Tuesday, February 19, 2013

Example: 1s level of hydrogen $\quad W = H_{Stark} = -q_e \vec{E}\cdot\vec{R} = -q_e|E|Z$

1st order: (energy) $\Delta E' = -q_e|E|\langle n_e=1, l=0, m_l=0| Z |n=1, l=0, m_l=0\rangle$

$$= -q_e|E| \,{}_{\ell}\langle n| \cancel{\langle F, m_F|} Z \cancel{|F, m_F\rangle} |n\rangle_{\ell}$$

I+S

$$= -q_e|E| \int \underbrace{|R_{10}(r)|^2}_{\text{even}} \underbrace{Z}_{\text{odd}}\, d\vec{r}^3$$

$$= 0$$

2nd order energy:

$$\Delta E'' = \sum_{\substack{n\neq 1\\ l, m_l\\ F, m_F}} \frac{|\langle n, l, m_l|\langle F, m_F| (-q_e E Z) |F, m_F\rangle |n=1, l=0, m_l=0\rangle|^2}{E_{1S_{1/2}} - E_{n l m_l, F, m_F, J}}$$

$$= q_e^2 |E|^2 \sum_{\substack{n\neq 1\\ l, m_l}} \frac{|\langle n, l, m_l| Z |n=1, l=0, m_l=0\rangle_J|^2}{\underbrace{E_{1S_{1/2}} - E_{n, l, m_l, J}}_{\text{negative}}}$$

+ continuum states

$$= \text{cst}\, |E|^2$$

$$= -\frac{1}{2}\alpha |E|^2 \qquad \alpha = \text{DC electric polarizability}$$

1st order eigenstate ("parity violation")

$$|\psi'\rangle = |n=1, l=0, m_l=0\rangle - q_e|E| \sum_{\substack{n\neq 1\\ l}} \frac{\overset{\text{odd}}{\langle n, l, m_l|}\, Z\, \overset{\text{even}}{|n=1, l=0, m_l=0\rangle}}{E_{1S_{1/2}} - E_{n, l, m_l, J}}$$

$$= |1S_{1/2}\rangle + \varepsilon |2P_{1/2}\rangle + \ldots$$

must be odd for non-zero contribution (p state, f-state) + continuum states

Selection rules for

$\langle n, l, m_l | z | n=1, l=0, m_l=0 \rangle \neq 0$ for $|n,l,m_l\rangle$ = odd

$\underset{\text{odd}}{\uparrow}$ $\quad \underbrace{n=1,\ l=0,\ m_l=0}_{\text{even}}$

since $\langle r | n=1, l=0, m_l=0\rangle = R_{10}(r)\, Y_0^0(\theta,\phi)$

$$= \frac{1}{\sqrt{4\pi}} R_{10}(r)$$

Also $z = R\cos\theta = \sqrt{\frac{4\pi}{3}}\, R\, Y_1^0(\theta,\phi)$

thus

$\langle n, l, m_l | z | n=1, l=0, m_l=0\rangle$

$$= \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2 dr \sin\theta\, d\theta\, d\phi \left\{ R_{nl}(r)\, Y_l^{m_l}(\theta,\phi) \sqrt{\frac{4\pi}{3}}\, R\, Y_1^0(\theta,\phi) \frac{1}{\sqrt{4\pi}} R_{10}(r) \right\}$$

$$= \frac{1}{\sqrt{3}} \int_0^\infty R_{nl}(r) R_{10}(r)\, r^3 dr \underbrace{\int_0^\pi\int_0^{2\pi} Y_l^{m_l}(\theta,\phi)\, Y_1^0(\theta,\phi) \sin\theta\, d\theta\, d\phi}_{\langle l=1, m_l=0 | l, m_l\rangle \neq 0 \text{ only for } l=1,\ m_l=0}$$

(orthonormality of Y_l^m)

$$= \begin{cases} \frac{1}{\sqrt{3}} \int_0^\infty R_{n1}(r) R_{10}(r)\, r^3 dr & \text{for } l=1, m_l=0 \\ =0 & \text{for } l\neq 1, m_l\neq 0 \end{cases}$$

in practice: truncate series to first few terms

$\frac{\langle 2,1,0 | z | 1,0,0\rangle}{\langle 3,1,0 | z | 1,0,0\rangle} \approx 2.5 \quad \Rightarrow \left(\frac{\langle 2,1,0 | z | 1,0,0\rangle}{\langle 3,1,0 | z | 1,0,0\rangle} \right)^2 \simeq 6.2$

useful formula for evaluating terms such as

$\langle n', l', m_l' | Z | n, l, m_l \rangle$:

(Sakurai & Napolitano p231, eq. 3.8.73)
(Cohen-Tannoudji p. 1037)

$$\int r^2 \sin\theta \, d\theta \, d\phi \left\{ Y_l^{m*}(\theta,\phi) Y_{l_1}^{m_1}(\theta,\phi) Y_{l_2}^{m_2}(\theta,\phi) \right\}$$

$$= \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} \langle l_1, l_2; m_{l_1}=0, m_{l_2}=0 | l_1, l_2; j=l, m_j=0 \rangle$$

$$\times \langle l_1, l_2; m_{l_1}, m_{l_2} | l_1, l_2; j=l, m_j=m \rangle$$

Clebsch-Gordan coefficients

alternatively,

$$\cos\theta \, Y_l^m(\theta,\phi) = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1}^m(\theta,\phi)$$

$$+ \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} Y_{l-1}^m(\theta,\phi)$$

(Cohen-Tannoudji p.689)

Variational Method

Approximation Method for computing ground state energy.

