Physics 522 Lecture 2

Review: The Schrödinger Equation

Dynamics:

"Of all the symmetries, the most important is "time translation" as it determines "dynamics"

The time evolution operator: $\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}$
Where $\hat{H}$ is the Hamiltonian

"Schrödinger picture" evolution of state

$$|\Psi(t)\rangle = \hat{U}(t)|\Psi(0)\rangle$$

"Heisenberg picture" evolution of observables

$$\hat{A}(t) = \hat{U}^{\dagger}(t)\,\hat{A}(0)\,\hat{U}(0)$$

Same predictions of measurement outcomes if

$$|\Psi_S(0)\rangle = |\Psi_H\rangle \qquad \hat{A}_S = \hat{A}_H(0)$$

Differential form:

$$\frac{\partial \hat{U}}{\partial t} = -\frac{i}{\hbar}\hat{H}\hat{U} \qquad \text{"Schrödinger equation"}$$

Schrödinger picture: $\frac{\partial}{\partial t}|\Psi(t)\rangle = \frac{\partial \hat{U}}{\partial t}|\Psi(0)\rangle = -\frac{i}{\hbar}\hat{H}|\Psi(t)\rangle$

Heisenberg picture: $\frac{\partial}{\partial t}\hat{A}(t) = \frac{\partial}{\partial t}\left(\hat{U}^{\dagger}(t)\hat{A}(0)\hat{U}(t)\right) = -\frac{i}{\hbar}[\hat{A}, \hat{H}]$

<u>Note:</u> In defining $\hat{U}$, I assume $\hat{H}$ had no explicit time dependence (e.g., through an external oscillating force)

More generally

$$\frac{\partial \hat{U}(t)}{\partial t} = -\frac{i}{\hbar} \hat{H}(t)\, \hat{U}(t)$$

$$\Rightarrow \hat{U}(t) = e^{-\frac{i}{\hbar}\int_0^t dt' \hat{H}(t')} \quad \text{if } [\hat{H}(t), \hat{H}(t')] = 0$$

$$\hat{U}(t) = \tilde{\mathcal{T}} \left\{ e^{-i\int_0^t dt' \hat{H}(t')} \right\} \qquad \begin{pmatrix}\text{Time-ordered} \\ \text{product}\end{pmatrix}$$

$$= \mathbb{1} - \frac{i}{\hbar}\int_0^t dt' \hat{H}(t') + \frac{1}{2}\left(\frac{i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' \hat{H}(t')\hat{H}(t'') + \cdots$$

<u>Time-independent Schrödinger Equation</u>

Of central importance in determining the properties of quantum systems is to solve for its energy eigenvalues and eigenstates:

$$\hat{H}|u_E\rangle = E|u_E\rangle$$

This is important for a number of reasons:

(1) "Coherent dynamics":

The time-evolution operator can be expressed

$$\hat{U} = e^{-\frac{i}{\hbar}\hat{H}t} = \sum_E e^{-\frac{i}{\hbar}Et} |u_E\rangle\langle u_E|$$

- Initial value problem: Given $|\psi(0)\rangle$ find $|\psi(t)\rangle$

$$|\psi(0)\rangle = \sum_E' c_E(0)\, |u_E\rangle$$

where $c_E(0) = \langle u_E | \psi(0)\rangle$

$$|\psi(t)\rangle = \hat{U}(t)\, |\psi(0)\rangle = \sum_E' e^{-iEt/\hbar}\, |u_E\rangle\langle u_E|\psi(0)\rangle$$

$$= \sum_E' \underbrace{c_E(0)\, e^{-iEt/\hbar}}_{c_E(t)}\, |u_E\rangle$$

(2) "Thermo dynamics"
From classical statistical physics we know that a system in thermal equilibrium the "state" of the system at a given temperature is determined by a Boltzmann distribution

$$P(E) = \frac{1}{Z} e^{-E/k_B T}$$

Z ← partition function

Quantum mechanically, we say that we have a "statistical mixture" of energy eigenstates written formally as a "density operator"

$$\hat{\rho} = \frac{1}{Z} e^{-\hat{H}/k_B T}$$

$$\Rightarrow \quad P(E) = \langle E | \hat{\rho} | E \rangle$$

Note: In the thermal state, we don't have a "coherent superposition", but instead the system is more a kin to classical probability distribution.

