Separation of variables in a central potential $V(r)$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\varphi)+V(r)\psi(r,\theta,\varphi)=E\psi(r,\theta,\varphi)$$

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

$$-\frac{\hbar^2}{2\mu}\left[\frac{\partial^2\psi}{\partial r^2}+\frac{2}{r}\frac{\partial\psi}{\partial r}\right]+\frac{\hat{L}^2}{2\mu r^2}\psi+V(r)\psi=E\psi$$

$$-\frac{\hbar^2}{2\mu}\left[\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right]Y_{\ell m}(\theta,\varphi)+\frac{R}{2\mu r^2}\underbrace{\hat{L}^2Y_{\ell m}}_{\hbar^2\ell(\ell+1)Y_{\ell m}}+V(r)RY_{\ell m}=ERY_{\ell m}$$

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

using $R(r)=u(r)/r$

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

(one-dimentional-like Schroedinger equation with effective potential

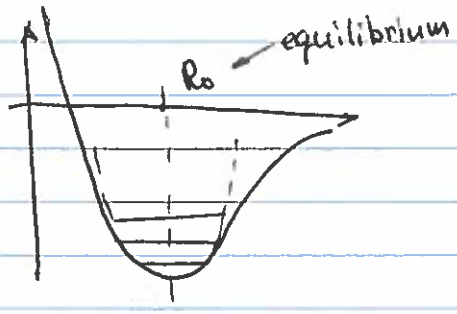
$$V_{eff}(r)=V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}$$

Note on quantum numbers: in 3D space we need 3 quantum numbers to define a bound energy level of a particle. Two comes from the spherical function $Y_{\ell m}$ → define angular distribution

One remaining comes from energy quantization from solving the Schroedinger equation.

Examples:

Molecular Vibration



$$V_{eff}(r) \approx V_{eff}(R_0) + \frac{1}{2}\left.\frac{d^2 V_{eff}}{dr^2}\right|_{R_0}(r-R_0)^2$$

SHO approximation

$$V_{eff}(r) \approx V_{eff}(R_0) + \frac{1}{2}\mu\omega^2(r-R_0)^2$$

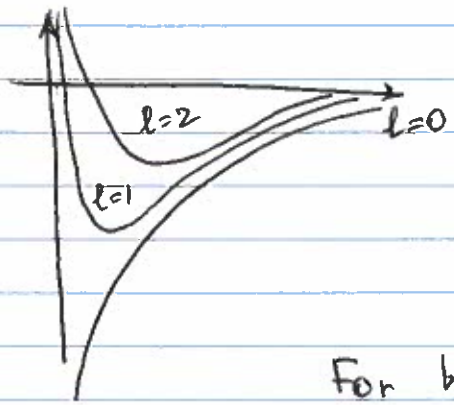
Here both ω and R_0 most likely depend on ℓ since $V_{eff}(r) = V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}$

$$E_{n_r} = \hbar\omega\left(n+\tfrac{1}{2}\right) \longrightarrow u_{n_r\ell}(r) \rightarrow \text{solutions of SHO}$$

$$\psi_{n\ell m}(r,\theta,\varphi) = \frac{u_{n_r,\ell}(r)}{r} Y_{\ell m}(\theta,\varphi)$$

The energy spectrum depends on n and ℓ, but not m $\longrightarrow$ degeneracy

Columb potential $V(r) = -ke^2/r$



$$V_{eff} = -\frac{ke^2}{r} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}$$

Only states with $\ell=0$ can have non-zero electron probability density at $r=0$

For higher ℓ we expect finding electrons farther from the nucleus

$$a = \frac{\hbar^2}{\mu k e^2} = 0.5 \cdot 10^{-10}\ m$$ Bohr's radius

$$E_{min} = -\frac{\mu (ke^2)^2}{2\hbar^2} = -\frac{1}{2}\mu c^2 \cdot \left(\frac{ke^2}{\hbar c}\right)^2 \cong -\frac{1}{2} m_e c^2 \cdot \alpha^2$$

$$\alpha = \frac{ke^2}{\hbar c} = \frac{1}{137}$$ fine-structure constant

$$\alpha^2 = 5.33 \cdot 10^{-5} \qquad E_{min} = -13.6\ eV = -E_R$$

Rydberg energy

Accurate solution

Step 1: convert equation into dimensionless units

position: $\rho = \sqrt{\frac{8\mu |E|}{\hbar^2}}\, r$ energy: $\lambda = \frac{ke^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$

$$\frac{d^2u(\rho)}{d\rho^2} - \frac{l(l+1)}{\rho^2}u(\rho) + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)u(\rho) = 0$$

