N 18.1

PHYS 621 Lecture Notes 21

The Hydrogen-Like Atom

Center-of-Mass and Relative Motion in a Central Potential:
Consider a general two-body problem with a central potential $V(|\vec{r}_{ij}|)$.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(|\vec{r}_1 - \vec{r}_2|)$$

Center-of-Mass: $\vec{R} \equiv \dfrac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$

Relative displacement: $\vec{r} \equiv \vec{r}_1 - \vec{r}_2$

Total mass $M \equiv m_1 + m_2$

Reduced mass $\mu \equiv \dfrac{m_1 m_2}{m_1+m_2}$

Chain rule:

$$\frac{\partial}{\partial x_{1i}} = \sum_j \frac{\partial r_j}{\partial x_{1i}}\frac{\partial}{\partial r_j} + \sum_j \frac{\partial R_j}{\partial x_{1i}}\frac{\partial}{\partial R_j} = \frac{\partial}{\partial r_{1i}} + \frac{m_1}{M}\frac{\partial}{\partial R_{1i}}$$

$$\frac{\partial}{\partial x_{2i}} = -\frac{\partial}{\partial r_{2i}} + \frac{m_2}{M}\frac{\partial}{\partial R_{2i}}$$

$$\Rightarrow \frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 = \frac{1}{m_1}\left(\nabla_{\vec{r}} + \frac{m_1}{M}\nabla_{\vec{R}}\right)^2 + \frac{1}{m_2}\left(-\nabla_{\vec{r}} + \frac{m_2}{M}\nabla_{\vec{R}}\right)^2$$

$$= \frac{1}{\mu}\nabla_{\vec{r}}^2 + \frac{1}{M}\nabla_{\vec{R}}^2$$

Time-Independent Schrödinger Eqn:

$$\left[-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2 + V(r)\right]\Psi(\vec{r},\vec{R}) = E_{Tot}\Psi(\vec{r},\vec{R})$$

Separation of Variables: Consider solution of the form

$$\Psi(\vec{r},\vec{R}) = \psi(\vec{r})\,\phi(\vec{R})$$

$$\left[-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\phi(\vec{R}) - E_{cm}\phi(\vec{R})\right]\psi(\vec{r}) + \left[-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi(\vec{r}) + V(r)\psi(\vec{r})\right]\phi(\vec{R})$$

$$= (E_{tot} - E_{cm})\psi(\vec{r})\phi(\vec{R})$$

$$\underbrace{\frac{1}{\phi(\vec{R})}\left[-\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\phi(\vec{R}) - E_{cm}\phi(\vec{R})\right]}_{\text{function of } \vec{R}} + \underbrace{\frac{1}{\psi(\vec{r})}\left[-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi(\vec{r}) + V(r)\psi(\vec{r})\right]}_{\text{Function of } \vec{r}}$$

$$= E_{tot} - E_{cm} \equiv E$$

For a function of $\vec{R}$ + a function of $\vec{r}$ to be a constant, each must be a constant. Choose the constant E_{cm} such that

$$\begin{cases} -\frac{\hbar^2}{2M}\nabla_{\vec{R}}^2\phi(\vec{R}) = E_{cm}\phi(\vec{R}) & \text{— CoM motion} \\ -\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2\psi(\vec{r}) + V(r)\psi(\vec{r}) = (E_{tot} - E_{cm})\psi(\vec{r}) = E\psi(r) & \text{— Relative motion} \end{cases}$$

N18.2 Hydrogen-Like Atom: has single electron of charge $q = -e$

Treat nucleus as a particle with charge $Q = Ze$

$m_e \ll m_N \rightarrow M \approx m_N$, $\mu \approx m_e$

electron mass (m_e) — Nuclear mass (m_N)

Coulomb potential $V(r) = -\frac{|Q||q|}{4\pi\epsilon_0}\frac{1}{r} \equiv -\frac{\tilde{Q}^2}{r}$

Relative motion describes the electron:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{\vec{r}}^2 + V(r)\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

Spherical Coordinates: $\nabla_{\vec{r}}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2}$

$$\psi(r,\theta,\phi) = R(r)\,Y_{\ell m}(\theta,\phi)$$

$$-\frac{\hat{L}^2}{\hbar^2}Y_{\ell m}(\theta,\phi) = -\ell(\ell+1)\,Y_{\ell m}(\theta,\phi)$$

$$\Rightarrow \left\{ -\frac{\hbar^2}{2\mu}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right] + V(r)\right\} R(r) = E\, R(r)$$

Solutions for $R(r)$ depend on E and ℓ, but not m.

