$\boxed{\text{Review of Central Potential}}$ – always covered in undergrad. Q.M.

$V(\vec{r}) = V(r)$ ⟵ spherically symmetric

$H = \frac{\vec{p}^{\,2}}{2m} + V(r)$

$\hookrightarrow \vec{p} = -i\hbar \vec{\nabla}$

$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{\hbar^2 r^2}$ ⟵ spherical coordinates

<u>Orbital angular momentum is conserved</u>

$$[L_z, \vec{p}^{\,2}] = [xp_y - yp_x, p_x^2 + p_y^2 + p_z^2]$$
$$= [xp_y, p_x^2] + \cancel{[xp_y, p_y^2]} + \cancel{[xp_y, p_z^2]} - \cancel{[yp_x, p_x^2]} - [yp_x, p_y^2] - \cancel{[yp_x, p_z^2]}$$
$$= xp_y p_x p_x - p_x \underbrace{p_x x}_{xp_x + \underbrace{[p_x, x]}_{-i\hbar}} p_y - yp_x p_y p_y + p_y \underbrace{p_y y}_{yp_y + \underbrace{[p_y, y]}_{-i\hbar}} p_x$$
$$= xp_y p_x p_x - p_x(xp_x - i\hbar)p_y - yp_x p_y p_y + p_y(yp_y - i\hbar)p_x$$
$$= xp_y p_x p_x - \underbrace{p_x x}_{xp_x + \underbrace{[p_x, x]}_{-i\hbar}} p_x p_y + i\hbar p_x p_y - yp_x p_y p_y + \underbrace{p_y y}_{yp_y + \underbrace{[p_y, y]}_{-i\hbar}} p_y p_x - i\hbar p_y p_x$$
$$= x\cancel{p_y p_x p_x} - [x\cancel{p_x} - i\hbar]\cancel{p_x p_y} + i\cancel{\hbar p_x p_y} - \cancel{yp_x p_y p_y} + \cancel{yp_y p_y p_x} - i\hbar \cancel{p_y p_x} - i\hbar \cancel{p_y p_x}$$
$$= 0$$

$[L_z, V(r)] = [-i\hbar \frac{\partial}{\partial \phi}, V(r)] = 0$

$\therefore$ similary $[L_x, U(r)] = [L_y, V(r)] = 0$

$\therefore [\vec{L}^2, V(r)] = 0$

$\therefore \boxed{\begin{matrix}[L_z, H] = 0 \\ [\vec{L}^2, H] = 0\end{matrix}} \longrightarrow$ orbital ang. mom. is converved

$\Longrightarrow$ Can make simultaneous eigenkets of $H, L_z, \vec{L}^2$

Schrodinger Equation for Central Potential

S.E. $\quad H\psi_E(r,\theta,\phi) = E\underbrace{\psi_E(r,\theta,\phi)}_{\boxed{R(r)Y_{lm}(\theta,\phi)}}$

$$\therefore \boxed{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}\Big[\underbrace{V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}}_{V_{eff}(r)} - E\Big]R = 0}$$

ang. mom. barrier

- Need $V(r)$ to solve
- $R = R(E, l, r)$
- No m dependence

Transform $R(r) = \frac{u(r)}{r}$ $\leftarrow$ need $u = rR \to 0$ as $r \to 0$ for well behaved R

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}\right]u = Eu}$$

Looks like 1-d S.E. but
- $V_{eff}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}$
- dif. eq. for each l
- $r \geq 0$
- $u = rR \to 0$ as $r \to 0$
- depends on l but not m $\therefore$ same E_l for $m = -l, \dots, l$

Solve for specific $V(r)$

① Free particle $V(r) = 0$

② Infinite square well
$$V(r) = \begin{cases} 0, & r \leq a \\ \infty, & r > a \end{cases}$$

③ Hydrogen "atom" (ion for $Z > 1$) $\quad V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$

$\boxed{\text{Hydrogen Atom}}$ $V(r) = -\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$

Radial equation: $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right]u = Eu$

$u = rR$ so that $u \to 0$ as $r \to 0$ for well behaved R

negative for bound states

Clean up notation: $\boxed{K = \sqrt{\frac{-2mE}{\hbar^2}}}$ $\boxed{\rho_0 = \frac{mZe^2}{2\pi\epsilon_0\hbar^2 K}}$ $\boxed{\rho = Kr}$

