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PHS-201(A).

E-Lecture-02.

Recap :- we have already discussed several approximation methods in quantum mechanics - time independent perturbation theory (applications like stark effect and zeeman effect). In this lecture we will learn about the variational method.

Suppose you want to calculate the ground state energy E_{gs} for a system described by Hamiltonian H, but you are unable to solve time independent Sch. equation. By the variational principle we will get the upper bound for E_{gs}, which is close to exact value.

Pick any normalised wave function ψ.

I claim $\boxed{E_{gs} \leq \langle \psi | H | \psi \rangle = \langle H \rangle}$

~~i.e.~~

To prove this let unknown eigenfunction of H form a complete set, we can express ψ as a linear combination of them.

$$\psi = \sum_n c_n \psi_n \quad \text{with} \quad \hat{H}\psi_n = E_n \psi_n$$

Since ψ is normalised.

$$1 = \langle \psi | \psi \rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{nm}}$$

$$\Rightarrow 1 = \sum_n |c_n|^2$$

$$\langle H \rangle = \left\langle \sum c_m \psi_m \middle| H \sum c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \underbrace{\langle \psi_m | \psi_n \rangle}_{\delta_{nm}}$$

$$= \sum_n E_n |c_n|^2$$

But the ground state energy by defination have smallest eigenvalue $E_{gs} \leq E_n$ hence,

$$\langle H \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

proved

There are four steps for variational method :-

Step-I. Based on the physical situation, make an intutive choise, of trail wave function for ground state, with adjustable parameters $\alpha_1, \alpha_2, \ldots$ i.e.

$$|\psi_0\rangle = |\psi_0(\alpha_1, \alpha_2, \ldots)\rangle$$

Step-II Calculate the approximate energy

$$E_0 = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \rightarrow \text{depends on } \alpha_1, \alpha_2, \ldots$$

Step-III Minimize $E_0(\alpha_1, \alpha_2, \ldots)$ with respect to $\alpha_1, \alpha_2, \ldots$

$$\frac{\partial E_0(\alpha_1, \alpha_2, \ldots)}{\partial \alpha_i} = 0$$ from this you will get the values of $\alpha_1, \alpha_2, \ldots$ etc.

Step-IV Substitute the value of $\alpha_1, \alpha_2, \ldots$ in the step 2. i.e. the expression for approximate energy. Then you will get upperbound of exact ground state energy.

Problem: All of you already know the ground state energy of 1-dimensional harmonic oscillator $H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$. We already know the exact answer $E_{gs} = \frac{\hbar\omega}{2}$. Repeat the problem by variational method.

Solution: Let the trial wave function as gaussian. $\psi(x) = Ae^{-bx^2}$ where A = Normalisation constant and b = parameter

Now. normalisation leads to $\langle \psi(x) | \psi(x) \rangle = 1$

$$\Rightarrow |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} dx = 1$$

$$\Rightarrow |A|^2 \sqrt{\frac{\pi}{2b}} = 1 \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$$

Now $\langle H \rangle = \langle T \rangle + \langle V \rangle$

$$\langle T \rangle = -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx$$

$$= \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \langle \psi | V | \psi \rangle = \frac{1}{2}m\omega^2 |A|^2 \int_{-\infty}^{\infty} x^2 e^{-2bx^2} dx$$

$$= \frac{m\omega^2}{8b}$$

$$\langle H\rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

Now $$\frac{d\langle H\rangle}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0$$

$$\Rightarrow b = \frac{m\omega}{\hbar}$$

Put this in $\langle H\rangle$ we get

$$\langle H\rangle_{min} = \frac{\hbar\omega}{2}.$$

Problem: Using variational method find out the ground state energy for delta function potential.

Solution: $$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\,\delta(x) \; ; \quad \alpha = \text{Constant}$$

Let the trial wave function is $\psi(x) = A e^{-bx^2}$. ($A \to$ Constant, $b \to$ parameter)

$$\langle T\rangle = \left\langle \psi(x) \left| -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \right| \psi(x) \right\rangle$$

$$= -\frac{\hbar^2}{2m}|A|^2 \int_{-\infty}^{\infty} e^{-bx^2}\frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx$$

$$= \frac{\hbar^2 b}{2m}$$

In the previous problem we get $\langle\psi(x)|\psi(x)\rangle = 1$
$\Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}$

$$\langle V\rangle = \langle\psi(x)|\hat{V}|\psi(x)\rangle$$

$$= -\alpha|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\,\delta(x)\,dx$$

$$= -\alpha\sqrt{\frac{2b}{\pi}}$$

$$\langle H\rangle = \langle T\rangle + \langle V\rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}$$

Now, $$\frac{d\langle H\rangle}{db} = 0$$

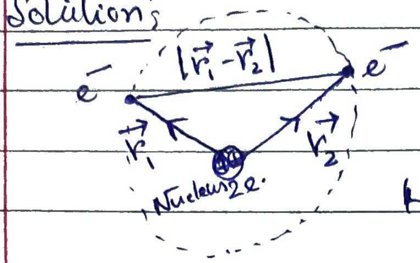
$$\Rightarrow \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0$$

$$\Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4}.$$

we get $$\langle H\rangle_{min} = -\frac{m\alpha^2}{\pi\hbar^2}$$

Problem: Estimate the ground state energy for He-atom.

