Quantum Mechanics Lectures

1 Time Independent Perturbation Theory

We start with the Hamiltonian $H = H_0 + H_p$ where we assume that we know the solution of the Schrödinger equation for the unperturbed Hamiltonian H_0

$$H_0|n\rangle = E_n|n\rangle$$

We assume that the perturbed Hamiltonian H_p is a relatively small change to H_0. We do not know the solution for the Schrödinger equation $H\psi = E\psi$. Assume for every wave function $|n\rangle$ there is a corresponding wave function ψ'_n which is a solution for the Hamiltonian H such that

$$H|\psi'_n\rangle = E'_n|\psi'_n\rangle$$

Assume all E_n are non degenerate (e.g., bound states in one dimension), we can write

$$|\psi'_n\rangle = |n\rangle + |\delta\psi_\perp\rangle$$

$\perp$ is used to indicate that the $|\delta\psi_\perp\rangle$ is supposed to be orthogonal to the unperturbed wave function $|n\rangle$,i.e. $\langle n|\delta\psi_\perp\rangle = 0$. Otherwise, we can write

$$|\psi'_n\rangle = |n\rangle + |\delta\psi_\perp\rangle + |\delta\psi_{||}\rangle = |n\rangle + (|\delta\psi\rangle - \langle n|\delta\psi\rangle|n\rangle) + \langle n|\delta\psi\rangle|n\rangle$$

$$|\psi'_n\rangle = (1 + \langle n|\delta\psi\rangle)|n\rangle + |\delta\psi_\perp\rangle$$

Let $\zeta = 1 + \langle n|\delta\psi\rangle$, therefore

$$\frac{1}{\zeta}|\psi'_n\rangle = |n\rangle + \frac{1}{\zeta}|\delta\psi_\perp\rangle$$

So always we can choose $|\delta\psi_{||}\rangle = 0$.
The Schrödinger equation for the perturbed Hamiltonian is given by $H|\psi'_n\rangle = E'_n|\psi'_n\rangle$, the right hand side can be written as $E'_n|n\rangle + E'_n|\delta\psi_\perp\rangle$. The left hand side consists of four terms

$$(H_0 + H_p)|\psi'_n\rangle = H_0|n\rangle + H_0|\delta\psi_\perp\rangle + H_p|n\rangle + H_p|\delta\psi_\perp\rangle \tag{1}$$

Multiply both sides by $\langle n|$, one gets

$$\langle n|H|\psi'_n\rangle = \langle n|E'_n|\psi'_n\rangle = \langle n|E'_n|n\rangle + \langle n|E'_n|\delta\psi_\perp\rangle = E'_n$$

$$\langle n|(H_0 + H_p)|\psi'_n\rangle = \langle n|H_0|n\rangle + \langle n|H_0|\delta\psi_\perp\rangle + \langle n|H_p|n\rangle + \langle n|H_p|\delta\psi_\perp\rangle$$
$$E'_n = E_n + \langle n|H_p|n\rangle + \langle n|H_p|\delta\psi_\perp\rangle \tag{2}$$

Now, multiplying (1) by $\langle m|$, where $m \neq n$, we get

$$E'_n\langle m|\delta\psi_\perp\rangle = \langle m|H_0|\delta\psi_\perp\rangle + \langle m|H_p|n\rangle + \langle m|H_p|\delta\psi_\perp\rangle = \langle m|H_p|n\rangle + \langle m|H_p|\delta\psi_\perp\rangle \tag{3}$$

Equations 2 and 3 have no approximation applied to them yet. Using the assumptions H_p and $\delta\psi_\perp$ are small, so we can ignore the last term in RHS of equations 2 and 3 at *first* order. Therefore for the first order approximation I do not need to know the perturbed wave function $|\delta\psi_\perp\rangle$. From 2,

$$E'_n = \langle n|H|n\rangle = E_n + \langle n|H_P|n\rangle. \tag{4}$$

From 3,

$$E'_n\langle m|\delta\psi_\perp\rangle = E_m\langle m|\delta\psi_\perp\rangle + \langle m|H_p|n\rangle$$
$$(E'_n - E_m)\langle m|\delta\psi_\perp\rangle = \langle m|H_p|n\rangle$$

To the first order approximation $E'_n = E_n$, so we get

$$(E_n - E_m)\langle m|\delta\psi_\perp\rangle = \langle m|H_p|n\rangle$$

$$\langle m|\delta\psi_\perp\rangle = \frac{\langle m|H_p|n\rangle}{E_n - E_m}$$

we can write the perturbed wave function to the first order approximation as follows

$$|\delta\psi_\perp\rangle = \sum_{n\neq m} \frac{\langle m|H_p|n\rangle}{E_n - E_m}|m\rangle \tag{5}$$

