Central potentials and hydrogen atom

Laplacian ∇^2 in spherical coordinates:

$$H = \frac{P^2}{2m} + V(|\vec{R}|) = \underset{\uparrow \atop -\frac{\hbar^2}{2m}\frac{1}{r}\left(\frac{\partial^2}{\partial r^2} r\right)}{\frac{P_r^2}{2m}} + \underbrace{\frac{L^2}{2mr^2} + V(|\vec{R}|)}_{V_{eff}(r)}$$

$\{H, L^2, L_z\}$ form a C.S.C.O.

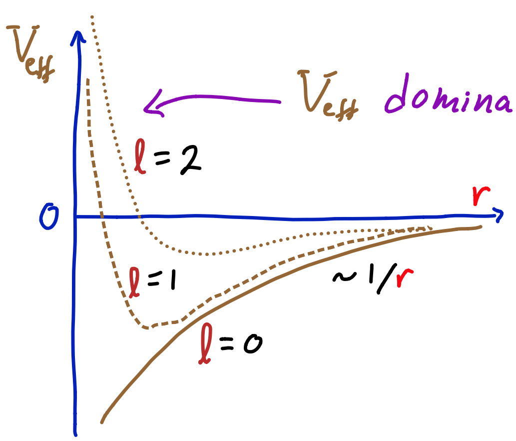
$$\left.\begin{aligned} H\varphi &= E\varphi \\ L^2\varphi &= \ell(\ell+1)\hbar^2\varphi \\ L_z\varphi &= m\hbar\,\varphi \end{aligned}\right\}$$

Separation of variables

$$\varphi(\vec{r}) = R_{k\ell}(r)\, Y_{\ell m}(\theta, \varphi)$$

Check: $\left\{-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{\ell(\ell+1)\hbar^2}{2mr^2} + V(r)\right\}R_{k\ell}(r) = E_{k\ell}R_{k\ell}(r)$

Coulomb potential: $V(r) = -q^2/r$



V_{eff} dominated by $1/r^2 \Rightarrow R(r) \to 0$

try $R(r) \sim r^s$ as $r \to 0$

$\Longrightarrow -s(s+1) + \ell(\ell+1) = 0$

$\Longrightarrow s = \ell$ or $s = -(\ell+1)$

$\therefore R_{k\ell}(r) \sim r^\ell$ as $r \to 0$

Atomic Units

$a_0 = \hbar^2/me^2 = 0.529\ \text{Å}$ "Bohr"

$E_I = me^4/2\hbar^2 = 13.6\ eV$ "Rydberg"

Scale: $r \to r/a_0$ $\quad E \to E/E_I$ $\qquad$ Substitute: $u_{kl}(r) = r R_{kl}(r)$

$$\Rightarrow \left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - \underbrace{\frac{2}{r}}_{-V} - \underbrace{E_{kl}}_{\substack{<0 \text{ for} \\ \text{bound state} \\ \equiv -\lambda_{kl}^2}} \right\} u_{kl}(r) = 0$$

Large r limit: $\quad u'' - \lambda^2 u = 0 \Rightarrow u \sim e^{\pm\lambda r}$ $\quad$ only $e^{-\lambda r}$ is normalizable

How to eliminate $u \sim e^{+\lambda r}$?

Combine large + small r: $\quad u(r) = r^{l+1} e^{-\lambda r} y(r) \qquad y(0) = 1$

Generic solution: $y(r) \sim e^{2\lambda r}$

Laguerre polynomial solution: $\lambda = \dfrac{1}{k+l} \qquad k \in \mathbb{N}_1 = \{1, 2, 3, \cdots\}$

$$E_{kl} = -\lambda^2 E_I = -\frac{E_I}{(k+l)^2}$$

"Accidental degeneracy" $\quad E_{20} = E_{11},\ E_{30} = E_{21} = E_{12}$, etc.

Degeneracy: Let $n = k + l \qquad E_{kl} = E_n = -\dfrac{E_I}{n^2}$

given n, allowed $l = 0, 1, \cdots, n-1$

given l, allowed m: $-l \le m \le l$

degeneracy $g_n = \displaystyle\sum_{l=0}^{n-1} (2l+1) = n^2 \in \{1, 4, 9, \cdots\}$

Radial functions $R_{k\ell}(r)$

$k=1 \quad \ell=0 \quad n=1 \ : \quad R_{10} \sim e^{-r/a_0}$ "1s"

$k=2 \quad \ell=0 \quad n=2 \ : \quad R_{10} \sim \left(1-\frac{r}{a_0}\right) e^{-r/2a_0}$ "2s"

$k=1 \quad \ell=1 \quad n=2 \ : \quad R_{11} \sim \frac{r}{a_0} e^{-r/2a_0}$ "2p"

notation: "$n\ell$"

$\ell = 0 \quad 1 \quad 2 \quad \cdots$
$\quad\ \ s \quad p \quad d$

Radiation: $n \to n'$ $\quad \hbar\Omega_{nn'} = E_{n'} - E_n = E_I\left(\frac{1}{n'^2} - \frac{1}{n^2}\right)$

Selection rule for electric dipole $\langle n'\ell'm' | \vec{D} = q\vec{R} | n\ell m\rangle \neq 0$

$\vec{R} \sim r\, Y_{1m}(\theta,\varphi) \Rightarrow \ell' = \ell, \ell \pm 1$

D_z requires $m = m'$