Spectroscopy

As we've discussed in central potential $V(r)$ we can describe the energy states of a system with three quantum numbers

n – principle q.n., depends on the potential

l – eigenvalue of $\hat{L}^2$

m – ——"—— $\hat{L}_z$

since $[\hat{H}, \hat{L}^2] = [\hat{H}, \hat{L}_z] = 0$

Coulumb potential $V(r) = ke^2/r$

$$\psi_{n,l,m}(r,\theta,\varphi) = \underbrace{R_{n,l}(r)}_{\text{radial wave-function component}} \underbrace{Y_{lm}(\theta,\varphi)}_{\text{spherical functions}}$$

Normalization $\int_0^\infty |\psi_{n,l,m}|^2 dV = \int_0^\infty |R_{n,l}(r)|^2 r^2 dr \times$ (= 1)

$$\times \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, |Y_{lm}(\theta,\varphi)|^2 \quad (= 1)$$

What is the probability density of finding an electron at distance r from the nucleus?

$$\int_r^{r+dr} r^2 \cdot dr \int_0^\pi \int_0^{2\pi} |\psi_{n,l,m}(r,\theta,\varphi)|^2 \sin\theta\, d\theta\, d\varphi = \int_r^{r+dr} |R_{n,l}(r)|^2 r^2 dr =$$

$$= |R_{n,l}(r)|^2 \cdot r^2$$

One can estimate that the density is highest at $r \sim n^2 a_0$, where $a_0 = \frac{\hbar^2}{\mu k e^2} = \frac{\hbar}{mcd}$

n	l	m	$\psi_{n,l,m}(r,\theta,\phi)$
1	0	0	$\frac{1}{\sqrt{\pi}a_0^{3/2}}e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}cos\ \theta$
2	1	±1	$\frac{1}{8\sqrt{3\pi}a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}sin\ \theta\ e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_o^2}\right)e^{-r/2a_o}$
3	1	0	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ cos\ \theta$
3	1	±1	$\frac{1}{81\sqrt{3\pi}a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\ sin\ \theta\ e^{\pm i\phi}$
3	2	0	$\frac{1}{81\sqrt{6\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ \left(3\ cos^2\ \theta-1\right)$
3	2	±1	$\frac{1}{81\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin\ \theta\ cos\ \theta\ e^{\pm i\phi}$
3	2	±2	$\frac{1}{162\sqrt{\pi}a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\ sin^2\ \theta\ e^{\pm 2i\phi}$

