Lecture 9 – 10/4

4) Atoms

a) Spectroscopic notation

- atom: nucleus (heavy) with charge Ze surrounded by Z electrons

  positively charged ions: same except for scaling factor

  negatively charged ions: bound much weaker

- Quantum numbers:

  main: n

  angular momentum: $\left\{ \begin{array}{ll} l \quad m & \text{(single electron)} \\ J,\ M_J & \text{(whole outer shell)} \end{array} \right.$

  nuclear — " — I

  each J has $2J+1$ values of M_J : $M_J = -J, -J+1, \dots +$

  L : orbital ang. mom., S : spin of e^-

$$\vec{J} = \vec{L} + \vec{S}$$

- atoms are designated by "term":

$$(n)\,^{2S+1}L_J$$

  where S, J are written numerically

$L =$ 0	1	2	3	4	....
"S"	"P"	"D"	"F"	"G"	
"sharp"	"principal"	"diffuse"	"fundamental"		

spectral lines of $1e^-$-atoms

examples:

$3\,^2S_{1/2}$ $\quad (\rightarrow n=3,\ S=\frac{1}{2},\ L=0,\ J=\frac{1}{2})$

- or in terms of "configuration"
  product of symbols $n l^k$ for k electrons in nl-shell,
  e.g. Ca: $(1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s)\, 3d$

  often only most significant

  (as "term": ${}^1D_2$, ${}^3D_{1,2,3}$
  split significantly in energy)

  Term is usually more important (it determines behavior of atom in fields

- "selection rules" $\Rightarrow$
  allowed ΔJ, ΔL, ΔS under transition

NB: "configuration" might not be pure: if two configurations give same term, often intra-atom electrostatic interaction mixes them: "configuration interaction" $\Rightarrow$ results in level shifts and line intensity changes.

b) Bohr atom

Schr Eq: $$\boxed{-\frac{\hbar^2}{2\mu}\vec{\nabla}^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi}$$

$$\mu = \frac{m_e m_n}{m_e + m_n} \quad (\approx m_e) \quad \text{"reduced mass"}$$

Spherical symm. $\Rightarrow$ choose polar coordinates

$$\vec{\nabla}^2 = \frac{1}{r^2}\partial_r r^2 \partial_r - \frac{1}{r^2}\hat{\vec{L}}^2$$

$$\hat{\vec{L}}^2 = -\frac{1}{\sin\vartheta}\partial_\vartheta \sin\vartheta\, \partial_\vartheta - \frac{1}{\sin^2\vartheta}\partial_\varphi^2$$

$$\hat{L}_\pm = e^{\pm i\varphi}(\pm\partial_\vartheta + i\cot\vartheta\, \partial_\varphi)$$

$$\hat{L}_z = -i\partial_\varphi$$

Separation of variables:

$$\psi(r,\vartheta,\varphi) = R(r)\, Y(\vartheta,\varphi)$$

$$\frac{1}{R}\partial_r r^2 \partial_r R - \frac{2\mu}{\hbar^2} r^2 (V-E) = \lambda \qquad (1a)$$

$$\hat{\vec{L}}^2 Y = \lambda Y \qquad (1b)$$

Angular part (Y):

$$Y(\vartheta,\varphi) = \Theta(\vartheta)\,\phi(\varphi)$$

$$\frac{\sin\vartheta}{\Theta}\partial_\vartheta \sin\vartheta\, \partial_\vartheta \Theta + \lambda \sin^2\vartheta = m^2 \qquad (2a)$$

$$\partial_\varphi^2 \phi = -m^2 \phi \qquad 2(b)$$

$$\Rightarrow \phi = A e^{im\varphi} + B e^{-im\varphi}$$

with $\phi(\varphi) \overset{!}{=} \phi(\varphi + 2\pi)$ $\Rightarrow$ $m \in \mathbb{Z}$

"magnetic q. number"

$\rightarrow \quad L_z \Phi = m \Phi$ and

$[\hat{\vec{L}}^2, \hat{L}_z] = [\hat{\vec{L}}^2, \hat{L}_\pm] = 0$

$\Rightarrow Y, \hat{L}_z Y, \hat{L}_\pm Y$ are all eigenfunctions of $\hat{\vec{L}}^2$ with same eigenvalue

$\hat{L}_\pm$ ($\propto e^{\pm i\varphi}$) : "raising / lowering" operators

$\exists\, m_{max} \equiv l$ (w/o proof, cf. to harm. osc.)