Note: $e^{-\tau \hat{H}} = \hat{U}(-i\hbar t)$ "imaginary time"

as $\tau \to \infty \Rightarrow T \to 0$ (temperature)

$\longrightarrow$ All population in lowest energy state (ground state)

In condensed matter, typically in equilibrium state

<u>Schrödinger equation in particle mechanics</u>

Consider a Hamiltonian of the form

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\text{Kinetic}} + \underbrace{\hat{V}(\vec{x})}_{\text{Potential}}$$

In position representation, the time-independent Schrödinger equation is

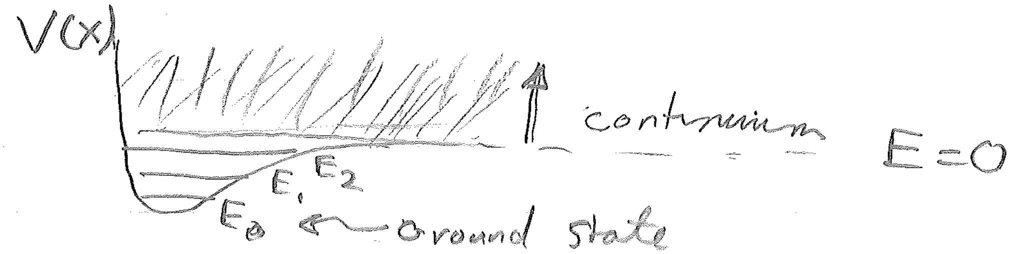
$$\langle \vec{x} | \hat{H} | \psi \rangle = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x}) \right) \psi(\vec{x})$$

$$= E \psi(\vec{x})$$

Potential well $\Rightarrow$ Bound & Unbound States

$\Rightarrow$ Spectrum divides into discrete allowed energy eigenvalues and continuum

1D



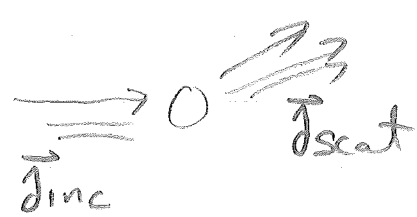
$$\Rightarrow \quad \hat{\mathbb{1}} = \sum_{n}^{n\ \text{bound}} |u_n\rangle\langle u_n| + \int dE\, |u(E)\rangle\langle u(E)|$$

<u>Bound States</u>: Only certain eigenvalues allowed
Goal: Find energy eigenvalues

<u>Continuum</u>: $\Rightarrow$ Scattering

Probability current $\vec{j} = \frac{1}{2}\Big[\psi^*(x)\left(\frac{\hbar}{im}\vec{\nabla}\right)\psi(x) + \left(\frac{\hbar}{im}\vec{\nabla}\psi\right)^* \psi(x)\Big]$

Scattering $\Rightarrow$ Change in probability current
1D: reflection & transmission
3D: differential scattering cross-section



3D, spherical symmetry, and separation of variables

Kinetic Energy: $\frac{\vec{p}^{\,2}}{2m} = \underbrace{\frac{\vec{p}_r^{\,2}}{2m}}_{\text{radial kinetic energy}} + \underbrace{\frac{L^2}{2mr^2}}_{\text{angular kinetic energy}}$

Where $\vec{L} = \vec{r} \times \vec{p}$ (angular momentum)

For a spherically symmetric potential $V(r)$

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

$\Rightarrow$ energy eigenfunctions are also eigenstates of $\hat{L}^2, \hat{L}_z$

$$\psi_{E,\ell,m}(r,\theta,\phi) = \underbrace{R_{E\ell}(r)}_{\text{Radial wavefunction}} \underbrace{Y_{\ell,m}(\theta,\phi)}_{\text{spherical Harmonic}}$$

T.I.S.E. $\Rightarrow$ Radial equation

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

or reduced $u(r) \equiv r R(r)$

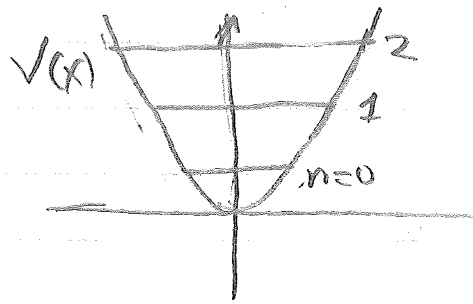
$$\Rightarrow \boxed{-\frac{\hbar^2}{2m}\frac{d^2}{\partial r^2} u + V_{eff}^{(\ell)} u = E R}$$

