Quantum Mechanics

The Variational Principle

We don't know the solutions or the energies but we want an upper bound on the ground state energy. Claim:

$$\boxed{E_{gs} \leq \langle\psi|H|\psi\rangle \equiv \langle H\rangle}$$

where $|\psi\rangle$ is any normalised state.

Proof: Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:

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

Since ψ is normalized,

$$1 = \langle\psi|\psi\rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* c_n \langle\psi_m|\psi_n\rangle = \sum_n |c_n|^2,$$

(assuming the eigenfunctions themselves have been orthonormalized: $\langle\psi_m|\psi_n\rangle = \delta_{mn}$). Meanwhile,

$$\langle H\rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle\psi_m|\psi_n\rangle = \sum_n E_n |c_n|^2.$$

But the ground state energy is, by definition, the *smallest* eigenvalue, so $E_{gs} \leq E_n$, and hence

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

Example Suppose we want to find the ground state energy for the one-dimensional harmonic oscillator:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2.$$

Gaussian trial wave function:

$$\psi(x) = Ae^{-bx^2},$$

where b is a constant, and A is determined by normalization:

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx = |A|^2 \sqrt{\frac{\pi}{2b}} \Rightarrow A = \left(\frac{2b}{\pi}\right)^{1/4}.$$

Now

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

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where, in this case,

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

and

$$\langle V \rangle = \frac{1}{2}m\omega^2|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2} x^2\, dx = \frac{m\omega^2}{8b}.$$

so

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

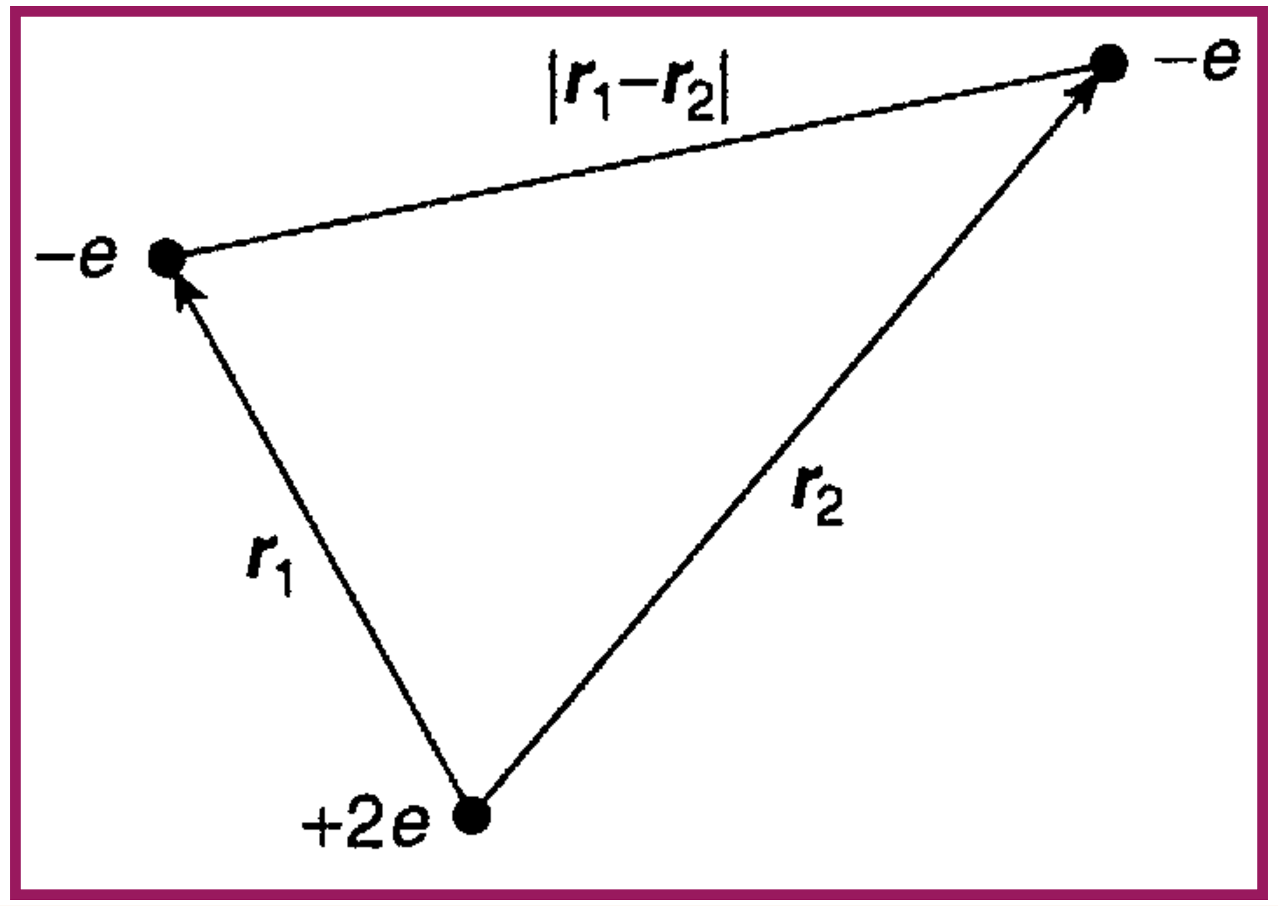
let's *minimize* $\langle H \rangle$:

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

Putting this back into $\langle H \rangle$, we find

$$\langle H \rangle_{\min} = \frac{1}{2}\hbar\omega.$$

The Ground State of Helium



The Hamiltonian for this system (ignoring fine structure and smaller corrections) is:

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

Our problem is to calculate the ground state energy, E_{gs}. Physically, this represents the amount of energy it would take to strip off both electrons.

The ground state energy of helium has been measured

$$E_{gs} = -78.975 \text{ eV} \quad \text{(experimental)}.$$

This is the number we would like to reproduce theoretically.

The trouble comes from the electron-electron repulsion,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}.$$

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If we ignore this term altogether, H splits into two independent hydrogen Hamiltonians (only with a nuclear charge of $2e$, instead of e); the exact solution is just the product of hydrogenic wave functions:

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

and the energy is $8E_1 = -109$ eV

To get a better approximation for E_{gs} we'll apply the variational principle, using ψ_0 as the trial wave function. This is a particularly convenient choice because it's an eigenfunction of *most* of the Hamiltonian:

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

Thus

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

where[8]

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

I'll do the $\mathbf{r}_2$ integral first; for this purpose $\mathbf{r}_1$ is fixed, and we may as well orient the $\mathbf{r}_2$ coordinate system so that the polar axis lies along $\mathbf{r}_1$

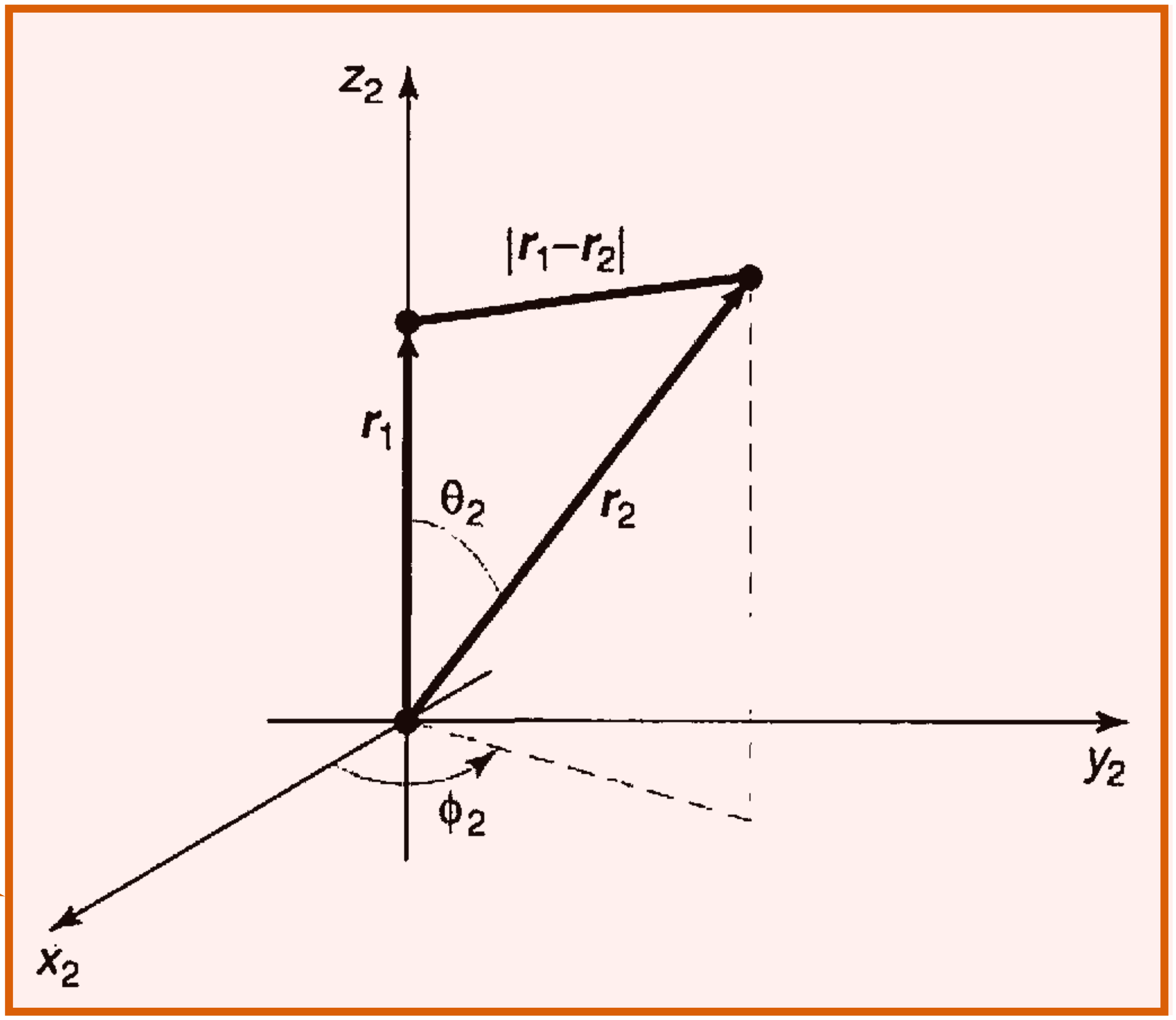
$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}.$$