$\Rightarrow \hat{L}_+ Y_l \overset{!}{=} 0$ $\Rightarrow$ spherical harmonics (see page from Foot)

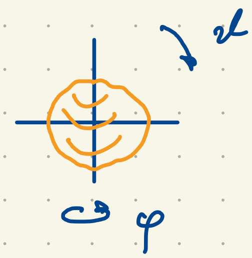
$\rightarrow$ into (1b) $\Rightarrow \lambda = l(l+1)$

l: "orbital q. number"

(same argument for $m_{min} \Rightarrow = -l$)

$Y = Y_{lm}(\vartheta, \varphi)$

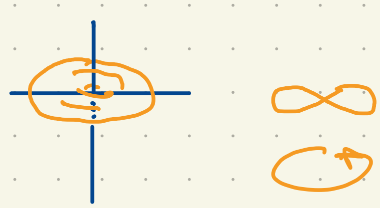
$|Y_{00}|^2$:



(spherically symm.)

$|Y_{10}|^2$:

$|Y_{1,\pm 1}|^2$:



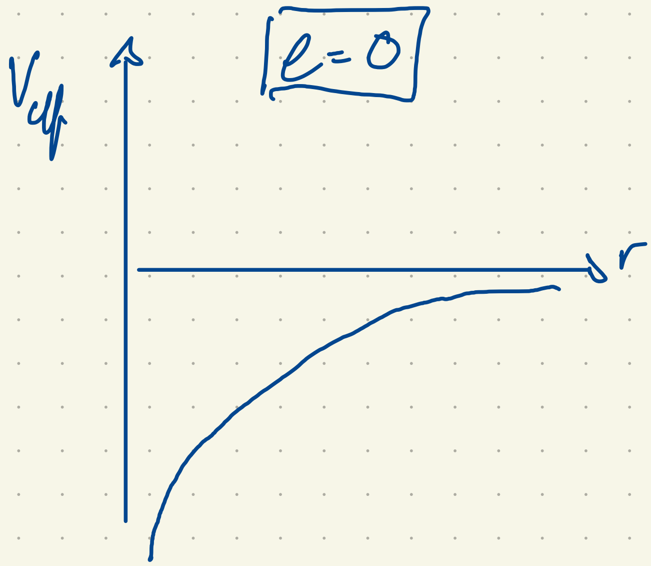
Radial equation:

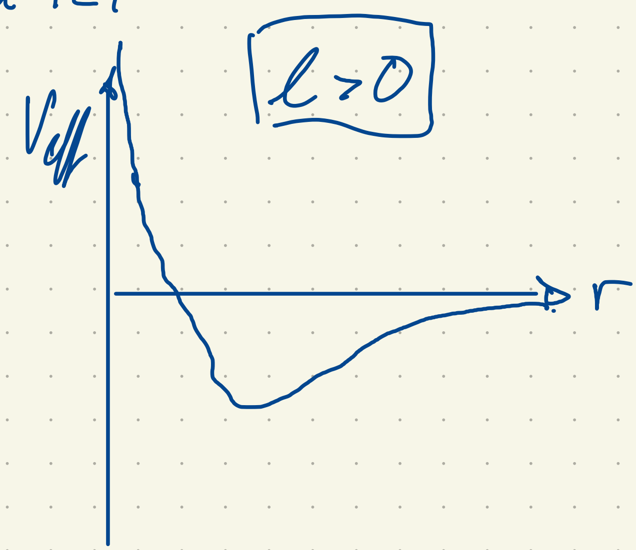
$$P(r) \equiv r\,R(r)$$

$$\rho^2 \equiv \frac{2\mu |E|}{\hbar^2}\, r^2$$

$$\partial_\rho^2 P(\rho) + \Big(+ \overbrace{\frac{l(l+1)}{\rho^2} - \frac{b}{\rho}}^{V_{eff}} + 1 \Big) P(\rho) = 0 \qquad (3)$$

where: $b = \dfrac{e^2}{4\pi\epsilon_0} \sqrt{\dfrac{2\mu}{\hbar^2 |E|}}$





$\Rightarrow$ • only for $l=0$ finite prob. density @ $r=0$

• all l have bound states

Solve (3) using series $\Rightarrow$ solution diverges unless $b = 2n$ (i.e. even integer) $n \in \mathbb{Z}^+$

only for $E<0$ (bound states)

$$\Rightarrow \boxed{E = -\frac{2\mu \left(\frac{e^2}{4\pi\epsilon_0}\right)^2}{\hbar^2} \frac{1}{b^2} = -\frac{Ry}{n^2}}$$

n : "principle q number"

→ for atom number Z (but only <u>one</u> e^-)

$$E_Z = -Z^2 \frac{Ry}{n^2}$$

$$R_{nl}(\rho) \propto \rho^{l+1} e^{-\rho/2} L_{n-l-1}(\rho)$$

$\downarrow$ "Laguerre polynomials"

normalized: $\int_0^\infty |R(r)|^2 r^2 \, dr = 1$