$$\psi_{E\ell m}(r,\theta,\phi) = R_{E\ell}(r)\, Y_{\ell m}(\theta,\phi)$$

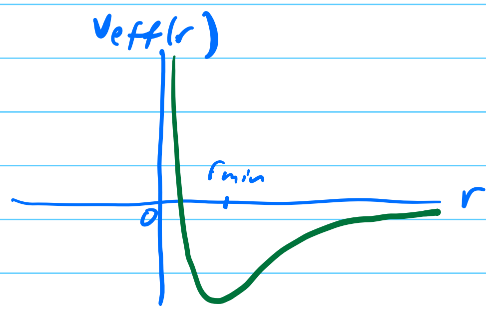
We can eliminate the $\frac{1}{r}\frac{d}{dr}$ term in the Schrödinger Eq. by defining

$$R(r) = \frac{\chi(r)}{r}$$

$$\Rightarrow \frac{d^2\chi}{dr^2} + \frac{2\mu}{\hbar^2}\left[-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2} + E - V(r)\right]\chi(r) = 0$$

$\rightarrow$ Like 1D Schrödinger Eq. with potential

$$V_{eff}(r) = -\frac{\tilde{Q}^2}{r} + \frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}$$, energy eigenvalue E



$$r_{min} = \frac{\ell(\ell+1)\hbar^2}{\tilde{Q}^2\mu}$$

Boundary Conditions: "Wall" at $r=0 \rightarrow$ $\boxed{\chi(r=0)=0}$

Normalizability: $\int_0^\infty |\psi|^2 r^2 dr\, d\Omega < \infty$

$$\Rightarrow \boxed{\int_0^\infty |\chi(r)|^2 dr < \infty}$$

$|\chi(r)| < \frac{A}{r^{1/2}}$ as $r\to\infty$ for some constant A.

★ There are also non-normalizable solutions that asymptote to $\chi(r) \sim e^{\pm ikr}$ as $r\to\infty$, for $E>0$. These describe states of the electron scattering off the nucleus.

Bound states: $E<0$. We would like to find the spectrum of states E_n.

Solution to radial equation: Compare with equation for Laguerre polynomials:

$$x L_n''(x) + (1-x)L_n'(x) + n L_n(x) = 0 \quad , \quad n \geq 0 \in \mathbb{Z}$$

polynomial solutions: $L_n(x) = e^x \dfrac{d^n}{dx^n}\left(e^{-x} x^n\right)$

Examples:

$L_0(x) = 1$

$L_1(x) = -x + 1$

$L_2(x) = x^2 - 4x + 2$

Associated Laguerre Polynomials

$L_j^k(x) \equiv (-1)^k \dfrac{d^k}{dx^k} L_{j+k}(x)$

$j, k \geq 0 \in \mathbb{Z}$

Associated Laguerre functions $y_j^k(x) \equiv e^{-x/2}\, x^{\frac{k+1}{2}}\, L_j^k(x)$

- satisfy $y_j^{k\,\prime\prime}(x) + \left(-\dfrac{1}{4} + \dfrac{2j+k+1}{2x} - \dfrac{k^2-1}{4x^2}\right) y_j^k(x) = 0$

Compare with the Schrödinger Eq for $\chi(r)$:

$$\frac{d^2\chi}{dr^2} + \frac{2\mu}{\hbar^2}\left[-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2} + E - \frac{\tilde{Q}^2}{r}\right]\chi(r) = 0$$

Define $x \equiv 2\sqrt{\dfrac{-2\mu E}{\hbar^2}}\; r \quad , \quad y(x) \equiv \chi(r(x))$

note $-E > 0$ for bound states

$$\frac{d^2 y}{dx^2}\left(-\frac{8\mu E}{\hbar^2}\right) + \left[\frac{8\mu E}{\hbar^2}\frac{\ell(\ell+1)}{x^2} + \frac{2\mu E}{\hbar^2} - \tilde{Q}^2 \frac{4\mu}{\hbar^2}\sqrt{\frac{-2\mu E}{\hbar^2}}\,\frac{1}{x}\right] y(x) = 0$$

$$\frac{d^2 y}{dx^2} + \left[-\frac{1}{4} + \tilde{Q}^2\sqrt{\frac{-\mu}{2\hbar^2 E}}\,\frac{1}{x} - \frac{\ell(\ell+1)}{x^2}\right] y(x) = 0$$

$y(x)$ satisfies the formula for $y_j^k(x)$, with

$$\ell(\ell+1) = \frac{k^2-1}{4}, \quad \sqrt{\frac{-\mu}{2\hbar^2 E}}\,\tilde{Q}^2 = \frac{2j+k+1}{2}$$

$$k^2 = 4\ell(\ell+1)+1 = (2\ell+1)^2 \quad \rightarrow k = 2\ell+1$$

$$\longrightarrow \sqrt{\frac{-\mu}{2\hbar^2 E}}\,\tilde{Q}^2 = j+\ell+1$$

$$E = -\frac{\mu \tilde{Q}^4}{2\hbar^2}\left(\frac{1}{j+\ell+1}\right)^2, \quad j+\ell \geq 0 \in \mathbb{Z}$$

