12.6 Solution of rotationally invariant problems.

The general state $|\psi\rangle$ is represented in the coordinate basis by a wave function $\psi(r,\vartheta,\varphi)$ which can be expanded into the complete set of angular momentum eigenstates as follows:

$$\psi(r,\vartheta,\varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} C_{\ell m}(r)\, Y_{\ell m}(\vartheta,\varphi)$$

where

$$C_{\ell m}(r) = \int d\Omega\, Y^*_{\ell m}(\vartheta,\varphi)\, \psi(r,\vartheta,\varphi)$$

We will now find the functions $C_{\ell m}(r)$ that solve the eigenvalue problem for $\hat{H}$.

Rotationally invariant problems have potentials that do not depend on the angles ϑ, φ:

$$\hat{H} = \frac{\hat{\vec{P}}^2}{2m} + V(\hat{R}) \qquad \hat{R} = \sqrt{\hat{X}^2 + \hat{Y}^2 + \hat{Z}^2}$$

The eigenvalue problem $\hat{H}|\psi\rangle = E|\psi\rangle$ in coordinate basis, using spherical coordinates, reads

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\left\{\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2}\underbrace{\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)}_{= -\frac{1}{\hbar^2}\hat{L}^2}\right\} + V(r)\right]\psi_E = E\,\psi_E(r,\vartheta,\varphi)}$$

Seeking simultaneous eigensolutions of $\hat{H}$ and $\hat{L}^2, \hat{L}_z$, we write

$$\psi_E(r,\vartheta,\varphi) = R_{E\ell m}(r)\, Y_{\ell m}(\vartheta,\varphi)$$

and note that the angular part of ∇^2 is just $-\frac{\hat{L}^2}{\hbar^2 r^2}$ (as indicated). We thus get the <u>radial equation</u>

$$\boxed{\left\{-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{\ell(\ell+1)}{r^2}\right] + V(r)\right\}R_{E\ell}(r) = E\,R_{E\ell}(r)}$$

Since the eigenvalues of $\hat{L}^2$ are independent of m, so are the radial solution $R_{E\ell}(r) \Rightarrow$ we have $(2\ell+1)$-fold degeneracy for each energy eigenvalue E.

This can be simplified by the ansatz

$$R_{E\ell} = \frac{1}{r}\,u_{E\ell}$$

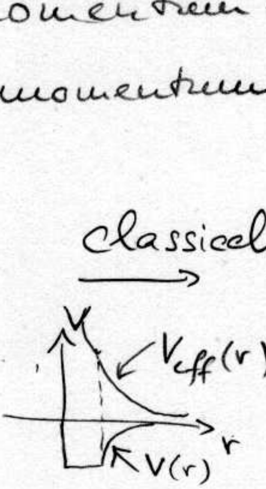
$$\Rightarrow \boxed{\left[\frac{d^2}{dr^2} + \frac{2\mu}{\hbar^2}\left(E - V(r) - \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right)\right]u_{E\ell}(r) = 0}$$

Note that the factor $\frac{1}{r}$ drops out in the normalization integral

$$\int_0^\infty r^2 dr\,|R_{E\ell}(r)|^2 = \int_0^\infty dr\, u_{E\ell}^2(r) = 1$$

We see that nonzero angular momentum appears in the form of an angular momentum barrier in the effective potential:

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



General properties of the eigenfunctions $U_{E\ell}(r)$

Limiting behavior at $r \to \infty$:

Bound states: Wave function must be normalizable to unity (discrete eigenvalues for E)

$$\Rightarrow \int_0^\infty |R_{E\ell}(r)|^2 r^2 dr = C < \infty$$

$$\Rightarrow \int_0^\infty |U_{E\ell}(r)|^2 dr = C \quad \Rightarrow \boxed{\lim_{r\to\infty} U_{E\ell}(r) = 0}$$

(bound)

Unbound (continuum) states:

$$\int_0^\infty R^*_{E\ell}(r)\, R_{E'\ell}(r)\, r^2 dr = \int_0^\infty U^*_{E\ell}(r)\, U_{E'\ell}(r)\, dr$$

$$\sim \delta(E-E')$$

$$\Rightarrow \boxed{\lim_{r\to\infty} U_{E\ell}(r) \sim e^{ikr}}$$ (unbound)

Limiting behavior at $r \to 0$:

(i) Case $\ell = 0$: $\psi(r) \sim R(r)\, Y_{00}(\vartheta, \varphi)$

If $\lim_{r\to 0} U(r) \neq 0$, then $\lim_{r\to 0} R(r) \sim \frac{1}{r^{1+\alpha}}$ $(\alpha > 0)$

But then $-\frac{\hbar^2}{2\mu}\nabla^2\psi$ has a term $\sim \nabla^2\left(\frac{1}{r^{1+\alpha}}\right)$

For $\alpha = 0$, $\nabla^2\left(\frac{1}{r}\right) = -4\pi \delta^{(3)}(\vec{r})$; unless the potential $V(r)$ also has a term $\sim \delta^{(3)}(\vec{r})$, this term cannot be cancelled in the eigenvalue equation, and therefore $\psi(\vec{r}) \sim \frac{1}{r}$ does not satisfy the S.Eq.

