Thursday, February 20, 2013

<u>Ritz Theorem</u>: $\delta \langle \psi | H | \psi \rangle = 0 \iff H|\psi\rangle = \langle H \rangle_\psi |\psi\rangle$ (eigenvalue/eigenfunction equation)

$\Rightarrow$ [i.e. $\delta \langle H \rangle_\psi = 0$]

alternatively, we can write

$$\delta \int \psi^*(r)\, H\, \psi(r)\, d^3r = 0 \iff H|\psi\rangle = \langle H \rangle_\psi |\psi\rangle$$

or even

$$\delta \int \psi^*(r)\, (H - E)\, \psi(r)\, d^3r = 0$$

$$\iff H|\psi\rangle = E|\psi\rangle$$

In other words, we can derive the schrodinger equation from a variational principle, where the eigenstates of the system lead to a local extremum of $H - E$.

↳ Many-body problems are sometimes written in this form.

How do you guess a good wavefunction for the ground state? (first excited state) etc..

<u>Oscillation theorem</u>: see { Landau & Lifshitz §21 (p60) ; Sturm-Liouville theory in Morse & Feshbach (p719) }

For ~~one~~ 1D schrodinger equations or effectively 1D schrodinger equations (i.e. when you can do separation of variables):

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x) = E\,\psi(x)$$

If this 1D Schrodinger equation has a discrete spectrum : $\{E_n, \{\psi_n(x)\}\}$ $n = 0, 1, 2, \ldots$
and $E_0 < E_1 < E_2 < \ldots < E_n$

then
- the ground state wavefunction $\psi_0(x)$ has no nodes
- the first excited state wavefunction $\psi_1(x)$ has one node
- the 2^{nd} excited state wavefunction $\psi_2(x)$ has two nodes
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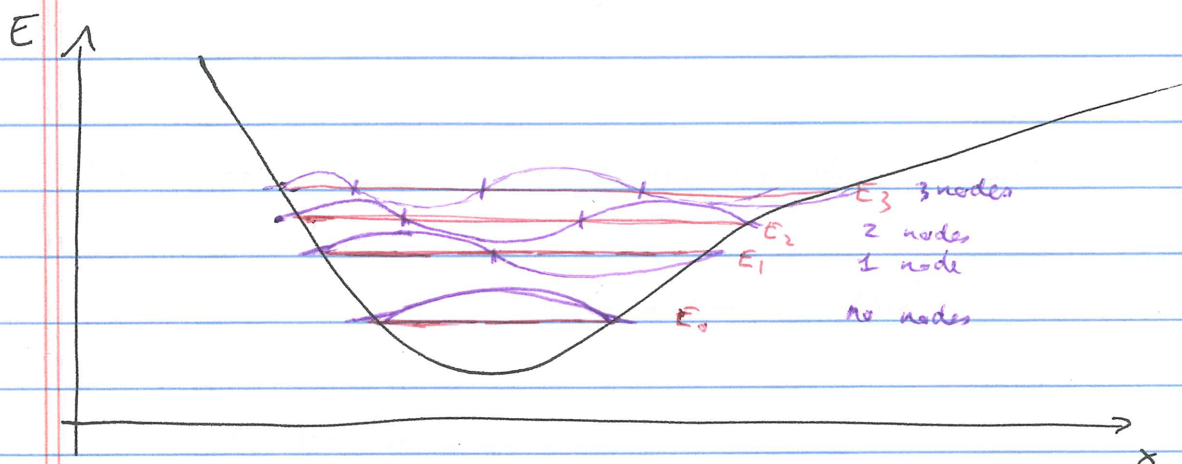
- the n^{th} excited state wavefunction $\psi_n(x)$ has n nodes



Ground state trial wavefunction :

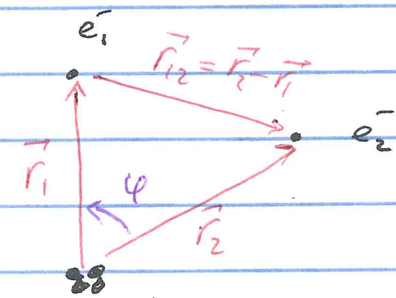
1. Motivate choice with physics
2. If "1D" problem, the pick a wavefunction with a single bump (i.e. Gaussian, Lorentzian, triangle, etc...