Solution:



The Hamiltonian for the system of ${}_2He^4$ atom is

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{|\vec{r}_1-\vec{r}_2|}\right)$$

our problem is to calculate $E_{gs} = ?$

Experimentally it is found that $E_{gs} = -78.975$ eV.

If we ignore the electron-electron repulsion term i.e. $V_{ee} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$ then the exact solution

$$\psi_0(\vec{r}_1,\vec{r}_2) = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a_0}$$

The energy $E_0 = 8E_1 = 8\times(-13.6)$ eV $= -109$ eV which is very far from -79 eV.

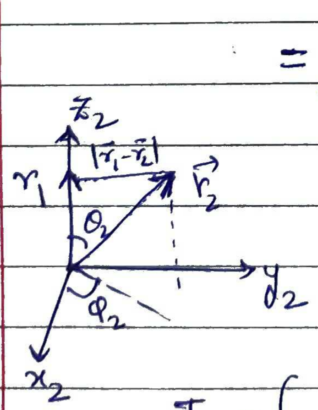
Let $\psi_0(\vec{r}_1,\vec{r}_2)$ be the trial wave function.

$$H|\psi_0\rangle = (8E_1 + V_{ee})|\psi_0\rangle$$

$$\Rightarrow \langle H\rangle = 8E_1 + \langle V_{ee}\rangle$$

where $\langle V_{ee}\rangle = \langle\psi_0|V_{ee}|\psi_0\rangle$

$$= \frac{e^2}{4\pi\epsilon_0}\left(\frac{8}{\pi a^3}\right)^2\int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1-\vec{r}_2|}\,d^3r_1\,d^3r_2$$



Now $|\vec{r}_1-\vec{r}_2| = \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}$

$$I_2 = \int \frac{e^{-4r_2/a}}{|\vec{r}_1-\vec{r}_2|}\,d^3r_2$$

Keep r_1 fixed do r_2 integral first

$$I_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\,r_2^2\sin\theta_2\,dr_2\,d\theta_2\,d\phi_2$$

ϕ_2 integral gives 2π

θ_2 integral $\longrightarrow$ $\displaystyle\int_0^{\pi} \frac{\sin\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}\, d\theta_2 = \left.\frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_2}}{r_1 r_2}\right|_0^{\pi}$

$$= \frac{1}{r_1 r_2}\left[\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right]$$

$$= \frac{1}{r_1 r_2}\left[r_1+r_2 - |r_1-r_2|\right]$$

$$= \begin{cases} \dfrac{2}{r_1} & \text{for } r_2 < r_1 \\ \dfrac{2}{r_2} & \text{for } r_2 > r_1 \end{cases}$$

Thus $\displaystyle I_2 = 4\pi \left[\frac{1}{r_1}\int_0^{r_1} e^{-\frac{4r_2}{a}} r_2^2\, dr_2 + \int_{r_1}^{\infty} e^{-4r_2/a} r_2\, dr_2\right]$

$$= \frac{\pi a^3}{8 r_1}\left[1 - \left(1+\frac{2r_1}{a}\right)e^{-4r_1/a}\right]$$

$$\langle V_{ee}\rangle = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{8}{\pi a^3}\right)\int \left[1-\left(1+\frac{2r_1}{a}\right)e^{-4r_1/a}\right]e^{-4r_1/a}\, r_1 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1$$

The angular part $\int \sin\theta_1\, d\theta_1\, d\phi_1 \longrightarrow 4\pi$

hence $\displaystyle\int\left[r e^{-4r/a} - \left(r+\frac{2r^2}{a}\right)e^{-8r/a}\right]dr = \frac{5a^2}{128}$

Now $\displaystyle\langle V_{ee}\rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\varepsilon_0}\right) = -\frac{5}{2}E_1 = -\frac{5}{2}\cdot(-13.6)\text{ eV} = 34\text{ eV}.$

$\langle H\rangle = -109\text{ eV} + 34\text{ eV} = -75\text{ eV}$, which is close to -79 eV.

Now we can think of more realistic function ψ_0

Each electron is a cloud of negative charge, which partially shields the nuclear charge, so that the other electrons see an effective nuclear charge $Z<2$. This suggest the trial wave function is

$$\psi(r_1, r_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

parameter

This is eigenstate of unperturb Hamiltonian.

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\vec{r}_1 - \vec{r}_2|}\right)$$

$$\langle H \rangle = 2Z^2 E_1 + 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle + \langle V_{ee} \rangle$$

We have already calculate $\langle V_{ee} \rangle = -\frac{5Z}{4}E_1$

Hence $\langle H \rangle = \left(2Z^2 - 4Z(Z-2) - \frac{5}{4}Z\right)E_1 = \left(-2Z^2 + \frac{27}{4}Z\right)E_1$

Now, $\frac{d}{dZ}\langle H \rangle = \left[-4Z + \frac{27}{4}\right]E_1 = 0$

or, $Z = \frac{27}{16} = 1.69$ which is less than 2.

$$\langle H \rangle = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 = -77.5\text{ eV}$$

x

H.W Find out the best bound state of first excited state of 1-dim harmonic oscillator with the trial wave function $\psi(x) = A x e^{-bx^2}$.

H.W Using the Gaussian trial wave function obtain the lowest upper bound of the potential $V(x) = \alpha|x|$.

x

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