

$$H = H_0 + H' = H_0 + \lambda W.$$

$H'$  is characterized by a small parameter  $\lambda$ . We would like to approach the eigensolution and eigenvalues as a series expansion starting from those of  $H_0$ . We assume  $H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$ , and first consider the simple case that the energy level  $E_n^{(0)}$  is well-separated from others. This case is called non-degenerate perturbation theory.

Let us expand

$$\left. \begin{aligned} E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \\ \psi_n &= \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots \end{aligned} \right\} \text{ plug into } \boxed{H \psi = E \psi}.$$

$$\Rightarrow \lambda^{(0)} \text{ order : } H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}$$

$$\lambda^1 \text{ order : } H_0 \psi_n^{(1)} + W \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$

$$\Rightarrow (H_0 - E_n^{(0)}) \psi_n^{(1)} = (E_n^{(1)} - W) \psi_n^{(0)}$$

$$\lambda^2 \text{ order : } H_0 \psi_n^{(2)} + W \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

$$\Rightarrow (H_0 - E_n^{(0)}) \psi_n^{(2)} = (E_n^{(1)} - W) \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

...

1st order: we use the zeroth order wavefunction as the bases

to expand  $\psi_n^{(1)} = \sum_{n'} a_{n'}^{(1)} \psi_{n'}^{(0)}$ .

$$\Rightarrow [H_0 - E_n^{(0)}] \psi_n^{(1)} = (E_n^{(1)} - W) \psi_n^{(0)}$$

$$\sum_{n'} a_{n'}^{(1)} [E_{n'}^{(0)} - E_n^{(0)}] \psi_{n'}^{(0)} = (E_n^{(1)} - W) \psi_n^{(0)}$$

$$\int \psi_m^{(0)*} \Rightarrow a_m^{(1)} (E_m^{(0)} - E_n^{(0)}) = E_n^{(1)} \delta_{mn} - \langle \psi_m^{(0)} | W | \psi_n^{(0)} \rangle$$

set  $m=n \Rightarrow E_n^{(1)} = \langle \psi_n^{(0)} | W | \psi_n^{(0)} \rangle$

$$m \neq n \Rightarrow a_m^{(1)} = - \frac{\langle \psi_m^{(0)} | W | \psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}}$$

or at 1st order  $\Rightarrow$

$$E_n = E_n^{(0)} + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle$$

$$\psi_n = \psi_n^{(0)} + \sum_m' \frac{\psi_m^{(0)} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

The summation  $\sum_m'$  excludes the term of  $m=n$ . The reason is that: according to the normalization condition

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^{(0)} + \lambda \psi_n^{(1)} | \psi_n^{(0)} + \lambda \psi_n^{(1)} \rangle = 1$$

Considering  $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1 \Rightarrow \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle = 0$

plug in  $\psi_n^{(1)} = \sum_{n'} a_{n'}^{(1)} \psi_{n'}^{(0)} \Rightarrow$  only  $n'=n$  term survives

$$\Rightarrow a_n^{(1)} + a_n^{(1)*} = 0 \Rightarrow a_n^{(1)} = i\gamma \quad (\gamma \text{ is real})$$

$$\Rightarrow \psi_n^{(0)}(1 + a_n^{(1)}) = e^{i\gamma\lambda} \psi_n^{(0)} \text{ which is just a phase shift}$$

$$\begin{aligned} \Rightarrow \psi_n &= e^{i\lambda\gamma} \psi_n^{(0)} + \lambda \sum_m' a_m^{(1)} \psi_m^{(0)} \\ &\approx e^{i\lambda\gamma} \left[ \psi_n^{(0)} + \lambda \sum_m' a_m^{(1)} \psi_m^{(0)} \right] + O(\lambda^2). \end{aligned}$$

usually, we approximate wavefunction up to first order. But for energy in many cases,  $\langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle = 0$  due to symmetry reasons, and we need to calculate up to  $\lambda^2$  order.