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

Assymptotic forms

large ρ: $\frac{d^2u}{d\rho^2} = u \rightsquigarrow u = Ae^{-\rho} + \cancel{Be^{\rho}}$

need $B=0$ to keep u finite when $\rho \to \infty$

small ρ: $\frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u \rightsquigarrow u = C\rho^{\ell+1} + \cancel{D\rho^{-\ell}}$

need $D=0$ to keep u finite when $\rho \to 0$

(Note: $\ell = 0 \longrightarrow u \sim D$
$rR \sim D$
cannot have $u \to 0$ as $r \to 0$)

Put in asymptotic behavior

$$u = e^{-\rho}\rho^{\ell+1}\underbrace{v(\rho)}_{\text{hope } v \text{ is simpler}}$$

$$\boxed{\rho\frac{d^2v}{d\rho^2} + 2(\ell+1-\rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)]v = 0}$$

Seek power series solution: $\boxed{v = \sum_{j=0}^{\infty} c_j \rho^j}$

$$\Longrightarrow \boxed{c_{j+1} = \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}c_j}$$

<u>Need j_{max} to have power series converge as $\rho \to \infty$</u>

– $e^{-\rho}$ will make R well behaved at large ρ <u>if</u> series is finite

<u>termination:</u> $2(\underbrace{j_{max} + l + 1}_{\equiv n}) - \rho_0 = 0$

$c_{j_{max}} \neq 0$

$c_{j_{max}+1} = 0$

$\equiv n$ ← integer

$\therefore \rho_0 = 2n$

$j_{max} \geq 0$

<u>quantum numbers:</u>

$l = 0, 1, 2, \ldots$

$j_{max} = 0, 1, 2, \ldots$

$\Big\} \; n = 1, 2, \ldots$

$1 = n = j_{max} + l + 1 \longrightarrow \underset{\geq 0}{l} = -\underset{\geq 0}{j_{max}} \longrightarrow l = 0$

$2 = n = j_{max} + l + 1 \longrightarrow \underset{\geq 0}{l} = 1 - \underset{\geq 0}{j_{max}} \longrightarrow l = 0, 1$

<u>etc.</u>

$l = 0, 1, \ldots, n-1$

$$\boxed{\begin{array}{l} n = 1, 2, \ldots \\ l = 0, 1, \ldots, n-1 \\ m = -l, -l+1, \ldots, l \end{array}}$$

Natural scaling of r

Recall $\kappa = \sqrt{\frac{-2mE}{\hbar^2}}$. $\rho_0 = \frac{mZe^2}{2\pi\epsilon_0 \hbar^2 \kappa}$. $\rho_0 = 2n$.

$$\rho = \kappa r = \frac{r}{\left(\frac{1}{\kappa}\right)}$$

$$\kappa = \frac{mZe^2}{2\pi\epsilon_0\hbar^2 \rho_0}$$

$$= \frac{mZe^2}{2\pi\epsilon_0\hbar^2 2n}$$

$$= \underbrace{\frac{me^2}{4\pi\epsilon_0\hbar^2}}_{\frac{1}{a_B}} \frac{Z}{n}$$

$$\frac{1}{a_B} \longrightarrow \boxed{a_B = \frac{4\pi\epsilon_0\hbar^2}{me^2}} = 0.0529 \text{ nm}$$

$$\boxed{\frac{1}{\kappa} = a_B \frac{n}{Z}}$$

bigger for bigger n

smaller for bigger Z

Energy eigenvalues

$$E = \frac{-\hbar^2\kappa^2}{2m} = -\frac{\cancel{\hbar^2}}{2\cancel{m}} \frac{Z^2}{\cancel{a_B^2} n^2} \frac{\cancel{a_B^2}}{} \frac{m^{\cancel{2}} e^4}{(4\pi\epsilon_0)^2 \hbar^{\cancel{4}\,2}}$$

$$\boxed{E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{Z^2}{n^2}}$$

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$$\psi_3^{(0)}(r) = \eta_1^{(0)\dagger}\eta_2^{(0)\dagger}r^2 e^{-r/3a_0} \propto \left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\frac{r^2}{a_0^2}\right)e^{-r/3a_0} \tag{64}$$

$$\psi_1^{(1)}(r) = re^{-r/2a_0} \tag{65}$$

$$\psi_2^{(1)}(r) = \eta_1^{(1)\dagger}r^2 e^{-r/3a_0} \propto r\left(1 - \frac{r}{6a_0}\right)e^{-r/3a_0} \tag{66}$$

$$\psi_1^{(2)}(r) = r^2 e^{-r/3a_0} \tag{67}$$

Exercise 8. Obtain the results stated in Eqs. (66) and (68).

