Lecture 16

Optional: Time Independent Pertubation Theory

Study Goal of This Lecture

- Pertubation theory (non-degenerate)
- First-order perturbation - Zeeman effect
- Second-order pertubation - Stark effect

16.1 Time Independent Perturbation Theory

We have briefly discussed the variational theory, in this lecture, we will discuss about another important approximation method in QM, the perturbation theory!

The idea is to treat a small addition to the Hamiltonian as a "perturbation" (small correction) to the eigenstates and eigenenergies of a set of already known eigenstates.

$$\hat{H} = \hat{H}_0 + \lambda V. \tag{16.1}$$

$\hat{H}_0$ is zero-th order Hamiltonian which can be exactly solved, it is an unperturbed system. It will satisfy:

$$\hat{H}_0 \left|\phi_n^{(0)}\right\rangle = E_n^{(0)} \left|\phi_n^{(0)}\right\rangle, \tag{16.2}$$

and λV stands for perturbation, it is a small correction to the $\hat{H}_0$. V is required to

be small, otherwise the perturbation theory is not applicable. λ is a number bewteen 0 and 1, it is used to effectly "turn on" the perturbation.

Note that we actually want to solve

$$\hat{H}\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle \tag{16.3}$$

with introduction of λ, $|\psi_n\rangle \equiv |\psi_n(\lambda)\rangle$, $E_n = E_n(\lambda)$. We expand the ture eigenwavefunction and energy with respect to λ. That is:

$$|\psi_n(\lambda)\rangle = |\psi_n(\lambda=0)\rangle + \overbrace{\frac{\partial\left|\psi_n(\lambda)\right\rangle}{\partial\lambda}\Big|_{\lambda=0}}^{\left|\psi_n^{(1)}\right\rangle}\lambda + \overbrace{\frac{1}{2!}\frac{\partial^2\left|\psi_n(\lambda)\right\rangle}{\partial\lambda^2}\Big|_{\lambda=0}}^{\left|\psi_n^{(2)}\right\rangle}\lambda^2 + \cdots, \tag{16.4}$$

$$E_n(\lambda) = E_n(\lambda=0) + \underbrace{\frac{\partial E_n}{\partial\lambda}\Big|_{\lambda=0}}_{E_n^{(1)}}\lambda + \underbrace{\frac{1}{2!}\frac{\partial^2}{\partial E_n^2}\Big|_{\lambda=0}}_{E_n^{(2)}}\lambda^2 + \cdots. \tag{16.5}$$

We rewrite:

$$|\psi_n\rangle = |\psi_n(\lambda=0)\rangle + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^{(2)}\right\rangle + \cdots, \tag{16.6}$$

$$E_n = E_n(\lambda=0) + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \tag{16.7}$$

We define some terms above as:

$\left|\psi_n^{(1)}\right\rangle$: First-order wavefunction correction

$E_n^{(1)}$: First-order energy correction

$E_n^{(2)}$: Second-order energy correction etc.

Clearly, $|\psi(\lambda=0)\rangle = \left|\psi_n^{(0)}\right\rangle$ and $E_n(\lambda=0) = E_n^{(0)}$ by letting λ goes to zero.

Now, we require that

$$\left\langle\psi_n^{(0)}\middle|\psi_n\right\rangle = 1 : \text{intermediate normalization}$$

. In this case, $\langle\psi_n|\psi_n\rangle \neq 1$, not normalized. Note that this will not change the eigenvalues. Also, $|\psi_n\rangle$ can be easily normalized in the end. So it does not affects the results, but will make the expressions much simpler.

Note that by multiply $\left\langle\psi_n^{(0)}\right|$ from the left in Equ (16.6), we obtain

$$1 = 1 + \lambda\left|\psi_n^{(1)}\right\rangle + \lambda^2\left|\psi_n^2\right\rangle + \cdots, \tag{16.8}$$

which must be satisfied by all $\lambda = 0 \cdots 1$. So $\left\langle \psi_n^{(0)} \middle| \psi_n^{(k)} \right\rangle = 0$, this implies that there is no $\left|\psi_n^{(0)}\right\rangle$ components in corrections.
Plug Equ (16.6), (16.7) into the Schrödinger equation for the full system, we obtain.