Consider

$$(H_0 - E_n^{(0)}) \psi_n^{(2)} = (E_n^{(1)} - W) \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

plug in  $\psi_n^{(2)} = \sum_m a_m^{(2)} \psi_m^{(0)}$

$$\text{and } \psi_n^{(1)} = \sum_m' \frac{\psi_m^{(0)} \langle \psi_m^{(0)} | W | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_m' a_m^{(1)} \psi_m^{(0)}$$

$$\Rightarrow \sum_m (E_m^{(0)} - E_n^{(0)}) a_m^{(2)} \psi_m^{(0)} = \sum_m' (E_n^{(1)} - W) a_m^{(1)} \psi_m^{(0)} + E_n^{(2)} \psi_n^{(0)}$$

$$\begin{aligned} \Rightarrow (E_{m'}^{(0)} - E_n^{(0)}) a_{m'}^{(2)} &= a_{m'}^{(1)} E_n^{(1)} - \sum_m \langle \psi_{m'}^{(0)} | W | \psi_m^{(0)} \rangle a_m^{(1)} \\ &\quad + E_n^{(2)} \delta_{n,m'} \end{aligned}$$

set  $m' = n$ , and notice that  $a_n^{(1)} = 0 \Rightarrow$

$$E_n^{(2)} = \sum_m' \langle \psi_n^{(0)} | W | \psi_m^{(0)} \rangle a_m^{(1)}$$

$$= + \sum_m' \frac{\langle \psi_n^{(0)} | W | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | W | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_m^{(0)})}$$

⇒ the second order correction to energy

$$E_n = E_n^{(0)} + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle + \sum_m' \frac{|\langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

★ Example: Polarizability of dielectric material

We can approximate dielectric materials as a bunch of bound charges, or, oscillators. Suppose we add an electric field  $\vec{E}$  along x-direction

$$H = \underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{H_0} + \underbrace{\frac{1}{2} m \omega_0^2 x^2}_{H'} - qEx$$

The "unperturbed" WF:  $\psi_n^{(0)}(x) = N_n H_n\left(\frac{x}{l}\right) e^{-\frac{x^2}{2l^2}}$ ,  $l = \sqrt{\frac{\hbar}{m\omega}}$

$$E_n^{(0)} = (n + \frac{1}{2}) \hbar \omega.$$

We need matrix element  $\langle m | H' | n \rangle = -qE \langle m | x | n \rangle$ .

we know  $x = l \frac{a + a^\dagger}{\sqrt{2}}$ ,  $\Rightarrow \langle m | x | n \rangle = \frac{l}{\sqrt{2}} \{ \langle m | a | n \rangle + \langle m | a^\dagger | n \rangle \}$

$$= l \left[ \sqrt{\frac{n+1}{2}} \delta_{m,n+1} + \sqrt{\frac{n}{2}} \delta_{m,n-1} \right]$$

$$E_n = E_n^{(0)} + \langle n | H' | n \rangle + \sum_m' \frac{|\langle m | H' | n \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\langle n | H' | n \rangle = 0$$

$$\Rightarrow E_n = (n + \frac{1}{2}) \hbar \omega + \frac{q^2 E^2}{\hbar \omega_0} \left[ \overbrace{|\langle n-1 | x | n \rangle|^2}^{\left(\frac{n}{2}\right)^2 \ell^2} - \overbrace{|\langle n+1 | x | n \rangle|^2}^{\left(\frac{n+1}{2}\right)^2 \ell^2} \right]$$

$$= (n + \frac{1}{2}) \hbar \omega - \frac{q^2 E^2 \ell^2}{2 \hbar \omega_0}$$

$$= (n + \frac{1}{2}) \hbar \omega - \frac{q^2 E^2}{2 m \omega_0^2}$$

(all the energy levels are lowered  
-  $q^2 E^2 / 2 m \omega_0^2$ )

wavefunction

$$\psi_n(x) = \psi_n^{(0)}(x) + \sum_m' \frac{\psi_m^{(0)} \langle \psi_m^{(0)} | H' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$= \psi_n^{(0)}(x) + \frac{(-qE)}{\hbar \omega_0} \ell \left[ -\sqrt{\frac{n+1}{2}} \psi_{n+1}^{(0)} + \sqrt{\frac{n}{2}} \psi_{n-1}^{(0)} \right]$$

$$= \psi_n^{(0)}(x) + \frac{qE}{\hbar \omega_0} \ell \left[ \sqrt{\frac{n+1}{2}} \psi_{n+1}^{(0)} - \sqrt{\frac{n}{2}} \psi_{n-1}^{(0)} \right]$$