Consider a Hamiltonian H with a discrete energy spectrum

$$H|\psi_n\rangle = E_n|\psi_n\rangle \qquad n = 0, 1, 2, \ldots$$

where $n=0$ correspond to the ground state

$$E_0 < E_{n\neq 0}$$

Consider a state $|\psi\rangle$ (any state)

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle$$

we define $\langle H\rangle_\psi$ as $\langle H\rangle_\psi = \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ $= E_\psi$ if $|\psi\rangle$ is an eigenstate

$\leftarrow$ in case $|\psi\rangle$ is not normalized

Theorem:

$$\langle H\rangle_\psi \geq E_0$$

Thus $\langle H\rangle_\psi$ provides an upper bound on E_0.

proof:

$$\langle\psi|H|\psi\rangle = \left(\sum_{n'} c_{n'}^* \langle\psi_{n'}|\right) \underbrace{H\left(\sum_n c_n|\psi_n\rangle\right)}_{E_n c_n |\psi_n\rangle}$$

$$= \sum_n |c_n|^2 E_n \geq \underbrace{\sum_n |c_n|^2}_{\langle\psi|\psi\rangle} E_0$$

thus $\langle\psi|H|\psi\rangle \geq \langle\psi|\psi\rangle E_0 \iff \dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$

Generalization: Ritz Theorem

$\langle H \rangle_\psi$ is stationary (i.e. extremum) if and only if $|\psi\rangle$ is an eigenstate of H.

i.e. $\delta \langle H \rangle_\psi = 0 \iff H|\psi\rangle = \langle H \rangle_\psi |\psi\rangle$

eigen energy ($\langle H \rangle_\psi$) — eigenstate ($|\psi\rangle$)

proof: we consider a small perturbation to $|\psi\rangle$

$$|\psi\rangle \to |\psi\rangle + \underbrace{|\delta\psi\rangle}_{\delta|\psi\rangle}$$

for $\delta \to 0 \Rightarrow$ get back $|\psi\rangle$

with $|\psi\rangle$ is any state vector (preferably orthogonal to $|\psi\rangle$)

$$\langle H \rangle_\psi = \frac{(\langle\psi| + \langle\delta\psi|)H(|\psi\rangle + |\delta\psi\rangle)}{(\langle\psi| + \langle\delta\psi|)(|\psi\rangle + |\delta\psi\rangle)} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

δ^2 neglect

$$= \frac{\langle\psi|H|\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle + \langle\delta\psi|H|\delta\psi\rangle}{\underbrace{\langle\psi|\psi\rangle + \langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle}_{\langle\psi|\psi\rangle\left[1 + \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle}\right]} + \langle\delta\psi|\delta\psi\rangle} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$$

δ^2 neglect

Taylor expand, keep only first order in δ

$$\simeq \left(\frac{\langle\psi|H|\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle}\right)\left[1 - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle}\right] - \cancel{\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}}^{\langle H \rangle_\psi}$$

$$\simeq \cancel{\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}}^{\langle H \rangle_\psi} + \frac{\langle\delta\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \cancel{\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}}^{\langle H \rangle_\psi}\frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} - \cancel{\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}}^{\langle H \rangle_\psi}\frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle}$$

+ higher order terms in δ^2

$$- \cancel{\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}} \to \langle H \rangle_\psi$$

$$\Rightarrow \quad \delta\langle H\rangle_\psi \approx \frac{\langle\delta\psi|\, H - \langle H\rangle_\psi \,|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\, H - \langle H\rangle_\psi \,|\delta\psi\rangle}{\langle\psi|\psi\rangle}$$

If $|\psi\rangle$ is an eigenstate of H then $H|\psi\rangle = \langle H\rangle_\psi|\psi\rangle$,

then $$\delta\langle H\rangle_\psi = \frac{\langle\delta\psi|\, \underset{\langle H\rangle_\psi}{\cancel{H}} - \langle \psi\rangle_\psi \,|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\, \underset{\langle H\rangle_\psi}{\cancel{H}} - \langle H\rangle_\psi \,|\delta\psi\rangle}{\langle\psi|\psi\rangle}$$

$$= 0$$

If $\delta\langle H\rangle_\psi = 0$ for any variation $|\delta\psi\rangle$,

then define $|\phi\rangle = (H - \langle H\rangle_\psi)|\psi\rangle$

thus $\langle\delta\psi|\phi\rangle + \langle\phi|\delta\psi\rangle = 0 \quad (*)$

if we choose $|\delta\psi\rangle = \delta\lambda|\phi\rangle$,

[we can do this: $\delta\langle H\rangle_\psi = 0$ for any $|\delta\psi\rangle$]

then

$(*) \Rightarrow \delta\lambda\langle\phi|\phi\rangle + \langle\phi|\phi\rangle\delta\lambda = 0$

$\Rightarrow \langle\phi|\phi\rangle = 0 \Rightarrow |\phi\rangle = 0 \Rightarrow (H - \langle H\rangle_\psi)|\psi\rangle = 0$

$\Rightarrow H|\psi\rangle = \langle H\rangle_\psi|\psi\rangle$

$\Rightarrow \begin{cases} \langle H\rangle_\psi \text{ is an eigen}\cancel{\text{state}}\text{ value} \\ |\psi\rangle \text{ is an eigenstate.} \end{cases}$