Physic 531: Atom/Molecular Structure

Lecture 1: Overview

Structure of Matter? "Reductionist atomistic viewpoint"
- Revolution of the 20^{th} century
- Atomic and subatomic particles
- Physics of atoms $\Rightarrow$ birth of quantum theory
    - Bohr - Atom
- Explanation of spectroscopy ; chemistry
- Build up

    atoms $\rightarrow$ molecules $\rightarrow$ condensed matter

Why continue to study it today
- Spectroscopy: Finger prints of universe
- Applications: • Designing new materials
    - Biological studies
    - Lasers
    - * Quantum Control - information
    - * Quantum degenerate gases

Probes into the structure of matter
- Spectrosopy: Light emitted by matter
    (Dark matter?)
- Scattering: Quintessential example: Rutherford
    Particle accelerators
- Cooperative effects $\rightarrow$ condensed matter

Quantum Mechanics – The description of matter at the atomic scale

Basic review:

- States: kets $\{|\psi\rangle\}$, vectors in Hilbert space
  Complex vector space (perhaps ∞-dim)

Inherently Statistical:

Given state $|\psi\rangle$, probability of find $|\phi\rangle$

$$P_{\phi|\psi} = |\langle\phi|\psi\rangle|^2 \quad \text{"Born rule"}$$

Superposition $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$

probability amplitudes (complex #s)

Suppose $\langle\psi_1|\psi_2\rangle = 0$ = orthogonal

$$P_{\psi_1|\psi} = |c_1|^2 \qquad P_{\psi_2|\psi} = |c_2|^2$$

Normalization: $|c_1|^2 + |c_2|^2 = 1$

But $P_{\phi|\psi} = |\langle\phi|\psi\rangle|^2 = |c_1\langle\phi|\psi_1\rangle + c_2\langle\phi|\psi_2\rangle|^2$

$$= |\langle\phi|\psi_1\rangle|^2|c_1|^2 + |\langle\phi|\psi_2\rangle|^2|c_2|^2$$

$$+ c_1c_2^*\langle\phi|\psi_1\rangle\langle\psi_2|\phi\rangle$$

$$+ c_1^*c_2\langle\psi_1|\phi\rangle\langle\phi|\psi_2\rangle$$

$$\Rightarrow P_{\phi|\psi} = \underbrace{P_{\phi|\psi_1} P_{\psi_1|\psi} + P_{\phi|\psi_2} P_{\psi_2|\psi}}^{\text{Classical logical reasoning}}$$

$$+ \underbrace{c_1 c_2^* \langle\phi|\psi_1\rangle\langle\psi_2|\phi\rangle + c.c.}_{\text{Interference of amplitudes!}}$$

• Observables: Hermitian Operators on Hilbert space $\{\hat{A}\}$

Eigenvalue eq. $\hat{A}|a\rangle = a|a\rangle$

eigenvector ← eigenvalue

$\{a\}$ = Spectrum of $\hat{A}$, real for Hermitian

$\Rightarrow$ Possible measurement outcomes

Complete orthonormal set: $\langle a|a'\rangle = \delta_{aa'}$

$$\sum_a |a\rangle\langle a| = \mathbb{1}$$ "resolution of identity"

Compatible observables: $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$

$\Rightarrow$ Can specify simultaneous states with definite $\hat{A}$ and $\hat{B}$

Complete set of commuting operators

$\Rightarrow$ Set needed to completely specify state

$$\{\hat{A}, \hat{B}, \hat{C}\} \Rightarrow |\underbrace{a, b, c}_{\text{"quantum numbers"}}\rangle$$

<u>Symmetries:</u> One of the most important ingredients in describing nature.

Symmetry = Physics invariant under some transformation

In Q.M. $\Rightarrow$ Probability of measurement outcomes is unchanged

$\Rightarrow$ Preserve inner product $\Rightarrow$ <u>Unitary operator</u>

$$|\psi\rangle \Rightarrow |\psi'\rangle = \hat{U}|\psi\rangle$$

$$|\phi\rangle \Rightarrow |\phi'\rangle = \hat{U}|\phi\rangle$$

$$\forall |\psi\rangle, |\phi\rangle, \ \langle\psi'|\phi'\rangle = \langle\psi|\hat{U}^\dagger\hat{U}|\phi\rangle = \langle\psi|\phi\rangle$$

$$\Rightarrow \hat{U}^\dagger\hat{U} = \mathbb{1}$$

Examples: Rotation, Parity, Translation

<u>Symmetries and degeneracies:</u>

Consider an observable unchanged by a symmetry

$$\hat{U}^\dagger\hat{A}\hat{U} = \hat{A} \quad \text{or} \quad [\hat{A}, \hat{U}] = 0$$