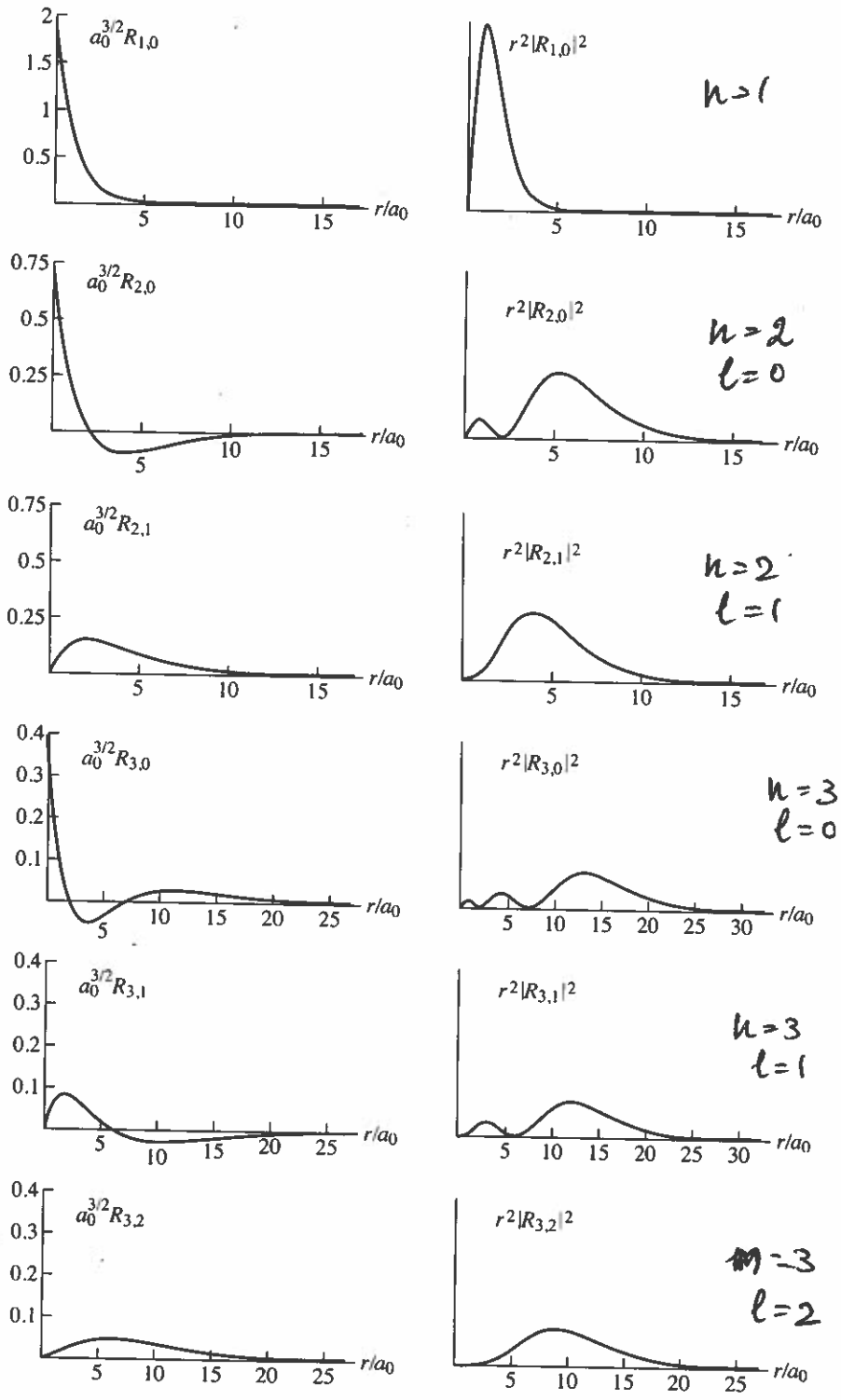
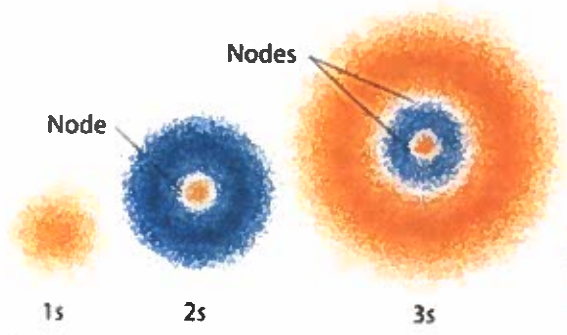
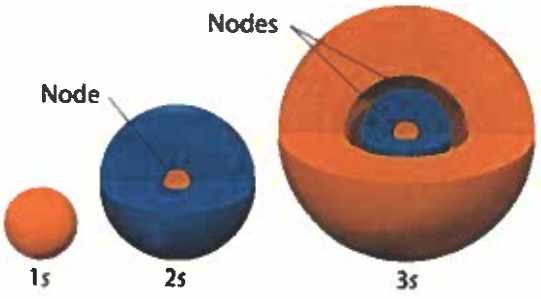


Figure 10.5 Plots of the radial wave function $R_{n,l}(r)$ and the radial probability density $r^2|R_{n,l}(r)|^2$ for the wave functions in (10.43), (10.44), and (10.45).

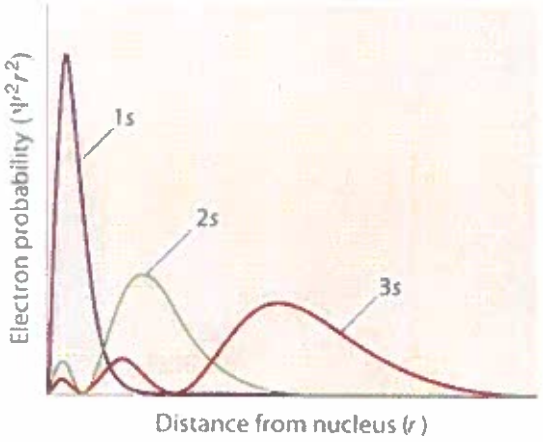
$$\int |\psi(\vec{r})|^2 \, d\tau = \int |R|^2 r^2 dr$$



(a) Electron probability



(b) Contour probability



(c) Radial probability

We can only extract information about the atomic structure from observing radiation emitted when electrons move from one level to another

$$\hbar\omega = 2\pi\hbar c/\lambda = E_{ini} - E_{fin} = E_R\left(\frac{1}{n_{fin}^2} - \frac{1}{n_{ini}^2}\right)$$

Because in H-atom the energies of lower states are so drastically different, the frequencies of emitted light are strongly influenced by the choice of the lower state and divided into series

