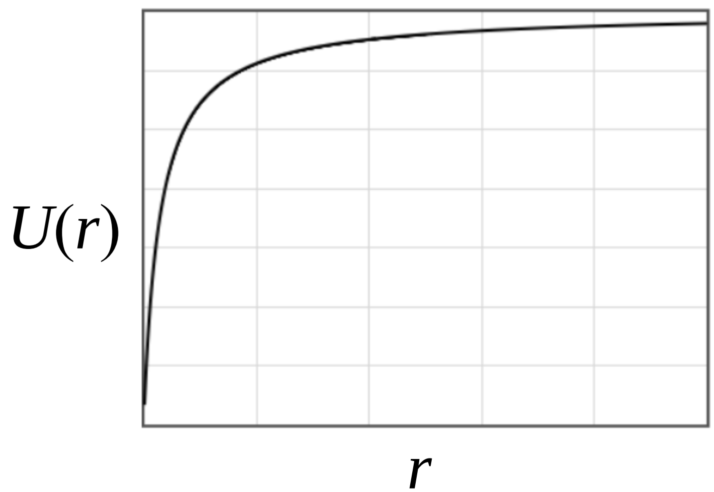
Hydrogen atom, Atomic Orbitals

Estimate the size of a hydrogen atom

Potential energy $$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$



Uncertainty relation $$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

For an atom: $\Delta x \sim r_0$

$$\Delta p_x \geq \frac{\hbar}{2r_0}$$

Estimate the size of a hydrogen atom

$$\Delta p_x \geq \frac{\hbar}{2r_0}$$

$$\Delta p_x = \sqrt{\left\langle p_x^2 \right\rangle - \left\langle p_x \right\rangle^2} \qquad \left\langle p_x \right\rangle = 0$$

$$\left(\Delta p_x\right)^2 = \left\langle p_x^2 \right\rangle \geq \left(\frac{\hbar}{2r_0}\right)^2$$

$$E_{kin} = \frac{mv^2}{2} = \frac{p^2}{2m}$$

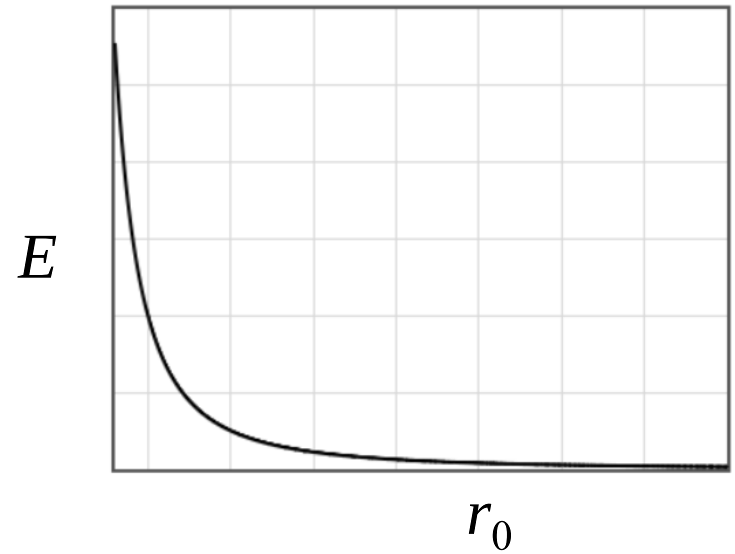
Kinetic energy in *x*-direction = $\left\langle E_{kin} \right\rangle = \dfrac{\left\langle p_x^2 \right\rangle}{2m} \geq \dfrac{\hbar^2}{8mr_0^2}$

Confinement energy

Kinetic energy in x-direction = $\langle E_{kin} \rangle = \dfrac{\langle p_x^2 \rangle}{2m} \geq \dfrac{\hbar^2}{8mr_0^2}$

Confinement energy:

$$\frac{\langle p_x^2 \rangle}{2m} + \frac{\langle p_y^2 \rangle}{2m} + \frac{\langle p_z^2 \rangle}{2m} \geq \frac{3\hbar^2}{8mr_0^2}$$



Estimate the size of a hydrogen atom

Total energy = Kinetic + Potential

$$E_{tot} = \frac{3\hbar^2}{8mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\frac{dE_{tot}}{dr} = \frac{-3\hbar^2}{4mr^3} + \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$r_0 = \frac{3\hbar^2 \pi\varepsilon_0}{me^2} = 4.0\times 10^{-11}\ \text{m}$$

$$a_0 = 5.3\times 10^{-11}\ \text{m}$$

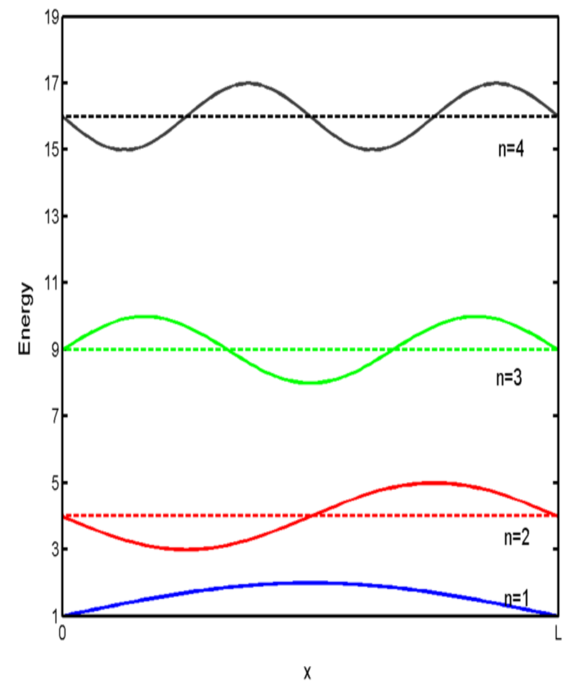
Confinement energy

$$\frac{-\hbar^2}{2m}\nabla^2\Psi - \frac{e^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