For $\alpha > 0$, the divergence at $r=0$ is worse, and the wave function does not yield a finite expectation value for the energy

$$\Longrightarrow \text{For } l=0, \quad \boxed{\lim_{r \to 0} u(r) = 0}$$

(ii) Case $l \neq 0$:

If we assume that $V(r)$ is less singular than $1/r^2$, then for $r \to 0$ the centrifugal barrier dominates over $V(r)$, and for $r \to 0$ the S.Eq. simplifies to

$$u_l'' = \frac{l(l+1)}{r^2} u_l + \text{less singular terms}$$

$$\Longrightarrow \lim_{r \to 0} u_l(r) = r^\alpha \quad \text{with} \quad \alpha(\alpha-1) = l(l+1)$$

$$\Longrightarrow \alpha = \begin{cases} l+1 & \text{or} \\ -l \end{cases}$$

$$\Longrightarrow \boxed{u_l(r) \sim \begin{cases} r^{l+1} & (\text{regular}) \\ r^{-l} & (\text{irregular}) \end{cases}} \quad \text{as } r \to 0$$

The irregular solution again gives infinite energy expectation value and is not even normalizable.

So we reject it,

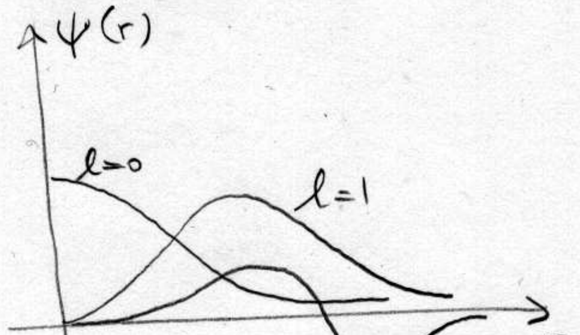
$$\Rightarrow \boxed{u_\ell(r) \xrightarrow[r\to 0]{} r^{\ell+1} \qquad (\ell \neq 0)}$$

For $\ell \neq 0$, $|\psi(r)|^2 \sim (r^\ell)^2 \xrightarrow[r\to 0]{} 0 \Rightarrow$ probability density vanishes at the origin

For $\ell = 0$, $u_\ell(r) \xrightarrow[r\to 0]{} r$ for the potentials we will consider in the following

($u_\ell(r)$ could also fall less quickly than r and still be normalizable, but this occurs only for very peculiar potentials.)

Then $|\psi(r)|^2 \xrightarrow[r\to 0]{}$ constant.



Asymptotic behavior as $r \to \infty$:

- If $V(r)$ does not vanish at $r \to \infty$, it will dominate the asymptotic behavior at $r \to \infty$

$\longrightarrow$ no general answer

(examples: $\frac{u(r)}{r} \sim \frac{\sin(qr)}{r}$ spherical well

$\sim r^k e^{-r^2/2}$ harmonic oscillator

$\sim r^k e^{-Zr}$ Coulomb)

- However, if $\boxed{\lim_{r\to\infty} r\,V(r) = 0}$, we see that the S.Eq. becomes for $r \to \infty$

$$\frac{d^2 u_E}{dr^2} = -\frac{2\mu E}{\hbar^2} u_E$$

(1) $\underline{E > 0}$: particle can escape to infinity,

$$\lim_{r\to\infty} u_E(r) \sim e^{\pm ikr} \quad \left(k = \sqrt{\frac{2\mu E}{\hbar^2}}\right)$$

(2) $\underline{E < 0}$: bound state: the region $r \to \infty$ is classically forbidden, and we expect $u_E(r)$ to fall exponentially for $r \to \infty$.

<u>Case (1)</u> Why did we require $\lim_{r\to\infty} r\,V(r) = 0$ and not simply $\lim_{r\to\infty} V(r) = 0$?

Let's write $u_E(r) = f(r)\, e^{\pm ikr}$ and plug it into the S.Eq. Assuming that $V(r)$ falls more slowly than $1/r^2$ we can ignore the centrifugal barrier and find for large r

$$f'' \pm (2ik) f' - \frac{2\mu V(r)}{\hbar^2} f = 0$$

Since we expect $f(r)$ to be slowly varying at $r \to \infty$ (we even suspect it may become constant), we ignore f'':

$$\frac{df}{f} = \pm \frac{i}{k} \frac{\mu}{\hbar^2} V(r)\, dr$$

$$\Rightarrow f(r) = f(r_0)\, e^{\mp \frac{i\mu}{\hbar^2 k} \int_{r_0}^{r} dr'\, V(r')}$$

If $V(r)$ falls faster than $\frac{1}{r}$, $\lim_{r\to\infty} r V(r) = 0$, then $\lim_{r\to\infty} \int_{r_0}^{r} dr'\, V(r')$ exists, and $\lim_{r\to\infty} f(r) = \text{const.}$ ✓

But for the Coulomb potential, $V(r) = -\frac{e^2}{r}$,

$$\lim_{r\to\infty} f(r) = f(r_0)\, e^{\pm \frac{i\mu e^2}{\hbar^2 k} \ln r/r_0}$$

and hence

$$\boxed{u_E(r) \sim e^{\pm i\left(kr + \frac{\mu e^2}{\hbar^2 k} \ln r/r_0\right)}}$$

"Coulomb phase"

The particle is never free from the Coulomb field, no matter how far from the origin.

Case (2) ($E<0$)

All results from case (1) carry over with substitution

$$k \longrightarrow i\kappa \qquad \kappa = \sqrt{\frac{2\mu|E|}{\hbar^2}}$$

$$\Rightarrow \quad u_E(r) \xrightarrow[r\to\infty]{} A e^{-\kappa r} + B e^{+\kappa r} \qquad \text{if } \lim_{r\to\infty} rV(r) = 0$$

The ratio A/B is determined by demanding

$u=0$ at $r=0$, and B is fixed by normalization.

For the Coulomb potential

$$u_E(r) \xrightarrow[r\to\infty]{} e^{\pm\kappa r}\, e^{\mp \frac{\mu e^2}{\hbar^2 \kappa} \ln r/r_0} = \left(\frac{r}{r_0}\right)^{\mp \frac{\mu e^2}{\hbar^2 \kappa}} e^{\pm \kappa r}$$

This is what we will find for the hydrogen atom.