Tuesday, January 29, 2013

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

$\langle\psi| x_1 x_2 |\psi\rangle = 0$, but $\langle\psi'| x_1 x_2 |\psi'\rangle \neq 0$

motion of e_1 & e_2 is correlated

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

Stopped here

Degenerate Perturbation theory

If 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 are g_j eigenstates $|\varphi_{j,1}\rangle \ldots |\varphi_{j,g_j}\rangle$ 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 correction to eigenstate has a divergence)

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

the "λ^1" equation reduces to

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

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

$E_j\langle\varphi_{j,n}|1\rangle$ $\qquad$ $\varepsilon_0 = E_j$ $\qquad$ $E_j\langle\varphi_{j,n}|1\rangle$

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

insert identity

$$\Rightarrow \sum_{i,\, j_i \to p \;\; p=1 \text{ to } g_i} \langle \varphi_{j,n} | \hat{w} | \varphi_{i,p} \rangle \underbrace{\langle \varphi_{i,p} | 0 \rangle}_{=0 \text{ for } i \neq j} = \varepsilon_i \langle \varphi_{j,n} | 0 \rangle$$

g_i = degeneracy of i^{th} energy level

$$\Rightarrow \sum_{p=1}^{g_j} \langle \varphi_{j,n} | \lambda \hat{w} | \varphi_{j,p} \rangle \langle \varphi_{j,p} | 0 \rangle = \lambda \varepsilon_i \langle \varphi_{j,n} | 0 \rangle$$

$\lambda \hat{W}_{np} |0\rangle = \lambda \varepsilon_i |0\rangle$ (line n, column p)

This is just an eigenvalue equation for the $\hat{w}$ or W operator in the degeneracy subspace of Energy level "j."

$\Rightarrow$ find the new eigenstates of W in the subspace spanned by the eigenstates of the E_j energy level.

$\hookrightarrow |\varphi_{j,p}\rangle_W$

$\Rightarrow$ c^{th} order correction to the eigenstate

pick the new eigenstate $|\varphi_{j,p}\rangle_W$ that you're interested in

1st order correction to energy

$$E_j' = E_j + \underbrace{{}_W\langle \varphi_{j,p} | W | \varphi_{j,p} \rangle_W}_{\text{"eigenenergies of } W\text{" in the degeneracy subspace of energy level "j"}}$$

Higher order:

version 1: If $\{E_j', |\varphi_{j,p}\rangle_W\}$ is now non-degenerate, then

the non-degenerate formulae apply but with a modified set of eigenstates: $|\varphi_i\rangle \to |\varphi_i\rangle_{(i \neq j)}$ and $|\varphi_{j,n}\rangle_W$ $n \neq p$

version 2: if $\{E_j', |\varphi_{j,p}\rangle_W\}$ is still degenerate see problem 5.12 Sakurai

remember 1st order means λ^1 in correction

2nd order means λ^2 in correction

the defining equations are still correct (but sometimes insufficient):

λ^0: $H_0|0\rangle = \varepsilon_0|0\rangle$

λ^1: $H_0|1\rangle + \hat{W}|0\rangle = \varepsilon_1|0\rangle + \varepsilon_0|1\rangle$

λ^2: $H_0|2\rangle + \hat{W}|1\rangle = \varepsilon_2|0\rangle + \varepsilon_1|1\rangle + \varepsilon_0|2\rangle$

Simple Example: 2-level system

original Hamiltonian: $H_0 = \begin{matrix} \\ \langle\varphi_1| \\ \langle\varphi_2| \end{matrix} \begin{matrix} \begin{matrix} |\varphi_1\rangle & |\varphi_2\rangle \end{matrix} \\ \begin{bmatrix} E_1 & 0 \\ 0 & E_1 \end{bmatrix} \end{matrix}$

Perturbation: $W = \begin{bmatrix} 0 & V \\ V^* & 0 \end{bmatrix}$ $\quad V > 0$

- Calculate the zeroth order & correction to the eigenstates
- Calculate the 1st order ~~correction to the~~ energie ~~t~~

$$\det(W - \lambda I) = 0 \iff \begin{vmatrix} -\lambda & V \\ V^* & -\lambda \end{vmatrix} = 0$$

$$\iff \lambda^2 - |V|^2 = 0 \implies \begin{cases} \lambda_+ = +|V| \\ \lambda_- = -|V| \end{cases}$$

$\lambda_+ = +|V|$:

$$\begin{pmatrix} -|V| & V \\ V^* & -|V| \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\implies |\varphi_+\rangle = \frac{V|\varphi_1\rangle + |V||\varphi_2\rangle}{\sqrt{V^2 + V^2}} = \frac{1}{\sqrt{2}}\left(|\varphi_1\rangle + |\varphi_2\rangle\right)$$

thus $E_+ = E_1 + \langle \varphi_+ | W | \varphi_+ \rangle$

$= E_1 + V$

$\underline{\lambda_- = -V}$: $\begin{pmatrix} V & V \\ V & V \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