"even" function if potential is symmetric

Example : Ground state energy of helium

(ignoring fermionic nature of e^-)

we assume an infinitely heavy nucleus



$$H = \underbrace{\frac{\vec{P}_1^{\,2}}{2m_e} - \frac{2e^2}{r_1}}_{H_{0,1}} + \underbrace{\frac{\vec{P}_2^{\,2}}{2m_e} - \frac{2e^2}{r_2}}_{H_{0,2}} + \frac{e^2}{r_{12}}$$

charge = $2|q_e|$

$$= H_{0,1} + H_{0,2} + \underbrace{\frac{e^2}{|\vec{r}_2 - \vec{r}_1|}}_{\text{interaction term}}$$

two approaches: 1) Perturbation theory with $W = \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$

2) Variational method.

Variational method:

Trial wavefunction

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{1s}(\vec{r}_1)\,\psi_{1s}(\vec{r}_2)$$

$$= R_{10}(r_1)\underbrace{Y_0^0(\theta_1,\phi_1)}_{\frac{1}{\sqrt{4\pi}}} R_{10}(r_2)\underbrace{Y_0^0(\theta_2,\phi_2)}_{\frac{1}{\sqrt{4\pi}}}$$

$(Z=2)$

$$= \frac{1}{4\pi}\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr_1/a_0}\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr_2/a_0}$$

$$= \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-\frac{Z}{a_0}(r_1+r_2)}$$

⚠ there is no free parameter to minimize

[equivalent to first order perturbation theory]

We can partially account for e^- screening of the nucleus of one e^- relative to the other e^- by making Z a free parameter that minimizes the energy.

$$\tilde{E}_0 = \langle H \rangle_\psi = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

$\langle \psi | \psi \rangle \rightarrow$ 1 in our case by construction

$$= \langle \psi | \frac{\vec{P}_1^2}{2m_e} + \frac{\vec{P}_2^2}{2m_e} | \psi \rangle - \langle \psi | \frac{2e^2}{r_1} + \frac{2e^2}{r_2} | \psi \rangle + \langle \psi | \frac{e^2}{|\vec{r}_2 - \vec{r}_1|} | \psi \rangle$$

$\vec{P}_1^2 \rightarrow \nabla_{r_1}^2$, $\vec{P}_2^2 \rightarrow \nabla_{r_2}^2$

$\nabla_{r_1}^2 \rightarrow \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2}(r_1 \psi)$ + angular parts

$= \frac{1}{r_1^2} \frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r}\right)$ + angular parts

Let's calculate:

$$\langle \psi | \frac{\vec{P}_1^2}{2m_e} | \psi \rangle = -\frac{\hbar^2}{2m_e} \int d^3r \left[\psi_1^*(\vec{r}_1) \frac{1}{r_1^2} \frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r}\right) \psi_1(\vec{r}_1) \right] \times \int d^3r\, \psi_2^*(\vec{r}_2)\, \psi_2(\vec{r}_2)$$

$\int d^3r\, \psi_2^*(\vec{r}_2)\, \psi_2(\vec{r}_2) = 1$ by construction (normalization)

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$$= \frac{-\hbar^2}{2m_e} \int d^3r\, \psi_1^*(\vec{r}_1) \frac{1}{r_1^2} \left(\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r} e^{-Zr_1/a_0} \right) \frac{1}{\sqrt{4\pi}} \left(\frac{Z}{a_0}\right)^{3/2}$$

$\frac{\partial}{\partial r} e^{-Zr_1/a_0} = -\frac{Z}{a_0} e^{-Zr_1/a_0}$

$\left(-\frac{Z}{a_0}\right) 2r_1 e^{-Zr_1/a_0} + r_1^2 \left(-\frac{Z}{a_0}\right) e^{-Zr_1/a_0}$

