Thursday, January 24, 2013 #1

**Example:** perturbation of a 2-level system

Consider
$$H_0 = \begin{array}{c|cc} & |\varphi_1\rangle & |\varphi_2\rangle \\ \hline \langle\varphi_1| & E_1 & 0 \\ \langle\varphi_2| & 0 & E_2 \end{array} \quad \text{and} \quad W = \begin{pmatrix} \cancel{\emptyset}\ \varepsilon_1 & V \\ V^* & \cancel{\emptyset}\ \varepsilon_2 \end{pmatrix}$$

1st order:
$$E_1' = E_1 + \langle\varphi_1|W|\varphi_1\rangle \xrightarrow{} \varepsilon_1 = E_1 + \varepsilon_1$$

$$E_2' = E_2 + \langle\varphi_2|W|\varphi_2\rangle \xrightarrow{} \varepsilon_2 = E_2 + \varepsilon_2$$

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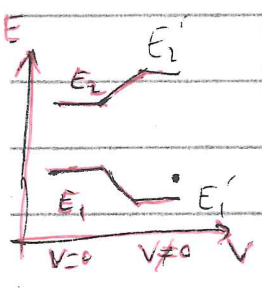
~~1st order~~
$$|\varphi_1\rangle' = |\varphi_1\rangle + \frac{\langle\varphi_2|W|\varphi_1\rangle}{E_1 - E_2}|\varphi_2\rangle$$
$$= |\varphi_1\rangle + \frac{V^*}{E_1 - E_2}|\varphi_2\rangle$$

$$|\varphi_2\rangle' = |\varphi_2\rangle + \frac{\langle\varphi_1|W|\varphi_2\rangle}{E_2 - E_1}|\varphi_1\rangle$$
$$= |\varphi_2\rangle + \frac{V}{E_2 - E_1}|\varphi_1\rangle$$

note: $\langle\varphi_1'|\varphi_2'\rangle = 0$

2nd order:
$$E_1'' = \cancel{E_1'}\ E_1 + \frac{|\langle\varphi_2|W|\varphi_1\rangle|^2}{E_1 - E_2} = E_1 + \frac{|V|^2}{E_1 - E_2}$$

$$E_2'' = \cancel{E_2'}\ E_2 + \frac{|\langle\varphi_1|W|\varphi_2\rangle|^2}{E_2 - E_1} = E_2 + \frac{|V|^2}{E_2 - E_1}$$




note: - if $E_1 < E_2$, then perturbed level repelled by off-diagonal coupling, $V = \langle\varphi_1|W|\varphi_2\rangle$

- if $E_2 > E_1$, same thing.

$\Rightarrow$ no level crossing theorem.

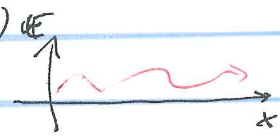
## Validity of perturbation theory

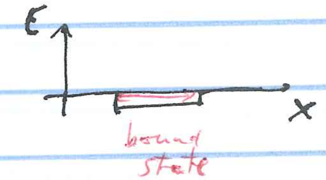
if $\left(\frac{\lambda}{\omega}\right)$ is sufficiently small then generally perturbation theory is valid.

Exception: In many-body system you can get a quantum phase transition in which the nature/symmetry of the wave function changes dramatically at a critical value of a Hamiltonian parameter.

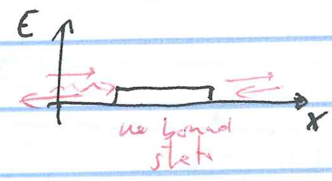
ex: 1) cooper-pairing in superconductivity

