

Consider the time independent Schroedinger equation

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

For a wave function  $\psi$  that is an exact solution,  $E$  is a number. However, when  $\psi$  is an approximate solution,  $E$  varies over the coordinates of  $\psi$ . For example, a two-electron atom does not have an exact solution, hence for an approximate  $\psi$  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 energy for the wave function. If the wave function  $\psi$  is a good approximation, then the errors should average out and  $\langle E \rangle$  will be close to the actual energy determined by experiment.

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

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

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

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

Reorder factors.

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

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  $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ .

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

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  $\psi$  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

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

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  $\psi$  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

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

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)

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

Summing over kinetic and potential energies we have

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

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

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

Solve for  $\alpha$  with  $Z = 2$  for helium.

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

Then for  $\alpha = 27/16$  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 observed value  $-79.0052 \text{ eV}$ .

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

To verify equation (4) we will now show that

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

where

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

Symbol  $r_{12}$  is the following distance function where  $\theta_{12}$  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  $\phi_2$ .

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

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  $\theta_2$ , 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  $\theta_1$  and  $\phi_1$ .

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

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.

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

The result vanishes for  $r_1 = \infty$  hence

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