{V}|\phi_n\rangle\right|^2\right) \\ &= \frac{1}{\Delta}\left(\langle\phi_n|\hat{V}^2|\phi_n\rangle - \langle\phi_n|\hat{V}|\phi_n\rangle^2\right). \end{aligned}$$

The condition $|E_n^{(2)}| \ll |E_n^{(1)}|$ is satisfied as long as,

$$\frac{1}{\Delta}\left(\langle\phi_n|\hat{V}^2|\phi_n\rangle - \langle\phi_n|\hat{V}|\phi_n\rangle^2\right) \ll \langle\phi_n|\hat{V}|\phi_n\rangle\ , \tag{6.23}$$

or equivalently, as long as:

$$\left|\frac{\langle\phi_n|\hat{V}^2|\phi_n\rangle}{\langle\phi_n|\hat{V}|\phi_n\rangle} - \langle\phi_n|\hat{V}|\phi_n\rangle\right| \ll \Delta\,. \tag{6.24}$$

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:

$$\left|\frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{\epsilon_n - \epsilon_m}\right| \ll 1.$$

6.1.1 Examples

Example 6.1.1. **Harmonic Oscillator Exposed to a Constant Force.** Suppose we consider particle in a Harmonic well subject to a constant force:

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - qEx\,. \tag{6.25}$$

We can write this Hamiltonian as $H = H_0 + \lambda V$ with

$$\begin{aligned} H_0 &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \\ V &= -qEx \end{aligned} \tag{6.26}$$

and $\lambda = 1$. We know the energies of H_0, as this is just the simple harmonic oscillator with energies

$$\epsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{6.27}$$

and eigenstates $|n\rangle$. To simplify things, we express V using the lowering and raising operators

$$V = -qEx = -qE\sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger) \tag{6.28}$$

with $a|n\rangle = \sqrt{n}|n-1\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$. To find the 1st order corrections to the energies, we use $E_n^{(1)} = \langle n|V|n\rangle$:

$$E_n^{(1)} = -qE\sqrt{\frac{\hbar}{2m\omega}}\langle n|(a + a^\dagger)|n\rangle = 0 \tag{6.29}$$

and thus the first order correction to the energy vanishes [1].

To find the 2nd order corrections to the energies, we write

$$\begin{aligned}
E_n^{(2)} &= \sum_{m\neq n} \frac{|\langle m|V|n\rangle|^2}{\epsilon_n - \epsilon_n} && (6.30)\\
&= \frac{q^2E^2\hbar}{2m\omega}\sum_{m\neq n}\frac{|\langle m|(a + a^\dagger)|n\rangle|^2}{\hbar\omega(n-m)} && (6.31)\\
&= \frac{q^2E^2}{2m\omega^2}\sum_{m\neq n}\frac{|\langle m|(a + a^\dagger)|n\rangle|^2}{(n-m)}\,. && (6.32)
\end{aligned}$$

To simplify this we use the fact that $a|n\rangle = \sqrt{n}|n-1\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$ to find

$$\begin{aligned}
E_n^{(2)} &= \frac{q^2E^2\hbar}{2m\omega}\sum_{m\neq n}\frac{|\sqrt{n}\langle m|n-1\rangle + \sqrt{n+1}\langle m|n+1\rangle|^2}{\hbar\omega(n-m)} && (6.33)\\
&= \frac{q^2E^2}{2m\omega^2}\left(\frac{|\sqrt{n}|^2}{n-(n-1)} + \frac{|\sqrt{n+1}|^2}{n-(n+1)}\right) && (6.34)\\
&= -\frac{q^2E^2}{2m\omega^2} && (6.35)
\end{aligned}$$

So, up to second order, we have

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{q^2E^2}{2m\omega^2}\,. \tag{6.36}$$

Note that for this simple example you can just solve this Hamiltonian exactly by seeing that a constant force simply shifts the equilibrium position (the position where the force vanishes) to $x_0 = qE/(m\omega^2)$ as

$$\begin{aligned}
H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 - qEx &= \frac{p^2}{2m} + \frac{1}{2}m\omega^2\left(x - \frac{qE}{m\omega^2}\right)^2 - \left(\frac{qE}{m\omega^2}\right)^2\\
&= \frac{p^2}{2m} + \frac{1}{2}m\omega^2\left(x - x_0\right)^2 - \frac{1}{2}m\omega^2x_0^2\,.
\end{aligned} \tag{6.37}$$

Thus you can see that the perturbation reduces the energy by $\frac{1}{2}m\omega^2x_0^2 = \frac{q^2E^2}{2m\omega^2}$. We therefore see that in this case 2nd order perturbation theory gives us the exact values of energies for the Hamiltonian. However, this is is only true for this simple example and not generally the case.

