

Helium

Consider the simplest Schroedinger equation.

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

For a wavefunction ψ that is an exact solution, energy E is a number. However, when ψ is an approximate solution, E varies over configuration space. For example, two electrons have six dimensions in configuration space so we have

$$\hat{H}\psi = E(r_1, r_2, \theta_1, \theta_2, \phi_1, \phi_2) \psi$$

We still want a single number for energy so we use the expected energy $\langle E \rangle$. The expected energy is the average value of function E over configuration space. If the wavefunction 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 wavefunction.

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

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 in the integrand. For the wavefunction 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 $\hbar = m_e = e = 4\pi\epsilon_0 = 1$.

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

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

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2 = 16\pi^2 \quad (1)$$

to obtain

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

Solve for each term separately, starting with the kinetic energy of the first electron.

$$\langle K_1 \rangle = 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(-\frac{1}{2}\nabla_1^2 \right) \psi r_1^2 r_2^2 dr_1 dr_2$$

The Laplacian 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 $\psi = \alpha^3/\pi \exp(-\alpha(r_1 + r_2))$ has no angular dependence we have for the first electron

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

It follows that

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

Hence

$$\langle K_1 \rangle = -8\alpha^6 \int_0^\infty \int_0^\infty \left(\alpha^2 - \frac{2\alpha}{r_1} \right) \exp(-2\alpha(r_1 + r_2)) r_1^2 r_2^2 dr_1 dr_2$$

The result is

$$\langle K_1 \rangle = \frac{1}{2}\alpha^2 \quad (2)$$

By symmetry $\langle K_1 \rangle = \langle K_2 \rangle$ so we can write

$$\langle K \rangle = \langle K_1 \rangle + \langle K_2 \rangle = \alpha^2$$

For the potential energy of the first electron we have

$$\langle V_1 \rangle = 16\pi^2 \int_0^\infty \int_0^\infty \psi \left(-\frac{Z}{r_1} \right) \psi r_1^2 r_2^2 dr_1 dr_2 = -Z\alpha \quad (3)$$

Again by symmetry we can write

$$\langle V \rangle = \langle V_1 \rangle + \langle V_2 \rangle = -2Z\alpha$$

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

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

Summing over kinetic and potential energies we have

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

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

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

Solve for α .

$$\alpha = Z - \frac{5}{16}$$

For helium with $Z = 2$ we have

$$\alpha = \frac{27}{16}$$

Hence the expected energy is

$$\langle E \rangle = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha = -\frac{729}{256} \text{ hartree}$$

The result is in hartrees because we used atomic units. Convert hartrees to electron volts.

$$\langle E \rangle = -\frac{729}{256} \text{ hartree} \times 27.2114 \frac{\text{eV}}{\text{hartree}} = -77.4887 \text{ eV}$$

It turns out that $\langle E \rangle$ differs from the observed value by about 2%.

$$\frac{77.4887}{79.0052} = 0.98$$

To verify equation (4) we will now show that

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

where

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

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 $r_2 > r_1$.

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

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

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

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.

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

Evaluate per limits.

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

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.

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

The result vanishes for $r_1 = \infty$ hence

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