

# Computer Lab 6.1: Hydrogen Atom Calculations

## Full kinetic energy operator in spherical coordinates:

Kinetic energy operator for s states:

$$-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot$$

Kinetic energy operator for p states:

$$-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \dots$$

$$+ \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)} \cdot \left[ \frac{d}{d\theta} \left( \sin(\theta) \cdot \frac{d}{d\theta} \right) \right] \dots$$

$$+ \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)^2} \cdot \frac{d^2}{d\phi^2} \cdot$$

Position operator:

$$r$$

Potential energy operator:

$$-\frac{1}{r}$$

Triple integral with volume element:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr$$

Orbitals:

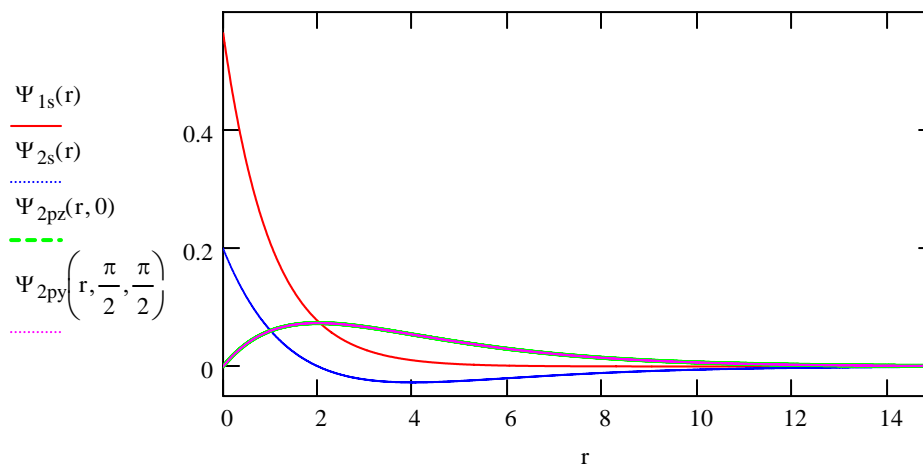
$$\Psi_{1s}(r) := \frac{1}{\sqrt{\pi}} \cdot \exp(-r)$$

$$\Psi_{2s}(r) := \frac{1}{\sqrt{32 \cdot \pi}} \cdot (2 - r) \cdot \exp\left(-\frac{r}{2}\right)$$

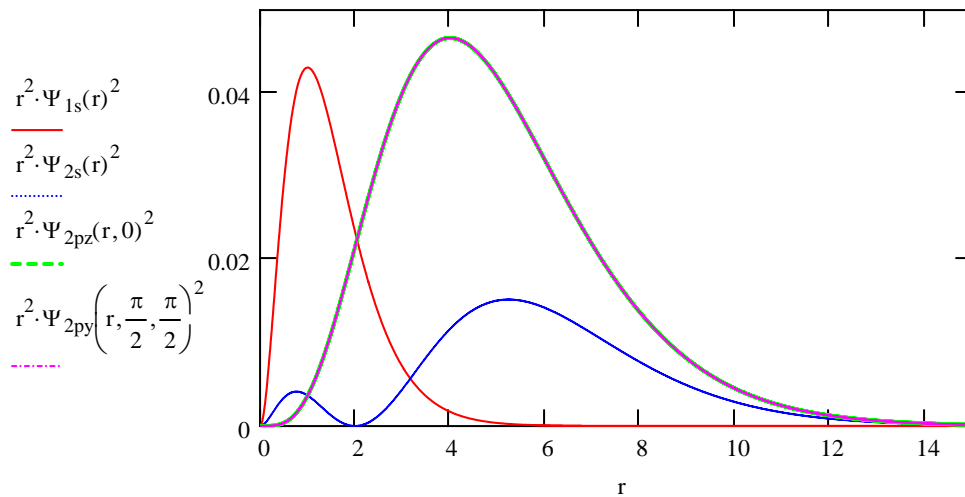
$$\Psi_{2pz}(r, \theta) := \frac{1}{\sqrt{32 \cdot \pi}} \cdot r \cdot \exp\left(-\frac{r}{2}\right) \cdot \cos(\theta)$$

$$\Psi_{2py}(r, \theta, \phi) := \frac{1}{\sqrt{32 \cdot \pi}} \cdot r \cdot \exp\left(-\frac{r}{2}\right) \cdot \sin(\theta) \cdot \sin(\phi)$$

Plot the wave functions on the same graph:



Plot the radial distribution functions for each orbital on the same graph:



Demonstrate that the 1s orbital is normalized:

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi_{1s}(r)^2 \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 1$$

Demonstrate that the 2s orbital is normalized:

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi_{2s}(r)^2 \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 1$$

Demonstrate that the 2p<sub>z</sub> orbital is normalized:

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi_{2p_z}(r, \theta)^2 \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 1$$

Demonstrate that the 1s and the 2p<sub>z</sub> orbitals are orthogonal:

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi_{1s}(r) \cdot \Psi_{2p_z}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

Demonstrate that 1s and 2s orbitals are orthogonal:

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi_{1s}(r) \cdot \Psi_{2s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

Demonstrate that the  $2p_y$  and the  $2p_z$  orbitals are orthogonal:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_y}(r, \theta, \phi) \cdot \Psi_{2p_z}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 0$$

Determine the most probable value for  $r$  using the Trace function and calculus:

$$\frac{d}{dr} r^2 \cdot \Psi_{1s}(r)^2 = 0 \text{ solve, } r \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Calculate the probability that an electron in the  $1s$  orbital will be found within one Bohr radius of the nucleus.