$$\bar{x}_n = \frac{\langle \psi_n | x | \psi_n \rangle}{\langle \psi_n | \psi_n \rangle} = \underbrace{\langle \psi_n^{(0)} | x | \psi_n^{(0)} \rangle}_0 + \underbrace{\langle \psi_n^{(0)} | x | \psi_n' \rangle}_n + \underbrace{\langle \psi_n' | x | \psi_n^{(0)} \rangle}_n$$

$$= \frac{2qE}{\hbar \omega_0} \ell \left\{ \langle \psi_n^{(0)} | x | \psi_{n+1}^{(0)} \rangle \sqrt{\frac{n+1}{2}} - \langle \psi_n^{(0)} | x | \psi_{n-1}^{(0)} \rangle \sqrt{\frac{n}{2}} \right\}$$

$$= \frac{2qE}{\hbar \omega_0} \ell^2 \left[ \left( \sqrt{\frac{n+1}{2}} \right)^2 - \left( \frac{n}{2} \right)^2 \right] = \frac{qE}{\hbar \omega_0} \frac{\hbar}{m \omega_0^2} = \frac{qE}{m \omega_0^2}$$

$\Rightarrow$  all the states, their position are shifted along the electric field  $\frac{qE}{m \omega_0^2}$

$$\Rightarrow \text{polarizability } \chi = \frac{q \cdot \bar{x}}{E} = \frac{q^2 E}{m \omega_0^2}.$$

This can also be obtained through the thermodynamic relation

$$\Delta E = -\frac{1}{2} \chi E^2 = -\frac{q^2 E^2}{2 m \omega_0^2} \Rightarrow \chi = \frac{q^2 E}{m \omega_0^2}.$$

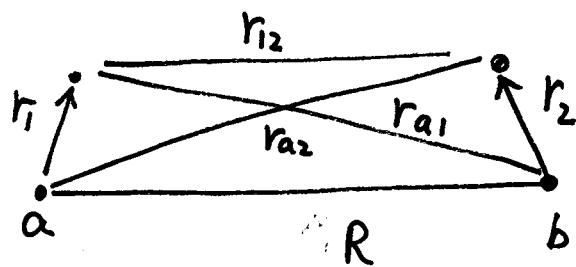
This problem can be solved exactly.  $\frac{1}{2} m \omega_0^2 x^2 - q E x$

The 2nd correction of energy is already correct!

$$= \frac{1}{2} m \omega_0^2 \left( x - \frac{q E}{m \omega_0^2} \right)^2 - \frac{q^2 E^2}{2 m \omega_0^2}.$$

## §2. Van der Waals force

Consider two hydrogen atoms a and b, each carries one proton and one electron.



$$H = H_0 + H'$$

$$H_0 = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

$$H' = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}}$$

$$\xrightarrow[\text{dipolar interaction}]{R \gg a_{\text{Bohr}}} \frac{\vec{D}_1 \cdot \vec{D}_2 - 3(\vec{D}_1 \cdot \hat{R})(\vec{D}_2 \cdot \hat{R})}{R^3}$$

where  $\vec{D}_1 = -e\vec{r}_1$   
 $\vec{D}_2 = -e\vec{r}_2$

When the atoms are in the ground states,

the overlap between wavefunctions are small, such that we can neglect the symmetry requirement of fermions.

$$\psi_0 = \psi_{L1s}(r_1) \psi_{R1s}(r_2)$$

$$E^{(1)}: \langle \psi_0 | H' | \psi_0 \rangle = 0$$

$$E^{(2)}: \sum_k' \frac{|\langle \psi_k | H' | \psi_0 \rangle|^2}{E_0 - E_k} \propto -\frac{1}{R^6}$$

$$|\psi_k\rangle \sim \psi_{L2p}(r_1) \psi_{R2p}(r_2)$$

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~~The first atom due to fluctuation (induced by the second one)~~

~~randomly generate a dipole moment  $P_1$ ,  $P_1$  will generate E field~~

~~$\propto \frac{P_1}{R^3}$  at the position of the second dipole. It induce the second~~

~~dipole  $\propto \chi \frac{P_1}{R^3}$ , and thus the energy lowered  $\propto -\frac{P^2}{R^6}$ .~~