It's orthogonal to $|n\rangle$. It tells us that the change we have to apply to $|n\rangle$ is dominated by those states $|m\rangle$ for which the overlap (numerator) is large and the denominator (energy difference) is small. For the perturbation expansion to work, we require $\langle\delta\psi_\perp|\delta\psi_\perp\rangle$ to be much less than one. The overlap between any two wave functions introduced by the Hamiltonian should be small. For the second order approximation for the new energy eigenvalue, we get

$$E'_n = E_n + \langle n|H_p|n\rangle + \langle n|H_p|\sum_{n\neq m} m\rangle \frac{\langle m|H_p|n\rangle}{E_n - E_m} = E_n + \langle n|H_p|n\rangle + \sum_{n\neq m} \frac{|\langle m|H_p|n\rangle|^2}{E_n - E_m} \tag{6}$$

1.1 Example 1: Harmonic Oscillator

The unperturbed Hamiltonian can be written as $H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$
The perturbed Hamiltonian is given by $H_p = d \cdot x$. The exact solution is

$$\psi_n'(x) = \phi_n(x + \frac{d}{m\omega^2})$$

$$E_n' = E_n - \frac{d^2}{2m\omega^2}$$

To the first order approximation $E_n' = E_n$ because d is very small and therefor d^2 can be neglected. Indeed, $\langle\phi_n|H_p|\phi_n\rangle = d\langle\phi_n|x|\phi_n\rangle = 0$ for all ϕ_n.

The wave function to the first order approximation is

$$|\delta\psi_\perp\rangle = \sum_{n\neq m} \frac{\langle\phi_m|dx|\phi_n\rangle}{(n-m)\hbar\omega}|\phi_m\rangle$$

In the first semester we already showed that

$$\langle\phi_{n+1}|\hat{X}|\phi_n\rangle = \sqrt{\frac{n+1}{2}} \tag{7}$$

$$\hat{X} = \frac{x}{\sqrt{\frac{\hbar}{m\omega}}}$$

$$\langle\phi_{n-1}|\hat{X}|\phi_n\rangle = \sqrt{\frac{n}{2}} \tag{8}$$

Equations (7) and (8) are the only non-zero matrix elements.Using the raising and lowering operators we can get the same results;

$$a = \frac{1}{\sqrt{2}}(\hat{X} + i\hat{P})$$

$$\hat{X} = \frac{1}{\sqrt{2}}(a + a^\dagger)$$

$$a^\dagger|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle$$

$$a|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle$$

Therefore the sum has only two values of nonzero contribution $x = \sqrt{\frac{\hbar}{m\omega}}\hat{X}$. The wave function in the first order approximation when $n > 0$ is given by

$$|\delta\psi_\perp\rangle = d\sqrt{\frac{\hbar}{m\omega}}(\frac{\sqrt{\frac{n+1}{2}}}{-\hbar\omega}|\phi_{n+1}\rangle + \frac{\sqrt{\frac{n}{2}}}{\hbar\omega}|\phi_{n-1}\rangle),$$

which means the wave function changes in the first order. Let $n = 0$:

$$|\delta\psi_\perp\rangle = -d\sqrt{\frac{\hbar}{2m\omega}}\frac{1}{\hbar\omega}|\phi_1\rangle = -d\sqrt{\frac{1}{2m\hbar\omega^3}}|\phi_1\rangle$$

$$|\phi_1\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\sqrt{\frac{1}{2^1\cdot 1!}}\left(2\sqrt{\frac{m\omega}{\hbar}}x\right)\exp(\frac{-m\omega x^2}{2\hbar}) \Rightarrow$$

$$|\delta\psi_\perp\rangle = -d\sqrt{\frac{1}{2m\hbar\omega^3}}\sqrt{\frac{2m\omega}{\hbar}}x\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\exp(\frac{-m\omega x^2}{2\hbar})$$

$$|\delta\psi_\perp\rangle = -d\sqrt{\frac{1}{\hbar^2\omega^2}}x|\phi_0(x)\rangle$$

which is the same answer that we get for the exact solution ψ_0' if we Taylor-expand it to first order in d:

$$\psi_0' = (\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}\exp(\frac{-m\omega(x+\frac{d}{m\omega^2})^2}{2\hbar}) = (\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}\exp(\frac{-m\omega x^2}{2\hbar} - \frac{xd}{\omega\hbar} - ...) \Rightarrow$$

$$\psi_0' = \phi_0(x)(1 - \frac{dx}{\hbar\omega}).$$

Now we need to evaluate the second order for E_n':

$$E_n' = E_n + \sum_{n\neq m}\frac{|\langle\phi_m|dx|\phi_n\rangle|^2}{E_n - E_m} = E_n + \frac{d^2\hbar}{m\omega}(\frac{n+1}{-2\hbar\omega} + \frac{n}{2\hbar\omega})$$

$$E_n' = E_n - \frac{d^2\hbar}{m\omega}(\frac{1}{2\hbar\omega}) = E_n - \frac{d^2}{2m\omega^2}$$

Which is the exact solution. Therefore the energy comes out right after only the second order approximation.