$n_{fin} = 1$ Lyman series

$$\hbar\omega = E_R\left(1 - \frac{1}{n^2}\right) \qquad n = 2, 3, \ldots$$

$\hbar\omega_{min} = \frac{3}{4}E_R \ (n=2)$ $\hbar\omega_{max} = E_R \ (n \to \infty)$

Photon energy 10–13 eV, deep UV light

$n_{fin} = 2$ Balmer series

$$\hbar\omega = E_R\left(\frac{1}{4} - \frac{1}{n^2}\right) \qquad n = 3, 4, \ldots$$

$\hbar\omega_{min} = E_R\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}E_R = 1.8\,eV$, $\hbar\omega_{max} = \frac{E_R}{4} = 3.4\,eV$

visible range

$n_{fin} = 3$ Paschen series

$$\hbar\omega = E_R\left(\frac{1}{9} - \frac{1}{n^2}\right) \qquad n = 4, 5, \ldots$$

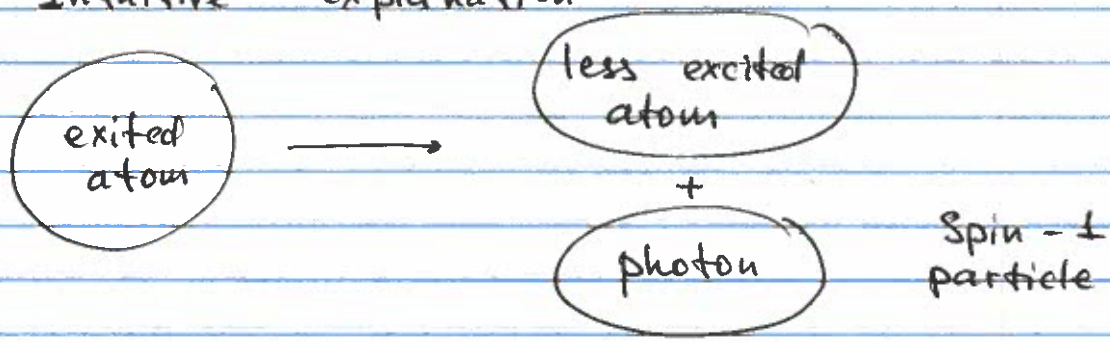
$\hbar\omega_{min} = \frac{7}{144}E_R = 0.66\,eV$ $\hbar\omega_{max} = \frac{E_R}{9} = 1.5\,eV$

near IR – vis range

Selection rules

Not every transition b/w different states are allowed! There are selection rules!

Intuitive explanation



Angular momentum conservation:
initial angular momentum of an atom = final angular momentum of an atom ± Angular momentum of a photon

$$\ell_{ini} = \ell_{fin} \pm 1$$
$$m_{ini} = m_{fin} \text{ or } m_{fin} \pm 1$$

A peculiar property of a Coulumb potential: eigen energies depend only on n, and not ℓ, m

$$E_n = -\frac{\mu (ke^2)^2}{2\hbar^2 n^2} = -\frac{E_R}{n^2} = -\frac{13.6\,eV}{n^2}$$