The kinetic energy term increases as the wavelength gets smaller

$$E_{kin} = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$p = mv \quad p = \hbar k \quad k = \frac{2\pi}{\lambda}$$



Atomic orbitals

$$\frac{-\hbar^2}{2m}\nabla^2\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

Z = effective nuclear charge

Solve with the boundary condition $\quad \Psi \to 0 \quad \text{as} \quad |\vec{r}| \to \infty$

Assume $\quad \Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$

Atomic orbitals

$$\phi_{1s}^{Z} = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-\frac{Zr}{a_0}},$$

$$\phi_{2s}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}},$$

$$\phi_{2px}^{Z} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta\cos\varphi,$$

$$\phi_{2py}^{Z} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \sin\theta\sin\varphi,$$

$$\phi_{2pz}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}} \cos\theta,$$

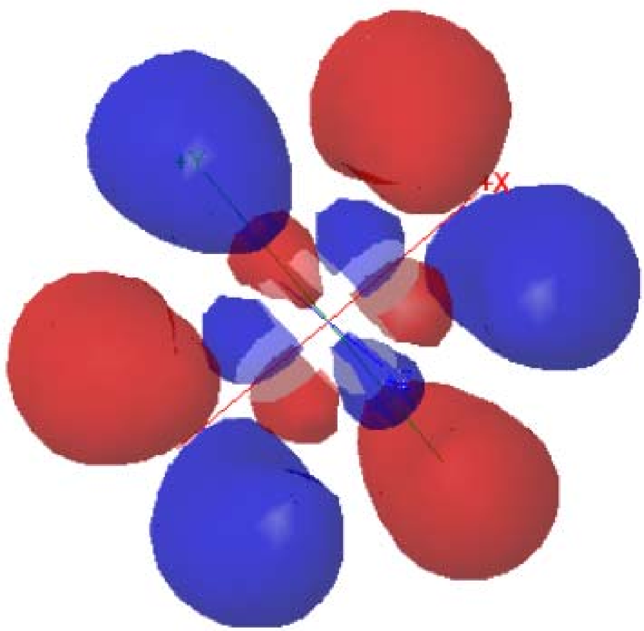
Z is the effective nuclear charge

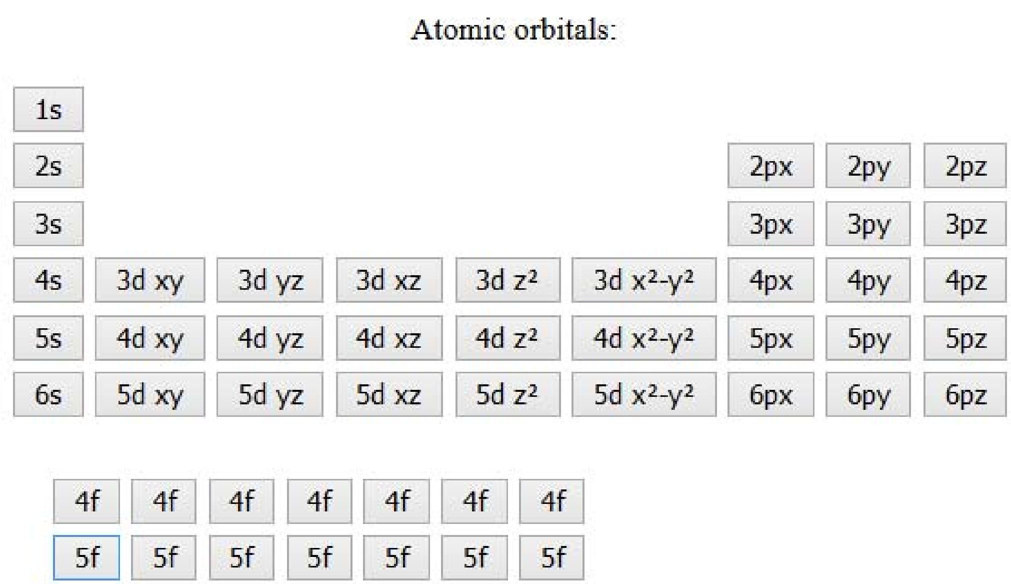
$$E = -\frac{Z^2 m e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} = -\frac{13.6 Z^2}{n^2}\ \text{eV}.$$

Atomic orbitals

http://lampx.tugraz.at/~hadley/ss1/molecules/atoms/AOs.php

5f





$$\langle \phi_m | H | \phi_n \rangle = \frac{-\hbar^2}{2m} \langle \phi_m | \nabla^2 | \phi_n \rangle - \frac{2e^2}{4\pi\varepsilon_0} \langle \phi_m | \frac{1}{|\vec{r}|} | \phi_n \rangle$$

Radial distribution function

$$P(r) = 4\pi r^2 |\psi|^2$$

$$\phi_{1s}^{Z} = \sqrt{\frac{Z^3}{\pi a_0^3}} \exp\left(-\frac{Zr}{a_0}\right)$$

$$\phi_{2s}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$$