$$\int_0^1 \int_0^\pi \int_0^{2\pi} \Psi_{1s}(r)^2 \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \text{ float, } 3 \rightarrow .325$$

Find the distance from the nucleus for which the probability of finding a  $1s$  electron is 0.75.

$$a := 2 \quad \text{Given} \quad \int_0^a \Psi_{1s}(r)^2 \cdot 4 \cdot \pi \cdot r^2 \, dr = .75 \quad \text{Find}(a) = 1.96$$

Calculate  $\langle T \rangle$ ,  $\langle V \rangle$ , and  $\langle r \rangle$  for the  $1s$  orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{1s}(r) \cdot \left(-\frac{1}{2r}\right) \cdot \frac{d^2}{dr^2} r \cdot \Psi_{1s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{1}{2}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{1s}(r) \cdot \left(-\frac{1}{r}\right) \cdot \Psi_{1s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow -1$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{1s}(r) \cdot r \cdot \Psi_{1s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{3}{2}$$

Calculate  $\langle T \rangle$ ,  $\langle V \rangle$ , and  $\langle r \rangle$  for the  $2s$  orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \left(-\frac{1}{2r}\right) \cdot \frac{d^2}{dr^2} r \cdot \Psi_{2s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{1}{8}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot \left(-\frac{1}{r}\right) \cdot \Psi_{2s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{-1}{4}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2s}(r) \cdot r \cdot \Psi_{2s}(r) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 6$$

Calculate  $\langle T \rangle$ ,  $\langle V \rangle$ , and  $\langle r \rangle$  for the  $2p_y$  orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_y}(r, \theta, \phi) \cdot \left[ \begin{aligned} & -\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi_{2p_y}(r, \theta, \phi) \dots \\ & + \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)} \cdot \left[ \frac{d}{d\theta} \left( \sin(\theta) \cdot \frac{d}{d\theta} \Psi_{2p_y}(r, \theta, \phi) \right) \right] \dots \\ & + \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)^2} \cdot \frac{d^2}{d\phi^2} \Psi_{2p_y}(r, \theta, \phi) \end{aligned} \right] \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{1}{8}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_y}(r, \theta, \phi) \cdot \left( -\frac{1}{r} \right) \cdot \Psi_{2p_y}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{-1}{4}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_y}(r, \theta, \phi) \cdot r \cdot \Psi_{2p_y}(r, \theta, \phi) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 5$$

Calculate  $\langle T \rangle$ ,  $\langle V \rangle$ , and  $\langle r \rangle$  for the  $2p_z$  orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}(r, \theta) \cdot \left[ \begin{aligned} & -\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi_{2p_z}(r, \theta) \dots \\ & + \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)} \cdot \left[ \frac{d}{d\theta} \left( \sin(\theta) \cdot \frac{d}{d\theta} \Psi_{2p_z}(r, \theta) \right) \right] \dots \\ & + \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)^2} \cdot \frac{d^2}{d\phi^2} \Psi_{2p_z}(r, \theta) \end{aligned} \right] \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{1}{8}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}(r, \theta) \cdot \left( -\frac{1}{r} \right) \cdot \Psi_{2p_z}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow \frac{-1}{4}$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2p_z}(r, \theta) \cdot r \cdot \Psi_{2p_z}(r, \theta) \cdot r^2 \cdot \sin(\theta) \, d\phi \, d\theta \, dr \rightarrow 5$$

Summarize your results in the following table:

$\Psi$	T	V	E	r
1s	0.5	-1	-0.5	1.5
2s	0.125	-0.25	-0.125	6
2pz	0.125	-0.25	-0.125	5
2py	0.125	-0.25	-0.125	5

Demonstrate that the 1s orbital is an eigenfunction of the energy operator. What is the eigenvalue?

$$T = -\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi \quad V = -\frac{1}{r} \quad H = T + V \quad \Psi(r) = \frac{1}{\sqrt{\pi}} \cdot \exp(-r)$$

$$\frac{-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi_{1s}(r) - \frac{1}{r} \cdot \Psi_{1s}(r)}{\Psi_{1s}(r)} \text{ simplify } \rightarrow \frac{-1}{2}$$

Demonstrate that the 2s orbital is an eigenfunction of the energy operator. What is the eigenvalue?

$$\frac{-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi_{2s}(r) - \frac{1}{r} \cdot \Psi_{2s}(r)}{\Psi_{2s}(r)} \text{ simplify } \rightarrow \frac{-1}{8}$$

Demonstrate that the 2p<sub>y</sub> orbital is an eigenfunction of the energy operator. What is the eigenvalue?

$$\frac{\left[ \begin{aligned} &-\frac{1}{2 \cdot r} \cdot \frac{d^2}{dr^2} r \cdot \Psi_{2py}(r, \theta, \phi) \dots \\ &+ \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)} \cdot \left[ \frac{d}{d\theta} \left( \sin(\theta) \cdot \frac{d}{d\theta} \Psi_{2py}(r, \theta, \phi) \right) \right] \dots \\ &+ \frac{-1}{2 \cdot r^2 \cdot \sin(\theta)^2} \cdot \frac{d^2}{d\phi^2} \Psi_{2py}(r, \theta, \phi) \end{aligned} \right]}{\Psi_{2py}(r, \theta, \phi)} - \frac{1}{r} \cdot \Psi_{2py}(r, \theta, \phi) \text{ simplify } \rightarrow \frac{-1}{8}$$