

LECTURE 1

Many-electron Schrödinger equation

$$H\psi = E\psi$$

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V_{ext}(\vec{r}_i) + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Use atomic units (Hartree units)

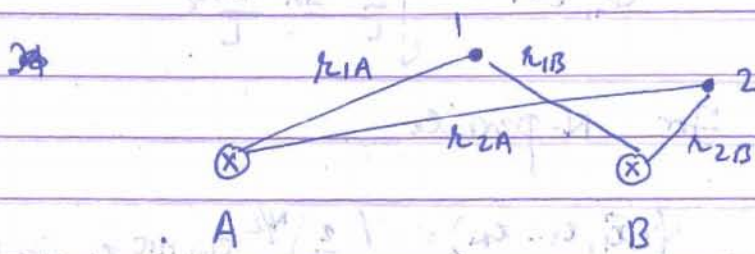
$$\hbar = m_e = |e| = 1$$

$$H = \sum_i -\frac{\nabla_i^2}{2} + \sum_i V_{ext}(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}$$

Examples: • two-electron atomic systems

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{e^2}{r_{12}}$$

• two-electron molecular system (H_2 molecule)



$$H = \underbrace{-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2}_T - \underbrace{\frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}}}_{V_{ext}(\vec{r}_1, \vec{r}_2)} + \underbrace{\frac{1}{r_{12}}}_{V_{ee}}$$

and solids where the external potential is given by ions.

②

Solution of Schrodinger equation without the interaction term:

$$H = \sum_{i=1}^N -\frac{\nabla_i^2}{2} + \sum_i V_{ext}(\vec{r}_i) = \Phi H$$

$$= \sum_{i=1}^N h_i$$

$$h_i = -\frac{\nabla_i^2}{2} + V_{ext}(\vec{r}_i)$$

Separation of variables:

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \phi_{\{\alpha_1\}}(\vec{r}_1) \phi_{\{\alpha_2\}}(\vec{r}_2) \dots \phi_{\{\alpha_N\}}(\vec{r}_N)$$

$\{\alpha_i\}$ = Set of quantum numbers.

$\phi_{\{\alpha_i\}}$ is a solution of

$$\left[-\frac{1}{2} \nabla_i^2 + V_{ext}(\vec{r}_i) \right] \phi_{\alpha_i} = E_i \phi_{\alpha_i}$$

Example: N , particles in a one-d box



$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

For N particles

$$\psi(\vec{r}_1, x_2, \dots, x_N) = \left(\frac{2}{L}\right)^{N/2} \sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L} \dots \sin \frac{n_N \pi x_N}{L}$$

How do we fill the levels. For electrons we cannot have more than two electrons - one with spin up and one with spin down - in any orbital. Electrons being Fermions obey Fermi-Dirac statistics.

$$\Psi(x_1 s_1; x_2 s_2 \dots x_N s_N)$$

$$= \left(\frac{2}{L}\right)^{N/2} \left(\sin \frac{k x_1}{L} \sin \frac{k x_2}{L} \dots\right) \left(\sin \frac{2k x_1}{L} \sin \frac{2k x_2}{L} \dots\right) \dots$$

Freely moving particles (Homogeneous gas of non-interacting fermions or non-interacting electrons)

Plays very important role in solid-state physics (plane waves)

$$H = \sum_i -\frac{1}{2} \nabla_i^2$$

$$\Psi(r_1, r_2, \dots) = \left(\prod_i \frac{1}{\sqrt{L}} e^{i \vec{k}_i \cdot \vec{r}_i}\right)$$

When periodic boundary conditions are applied over a cube of length L .

$$\Rightarrow e^{i \vec{k}_i \cdot (\vec{r}_i + \hat{z}L)} = e^{i \vec{k}_i \cdot \vec{r}_i}$$

$$\Rightarrow k_x L = 2n\pi \quad k_x = \frac{2n\pi}{L}$$

Similarly $k_y = \frac{2n\pi}{L}$ & $k_z = \frac{2n\pi}{L}$

Expectation values:

$$\Psi = \prod_i \phi_{\alpha_i}(\vec{r}_i)$$

$$\langle \Psi | H | \Psi \rangle = \sum_i \langle \phi_{\alpha_i} | h | \phi_{\alpha_i} \rangle$$

$$= \sum_i \epsilon_i$$

or write it more generally as $\sum_i f_i \epsilon_i$

For plane waves (HEG without interactions),

$$\sum_i \frac{k_i^2}{2}$$

(4)

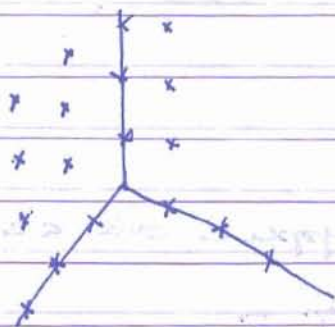
A little calculation with homogeneous electron gas

(Useful for later purposes also)