[1] An alternative way of seeing this would be to note that $|n\rangle$ are even under reflections $x \to -x$ but x is of course odd and the above equation corresponds to integrating an odd function for $x = -\infty$ to $x = \infty$.

Example 6.1.2. **Potential of a Diatomic Molecule.** Consider the following Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ with:

$$\begin{cases} \hat{H}_0 = \frac{\hat{p}^2}{2} + \frac{\hat{x}^2}{2}, \\ \hat{V} = c\hat{x}^3 + q\hat{x}^4, \end{cases}$$

for $c \geq 0$ and $q \leq 0$. Note that to make our life less miserable here we have picked units such that $\hbar\omega = m = 1$ (in contrast to the previous example).

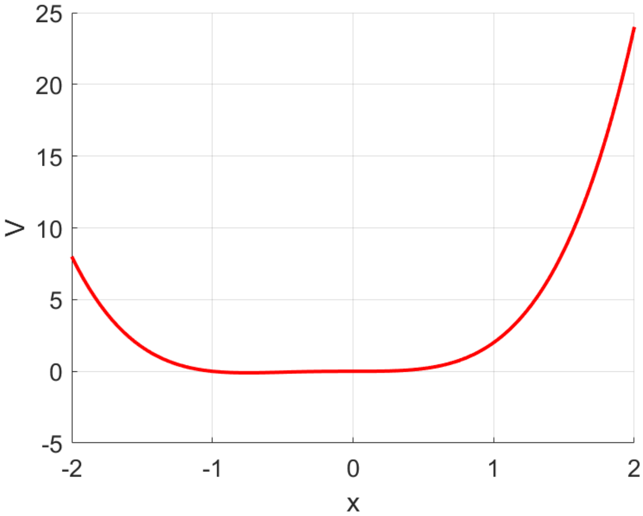

Figure 6.2: Correction to the potential

The energy and eigenstates of $\hat{H}_0$ for the system are already known- this is just a standard quantum harmonic osccilator. Concretely, we have $\epsilon_n = (n + \frac{1}{2})$. The goal is to determine the $E_n^{(k)}$ for a fixed n. From Eq. (6.9) the first order correction to the eigenenergies is given by:

$$E_n^{(1)} = \langle n | c\hat{x}^3 + q\hat{x}^4 | n \rangle \,.$$

To evaluate this let's introduce creation and annihilation operators such that $\hat{x} = \hat{a} + \hat{a}^\dagger$. It is immediately noticed that the term $c\hat{x}^3$ does not contribute because only terms with the same number of $\hat{a}^\dagger$ and $\hat{a}$ operators give rise to non-zero coefficients (alternatively, note that the eigenstates $|n\rangle$ are symmetric under $\hat{x} \to -\hat{x}$). Next we note that:

$$\begin{aligned}
\hat{x}^4 &= \left(\hat{a} + \hat{a}^\dagger\right)^4 = \left((\hat{a})^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} + \hat{a}^{\dagger 2}\right)^2 \\
&= (\hat{a})^4 + (\hat{a})^2\hat{a}^{\dagger 2} + (\hat{a})^3\hat{a}^\dagger + (\hat{a})^2\hat{a}^\dagger\hat{a} \\
&+ \hat{a}^{\dagger 2}(\hat{a})^2 + \hat{a}^{\dagger 4}\hat{a}^{\dagger 2}\hat{a}\hat{a}^\dagger + \hat{a}^{\dagger 3}\hat{a} + \hat{a}\hat{a}^\dagger(\hat{a})^2 \\
&+ \hat{a}\hat{a}^{\dagger 3} + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} + \hat{a}^\dagger(\hat{a})^3 \\
&+ \hat{a}^\dagger\hat{a}\hat{a}^{\dagger 2} + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} \\
&= (\hat{a})^2\,\hat{a}^{\dagger 2} + \hat{a}^{\dagger 2}\,(\hat{a})^2 + \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a},
\end{aligned}$$

where the last equality is obtained by again noting that only terms with equal numbers of creation and annihilation operators lead to non-zero contributions. Thus (after a bunch of algebra which I will leave it up to you to fill in) we find:

$$\langle n | \left(\hat{a}^\dagger + \hat{a}\right)^4 | n \rangle = \langle n | (\hat{a})^2\,\hat{a}^{\dagger 2} | n \rangle + \langle n | \hat{a}^{\dagger 2}\,(\hat{a})^2 | n \rangle + \langle n | \hat{a}\hat{a}^\dagger\hat{a}^\dagger\hat{a} | n \rangle + \langle n | \hat{a}^\dagger\hat{a}\hat{a}\hat{a}^\dagger | n \rangle + \langle n | \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger | n \rangle + \langle n | \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} | n \rangle \quad =$$

And so we have

$$\epsilon_n \approx \left(n+\frac{1}{2}\right) - 6|q|\left(n^2+n-\frac{1}{2}\right). \tag{6.38}$$

6.2 Degenerate Time-Independent Perturbation Theory

As mentioned earlier, the approach described above fails when $\hat{H}_0$ has degenerate eigenvalues because of terms of the form $\frac{1}{\epsilon_n-\epsilon_m} = \frac{1}{0}$ in Eq. (6.18). In this section we show how we can deal with this case.

For simplicity, we assume for now that only for the n$_{th}$ energy state is there an N-fold degeneracy. That is, we suppose that the initial Hamiltonian H_0 has energy ϵ_n with N degenerate states ϕ_{n_i}, $i = 1,\dots,N$.

Let us start by finding the first order corrections $E_n^{(1)}$. To do so, we expand our eigenstate $|\psi_n\rangle$ in powers of λ. However, this time we replace the 0-th order term $|\phi_n\rangle$ with a linear combination $\sum_j c_j|\phi_{n_j}\rangle$ of the degenerate states because we are unsure of what combination of these states yields the "correct" 0-th order contribution to $|\psi_n\rangle$. That is, we can write:

$$|\psi_n\rangle = \sum_j c_j|\phi_{n_j}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \dots \tag{6.39}$$

and the energy is given by

$$E_n = \epsilon_n + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \tag{6.40}$$

as previously. Again, working from the Schrödinger equation $H|\psi_n\rangle = E_n|\psi_n\rangle$ to first order in λ we have:

$$H_0|\psi_n^{(1)}\rangle + \sum_j c_j V|\phi_{n_j}\rangle = \epsilon_n|\psi_n^{(1)}\rangle + E_n^{(1)}\sum_j c_j|\phi_{n_j}\rangle$$

Similarly to the non-degenerate case we next bra through with $\langle\phi_{n_i}|$,

$$\langle\phi_{n_i}|H_0|\psi_n^{(1)}\rangle + \sum_j c_j\langle\phi_{n_i}|V|\phi_{n_j}\rangle = \epsilon_n\langle\phi_{n_i}|\psi_n^{(1)}\rangle + E_n^{(1)}\sum_j c_j\langle\phi_{n_i}|\phi_{n_j}\rangle$$

and cancel the ϵ_n terms to give:

$$\sum_j\langle\phi_{n_i}|V|\phi_{n_j}\rangle c_j = E_n^{(1)}\sum_j c_j\langle\phi_{n_i}|\phi_{n_j}\rangle = E_n^{(1)}\sum_j c_j\delta_{ij} = E_n^{(1)}c_i$$

The terms $\langle\phi_{n_i}|V|\phi_{n_j}\rangle = V_{ij}$ are the matrix elements of V in the $\{|\phi_{n_i}\rangle\}$ basis of degenerate 0-th order states. Thus we have:

$$\sum_j V_{ij}c_j = E_n^{(1)}c_i$$

This is precisely an eigenvalue equation. The first order corrections $E_n^{(1)}$ are the eigenvalues of V in the degenerate state basis and the corresponding vectors c_i characterize the "correct" linear combination $\sum_j c_j|\phi_{n_j}\rangle$ in the 0-th order term of the eigenstate $|\psi_n\rangle$.

Finding eigenvalues and eigenvectors of a matrix are equivalent to diagonalizing it - so, when we carry about this procedure for finding the 1st order corrections to the energies of degenerate states, we just diagonalize the perturbation Hamiltonian V.

Comment 1. Note that in the context of perturbation theory for a non-degenerate physical system, the perturbation appears at order 1 in λ, while here we have a correction to the zero-th order state.