Like 1D problem $0 \le r \le \infty$

Two important Problems

1D: Simple Harmonic Oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$



Only bound-states

Characteristic scales: $\hbar, m, \omega$

$$\Rightarrow \quad E_c = \hbar\omega, \quad p_c = \sqrt{m E_c} = \sqrt{\hbar m \omega}$$

$$x_c = \frac{\hbar}{p_c} = \sqrt{\frac{\hbar}{m\omega}}$$

$$\Rightarrow \hat{H} = \hbar\omega\left(\frac{\hat{X}^2 + \hat{P}^2}{2}\right) \qquad \text{where } \hat{X} = \frac{\hat{x}}{x_c}, \quad \hat{P} = \frac{\hat{p}}{p_c}$$

Define $\hat{a} = \hat{X} + i\hat{P} \Rightarrow [\hat{a}, \hat{a}^\dagger] = 1$

$$\hat{H} = \hbar\omega\left(\frac{\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger}{2}\right) = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right)$$

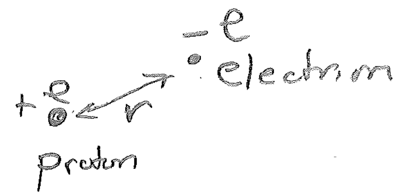
Solution to $\quad \hat{H}|E_n\rangle = E_n|E_n\rangle$

$$\Rightarrow E_n = \hbar\omega\left(n + \frac{1}{2}\right) \qquad n = 0, 1, 2, \ldots, \infty$$

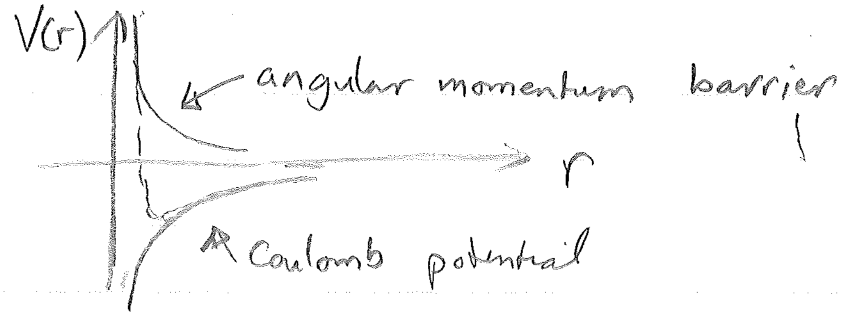
$|E_n\rangle \equiv |n\rangle \qquad a^\dagger a|n\rangle = n|n\rangle \qquad a|n\rangle = \sqrt{n}\,|n-1\rangle$

$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$

Hydrogen Atom:



Center of mass ≈ @ position of proton.
With proton @ origin $V(r) = -\frac{e^2}{r}$ (cgs units)



Bound-state solution

$$H\,\psi_{n_r,\ell,m}(r,\theta,\phi) = E_{n_r,\ell}\,\psi_{n_r,\ell,m}(r,\theta,\phi)$$

$$E_{n_r,\ell} = \underbrace{\frac{-e^2}{2a_0}}_{\text{Rydberg} = 13.6\text{ eV} = \mathbb{R}}\frac{1}{(n_r+\ell+1)^2}, \quad a_0 = \frac{\hbar^2}{m_e e^2} \text{ (Bohr radius)}$$

$$\psi_{n_r,\ell,m}(r,\theta,\phi) = \frac{1}{(a_0)^{3/2}}\,\bar{r}^{\,\ell}\, e^{-\frac{\bar{r}}{n}}\,\mathcal{L}_{n_r}^{2\ell+1}\left(\frac{2\bar{r}}{n}\right) Y_{\ell,m}(\theta,\theta)$$