and hence

$$I_2 \equiv \int \frac{e^{-4r_2/a}}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3 r_2 = \int \frac{e^{-4r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}} r_2^2 \sin\theta_2\, dr_2 d\theta_2 d\phi_2.$$

The ϕ_2 integral is trivial (2π); the θ_2 integral is

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



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$$= \frac{1}{r_1 r_2}\left(\sqrt{r_1^2 + r_2^2 + 2r_1 r_2} - \sqrt{r_1^2 + r_2^2 - 2r_1 r_2}\right)$$

$$= \frac{1}{r_1 r_2}\left[(r_1 + r_2) - |r_1 - r_2|\right] = \begin{cases} 2/r_1, & \text{if } r_2 < r_1, \\ 2/r_2, & \text{if } r_2 > r_1. \end{cases}$$

Thus

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

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

It follows that $\langle V_{ee}\rangle$ is equal to

$$\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{8}{\pi a^3}\right)\int\left[1 - \left(1 + \frac{2r_1}{a}\right)e^{-4r_1/a}\right]e^{-4r_1/a} r_1 \sin\theta_1\, dr_1 d\theta_1 d\phi_1.$$

The angular integrals are easy (4π), and the r_1 integral becomes

$$\int_0^{\infty}\left[re^{-4r/a} - \left(r + \frac{2r^2}{a}\right)e^{-8r/a}\right]dr = \frac{5a^2}{128}.$$

Finally, then,

$$\langle V_{ee}\rangle = \frac{5}{4a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5}{2}E_1 = 34\ \text{eV},$$

and therefore

$$\langle H\rangle = -109\ \text{eV} + 34\ \text{eV} = -75\ \text{eV}.$$

Not bad (remember, the experimental value is -79 eV). But we can do better.

We need to think up a more realistic trial function than ψ_0 (which treats the two electrons as though they did not interact at all). Rather than completely *ignoring* the influence of the other electron, let us say that, on the average, each electron represents a cloud of negative charge which partially *shields* the nucleus, so that the other electron actually sees an *effective* nuclear charge (Z) that is somewhat *less* than 2. This suggests that we use a trial function of the form

$$\psi_1(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}.$$

We'll treat Z as a variational parameter, picking the value that minimizes H.

This wave function is an eigenstate of the "unperturbed" Hamiltonian (neglecting electron repulsion), only with Z, instead of 2, in the Coulomb terms. With this in mind, we rewrite H

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)$$

$$+ \frac{e^2}{4\pi\epsilon_0}\left(\frac{(Z-2)}{r_1} + \frac{(Z-2)}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right).$$

The expectation value of H is evidently

$$\langle H\rangle = 2Z^2 E_1 + 2(Z-2)\left(\frac{e^2}{4\pi\epsilon_0}\right)\left\langle\frac{1}{r}\right\rangle + \langle V_{ee}\rangle.$$

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Here $\langle 1/r\rangle$ is the expectation value of $1/r$ in the (one-particle) hydrogenic ground state ψ_{100} (but with nuclear charge Z);

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a}.$$

The expectation value of V_{ee} is the same as before except that instead of $Z = 2$ we now want *arbitrary* Z—so we multiply a by $2/Z$:

$$\langle V_{ee}\rangle = \frac{5Z}{8a}\left(\frac{e^2}{4\pi\epsilon_0}\right) = -\frac{5Z}{4}E_1.$$

Putting all this together, we find

$$\langle H\rangle = \left[2Z^2 - 4Z(Z-2) - (5/4)Z\right]E_1 = [-2Z^2 + (27/4)Z]E_1.$$

According to the variational principle, this quantity exceeds E_{gs} for *any* value of Z. The *lowest* upper bound occurs when $\langle H\rangle$ is minimized:

$$\frac{d}{dZ}\langle H\rangle = [-4Z + (27/4)]E_1 = 0,$$

from which it follows that

$$Z = \frac{27}{16} = 1.69.$$

This seems reasonable; it tells us that the other electron partially screens the nucleus, reducing its effective charge from 2 down to about 1.69. Putting in this value for Z, we find

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

Reading assignment: Hydrogen Molecule Ion