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$$= \frac{-\hbar^2}{2m_e} \int d^3r\, \psi_1^*(\vec{r}_1) \left(-\frac{Z}{a_0}\right)\left[\left(\frac{2}{r_1}\right) - \left(\frac{Z}{a_0}\right)\right] \underbrace{e^{-Zr/a_0} \frac{1}{\sqrt{4\pi}} \left(\frac{Z}{a_0}\right)^{3/2}}_{\psi_1(\vec{r}_1)}$$

$$= +\frac{\hbar^2}{2m_e}\left(\frac{Z}{a_0}\right) \int d^3r\, \psi_1^* \left[\left(\frac{2}{r_1}\right) - \left(\frac{Z}{a_0}\right)\right] \psi_1(\vec{r}_1)$$

$a_0 = \frac{\hbar^2}{m_e e^2}$

$$= \frac{\hbar^2}{2m_e}\frac{Z}{a_0}\left[2\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle - \left(\frac{Z}{a_0}\right)\langle\psi_1|\psi_1\rangle\right]$$

$\frac{\hbar^2}{m_e} \to a_0 e^2$; $\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle \to \frac{Z}{a_0}$ see Sakurai & Napolitano appendix B; $\langle\psi_1|\psi_1\rangle \to 1$ (normalization); bracket $\to \frac{Z}{a_0}$

$$= \frac{1}{2} Z^2 \frac{e^2}{a_0}$$

Similarly, $\langle\psi|\frac{\vec{P}_2^2}{2m_e}|\psi\rangle = \frac{1}{2} Z^2 \frac{e^2}{a_0}$

$$\langle\psi|\frac{Ze^2}{r_1}|\psi\rangle = Ze^2 \underbrace{\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle}_{\frac{Z}{a_0}} \langle\psi_2|\psi_2\rangle = Z Z \frac{e^2}{a_0}$$

($\langle\psi_2|\psi_2\rangle \to 1$)

and $\langle\psi|\frac{Ze^2}{r_2}|\psi\rangle = \frac{Z Z e^2}{a_0}$

finally, we have

$$\langle\psi|\frac{e^2}{|\vec{r}_2 - \vec{r}_1|}|\psi\rangle = \text{see problem set and also Sakurai \& Napolitano p 456-7} = \frac{5}{8} Z \frac{e^2}{a_0}$$

$$\frac{1}{|\vec{r}_2 - \vec{r}_1|} = \begin{cases} \frac{1}{r_1} \sum_{\ell=0}^{\infty} \left(\frac{r_2}{r_1}\right)^{\ell} P_\ell(\cos\varphi) & \text{for } r_1 > r_2 \\ \frac{1}{r_2} \sum_{\ell=0}^{\infty} \left(\frac{r_1}{r_2}\right)^{\ell} P_\ell(\cos\varphi) & \text{for } r_2 > r_1 \end{cases}$$

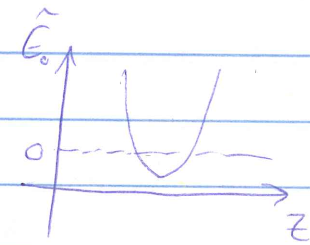
also $P_\ell(\cos\varphi) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\theta_1,\phi_1)\, Y_\ell^m(\theta_2,\phi_2)$