$$n \equiv n_r + \ell + 1, \quad \bar{r} \equiv \frac{r}{a_0}$$

<u>Note:</u> Energy doesn't depend on n_r and ℓ independently

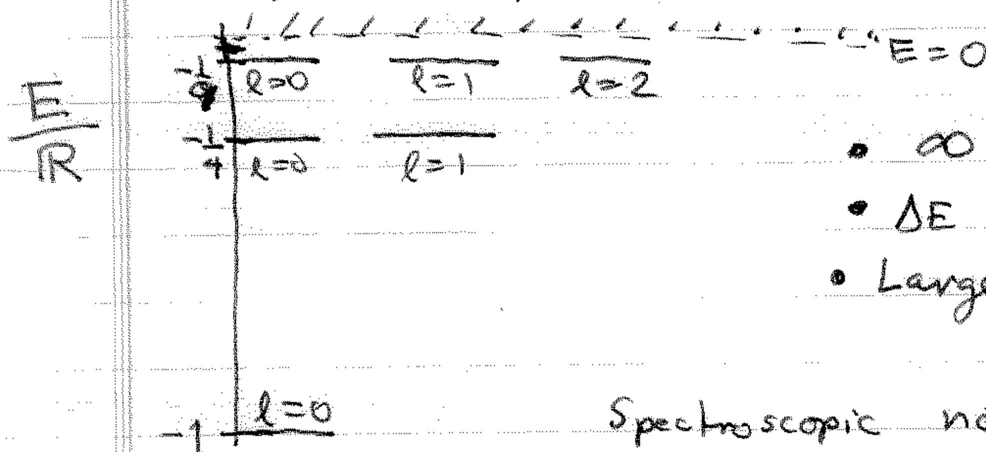
$$E_n = \frac{-\mathbb{R}}{n^2} \quad n = \text{principle quantum \#}$$

Bound-state eigenvalues

$$\boxed{\begin{aligned} E_{n_r,\ell} &= \frac{-E_0}{2(n_r+\ell+1)^2} \equiv \frac{-E_0}{2n^2} \\ \text{Hydrogen} &= -\frac{\mathbb{R}}{n^2} = -\frac{1}{n^2}(13.6\,eV) \quad \text{Balmer series} \end{aligned}}$$

Principle quantum # $n \equiv n_r + \ell + 1$

For given n, $\ell = 0, 1, 2, \ldots, n-1$ since $n_r = 0, 1, \ldots$



- ∞ # of bound-states
- ΔE gets smaller near $E=0$
- Large $n \Rightarrow$ "Rydberg states"

Spectroscopic notation

$\ell=0$: s-states ("sharp")
$\ell=1$: p-states ("principle")
$\ell=2$: d-states ("distinct")
$\ell=3$: f-states ("fine")

Degeneracy: Given n (excluding spin)

$$g_n = \sum_{\ell=0}^{n-1} \sum_{m=-\ell}^{\ell} 1 = \sum_{\ell=0}^{n-1} (2\ell+1) = n^2$$

Including electron spin $g_n = 2n^2$

"Accidental degeneracy"

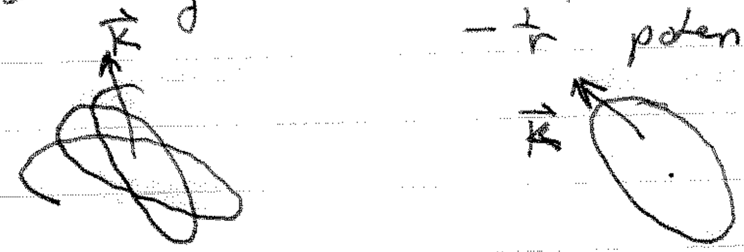
E_n depends only on $n_r + l$ and not on n_r and l independently:

Hidden symmetry: The Runge-Lenz vector

$$\hat{\vec{K}} = \frac{1}{2me^2}\left(\hat{\vec{L}} \times \hat{\vec{p}} - \hat{\vec{p}} \times \hat{\vec{L}}\right) + \frac{\hat{\vec{x}}}{r}$$

$\hat{\vec{K}}$ is a conserved quantity

Classically $\Rightarrow$ no precession of orbit for $-\frac{1}{r}$ potential



$V(r) \neq \frac{-1}{r}$ $\qquad\qquad$ $V(r) = -\frac{1}{r}$

New symmetry $\Rightarrow$ Another set of commuting operators

$\Rightarrow$ Can separate in parabolic coordinates

Suppose we add a small potential $V_{int} = \frac{\lambda}{r^2}$

$$\Rightarrow \quad E_{n_r, l} \cong \frac{-E_0}{2\left(n_r + \frac{1}{2} + \sqrt{(l + \frac{1}{2})^2 + \lambda^2}\right)^2}$$

"Breaks" the degeneracy