2.15: Quantum Mechanical Calculations for the Hydrogen Atom

Full kinetic energy operator in spherical coordinates:

Kinetic energy operator for s states:

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

Kinetic energy operator for p states:

$$\begin{gathered}-\frac{1}{2r}\frac{d^2}{dr^2}r\blacksquare\ldots\\+\frac{-1}{2r^2\sin(\theta)}\left[\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\blacksquare\right)\right]\ldots\\+\frac{-1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\blacksquare\end{gathered}$$

Position operator: r

Potential energy operator: $-\frac{1}{r}$

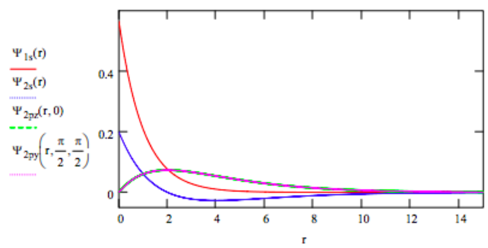
Triple integral with volume element: $\int_0^\infty\int_0^\pi\int_0^{2\pi}\blacksquare r^2\sin(\theta)d\phi d\theta dr$

Orbitals:

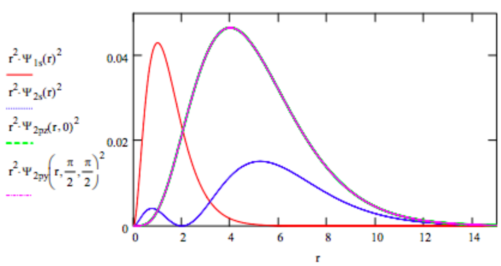
$$\Psi_{1s}(r)=\frac{1}{\sqrt{\pi}}\exp(\text{-r}) \qquad \Psi_{2s}(r)=\frac{1}{\sqrt{32\pi}}(2-r)\exp\left(-\frac{r}{2}\right)$$

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

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:

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

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

Demonstrate that the 2pz orbital is normalized:

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

Demonstrate that the 1s and the 2pz orbitals are orthogonal:

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

Demonstrate the 1s and 2s orbitals are orthogonal:

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

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

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

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

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

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

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

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

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

Calculate <T>, <V>, and <r> for the 1s orbital. Is the virial theorem obeyed? Explain.

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

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

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

Calculate <T>, <V>, and <r> for the 2s orbital. Is the virial theorem obeyed? Explain.

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

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

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

Calculate <T>, <V>, and <r> for the $2p_y$ orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2py}(r,\ \theta,\ \phi) \left[\begin{array}{c} -\frac{1}{2r}\frac{d^2}{dr^2} r \Psi_{2py}(r,\ \theta,\ \phi)\ldots \\ +\frac{-1}{2r^2 \sin(\theta)}\left[\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\Psi_{2py}(r,\ \theta,\ \phi)\right)\right]\ldots \\ +\frac{-1}{2r^2 \sin(\theta)^2}\frac{d^2}{d\phi^2}\Phi_{2py}(r,\ \theta,\ \phi) \end{array}\right] r^2 \sin(\theta) d\phi d\theta dr \rightarrow \frac{1}{8}$$

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

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

Calculate <T>, <V>, and <r> for the 2pz orbital. Is the virial theorem obeyed? Explain.

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi_{2pz}(r,\ \theta) \begin{bmatrix} -\frac{1}{2r}\frac{d^2}{dr^2} r\Psi_{2pz}(r,\ \theta)\ldots \\ +\frac{-1}{2r^2\sin(\theta)}\left[\frac{d}{d\theta}\left(\sin(\theta)\frac{d}{d\theta}\Psi_{2pz}(r,\ \theta)\right)\right]\ldots \\ +\frac{-1}{2r^2\sin(\theta)^2}\frac{d^2}{d\phi^2}\Phi_{2pz}(r,\ \theta) \end{bmatrix} r^2 \sin(\theta) d\phi d\theta dr \rightarrow \frac{1}{8}$$

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

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

Summarize your results in the following table:

$$\begin{pmatrix} \Psi & \text{T} & \text{V} & \text{E} & \text{r} \\ \text{1s} & 0.5 & -1 & -0.5 & 1.5 \\ \text{2s} & 0.125 & -0.25 & -0.125 & 6 \\ \text{2pz} & 0.125 & -0.25 & -0.125 & 5 \\ \text{2py} & 0.125 & -0.25 & -0.125 & 5 \end{pmatrix}$$

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

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

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

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

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

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

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