$\Rightarrow$ { angular integration is straight forward
radial somewhat involved

Thus

$$\tilde{E}_0 = \langle \psi | H | \psi \rangle = 2 \times \frac{Z^2}{2}\frac{e^2}{a_0} - 2 \times 2Z\frac{e^2}{a_0} + \frac{5}{8} Z \frac{e^2}{a_0}$$

$$= \left(Z^2 - \frac{27}{8} Z\right)\frac{e^2}{a_0}$$



$$\frac{\partial \tilde{E}_0}{\partial Z} = 0 \Leftrightarrow \frac{e^2}{a_0}\left(2Z - \frac{27}{8}\right) = 0$$

$$Z = \frac{27}{16} = 1.6875$$ $\leftarrow \sim 84\%$ of nuclear charge
$\llcorner \sim 16\%$ effective screening

thus $E_0 \leq \tilde{E}_0 \Big|_{min} = \left[\left(\frac{27}{16}\right)^2 - \frac{27}{8}\frac{27}{16}\right] \frac{e^2}{a_0}$

$$= -\left(\frac{27}{16}\right)^2 \frac{e^2}{a_0} = -2\left(\frac{27}{16}\right)^2 \frac{e^2}{2a_0}$$

($\frac{e^2}{2a_0}$ =) 13.6 eV

$$\simeq -77.5 \text{ eV}$$

Experiment : $E_0 = -78.8$ eV $\leftarrow$ off by 1.7%

<u>Can you use variational method for excited states?</u> yes... kind of

The 1st excited state is the state $|\psi_1\rangle$ with minimum $\langle H\rangle_{\psi_1}$ among all states $|\psi\rangle$ which are orthogonal to the ground state.

... what if you don't know ground state?

<u>physics idea</u>

Get the "ground state" $|\psi_0'\rangle$ using the variational method, next pick a "1st excited state" $|\psi_1'\rangle$ that is orthogonal to $|\psi_0'\rangle$ (and with only one node, if in 1D), then compute $\tilde{E}_1\big|_{min} = \langle \psi_1' | H | \psi_1' \rangle$

... you can then estimate $\tilde{E}_2$, $|\psi_2'\rangle$, and so on...

<u>Mini-max principle</u> (or Maxim-minimum principle)
Courant & Hilbert

<u>Theorem</u>:

Consider all normalized ψ satisfying $\langle \psi_0' | \psi \rangle = 0$ (*) where $|\psi_0'\rangle$ is a given state. For that $|\psi_0'\rangle$, let E_1' be the <u>minimum</u> of $\langle \psi | H | \psi \rangle$ for all ψ satisfying (*).

When $|\psi_0'\rangle$ is varied, the <u>maximum</u> of E_1' is the 1st excited state energy (eigenenergy) of H.

Physics: if ψ_0' is close to the ground state but not quite, then $|\psi\rangle$ such $\langle \psi_0' | \psi \rangle = 0$ means that

$|\psi\rangle = |\psi_1\rangle + \varepsilon |\psi_0\rangle + \dots$

↑ ground state contamination lowers E_1' with respect to E_1

proof: consider the representation where H is diagonal

$$H = \begin{pmatrix} E_0 & & & 0 \\ & E_1 & & \\ & & \ddots & \\ 0 & & & E_n \end{pmatrix}$$

$E_0 \leq E_1 \leq E_2 \ldots$ (ok if there is degeneracy)

$|\psi_0\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$; $|\psi_1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$; let $|\psi_0'\rangle = \begin{pmatrix} g_0 \\ g_1 \\ g_2 \\ \vdots \end{pmatrix}$ (normalized)

a) We first show that $E_1' \leq E_1$

consider $|\psi\rangle = \begin{pmatrix} e_0 \\ e_1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$ (normalized), then $\langle \psi_0' | \psi \rangle = 0$

$\Leftrightarrow g_0^* e_0 + g_1^* e_1 = 0$

↳ one can always find a $|\psi\rangle$ satisfying (*)

in this case,

$E_1' \leq \langle \psi | H | \psi \rangle = |e_0|^2 E_0 + |e_1|^2 E_1 \leq E_1$

normalization $|e_0|^2 + |e_1|^2 = 1$

$|e_0|^2 E_0 + |e_1|^2 E_1 \leq |e_0|^2 E_1 + |e_1|^2 E_1 = E_1$

↑ $E_0 \leq E_1$

b) So is the maximum of E_1' exactly E_1?

Yes → take $|\psi_0'\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$, then $E_1' = E_1$