Consider the time independent Schroedinger equation

$$\hat{H}\psi = E\psi$$

For an eigenfunction ψ that is an exact solution, E is a number. However, when ψ is an approximate solution, E varies over the coordinates of ψ. For example, a two-electron atom does not have an exact solution, hence for an approximate ψ we have

$$\hat{H}\psi = E(\vec{r}_1, \vec{r}_2)\psi$$

where $E(\vec{r}_1, \vec{r}_2)$ is a function of the electron coordinates. We still want a single number for the energy, so we use the expected energy $\langle E \rangle$. The expected energy is basically the average value of $E(\vec{r}_1, \vec{r}_2)$. If the eigenfunction ψ is a good approximation then $\langle E \rangle$ should be close to the actual energy determined by experiment.

For a helium atom, find the expected energy $\langle E \rangle$ given the following approximate eigenfunction.

$$\psi = \frac{\alpha^3}{\pi} \exp\left(-\alpha(r_1 + r_2)\right)$$

Recall that $|\psi|^2 = \psi^* \psi$ is a probability density function. Hence the expected energy is

$$\langle E \rangle = \int E \, |\psi|^2 \, dV_1 \, dV_2$$

Reorder factors. (For the eigenfunction given above, $\psi^* = \psi$.)

$$\langle E \rangle = \int \psi E \psi \, dV_1 \, dV_2$$

Replace $E\psi$ with $\hat{H}\psi$.

$$\langle E \rangle = \int \psi \hat{H} \psi \, dV_1 \, dV_2$$

This is a simplified Hamiltonian for helium, in atomic units of $\hbar = m_e = e = 4\pi\epsilon_0 = 1$.

$$\hat{H} = -\underbrace{\frac{1}{2}\nabla_1^2}_{\substack{\text{kinetic energy} \\ \text{electron 1}}} - \underbrace{\frac{1}{2}\nabla_2^2}_{\substack{\text{kinetic energy} \\ \text{electron 2}}} - \underbrace{\frac{Z}{r_1}}_{\substack{\text{potential energy} \\ \text{electron 1}}} - \underbrace{\frac{Z}{r_2}}_{\substack{\text{potential energy} \\ \text{electron 2}}} + \underbrace{\frac{1}{r_{12}}}_{\substack{\text{potential energy} \\ \text{inter-electron}}}$$

Hence

$$\langle E \rangle = \int \psi \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \psi \, dV_1 \, dV_2$$

The measure $dV_1 \, dV_2$ is the product of two volume elements.

$$dV_1 \, dV_2 = r_1^2 r_2^2 \sin\theta_1 \sin\theta_2 \, dr_1 \, dr_2 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2$$

Since ψ has no angular dependence, we can use the identity

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} \sin\theta_1 \sin\theta_2 \, d\theta_1 \, d\theta_2 \, d\phi_1 \, d\phi_2 = 16\pi^2 \tag{1}$$

to obtain

$$\langle E\rangle = 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \psi \, r_1^2 r_2^2 \, dr_1 \, dr_2$$

We now proceed to integrate each term separately. The Laplacian in spherical coordinates is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial \phi^2}$$

Since ψ has no angular dependence we have

$$\nabla_1^2 \psi = \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1}\right)\psi = \left(\alpha^2 - \frac{2\alpha}{r_1}\right)\psi$$

Hence for kinetic energy we have

$$\begin{aligned}
\langle K\rangle &= 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(-\frac{1}{2}\nabla_1^2 \right) \psi \, r_1^2 r_2^2 \, dr_1 \, dr_2 \\
&= -8\alpha^6 \int_0^\infty \int_0^\infty \left(\alpha^2 - \frac{2\alpha}{r_1}\right) \exp\left(-2\alpha(r_1 + r_2)\right) \, r_1^2 \, r_2^2 \, dr_1 \, dr_2 \\
&= \tfrac{1}{2}\alpha^2
\end{aligned} \tag{2}$$

For potential energy we have

$$\langle V\rangle = 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(-\frac{Z}{r_1} \right) \psi \, r_1^2 r_2^2 \, dr_1 \, dr_2 = -Z\alpha \tag{3}$$

Finally, for inter-electron potential energy we have (derivation is below)

$$\langle U\rangle = 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(\frac{1}{r_{12}} \right) \psi \, r_1^2 r_2^2 \, dr_1 \, dr_2 = \tfrac{5}{8}\alpha \tag{4}$$

Summing over kinetic and potential energies we have

$$\langle E\rangle = 2\langle K\rangle + 2\langle V\rangle + \langle U\rangle = \alpha^2 - 2Z\alpha + \tfrac{5}{8}\alpha$$

Next, find α that minimizes $\langle E\rangle$.

$$\frac{d}{d\alpha}\langle E\rangle = 2\alpha - 2Z + \tfrac{5}{8} = 0$$

Solve for α with $Z = 2$ for helium.

$$\alpha = Z - \tfrac{5}{16} = \tfrac{27}{16}$$

Then for $\alpha = 27/16$ and $Z = 2$ we have

$$\langle E\rangle = -2.84766 \, \text{hartree}$$

Hartree is the atomic unit of energy. Convert hartrees to electron volts.

$$\langle E\rangle = -2.84766 \, \text{hartree} \times 27.2114 \, \frac{\text{eV}}{\text{hartree}} = -77.4888 \, \text{eV}$$

It turns out that $\langle E \rangle$ is about 2% higher than the actual measured value of $-79.0052\,\text{eV}$.