Consider eigenvector $\hat{A}|a\rangle = a|a\rangle$

Let $|a'\rangle = \hat{U}|a\rangle$

$$\hat{A}|a'\rangle = \hat{A}\hat{U}|a\rangle = \hat{U}\hat{A}|a\rangle = a\hat{U}|a\rangle$$
$$= a|a'\rangle \quad : \text{Degenerate!}$$

Key Transformation: Dynamics

Time translation operator $\hat{U}(t)$

Given state $|\psi(0)\rangle \Rightarrow |\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle$

Generator of time translation: Hamiltonian

Time dependent Schrödinger Eqn.

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

If $\hat{H}$ independent of t $\quad \hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}t}$

Special states: Eigenstates of Hamiltonian

$\Rightarrow \boxed{\hat{H}|\psi_E\rangle = E|\psi_E\rangle}$ Time independent Schrödinger Eq.

$\{E\} \Rightarrow$ Energy levels $\rightarrow$ Define the structure

Bohr rule: Quantum Jumps $E_i \rightarrow E_f$

$\Rightarrow$ Emitted photon: $\boxed{\hbar\omega_{fi} = E_f - E_i}$

Studying the structure of atoms and molecules

$\equiv$ Solving the T.I.S.E.

Wave Mechanics $\psi(\vec{x}) = \langle \vec{x} | \psi \rangle$

$|\psi(\vec{x})|^2$ = Probability density to find a particle near $\vec{x}$

Simple Hamiltonian $\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\text{kinetic energy}} + \underbrace{V(\vec{x})}_{\text{potential energy}}$

$$\hat{H}|\psi\rangle = E|\psi\rangle \Rightarrow \langle \vec{x}|\hat{H}|\psi\rangle = E\langle \vec{x}|\psi\rangle$$

$$\Rightarrow \boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{x})\right)\psi(\vec{x}) = E\psi(\vec{x})}$$

Solving P.D.E's

Many-body case

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + \cdots \frac{\hat{p}_N^2}{2m_N} + V(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$$

$$\Rightarrow \left[-\frac{\hbar^2}{2}\left(\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 + \cdots + \frac{1}{m_N}\nabla_N^2\right) + V(\vec{x}_1, \vec{x}_2, \ldots \vec{x}_N)\right]\psi(\vec{x}_1, \ldots \vec{x}_N)$$

$$= E\,\psi(\vec{x}_1, \ldots, \vec{x}_N)$$

Other complication

- Identical particles $\Leftrightarrow$ exchange symmetry
- Spin and relativistic corrections

Approximation Methods

The number of physical problems with exact solution to the Schrödinger equation are extremely limited. The art of solving physics problems is the art of approximations.

Variational method

Consider the expectation value of the Hamiltonian

$$\bar{H}[\psi] = \langle\psi|\hat{H}|\psi\rangle / \langle\psi|\psi\rangle \leftarrow (\psi \text{ unnormalized})$$

$\uparrow$ "functional" of the wave function

Consider variation $|\psi\rangle \Rightarrow |\psi\rangle + |\delta\psi\rangle$

$$\delta\bar{H} = \frac{(\langle\psi| + \langle\delta\psi|)\,\hat{H}\,(|\psi\rangle + |\delta\psi\rangle)}{(\langle\psi| + \langle\delta\psi|)(|\psi\rangle + |\delta\psi\rangle)} - \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