2) Mott-Insulator transition

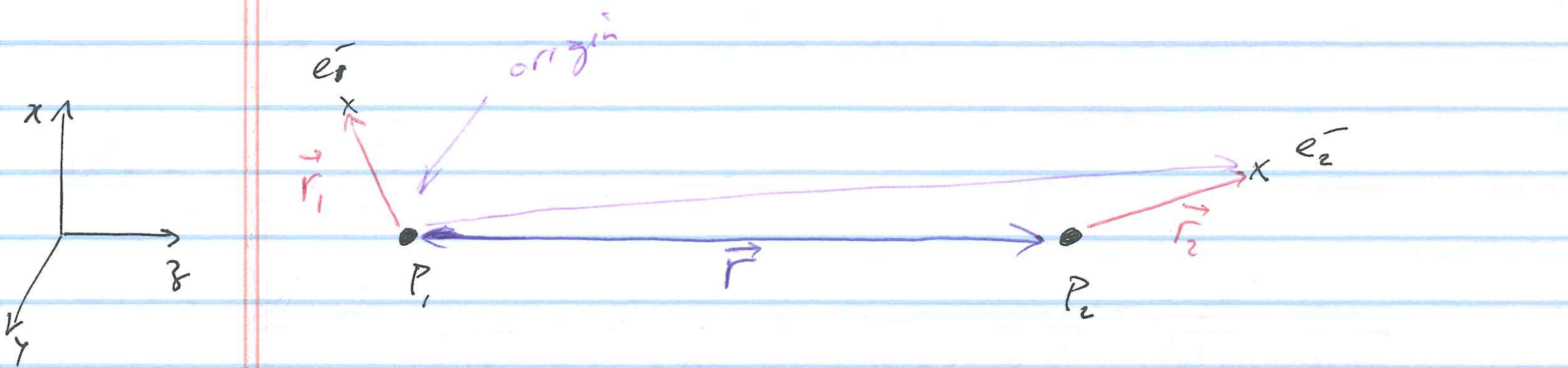
3) 


(see Sakurai & Napolitano) p 305 eq. 5.1.15



Example : van der waals force between two H atoms




$$H = \underbrace{H_{0,1} + H_{0,2}}_{H_0} + H_{int}$$

$$H_{0,1} = \frac{P_1^2}{2\mu_1} \cancel{+} - \frac{e^2}{r_1} \quad ; \quad H_{0,2} = \frac{P_2^2}{2\mu_2} - \frac{e^2}{r_2}$$

$$e^2 = \frac{q^2}{4\pi\varepsilon_0} \quad ; \quad \mu_1 = \mu_2 = \frac{m_e m_p}{m_e + m_p}$$

$$H_{int} = \underbrace{\frac{e^2}{r}}_{P_1, P_2} + \underbrace{\frac{e^2}{|\vec{r} + \vec{r}_2 - \vec{r}_1|}}_{e_1^-, e_2^-} - \underbrace{\frac{e^2}{|\vec{r} - \vec{r}_1|}}_{P_2, e_1^-} - \underbrace{\frac{e^2}{|\vec{r} + \vec{r}_2|}}_{P_1, e_2^-}$$

If both atoms are in the ground state $|n, l, m_l\rangle = |1, 0, 0\rangle$, then the wavefunction for the unperturbed Hamiltonian $H_0 = H_{0,1} + H_{0,2}$ is given by

$$|\psi\rangle = |n_1, l_1, m_1\rangle |n_2, l_2, m_2\rangle = |1,0,0\rangle_1 |1,0,0\rangle_2$$

$$\langle r_1 | \langle r_2 | \psi \rangle = \psi_{1,0,0}(\vec{r}_1)\ \psi_{1,0,0}(\vec{r}_2)$$

wavefunction for the g.s of $H_{0,1}$

wavefunction for the g.s. of $H_{0,2}$

We will treat $H_{int}$ as the perturbation, i.e. $W = H_{int}$

~~state~~ let's simplify $H_{int}$:

note: $\underset{\uparrow \text{ unperturbed}}{E_0} = \langle\psi|H_0|\psi\rangle = 2\times(-13.6\,eV)$ ← no "r" dependence

$$\cancel{H_{int} = \frac{e^2}{r}\{r+}$$

$$H_{int} = \frac{e^2}{r} + \frac{e^2}{\sqrt{(x_2-x_1)^2 + (y_2-y_1)^2 + \underbrace{(r+z_2-z_1)^2}_{r^2+2r(z_2-z_1)+(z_2-z_1)^2}}} - \frac{e^2}{\sqrt{x_1^2+y_1^2+(r-z_1)^2}}$$

$$- \frac{e^2}{\sqrt{x_2^2+y_2^2+\underbrace{(r+z_2)^2}_{r^2+2rz_2+z_2^2}}}$$

$$= \frac{e^2}{r} + \frac{e^2}{r}\frac{1}{\left[1 + \frac{2(z_2-z_1)}{r} + \frac{(\vec{r}_2-\vec{r}_1)^2}{r^2}\right]^{1/2}}$$