Comment 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. This links back to the previous comment - it is because the degeneracy is lifted that the 0th order contribution changes.

6.2.1 Examples

Example 6.2.1. **Trivial example.** We first note that this approach trivially works for the case of a Hamiltonian $H = H_0 + V$ with $H_0 = aI$. In this case eigenstates of H_0 are trivially degenerate and the eigenvalues and eigenvectors of the perturbed Hamiltonian can be found by finding the eigenvalues and eigenvectors of the perturbation V.

Example 6.2.2. **The Stark Effect.** The Stark effect is an important phenomenon in atomic physics where one observes the splitting of the degeneracy of one-electron atoms in an electric field. In this example we consider the Hamiltonian of a one-electron atom (e.g. Hydrogen) in a constant, uniform electric field E which points only in the z direction. We neglect spin in this example. (If you can't remember the physics of the hydrogen atom now is a good moment to recap it!) The Hamiltonian of such a system is

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} - e\mathcal{E}z = H_0 + V$$

where V is identified with the term $-e\mathcal{E}z$. The n_{th} energy eigenvalue of the unperturbed Hamiltonian is n^2-fold degenerate. In this example, we will consider the case of $n = 2$, which has a 4-fold degeneracy; the corresponding degenerate eigenstates are given in $|nlm\rangle$ notation by $|200\rangle$, $|211\rangle$, $|210\rangle$, $|21-1\rangle$.

To find the 0th order correction to the eigenstate and 1st order contribution to the eigenenergy we need to diagonalize V in the eigen-space spanned by $|200\rangle$, $|211\rangle$, $|210\rangle$, $|21-1\rangle$. I.e., we need to find the eigenvalues and eigenvectors of:

$$\tilde{V} = \begin{bmatrix} (200|V|200) & (200|V|210) & (200|V|211) & (200|V|21-1) \\ (210|V|200) & (210|V|210) & (210|V|211) & (210|V|21-1) \\ (211|V|200) & (211|V|210) & (211|V|211) & (211|V|21-1) \\ (21-1|V|200) & (21-1|V|210) & (21-1|V|211) & (21-1|V|21-1) \end{bmatrix} \tag{6.41}$$

This looks like a nasty thing to work with but luckily it turns out most of the terms are zero. Each of the 16 matrix elements is of the form:

$$V_{lm,l'm'} = \langle 2,l,m|z|2,l',m'\rangle = \iiint u_{lm}^*(r\cos\theta)u_{l'm'}r^2\sin\theta d\theta d\phi dr \tag{6.42}$$

where we recall that

$$\begin{aligned} u_{00} &\propto \left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} \\ u_{10} &\propto r\cos\theta e^{-r/2a_0} \\ u_{11} &\propto r\sin\theta e^{i\phi}e^{-r/2a_0} \\ u_{1-1} &\propto r\sin\theta e^{-i\phi}e^{-r/2a_0} \end{aligned} \tag{6.43}$$

where a_0 is the Bohr radius. Looking first at parity, it is clear that $z = r\cos(\theta)$ has odd parity. And thus any term along the diagonal is the integral over an odd function and so is zero. Similar parity arguments apply for $V_{1-1,11}$ terms. Secondly, $\int_0^{2\pi} e^{i\phi}d\phi = 0$, so any term with a single u_{11}

or u_{1-1} contribution vanishes, e.g. $V_{00,1-1} = V_{11,00} = V_{1-1,00} = 0$. Thus we end up with only two non-zero terms corresponding to $V_{00,01}$. Thus we have left with:

$$\tilde{V} = \begin{bmatrix} 0 & \alpha & 0 & 0 \\ \alpha^* & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

where (if you do the integrals) $\alpha = -3e\mathcal{E}a_0$. It is now easy to see[2] that the eigenvalues of $\tilde{V}$ are $\pm 3e\mathcal{E}a_0$ and 0. The corresponding eigenkets are $2^{-1/2}(1, \pm 1, 0, 0)$, $(0, 0, 1, 0)$ and $(0, 0, 0, 1)$ (with the final two eigenstates still degenerate). We conclude that as soon as the slightest perturbation is switched on, the system is in the state of lowest energy, i.e.,

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|200\rangle + |210\rangle\right) \tag{6.44}$$

with energy $E_b = -3a_0e\mathcal{E}$.

[2]The top left hand block just corresponds to diagonalizing σ_x, and the lower block is just the all zero matrix.