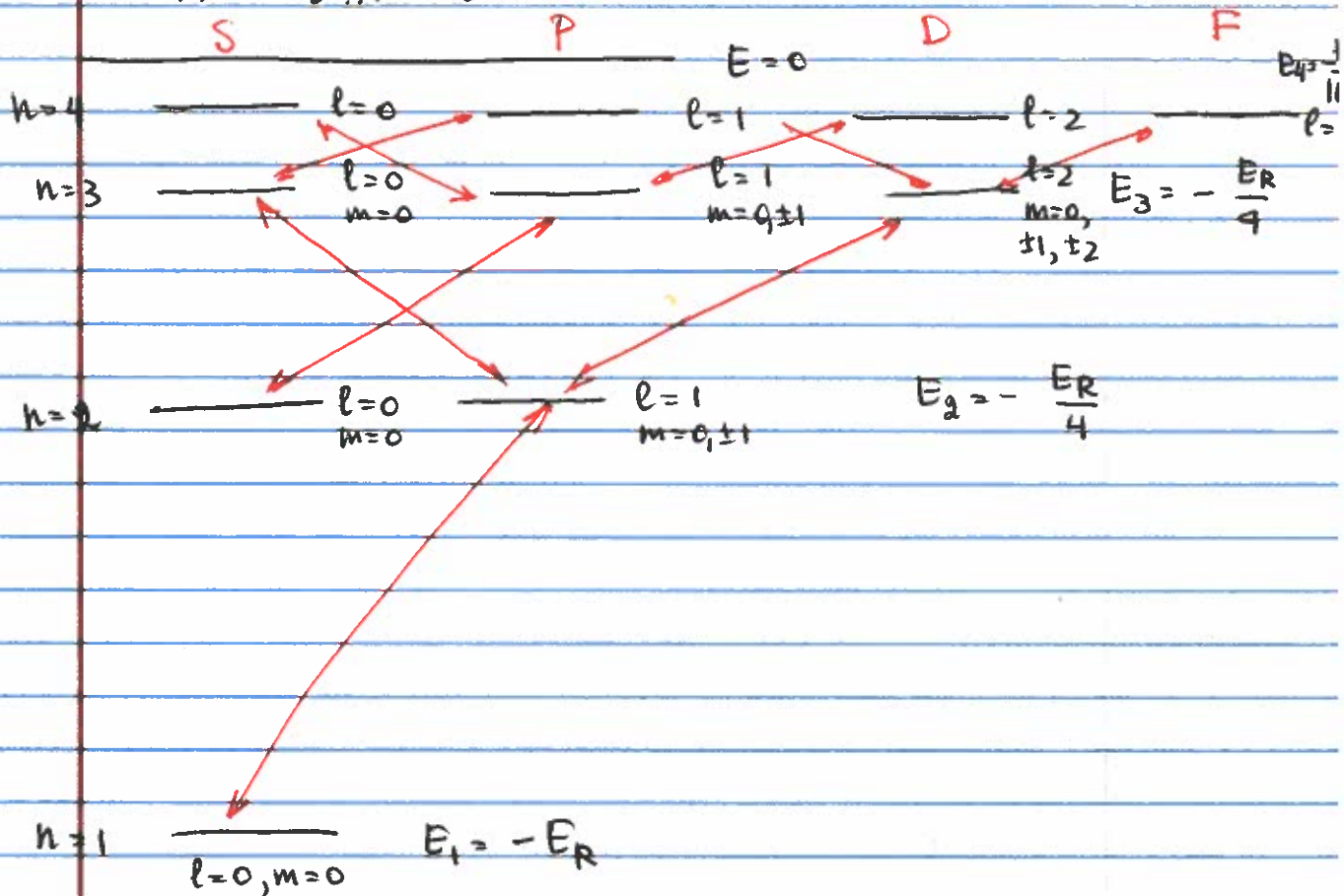
For a hydrogen-like ions ($+Ze$ nucleus and a single electron)

$$E_n = -\frac{Z^2 E_R}{n^2}$$

$n = 1, 2 \ldots \infty$

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

$m = -\ell \ldots +\ell$



Spectroscopic orbital names:

$\ell=0$	S	(sharp)
$\ell=1$	P	(principle)
$\ell=2$	D	(diffuse)
$\ell=3$	F	(fundamental)

Angular component of the wavefunction determines the selection rules!

Electro-dipole transition $\hat{V}_{int} = -\hat{\vec{d}} \cdot \vec{E} =$

$= e \hat{\vec{r}} \cdot \vec{E} = e(x \cdot E_x + y E_y + z \cdot E_z) =$

$= er(\sin\theta \cos\varphi \cdot E_x + \sin\theta \sin\varphi \cdot E_y + \cos\theta \cdot E_z)$

~~Interaction strength~~ Transition probability b/w two states $|n, l, m\rangle$ and $|n_1, l_1, m_1\rangle$ is defined by the $\langle n, l, m | \hat{V}_{in} | n_1, l_1, m_1 \rangle$

$$\langle n, l, m | \hat{V}_{in} | n_1, l_1, m_1 \rangle = e \int r^2 dr \langle nl | r | n_1, l_1 \rangle \times$$

$$\times \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \; Y^*_{lm} (\sin\theta \cos\varphi E_x + \sin\theta \sin\varphi E_y + \cos\theta E_z) Y_{l_1 m_1}$$

The radial integral ~~de~~ affects the interaction strength, but does not ~~de~~ select any states

$$Y_{lm} = A_{lm} P_l^m(\cos\theta) e^{im\varphi}$$

m selection rules $\int d\varphi \; e^{-im\varphi} \begin{Bmatrix} \cos\varphi \\ \sin\varphi \\ 1 \end{Bmatrix} e^{im_1\varphi} \neq 0$

only if $\Delta m = m - m_1 = \pm 1$ (top brackets) E_x, E_y

$\Delta m = 0$ (bottom bracket E_z

l selection rules

$$\int P_l^{m*}(\cos\theta) \begin{Bmatrix} \cos\theta \\ \sin\theta \end{Bmatrix} P_{l_1}^{m_1}(\cos\theta) \sin\theta \, d\theta \neq 0 \quad \text{only if } \Delta l = \pm 1$$

$\Delta l = \pm 1 \qquad l - l_1 = \pm 1$