THE VARIATIONAL METHOD

Goal: given H, estimate E_0

① Choose a trial state $|\Psi(a_i)\rangle$

some parameters

② Normalize

③ Calculate $E_\psi(a_i) = \langle \Psi(a_i) | H | \Psi(a_i) \rangle$

④ Minimize over $a_i \longrightarrow E_\psi^{min}$

Result: $E_0 \leq E_\psi^{min}$ ← this is our estimate

The Variational Method

Question: In a spin $\frac{1}{2}$ system with Hamiltonian H
Katie evaluates $\langle x|H|x\rangle$ for $|x\rangle = |\uparrow\rangle + |\downarrow\rangle$
and finds $0.2\,eV$. She can conclude that:

1. $E_0 \leq 0.2\,eV$
2. $E_0 \geq 0.2\,eV$
3. $E_0 \leq 0.1\,eV$
4. $E_0 \geq 0.1\,eV$
5. $E_0 \leq 0.4\,eV$
6. $E_0 \geq 0.4\,eV$

Normalized ~~state~~ is $|\Psi\rangle = \frac{1}{\sqrt{2}}|x\rangle$

$$E_0 \leq \langle \Psi|H|\Psi\rangle = \frac{1}{2}\langle x|H|x\rangle = 0.1\,eV$$

The Variational Method

Question: For a quantum system with 3-dimensional Hilbert space and Hamiltonian represented as

$$H = E\begin{pmatrix} 4 & 2 & 7 \\ 2 & 1 & 3 \\ 7 & 3 & 5 \end{pmatrix}$$

what is the upper bound that we can place on the ground state energy by considering a trial state $|\Psi\rangle$ represented as $\begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix}$ for some fixed θ?

EXTRA: What is the best we can do if we consider all possible θ?

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Question: For a quantum system with 3-dimensional Hilbert space and Hamiltonian represented as

$$H = E\begin{pmatrix} 4 & 2 & 7 \\ 2 & 1 & 3 \\ 7 & 3 & 5 \end{pmatrix}$$

what is the upper bound that we can place on the ground state energy by considering a trial state $|\Psi\rangle$ represented as $\begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix}$ (for some fixed θ).

① $4E\cos^2\theta$

② $4E\cos^2\theta + E\sin^2\theta$

③ $E\sin^2\theta$

④ $\boxed{4E\cos^2\theta + 4E\cos\theta\sin\theta + E\sin^2\theta}$

⑤ E

$$\langle\Psi|H|\Psi\rangle = (\cos\theta \;\; \sin\theta \;\; 0)\cdot E\begin{pmatrix} 4 & 2 & 7 \\ 2 & 1 & 3 \\ 7 & 3 & 5 \end{pmatrix}\begin{pmatrix} \cos\theta \\ \sin\theta \\ 0 \end{pmatrix}$$

$$= E(\cos\theta \;\; \sin\theta \;\; 0)\begin{pmatrix} 4\cos\theta + 2\sin\theta \\ 2\cos\theta + \sin\theta \\ 7\cos\theta + 3\sin\theta \end{pmatrix}$$

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$$E_0 \leq E(2\cos\theta + \sin\theta)^2$$

Minimum when $2\cos\theta + \sin\theta = 0$

$$\Rightarrow \tan\theta = -2$$

$$\therefore E_0 \leq 0$$

The Variational Method

Question: A particle in 1D has a Hamiltonian

$$H = \frac{p^2}{2m} + \lambda x^4$$

If we use a properly normalized trial wavefunction $\psi(x)$ for our variational method, what is the bound on E_0?

The Variational Method

Question: A particle in 1D has a Hamiltonian

$$H = \frac{p^2}{2m} + \lambda x^4$$

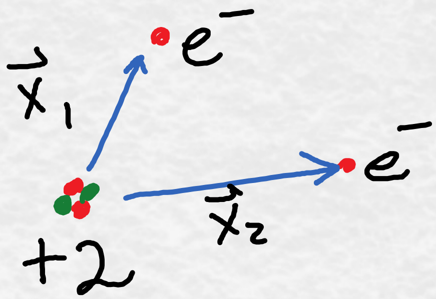
If we use a properly normalized trial wavefunction $\psi(x)$ for our variational method, what is the bound on E_0?