If $\rho \to \infty$

$$\frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0$$

$u(\rho) \propto e^{-\rho/2}$

(since $u(\rho) \xrightarrow{\rho\to\infty} 0$)

If $\rho \to 0$

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}u = 0$$

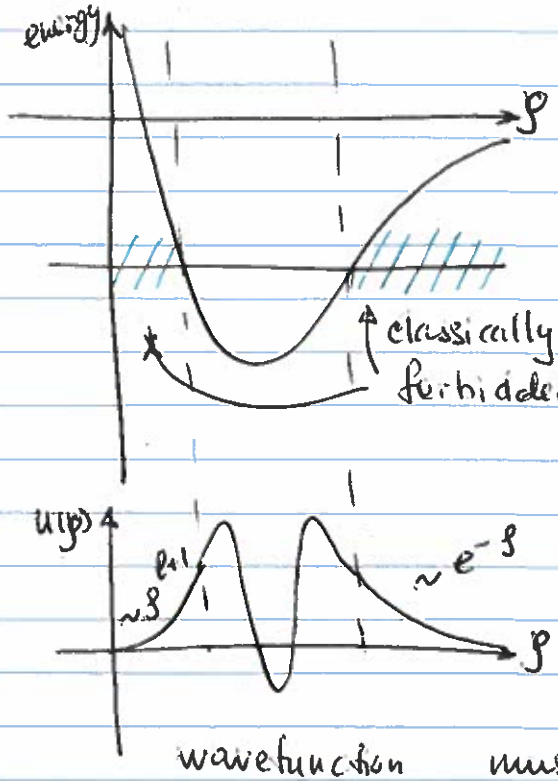
$u(\rho) = \rho^s$

$s(s-1)\rho^{s-2} - l(l+1)\rho^{s-2} = 0$

$s(s-1) = l(l+1)$

$s = l+1$

$u(\rho) \propto \rho^{l+1}$



wavefunction must decay in the forbidden region can oscillate in the allowed region

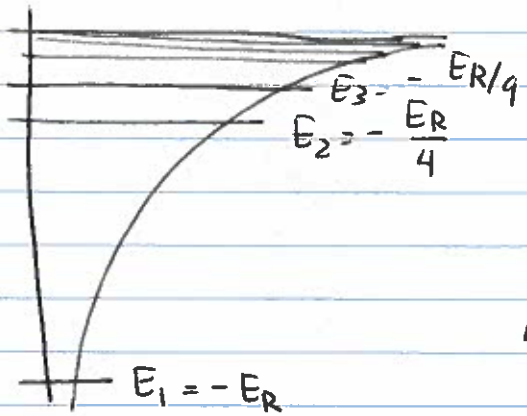
General solution $u(\rho) = \rho^{\ell+1} e^{-\rho/2} \underbrace{L^{2\ell+1}_{n-\ell-1}(\rho)}_{\text{associate Laguerre polynomials}}$

It exists only if $\lambda = n$, or

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

For hydrogen-like ions: nucleus + single electron

$+Ze$ $\quad -e$ $\qquad E_n = -\dfrac{Z^2 E_R}{n^2}$



n - principle quantum number

Surprisingly, E_n does not depend on ℓ (even though the wavefunctions do!)

Each E_n is degenerate

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

$m = 0, \pm 1, \ldots \pm\ell \rightarrow 2\ell+1$ values

Total degeneracy $\sum_{\ell=0}^{n-1} (2\ell+1) = \frac{1+2n-1}{2} \cdot n = n^2$

(actually $2n^2$ if we include electron spins)

Possible electron transitions (emission)

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

There are no selection rules for n