The customary notation for these radial wavefunctions is R_{nl}, where $n = l + j$. With this notation, and with the appropriate normalization factors, Eqs. (62)–(67) become

$$R_{10}(r) = \frac{2}{a_0^{3/2}}e^{-r/a_0} \tag{68}$$

$$R_{20}(r) = \frac{2}{(2a_0)^{3/2}}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} \tag{69}$$

$$R_{30}(r) = \frac{2}{(3a_0)^{3/2}}\left(1 - \frac{2}{3}\frac{r}{a_0} + \frac{2}{27}\frac{r^2}{a_0^2}\right)e^{-r/3a_0} \tag{70}$$

$$R_{21}(r) = \frac{1}{(2a_0)^{3/2}}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0} \tag{71}$$

$$R_{31}(r) = \frac{1}{(3a_0)^{3/2}}\frac{4\sqrt{2}}{3}\frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right)e^{-r/3a_0} \tag{72}$$

$$R_{32}(r) = \frac{1}{(3a_0)^{3/2}}\frac{2\sqrt{2}}{27\sqrt{5}}\frac{r^2}{a_0^2}e^{-r/3a_0} \tag{73}$$

The normalization condition satisfied by these radial wavefunctions is similar to Eq. (34):

$$\int_0^\infty (R_{nl})^2 r^2\,dr = 1$$

The normalization of the wavefunctions R_{nl} can be checked by evaluating this integral. Alternatively, we can use the results of Section 6.3 (see Problem 10).