1. $\int dx \, \lambda x^4 |\psi(x)|^2$
2. $\boxed{2}$ $\int dx \left\{ -\frac{\hbar^2}{2m} \psi^*(x) \psi''(x) + \lambda x^4 |\psi(x)|^2 \right\}$
3. $\int dx \, \lambda |\psi(x)|^4$
4. $\frac{1}{2}\hbar\omega$

$$\langle \Psi | p^2 | \Psi \rangle = \int dx \, \psi^*(x) \left(\frac{\hbar}{i} \frac{d}{dx} \right)^2 \psi(x)$$

$$\langle \Psi | x^4 | \Psi \rangle = \int dx \, \psi^*(x) \lambda x^4 \psi(x)$$

THE VARIATIONAL METHOD: Helium atom



Discussion questions (breakout groups)

① What is the "position space" description of the two electrons in a Helium atom?

e.g: two wavefunctions $\psi_1(\vec{x}), \psi_2(\vec{x})$

one wavefunction $\psi(\vec{x}_1, \vec{x}_2)$

wavefunctions $\psi_1(\vec{x}_1, \vec{x}_2), \psi_2(\vec{x}_1, \vec{x}_2)$

Basis $|x_1\rangle \otimes |x_2\rangle$. Wavefn is coefficient of this state in general superposition

② What is the Hamiltonian that describes the two electrons in a Helium atom?

(hint: it's also the energy operator)

(see next)

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Helium atom Hamiltonian:

$$H = \frac{p_1^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1|} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_2|} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1 - \vec{x}_2|}$$

THE VARIATIONAL METHOD

Helium atom Hamiltonian:

$$
\begin{aligned}
H = {} & \left.\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1|}\right\} \text{Hamiltonian for He}^+ \text{ ion} \\
& + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_2|} \\
& + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1 - \vec{x}_2|}
\end{aligned}
$$

Ground state is $\psi^{Z}_{100}(\vec{x})$

THE VARIATIONAL METHOD

Helium atom Hamiltonian:

$$H = \left.\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1|}\right\} \text{Hamiltonian for He}^+ \text{ ion}$$

$$+ \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_2|}$$

$$+ \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1 - \vec{x}_2|}$$

Ground state is

$$\psi_{100}^{Z=2}(\vec{x}) = e^{-Zr/a} \times N$$

Simple trial state: both electrons independently in this state.

$$① \quad \boxed{\psi(\vec{x}_1, \vec{x}_2) = \psi_{100}^{Z=2}(\vec{x}_1)\, \psi_{100}^{Z=2}(\vec{x}_2)}$$

e.g. $P(A \text{ and } B) = P(A) \times P(B)$

Q: Does that mean: ② $\psi(\vec{x}_1, \vec{x}_2) = \psi_{100}^{Z=2}(\vec{x}_1) + \psi_{100}^{Z=2}(\vec{x}_2)$

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arbitrary parameter.

TRIAL STATE #2 : $\psi(\vec{x}_1, \vec{x}_2) = \psi^{Z}_{100}(\vec{x}_1)\, \psi^{Z}_{100}(\vec{x}_2)$

Motivation:

If the first electron is in a spherically symmetric configuration about the He nucleus, what potential is felt by the second electron when it is far away?

$$\boxed{① \quad -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$

$$② \quad -\frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r}$$

$$③ \quad \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$④ \quad \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r}$$

⑤ $\emptyset$

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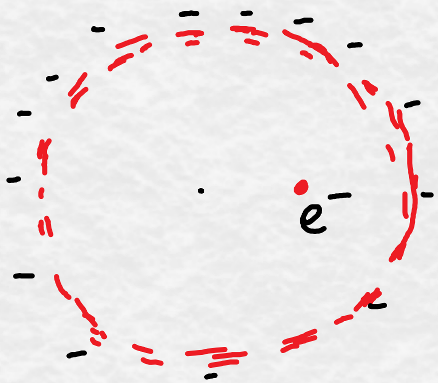
Q: The electron shown is inside a spherically symmetric shell of negative charge.



The force felt by the electron is

1. To the left
2. To the right
3. Zero.

Shell theorem from classical electrostatics

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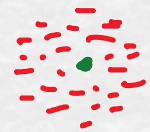
Helium atom Hamiltonian:

$$H = \frac{p_1^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1|} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_2|} + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{x}_1 - \vec{x}_2|}$$



Summary: each electron partly "screens" charge of nucleus; this motivates trial wavefn.

$$\psi_{100}^{Z}(\vec{x}_1)\,\psi_{100}^{Z}(\vec{x}_2) \qquad 1 \leqslant Z \leqslant 2$$