$$\frac{(-77.4888) - (-79.0052)}{|-79.0052|} = 0.019$$

To verify equation (4) we will now show that

$$\int \frac{\psi_1^2 \psi_2^2}{r_{12}}\, dV_1\, dV_2 = \tfrac{5}{8}\alpha$$

where

$$\psi_j = \sqrt{\frac{\alpha^3}{\pi}} \exp\left(-\alpha r_j\right)$$

Symbol r_{12} is the following distance function where θ_{12} is angular separation.

$$r_{12} = \sqrt{r_1^2 + r_2^2 - r_1 r_2 \cos\theta_{12}}$$

Let $I(r_1)$ be the following integral over V_2.

$$I(r_1) = \int \frac{\psi_2^2}{r_{12}}\, dV_2$$

The measure dV_2 is a volume element in spherical coordinates.

$$dV_2 = r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2$$

Write out the full integral and make $\theta_2 = \theta_{12}$ by independence of the coordinate system.

$$I(r_1) = \frac{\alpha^3}{\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \frac{\exp(-2\alpha r_2)}{\sqrt{r_1^2 + r_2^2 - r_1 r_2 \cos\theta_2}}\, r_2^2 \sin\theta_2\, dr_2\, d\theta_2\, d\phi_2$$

Integrate over ϕ_2.

$$I(r_1) = 2\alpha^3 \int_0^{\pi} \int_0^{\infty} \frac{\exp(-2\alpha r_2)}{\sqrt{r_1^2 + r_2^2 - r_1 r_2 \cos\theta_2}}\, r_2^2 \sin\theta_2\, dr_2\, d\theta_2$$

Expand $1/r_{12}$ in Legendre polynomials. The first integral is over $r_2 < r_1$ and the second integral is over $r_2 > r_1$.

$$\begin{aligned} I(r_1) = 2\alpha^3 \int_0^{\pi} \int_0^{r_1} \exp(-2\alpha r_2) \left(\sum_{k=0}^{\infty} \frac{r_2^k}{r_1^{k+1}} P_k(\cos\theta_2) \right) r_2^2 \sin\theta_2\, dr_2\, d\theta_2 \\ + 2\alpha^3 \int_0^{\pi} \int_{r_1}^{\infty} \exp(-2\alpha r_2) \left(\sum_{k=0}^{\infty} \frac{r_1^k}{r_2^{k+1}} P_k(\cos\theta_2) \right) r_2^2 \sin\theta_2\, dr_2\, d\theta_2 \end{aligned}$$

It turns out that, after integrating over θ_2, all summands vanish except for $k = 0$.

$$\int_0^{\pi} P_k(\cos\theta_2) \sin\theta_2\, d\theta_2 = \begin{cases} 2, & k = 0 \\ 0, & k > 0 \end{cases} \tag{5}$$

Hence

$$I(r_1) = \frac{4\alpha^3}{r_1} \int_0^{r_1} \exp(-2\alpha r_2)\, r_2^2\, dr_2 + 4\alpha^3 \int_{r_1}^{\infty} \exp(-2\alpha r_2)\, r_2\, dr_2$$

Solve the integrals.

$$I(r_1) = \frac{4\alpha^3}{r_1} \exp(-2\alpha r_2) \left(-\frac{r_2^2}{2\alpha} - \frac{r_2}{2\alpha^2} - \frac{1}{4\alpha^3} \right) \Bigg|_0^{r_1} + 4\alpha^3 \exp(-2\alpha r_2) \left(-\frac{r_2}{2\alpha} - \frac{1}{4\alpha^2} \right) \Bigg|_{r_1}^{\infty}$$

Evaluate per limits.

$$I(r_1) = \frac{1}{r_1} - \frac{1}{r_1} \exp(-2\alpha r_1) - \alpha \exp(-2\alpha r_1) \tag{6}$$

Having obtained $I(r_1)$ we can now evaluate the integral over V_1.

$$I = \frac{\alpha^3}{\pi} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \exp(-2\alpha r_1) I(r_1)\, r_1^2 \sin\theta_1\, dr_1\, d\theta_1\, d\phi_1$$

Integrate over θ_1 and ϕ_1.

$$I = 4\alpha^3 \int_0^{\infty} \exp(-2\alpha r_1) I(r_1)\, r_1^2\, dr_1$$

Expand the integrand.

$$I = 4\alpha^3 \int_0^{\infty} \exp(-2\alpha r_1)\, r_1\, dr_1 - 4\alpha^3 \int_0^{\infty} \exp(-4\alpha r_1)\, r_1\, dr_1 - 4\alpha^4 \int_0^{\infty} \exp(-4\alpha r_1)\, r_1^2\, dr_1$$

Solve the integrals.

$$I = \exp(-2\alpha r_1) \left(-2\alpha^2 r_1 - \alpha \right) \Big|_0^{\infty} - \exp(-4\alpha r_1) \left(-\alpha^2 r_1 - \tfrac{1}{4}\alpha \right) \Big|_0^{\infty} - \exp(-4\alpha r_1) \left(-\alpha^3 r_1^2 - \tfrac{1}{2}\alpha^2 r_1 - \tfrac{1}{8}\alpha \right) \Big|_0^{\infty}$$

The result vanishes for $r_1 = \infty$ hence

$$I = 0 - \left(-\alpha + \tfrac{1}{4}\alpha + \tfrac{1}{8}\alpha \right) = \tfrac{5}{8}\alpha \tag{7}$$