$$\begin{aligned} &(\hat{H}_0 + \lambda V)(\left|\psi_n^{(0)}\right\rangle + \lambda \left|\psi_n^{(1)}\right\rangle + \lambda^2 \left|\psi_n^{2}\right\rangle + \cdots) \\ &= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(\left|\psi_n^{(0)}\right\rangle + \lambda \left|\psi_n^{(1)}\right\rangle + \lambda^2 \left|\psi_n^{2}\right\rangle + \cdots) \end{aligned} \tag{16.9}$$

expand the expression and collec in powers of λ, we obtain:

$$\begin{aligned} &\hat{H}_0 \left|\psi_n^{(0)}\right\rangle + \lambda(\hat{V} \left|\psi_n^{(0)}\right\rangle + \hat{H}_0 \left|\psi_n^{(1)}\right\rangle) + \lambda^2(\hat{V} \left|\psi_n^{1}\right\rangle + \hat{H}_0 \left|\psi_n^{2}\right\rangle) \\ &= E_n^{(0)} \left|\psi_n^{(0)}\right\rangle + \lambda(E_n^1 \left|\psi_n^{0}\right\rangle + E_n^0 \left|\psi_n^{(1)}\right\rangle) \\ &+ \lambda^2(E_n^{(2)} \left|\psi_n^{(0)}\right\rangle + E_n^1) \left|\psi_n^{(1)}\right\rangle + E_n^{(0)} \left|\psi_n^{(2)}\right\rangle) + \cdots \end{aligned} \tag{16.10}$$

for the equation to hold with arbitrary valid λ, we require the coefficents of same term to be the same on both side. Therefore,

$$\lambda^0 : \ \hat{H}_0 \left|\psi_n^{(0)}\right\rangle = E_n^{(0)} \left|\psi_n^{(0)}\right\rangle \tag{16.11}$$

$$\lambda^1 : \ \hat{V} \left|\psi_n^{(0)}\right\rangle + \hat{H}_0 \left|\psi_n^{(1)}\right\rangle = E_n^1 \left|\psi_n^{0}\right\rangle + E_n^0 \left|\psi_n^{(1)}\right\rangle \tag{16.12}$$

$$\lambda^2 : \ \hat{V} \left|\psi_n^{1}\right\rangle + \hat{H}_0 \left|\psi_n^{2}\right\rangle = E_n^{(2)} \left|\psi_n^{(0)}\right\rangle + E_n^1) \left|\psi_n^{(1)}\right\rangle + E_n^{(0)} \left|\psi_n^{(2)}\right\rangle \tag{16.13}$$

Actually, we now can obtain the form of all corretion term now by comparing the both side of the equal sign. We take a close look at several terms:

16.1.1 The first-order energy correction

We mutiply λ^1 term with $\left\langle \psi_n^{(0)} \right|$,

$$\left\langle \psi_n^{(0)} \middle| \hat{H}_0 \middle| \psi_n^{(1)} \right\rangle + \left\langle \psi_n^{(0)} \middle| \hat{V} \middle| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left\langle \psi_n^{(0)} \middle| \psi_n^{(0)} \right\rangle \tag{16.14}$$

note that $\left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle = 0$ and

$$\left\langle \psi_n^{(0)} \middle| \hat{H}_0 \middle| \psi_n^{(1)} \right\rangle = \left\langle \psi_n^{(0)} \middle| \hat{H}_0 \middle| \psi_n^{(0)} \right\rangle^* = \left\langle \psi_n^{(1)} \middle| E_n^{(0)} \middle| \psi_n^{(0)} \right\rangle^* = E_n^{(0)} \left\langle \psi_n^{(0)} \middle| \psi_n^{(1)} \right\rangle = 0 \tag{16.15}$$

so

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \middle| \hat{V} \middle| \psi_n^{(0)} \right\rangle \tag{16.16}$$

The first-order energy correction is the diagonal matrix element of $\hat{V}$.

16.1.2 The first order wavefunction correction

We expand $\left|\psi_n^{(1)}\right\rangle$ in terms of the complete orthonormal set of unperturbed eigenfunctions $\left|\psi_m^{(0)}\right\rangle$ for $m \neq n$ (required: $\left\langle\psi_n^{(0)}\middle|\psi_n^{(1)}\right\rangle = 0$):

$$\left|\psi_n^{(1)}\right\rangle = \sum_m a_m \left|\psi_m^{(0)}\right\rangle \tag{16.17}$$

where $a_m = \left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle$. Mutiply $\left\langle\psi_m^{(0)}\right|$ to the λ^1 equation, we obtain

$$E_m^{(0)}\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle + \left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle = E_n^{(0)}\left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle + E_n^{(1)}\cancelto{0}{\left\langle\psi_m^{(0)}\middle|\psi_n^{(0)}\right\rangle} \tag{16.18}$$

therefore,

$$a_m = \left\langle\psi_m^{(0)}\middle|\psi_n^{(1)}\right\rangle = \frac{\left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}, \tag{16.19}$$

$$\left|\psi_n^{(1)}\right\rangle = \left|\psi_n^{(0)}\right\rangle + \sum_{m\neq n}\frac{\left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}}. \tag{16.20}$$

Off-diagonal terms ($m \neq n$) in $\hat{V}$ will "mix" zero-th order states, this is actually the core of all dynamics.