$$- \frac{e^2}{r}\frac{1}{\left[1 - \frac{2z_1}{r} + \frac{r_1^2}{r^2}\right]^{1/2}} - \frac{e^2}{r}\frac{1}{\left[1 + \frac{2z_2}{r} + \frac{r_2^2}{r^2}\right]^{1/2}}$$

recall: $(1+\varepsilon)^{1/2} = 1 + \frac{1}{2}\varepsilon - \frac{1}{8}\varepsilon^2 + \dots$, $(1+\varepsilon)^{-1/2} = 1 - \frac{1}{2}\varepsilon + \frac{3}{8}\varepsilon^2 - \dots$ for $\varepsilon \ll 1$

~~note: $x_1, x_2, r_1, r_2, z_1, z_2 \ll r$~~

1/r expansion: note: $\overbrace{r_1, r_2, z_1, z_2}^{\sim a_0} \ll r$. we ~~oper~~ will work in this limit.

$$H_{int} \simeq \cancel{\frac{e^2}{r}} + \frac{e^2}{r}\left[\cancel{1} - \cancel{\frac{(z_2-z_1)}{r}} - \cancel{\frac{1}{2}\frac{(\vec{r}_2-\vec{r}_1)^2}{r^2}} + \frac{3}{8}\cancel{\left(\frac{2(z_2-z_1)}{r}\right)^2} + \Theta\left(\frac{1}{r^3}\right)\right]$$

$$+ \frac{\vec{r}_2\cdot\vec{r}_1}{r^2} \qquad - \frac{3 z_2 z_1}{r^2}$$

$$- \frac{e^2}{r}\left[\cancel{1} + \cancel{\frac{z_1}{r}} - \cancel{\frac{1}{2}\frac{r_1^2}{r^2}} + \cancel{\frac{3}{8}\left(\frac{2z_1}{r}\right)^2} + \Theta(1/r^3)\right]$$

$$- \frac{e^2}{r}\left[\cancel{1} - \cancel{\frac{z_2}{r}} - \cancel{\frac{1}{2}\frac{r_2^2}{r^2}} + \cancel{\frac{3}{8}\left(\frac{2z_2}{r}\right)^2} + \Theta(1/r^3)\right]$$

thus

$$H_{int} \simeq \frac{e^2}{r^3}\left\{ \underbrace{\vec{r}_2 \cdot \vec{r}_1}_{x_1 x_2 + y_1 y_2 + z_1 z_2} - 3 z_2 z_1 \right\} + \mathcal{O}\left(\frac{1}{r^4}\right)$$

$$\simeq \frac{e^2}{r^3} \underbrace{\left[ x_1 x_2 + y_1 y_2 - 2 z_1 z_2 \right]}_{\text{dipole-dipole interaction}} + \mathcal{O}\left(\frac{1}{r^4}\right)$$

(see for example Griffiths 3rd ed. p. 165 eq. 4.7)

<u>Q</u>: what is the electric dipole moment of H in the ground state?

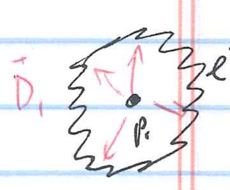
Electric Dipole moment observable / operator

$$\vec{D}_1 = q \underset{\substack{\uparrow \\ \text{classical}}}{\vec{r}_1} \equiv q \underset{\substack{\uparrow \\ \text{quantum}}}{\vec{R}_1}$$

$$\langle \vec{D}_1 \rangle = q \langle 1,0,0 | (X_1, Y_1, Z_1) | 1,0,0 \rangle \qquad r_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$$

$$= q \underbrace{\int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \int_0^{\infty} r_1^2 dr}_{\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1} \underbrace{\left[ \underbrace{\frac{1}{\sqrt{4\pi}} \frac{2}{a_0^{3/2}} e^{-r_1/a_0}}_{\text{even function}} \right]^2}_{\text{even function}} \underbrace{(X_1, Y_1, Z_1)}_{\text{odd functions}}$$

$$= 0$$




$\Rightarrow$ the average dipole moment is <u>zero</u>

however, specific measurements of $\vec{D}_1$ will be non-zero (i.e. quantum fluctuations of $\vec{D}_1$)