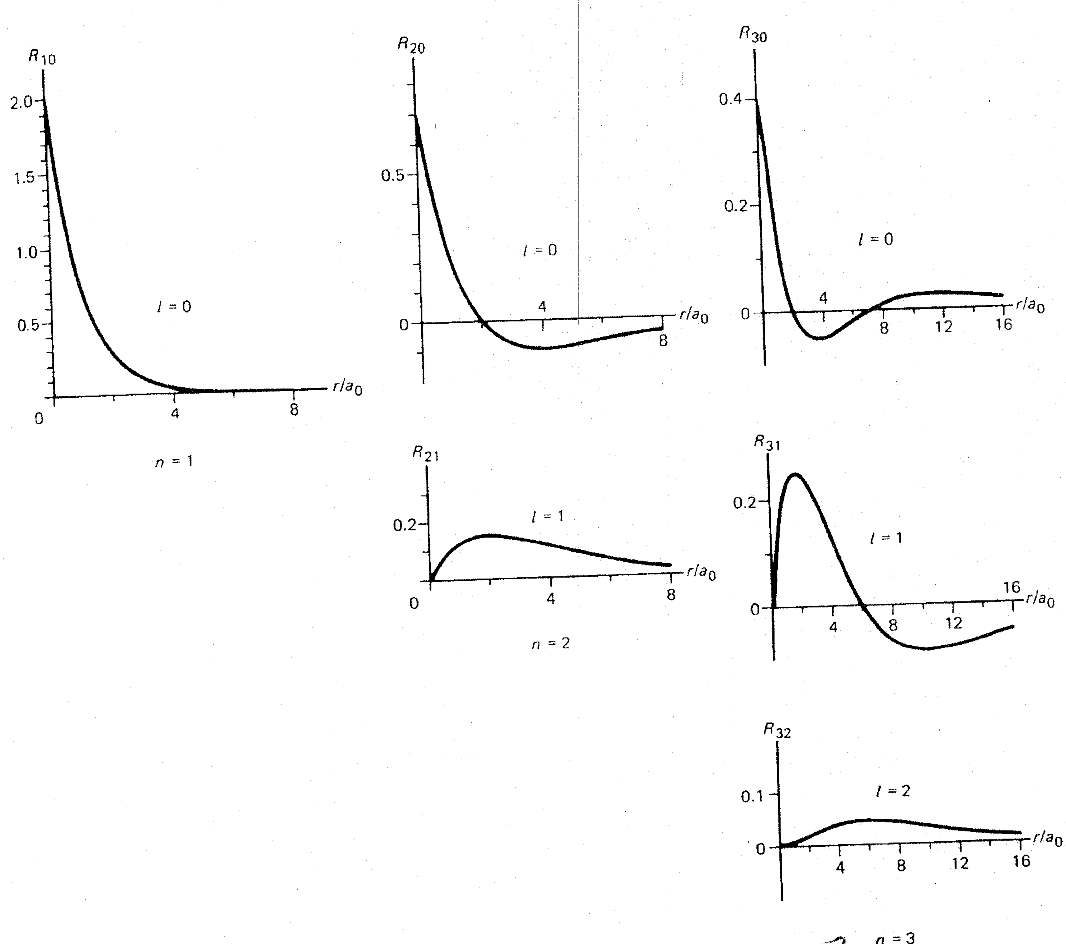

Fig. 8.3 Plots of the radial wavefunctions R_{10}, R_{20}, R_{30}, R_{21}, R_{31}, and R_{32}.

Figure 8.3 shows plots of the radial wavefunctions R_{nl}. All the wavefunctions with $l = 0$ have a maximum at $r = 0$. The other wavefunctions all vanish at $r = 0$. This says that when the electron is in a state of zero angular momentum, the probability for finding the electron in a volume element $dV = dx\,dy\,dz$ is largest at the nucleus.[1] Note, however, that the large probability per unit volume at $r = 0$ does not necessarily mean that this is the most proba-

[1] The electron does not interact with the nuclear material except by the Coulomb interaction; thus, the electron can move through the nucleus without hindrance.