$\Rightarrow |\varphi_-\rangle = \frac{1}{\sqrt{2}}\left(|\varphi_1\rangle - |\varphi_2\rangle\right)$

thus $E_- = E_1 + \langle \varphi_- | W | \varphi_- \rangle$

$= E_1 - V$

note: trivial example of the no crossing theorem

Lowest order relativistic correction to the hydrogen atom

(see Sakurai & Napolitano p321-323)

We can include a relativistic correction to the basic Hamiltonian $H_0 = \underbrace{\frac{p^2}{2\mu}}_{\text{kinetic energy}} - \frac{e^2}{R}$ by using the relativistic momentum and kinetic energy

$\vec{p} \rightarrow \vec{p}_{rel} = \gamma m_0 \vec{v}$ $\qquad \gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$

$E_{kinetic} \rightarrow E_{\substack{kinetic \\ rel}} = \sqrt{c^2 \vec{p}_{rel}^{\,2} + m_0^2 c^4}$

$= m_0 c^2 \sqrt{1 + \frac{\vec{p}_{rel}^{\,2}}{m_0^2 c^2}}$

$\simeq m_0 c^2 \left(1 + \frac{1}{2}\frac{\vec{p}_{rel}^{\,2}}{m_0^2 c^2} - \frac{1}{8}\left(\frac{\vec{p}^{\,2}}{m_0^2 c^2}\right)^2 + \cdots\right)$

$$\Rightarrow E_{\substack{\text{kinetic}\\ \text{rel.}}} \simeq m_0 c^2 + \frac{\vec{p}_{rel}^{\,2}}{2m_0} - \frac{\vec{p}_{rel}^{\,4}}{8m_0^3 c^2} + \dots$$

$m_0 c^2$: eliminate (constant offset)

$$\langle r | \vec{p}_{rel} | r \rangle \rightarrow \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$$

$\vec{p}$

Thus the Hamiltonian can be rewritten as

$$H = E_{\substack{\text{kinetic}\\ \text{rel.}}} + V = \frac{\vec{p}^{\,2}}{2m_0} - \frac{\vec{p}^{\,4}}{8m_0^3 c^2} - \frac{e^2}{r}$$

$\mu \simeq m_0$ (reduced mass $\simeq$ rest mass of e^-)

$$= H_0 - \underbrace{\frac{p^4}{8m_0^3 c^2}}_{W}$$

we can treat the correction to the kinetic energy using perturbation theory:

$$W = -\frac{p^4}{8m_0^3 c^2}$$

In principle, we must invoke degenerate perturbation theory since E_n, ~~$|n, l, m_l\rangle$~~ does not depend $\underline{\underline{l}}$.

However $[L, p^2] = 0 \Rightarrow [L, p^4] = 0 \Rightarrow [L, W]$

so L and W share the same eigenstates.

↳ W is a diagonal in the $|n, l, m_l\rangle$

$\Rightarrow$ there is no zeroth order correction to eigenvector states

the 1st order correction to the energy is

$$E_{n\ell m} = E_n + \langle n\ell m_\ell | W | n\ell m_\ell \rangle$$

4th order derivatives

$$= E_n + \langle n\ell m_\ell | \frac{P^4}{8m_0^3c^2} | n\ell m_\ell \rangle$$

Stopped here

trick: $\frac{P^4}{8m_0^3c^2} = \frac{1}{2m_0c^2}\left(\frac{P^2}{2m_0}\right)^2 = \frac{1}{2m_0c^2}\left(H_0 + \frac{e^2}{R}\right)^2$

$$\langle n,\ell,m_\ell | \frac{-P^4}{8m_0^3c^2} | n,\ell,m_\ell \rangle = \frac{-1}{2m_0c^2} \langle n,\ell,m_\ell | \left(H_0 + \frac{e^2}{R}\right)^2 | n,\ell,m_\ell \rangle$$

$$= \frac{-1}{2m_0c^2}\Big\{ \underbrace{\langle n,\ell,m_\ell | H_0^2 | n,\ell,m_\ell \rangle}_{E_n^2} + \underbrace{\langle n,\ell,m_\ell | H_0 \frac{e^2}{R} | n,\ell,m_\ell \rangle}_{E_n \langle n,\ell,m_\ell |} + \langle n,\ell,m_\ell | \frac{e^2}{R} \underbrace{H_0 | n,\ell,m_\ell \rangle}_{E_n | n,\ell,m_\ell \rangle} + \langle n,\ell,m_\ell | \frac{e^4}{R^2} | n,\ell,m_\ell \rangle \Big\}$$

$$= -\frac{1}{2m_0c^2}\Big\{ E_n^2 + 2E_n \langle n,\ell,m_\ell | \frac{e^2}{R} | n,\ell,m_\ell \rangle + \langle n,\ell,m_\ell | \frac{e^4}{R^2} | n,\ell,m_\ell \rangle \Big\}$$

$E_n = -\frac{e^2}{2n^2a_0}$ where $e^2 = \frac{q_e^2}{4\pi\varepsilon_0}$ — See Sakurai Appendix on H atom

$\frac{e^2}{R} = -2E_n$ where $\frac{e^2}{n^2a_0}$

$\frac{e^4}{R^2}$ where $\frac{e^4}{n^3a_0^2(\ell+\frac{1}{2})}$

$\frac{4n}{\ell+\frac{1}{2}} E_n^2$