$\left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle$ is the coupling.

16.1.3 The second-order energy correction

One can then evaluate from λ^2 equation that

$$E_n^{(2)} = \sum_{n\neq m}\frac{\left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle\left\langle\psi_n^{(0)}\middle|\hat{V}\middle|\psi_m^{(0)}\right\rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_{n\neq m}\frac{\left|\left\langle\psi_m^{(0)}\middle|\hat{V}\middle|\psi_n^{(0)}\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{16.21}$$

note that for ground state, $E_n^{(0)} - E_m^{(0)} < 0$. So, the second-order energy correction is always "negative". Second-order perturbation always lowers the groundstate energy. Also note that the energy correction is quadratic in the coupling matrix element. This is frequently encounter in chemical physics.

When implementing the perturbation theory, needs for higher order is not worthy. If one are going to use third or even fourth-order correction, he/she should consider change his/her method.

16.1.4 Example: Zeeman Effect and Stark Effect

Zeeman effect is stemed from the first-order perturbation and the Stark effect come from second-order perturbation.

Consider the hydrogen atom in its $1s$ groundstate in an electric field. The interaction energy is described by the Stark Hamiltonian for a E-field interacting with the electric dipole moment $q\dot{R}$ of the atom:

$$\hat{V}_s = -q\vec{E} \cdot \vec{R} = -q\epsilon\hat{z} \tag{16.22}$$

consider first order perturbation:

$$E^{(1)} = \langle 1s|\hat{V}_s|1s\rangle = 0 \quad (\because \hat{V}_s \text{ is odd}) \tag{16.23}$$

The lowest non-zero correction is the second-order term.

$$E^{(2)} = q^2\epsilon^2 \sum_{n\neq 1,l,m} \frac{|\langle 1,0,0|z|n,l,m\rangle|^2}{E_1 - E_n} \tag{16.24}$$

note that the energy correction is "negative" and quadratic in the E field. The trick to evaluate the correction energy is put below, but we show the plot of energy and intensity of field first:

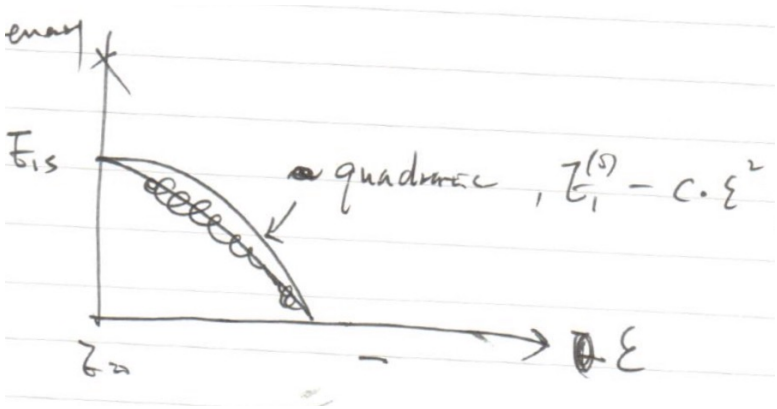

Figure 16.1: Stark effect

By directly observe, we find that the energy of $1s$ orbital change under the influence of electric field, this is Stark effect.

Trick to evaluate $\langle 1,0,0|z|n,l,m\rangle$:

$$\psi_{n,l,m} = R_{n,l}(r)Y_l^m(\theta,\phi), \quad \psi_{1,0,0} = R_{10}(r)Y_0^0(\theta,\phi) = R_{10}(r)\sqrt{\frac{1}{4\pi}}, \tag{16.25}$$

and

$$z = r\cos\theta = r\Big(\frac{4\pi}{3}^{\frac{1}{2}}\Big)Y_1^0. \tag{16.26}$$

Therefore,

$$\begin{aligned}
\langle 1,0,0|z|n,l,m\rangle &= \int R_{10}(r)\sqrt{\frac{1}{4\pi}} \times r \times \Big(\frac{4\pi}{3}^{\frac{1}{2}}\Big)Y_1^0 \times R_{nl}(r)Y_l^m(\theta,\phi)d\tau \\
&= \frac{1}{\sqrt{3}}\int_{-\infty}^{\infty}\int_0^{\pi}\int^{2\pi} R_{10}(r)rR_{nl}(r)\cdot Y_1^0 Y_l^m r^2\sin\theta dr d\theta d\phi \\
&= \frac{1}{\sqrt{3}}\int_{-\infty}^{\infty} r^3 R_{10}(r)R_{nl}(r)\underbrace{\iint Y_1^0 Y_l^m \sin\theta d\theta d\phi}_{\delta_{l,1}\delta_{m,0}}
\end{aligned} \tag{16.27}$$