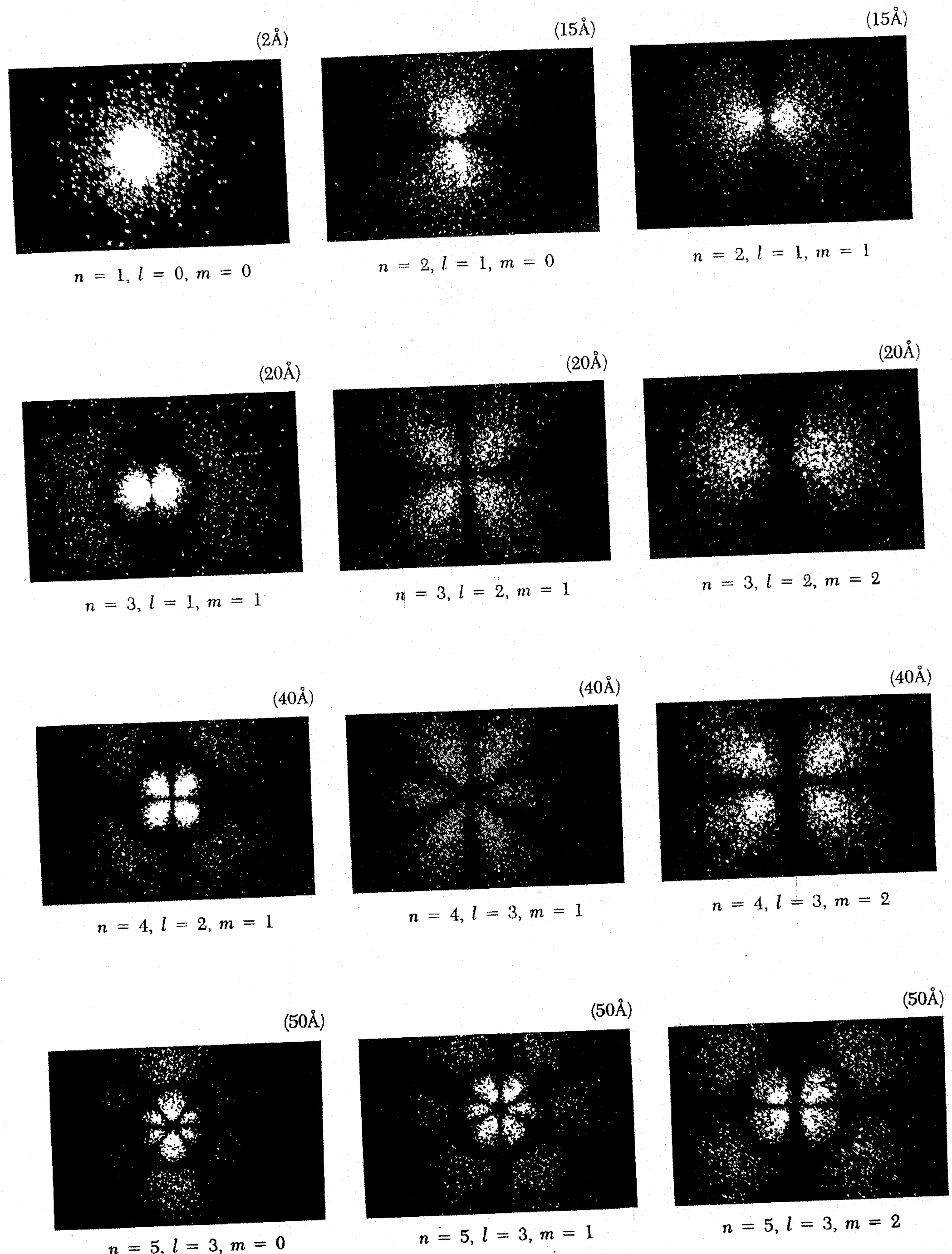

Fig. 8.5 Pictures of the probability distributions $|\psi_{nlm_l}(r, \theta, \phi)|^2$ for some states of the hydrogen atom. The density of dots in these pictures is proportional to the probability. These pictures were generated by a Monte-Carlo computer program that selected points r, θ, ϕ at random, and then decided to plot them or not plot them according to the value of $|\psi_{nlm_l}(r, \theta, \phi)|^2$. (Courtesy A. F. Burr and A. Fisher, New Mexico State University.)

Free Particle — Spherical Coordinates

$\boxed{\text{Summary only}}$

$$H = \frac{\vec{p}^{\,2}}{2m}$$
$$= -\frac{\hbar^2}{2m}\vec{\nabla}^2$$
$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\vec{L}^2}{\hbar^2 r^2}\right]$$
$$= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\frac{\vec{L}^2}{2mr^2}}_{\text{all angular dep.}}$$

<u>Look for separable solution</u>: $R(r)\,Y_{\ell m}(\theta,\phi)$

$$E R Y_{\ell m} = \left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right] R Y_{\ell m}$$

now any >0 energy is possible

Let $E = \frac{\hbar^2 k^2}{2m}$ ⇐ defines k

$$0 = \left[\frac{\cancel{\hbar^2}k^2}{\cancel{2m}} + \frac{\cancel{\hbar^2}}{\cancel{2m}}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{\cancel{\hbar^2}}{\cancel{2m}}\frac{\ell(\ell+1)}{r^2}\right]R(r)$$
$$= \left[1 + \frac{1}{(kr)^2}\frac{\partial}{\partial(kr)}\left((kr)^2\frac{\partial}{\partial(kr)}\right) - \frac{\ell(\ell+1)}{(kr)^2}\right] j_\ell(kr)$$

⟹ Well behaved solutions

<u>spherical Bessel functions</u>
$$j_\ell(kr) = (kr)^\ell\left(-\frac{1}{kr}\frac{d}{d(kr)}\right)^\ell \frac{\sin(kr)}{kr}$$

e.g. $j_0(\rho) = \frac{\sin\rho}{\rho}$

$$j_1(\rho) = \frac{\sin\rho}{\rho^2} - \frac{\cos\rho}{\rho}$$

$$j_2(\rho) = \left(\frac{3}{\rho^3} - \frac{1}{\rho}\right)\sin\rho - \frac{3}{\rho^2}\cos\rho$$

Expand functions in complete set

$$e^{ikz} = \sqrt{4\pi} \sum_{l=0}^{\infty} \sqrt{2l+1}\, i^l\, Y_{l0}(\theta,\phi)\, j_l(kr)$$

plane wave — important because used in scattering theory