## $1^{st}$ order perturbation theory

$$\langle \psi | H_{int} | \psi \rangle = \int dx_1 \int dy_1 \int dz_1 \int dx_2 \int dy_2 \int dz_2$$

$$\underbrace{|\psi_{1,0,0}(\vec{r}_1)|^2}_{\text{even}} \underbrace{|\psi_{1,0,0}(\vec{r}_2)|^2}_{\text{even}} \frac{e^2}{r^3} [\overset{\text{odd}}{x_1x_2 + y_1y_2 - 2z_1z_2}]$$

odd

$r$: not quantized, treated as a parameter

$$= 0$$

## $2^{nd}$ order perturbation theory (for $|\varphi_j\rangle$ state)

$E_j$ energy

$$E_{int} \simeq \sum_{i \neq j} \frac{|\langle \varphi_i | W | \varphi_j \rangle|^2}{E_j - E_i}$$

$$= \sum_{\substack{(n_1,l_1,m_1) \neq (1,0,0)_1 \\ (n_2,l_2,m_2) \neq (1,0,0)_2}} \frac{e^4}{r^6} \frac{|\overset{\text{even/odd}}{\langle n_1,l_1,m_1|} \overset{\text{even/odd}}{\langle n_2,l_2,m_2|} \overbrace{(x_1x_2 + y_1y_2 - 2z_1z_2)^2}^{\text{no ~~fixed~~ parity}} \overset{\text{even}}{|1,0,0\rangle_1} \overset{\text{even}}{|1,0,0\rangle_2}|^2}{\underbrace{E_0 - E_1(n_1,l_1,m_1) - E_2(n_2,l_2,m_2)}_{\text{always negative for bound states}}}$$

$E_0$: $2 \times (-13.6\,eV)$

[in principle, one should consider continuum states, but they have a very minor contribution]

$$\simeq -\frac{1}{r^6} \underbrace{6.5\, e^2 a_0^5}_{\text{see Schiff p.263}}$$

A few comments:

- $E_{int}$ is always negative $\Rightarrow$ attractive interaction
- $E_{int} \propto \frac{1}{r^6} \Rightarrow f_{int} \propto \frac{1}{r^7}$
- $E_{int}$ is due to the quantum fluctuations of dipole in one atom inducing a dipole moment in the other atom

this correlation can be seen in that the ~~#~~ 1st order correction to eigenstate $|\psi'\rangle$ involves ~~so~~ inter atom correlations

~~while~~ $\langle \psi | x_1 x_2 | \psi \rangle = 0$ , but $\underbrace{\langle \psi' | x_1 x_2 | \psi' \rangle \neq 0}_{\text{motion of } e_1 \,\&\, e_2 \text{ is correlated.}}$

see discussion in Cohen-Tannoudji (Complement $C_{XI}$)

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Degenerate Perturbation theory

If ~~the s~~ we want to study what happens when a perturbation $W$ is applied to an energy level $E_j$ that is $g_j$ times degenerate (i.e. there $g_j$ eigenstates $|\varphi_{j,1}\rangle \ldots |\varphi_{j,g}\rangle$ with energy $E_j$)

then it is unclear which eigenstate should be identified with $|0\rangle$ in the derivation of the perturbation theory : $|0\rangle \overset{?}{=} |\varphi_{j,n}\rangle$

↑ which n? or it could be a linear combination

(also ~~1st order~~ 1st order correction to eigenstate has a divergence)

but "$\lambda^0$" is valid $H_0|0\rangle = E_j|0\rangle$

the "$\lambda^1$" equation reduces to

Apply $\langle \varphi_{j,n}|$

$$\underbrace{\langle \varphi_{j,n}| H_0 |1\rangle}_{E_j \langle \varphi_{j,n}|1\rangle} + \langle \varphi_{j,n}|\hat{W}|0\rangle = \langle \varphi_{j,n}|\varepsilon_1|0\rangle + \underbrace{\langle \varphi_{j,n}|\varepsilon_0|1\rangle}_{E_j \langle \varphi_{j,n}|1\rangle}$$

thus $\langle \varphi_{j,n}|\hat{w}|0\rangle = \varepsilon_1 \langle \varphi_{j,n}|0\rangle$