$\rightarrow$ define $n \equiv j+\ell+1 \geq 1 \in \mathbb{Z}$

$\rightarrow \boxed{n \geq \ell+1}$

$$E_n = -\frac{\mu \tilde{Q}^4}{2\hbar^2}\frac{1}{n^2} \equiv -\frac{\hbar^2 Z^2}{2\mu a_0^2}\frac{1}{n^2}$$

a_0 = Bohr radius $= \frac{\hbar^2}{m_e e^2} = 0.529\ \text{Å}$

$\mu \simeq m_e = 0.511\ \text{MeV}/c^2$

$(hc) = (2\pi\hbar c) = 1.24\times 10^4\ \text{eV}\cdot\text{Å}$

$e^2 = 14.42\ \text{eV}\cdot\text{Å}$

Exercise

Exercise

$$\boxed{E_n \equiv -\frac{E_R Z^2}{n^2}}, \quad E_R = \frac{\hbar^2}{2m_e a_0^2} = -13.6\ \text{eV}$$

Wavefunctions: $R(r) = \frac{y(r)}{r}$

$$\rightarrow R_{n,\ell}(r) = A\, e^{-Zr/na_0}\left(\frac{2rZ}{na_0}\right)^{\ell+1} L_{n-\ell-1}^{2\ell+1}\left(\frac{2rZ}{na_0}\right)$$

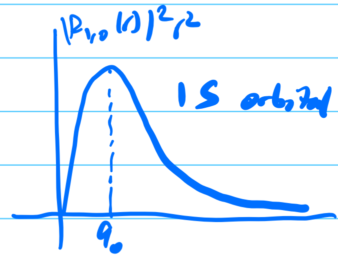
Examples (normalized):

$R_{1,0}(r) = 2a_0^{-3/2}e^{-r/a_0}$ — 1S orbital

$R_{2,0}(r) = \frac{1}{\sqrt{2}}a_0^{-3/2}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$ — 2S orbital

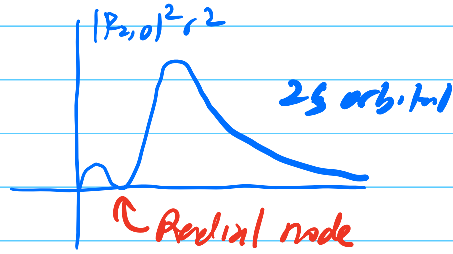
$\}$ $S \rightarrow \ell = 0$

$R_{2,1}(r) = \frac{1}{\sqrt{24}}a_0^{-3/2}\frac{r}{a_0}e^{-r/2a_0}$ — 2p orbital $\}$ $p \rightarrow \ell = 1$



$$\int dr\, \underbrace{|R(r)|^2 r^2}_{} = 1$$

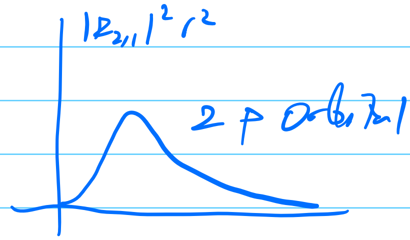
Radial probability density
$|R(r)|^2 r^2$



Average radial position:

$$\langle r \rangle_{n\ell} = \frac{3}{2}\frac{a_0}{Z}\left[n^2 - \frac{\ell(\ell+1)}{3}\right]$$

Shells around radius that grows as n^2.



$$\psi_{n,\ell,m}(r,\theta,\phi) = R_{n,\ell}(r)\, Y_{\ell,m}(\theta,\phi)$$

Normalized so that $\int d\Omega\, |Y_{\ell,m}(\theta,\phi)|^2 = 1$

Normalized so that $\int_0^\infty dr\, |R_{n,\ell}(r)|^2 r^2 = 1$

Angular dependence of orbitals:

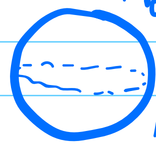
$$Y_{0,0} = \frac{1}{\sqrt{4\pi}}, \quad Y_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$Y_{1,1} = -\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{i\phi}$$

$$Y_{1,-1} = -\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{-i\phi}$$

Magnitude of Y_{lm} as distance from origin:

$|Y_{0,0}|^2$ $\quad$ $|Y_{1,0}|^2$ $\quad$ $|Y_{1,1}|^2$



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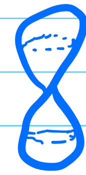
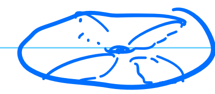
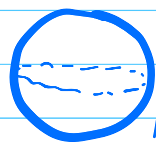




Superpositions of $Y_{1,1}$ and $Y_{1,-1}$ give $2p_x$, $2p_y$ orbitals like $2p_z$ with symmetry axes along $\vec{e}_x$, $\vec{e}_y$ respectively.

Surfaces of constant $|\psi_{nlm}(r,\theta,\phi)|^2$



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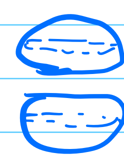

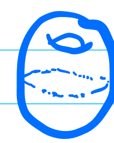

$2p_z$

$|\psi_{100}|^2$ $\quad$ $|\psi_{210}|^2$ $\quad$ $|\psi_{211}|^2$