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

H' is characterized by a small parameter λ. We would like to approch the eigensolution and eigenvalues as a series expansion starting from these 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-seperated from others. This case is called non-degenerate perturbation theory.

Let us expand

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

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

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

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

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

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

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1st order : we use the zeroth order eveafunctiun as the bases to expand $\psi_n^{(1)} = \sum_{n'} a_{n'}^{(1)} \psi_{n'}^{(0)}$.

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

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

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

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

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

or at 1st order $\Rightarrow$

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

The summation $\sum_m{}'$ excludes the term of $m = n$. The reason is that: according to the normalizatiun cnelitiun

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

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

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

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

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

$$\Rightarrow \quad \psi_n = e^{i\lambda\gamma}\, \psi_n^{(0)} + \lambda \sum_m{}' a_m^{(1)}\, \psi_m^{(0)}$$

$$\simeq e^{i\lambda\gamma} \left[\psi_n^{(0)} + \lambda \sum_m{}' a_m^{(1)}\, \psi_m^{(0)} \right] + O(\lambda^2).$$

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 λ^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 $\quad \psi_n^{(2)} = \sum_m a_m^{(2)}\, \psi_m^{(0)}$

and $\quad \psi_n^{(1)} = \sum_m{}' \dfrac{\psi_m^{(0)} \langle \psi_m^{(0)} | \; W \; | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} = \sum_m{}' a_m^{(1)}\, \psi_m^{(0)}$

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

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

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

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

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

$\Rightarrow$ the second order correction to energy

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

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Example: Polarizibility of dielectric material

We can approximate dielectric materials as a bounch ⊖∿⊕ of bound charges, or, oscillaters. Suppose we add an electric field $\vec{E}$ along x-direction $H = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega_0^2 x^2}_{H_0} \underbrace{- qEx}_{H'}$

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

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

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

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

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

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

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

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

$$\left(\frac{n}{2}\right)\ell^2 \qquad \left(\frac{n+1}{2}\right)\ell^2$$

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

$$= (n+\tfrac{1}{2})\hbar\omega - \frac{q^2E^2}{2m\omega_0^2} \quad \text{(all the energy levels are lowered } -q^2E^2/2m\omega_0^2\text{)}$$

wavefunction

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

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

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

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

$$\langle\psi_n^0|x|\psi_n^0\rangle = 0$$

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

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

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

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$\Rightarrow$ polarizibility $\chi = \dfrac{q\cdot\bar{x}}{E} = \dfrac{q^2 E}{m\omega_0^2}$.

This can also be obtained through the thermodynamic relation

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

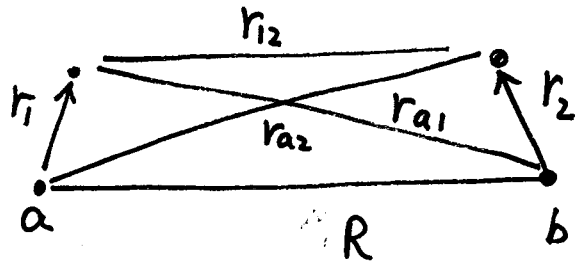
This problem can be solved exactly. $\frac{1}{2}m\omega_0^2 x^2 - qEx$

The 2nd correction of energy is already correct!

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

§2. Van der Waals force

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



$$H = H_0 + H'$$

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

$$H' = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} \xrightarrow[\text{dipolar interaction}]{R \gg a_{Bohr}} \frac{\vec{D}_1\cdot\vec{D}_2 - 3(\vec{D}_1\cdot\hat{R})(\vec{D}_2\cdot\hat{R})}{R^3}$$

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.

$$\psi_0 = \psi_{L1S}(r_1)\ \psi_{R1S}(r_2)$$

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

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

$$|\psi_k\rangle \sim \psi_{L2p}(r_1)\,\psi_{R,2p}(r).$$

The first ~~atom~~ due to fluctuation (induced by the second one) randomly generate a dipole moment P_1. P_1 will generate E filed $\propto \frac{P_1}{R^3}$ at the position of the second dipole. It induce the second dipole $\propto \frac{\chi P_1}{R^3}$, and thus the energy lowered $\propto -\frac{P^2}{R^6}$.

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