Expand in a Taylor series

$$\Rightarrow \delta\bar{H} = \frac{\left(\langle\psi|\hat{H}|\psi\rangle + \langle\delta\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{H}|\delta\psi\rangle\right)}{\langle\psi|\psi\rangle}\left(1 - \frac{\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle}\right)$$

$$- \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} + O(\delta\psi^2)$$

$$\Rightarrow \langle\psi|\psi\rangle^2 \,\delta\bar{H} = \langle\psi|\psi\rangle \left(\langle\delta\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{H}|\delta\psi\rangle\right)$$

$$- \langle\psi|\hat{H}|\psi\rangle \left(\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle\right)$$

$$+ \mathcal{O}(\delta\psi^2)$$

Suppose $|\psi\rangle$ is a normalized eigenstate of $\hat{H}$

$\langle\psi|\psi\rangle = 1$, $\quad \hat{H}|\psi\rangle = E|\psi\rangle$, $\quad \langle\psi|\hat{H} = E\langle\psi|$

$$\Rightarrow \delta\bar{H} = E\left(\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle\right)$$

$$- E\left(\langle\psi|\psi\rangle + \langle\psi|\delta\psi\rangle\right) + \mathcal{O}(\delta\psi^2)$$

$$\Rightarrow \boxed{\delta\bar{H} = \mathcal{O}(\delta\psi^2)}$$

Thus $\langle\hat{H}\rangle$ is stationary to variations in the wave function to first order in ψ

This result is used to find approximate solutions to the Schrödinger equation by a well informed choice of a "trial wave function" as a function of parameters $\alpha, \beta, \gamma \cdots$

Look for the choice of parameters such that

$$\frac{\partial}{\partial\alpha}\langle\hat{H}\rangle = \frac{\partial}{\partial\beta}\langle\hat{H}\rangle = \frac{\partial}{\partial\gamma}\langle\hat{H}\rangle = \cdots = 0$$

The most common use of the variational method is to find an upper bound on the ground state energy.

Note $\langle \hat{H} \rangle \geq E_{min}$ (Energy is bounded by a minimum #).
$= E_{ground}$

Thus $\text{Min} \langle \hat{H} \rangle \geq E_{ground}$

$\Rightarrow$ $\boxed{\text{Minimize } \langle \hat{H} \rangle \text{ for a well chosen trial wave function to get upper bound on ground state } E}$

Perturbation theory

Another important method for finding approximate solutions to the Schrödinger equation applies to problems when the Hamiltonian has the form

$$\hat{H} = \hat{H}_0 + \epsilon \hat{H}_1$$

$\hat{H}_0$ = "zeroth" order Hamiltonian with known bound-state spectrum

$$\hat{H}_0 |u_n^{(0)}\rangle = E_n^{(0)} |u_n^{(0)}\rangle$$

$\hat{H}_1$ = "Perturbation" - small correction of order "ϵ".

First order corrections to spectrum of bound states

$$\boxed{\begin{aligned} \Delta E_n^{(1)} &= \langle u_n^{(0)} | \hat{H}_1 | u_n^{(0)} \rangle \\ | u_n^{(1)} \rangle &= \sum_{m \neq n}' \frac{\langle u_m^{(0)} | \hat{H}_1 | u_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} | u_m^{(0)} \rangle \end{aligned}}$$

Notes: (i) This formula requires nondegenerate eigenvalues. More on degenerate case below
(ii) the perturbation "mixes" in other states to get the new eigenstate

Second order shift

$$\boxed{\Delta E_n^{(2)} = \sum_{m \neq n}' \frac{|\langle u_m^{(0)} | \hat{H}_1 | u_n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$

Go to second order when first order vanishes (sometime due to symmetry)

Small parameter of expansion:

- Characteristic scale of matrix elements of $\hat{H}_1$ compared to energy level splitting of the unperturbed spectrum.

Degenerate Perturbation theory

If there is a manifold of states with the same energy, standard perturbation theory can break down. Typically, degeneracy is due to symmetry. If the perturbation does not respect this symmetry, the degeneracy will be broken.

Consider Set $\{|u_{n,i}^{(0)}\rangle, \; i = 1, 2, 3, \ldots \underset{\substack{\uparrow \\ \text{degeneracy}}}{g_n}\}$

Diagonalize (i.e. find eigenvectors and eigenvalues) of $\hat{H} = \hat{H}_0 + \hat{H}_1$ is basis $\{|u_{n,i}^{(0)}\rangle\}$

$$\text{Matrix} \quad H_{ij} = \langle u_{n,i}^{(0)} | \hat{H} | u_{n,j}^{(0)} \rangle$$

$$= \underbrace{E_n^{(0)} \delta_{ij}}_{\text{already diagonal}} + H_{ij}^{(1)}$$

$\Rightarrow$ Diagonalize $H_{ij}^{(1)}$ $g_n \times g_n$ matrix

$\Rightarrow$ New eigenvectors and first order shifts in energy within degenerate manifold.