Total energy = kinetic energy

$$= \sum_i \left(\frac{k_i^2}{2} \right)$$

$$\vec{k} = \frac{2\pi}{L} (n_x \hat{i} + n_y \hat{j} + n_z \hat{k})$$



Every $\left(\frac{2\pi}{L}\right)^3$ has one \vec{k}

density of \vec{k} points = $\left(\frac{V}{8\pi^3}\right)$

Each \vec{k} point has two electrons

$$\text{No. of electrons} = 2 \cdot \int_0^{k_F} 4\pi k^2 dk \cdot \frac{V}{8\pi^3} = N$$

$$\left(\frac{k_F^3}{3\pi^2}\right) = \left(\frac{N}{V}\right) \Rightarrow k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3}$$

Kinetic energy:

$$\sum_i \frac{k_i^2}{2} = \frac{V}{8\pi^3} \cdot 2 \cdot \int_0^{k_F} \frac{k^2}{2} \cdot 4\pi k^2 dk$$

$$= \frac{V}{2\pi^2} \frac{k_F^5}{5}$$

$$= \left(\frac{3}{10} \cdot k_F^2\right) N$$

$$\text{kinetic energy per particle} = \frac{3}{10} k_F^2$$

These are simple cases where the Schrödinger equation can be solved easily
What do we do in cases when this is not possible even for non-interacting
systems: For example a potential like

A possible approach in this case is to solve the equations numerically.
 Another approach is perturbation theory if the potential can be written as slightly deviated for a known, solvable potential.

Their approach is provided by the variational principle for the energy. We discuss that now.

VARIATIONAL PRINCIPLE: Given a Hamiltonian H , if we assume an approximate wavefunction ψ , then

$$E_0 \leq \langle \psi | H | \psi \rangle \quad \left(\begin{array}{l} \text{NOTE: This is true only if} \\ |\psi\rangle \text{ is Normalized} \end{array} \right)$$

Therefore if we search all over the function space and keep taking the expectation value of a given Hamiltonian, we have

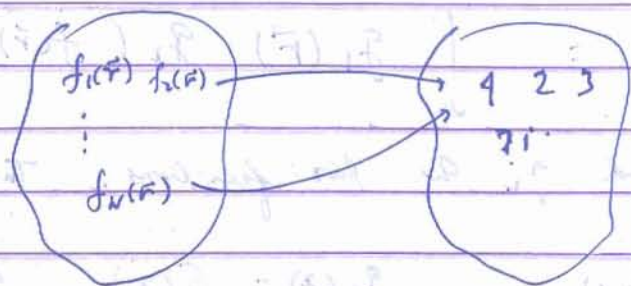
$$E_0 \leq \langle \psi | H | \psi \rangle$$

This then offers a way of finding or rather searching for the ground-state wavefunction.

DIGRESSION

Mathematical handling of the variational principle and its effective use requires familiarity with a mathematical entity called a functional; we discuss that now.

FUNCTIONAL: A functional is a map from functions to numbers



Functions

Real Numbers

Cautionary note: A functional is NOT a function of a function

Let us then first see what it is not

⑥

$\sin(\cos x)$ is NOT a functional

because $f(y) = y^2$ whereas $y = \cos x$ i.e. $f(\cos x) = \cos^2 x$

$f(x) = \cos^2 x$ is NOT a functional

In other words $g(f(x))$ is not a functional

On the other hand

map $F[f] = f(x=0)$ is a functional

(NOTE: This is a linear map)

$$F[\sin x] = f(\sin 0) = 0$$

$$F[\cos x] = \cos 0 = 1$$

$$F[e^x] = e^0 = 1$$

$$F\left[\frac{1}{5+x^2}\right] = \frac{1}{5} = 0.2$$

is a functional.

$F[f] = f(x = \pi/2)$ is also a functional

In general a functional can be written as an integral

$$F[f] = \int g_1(x) g_2(f(x)) dx$$

$$= \int g_1(\vec{r}) g_2(f(\vec{r})) d\vec{r}$$

when g_1 and g_2 are two functions. Thus

$$F[f] = f(0) \quad g_1(x) = \delta(x) \quad g_2(x) = x$$

$$F[f] = f(\pi/2) \quad g_1(x) = \delta(x - \pi/2) \quad g_2(x) = x$$

$$\text{Similarly } F[f] = \int f(x) dx \quad ; \quad \int |\nabla f(\vec{r})|^2 d\vec{r}$$

Other examples of a functional are: time taken by a particle (7)

to slide over a curve from $(0, h)$ to $(x_0, 0)$ $T[y] = \int \frac{ds}{v} = \int \frac{\sqrt{1+y'^2}}{\sqrt{2g(h-y)}} dx$

(ii) Area under a curve $y(x)$.

Connection with Quantum mechanics / Variational principle / Classical mechanics

A functional most familiar to us in physics is the action functional

$$A[q(t)] = \int_{t_0}^{t_1} L(q, \dot{q}, t) dt$$

$$= \int_{t_0}^{t_1} (T - V) dt$$

Given a $q(t)$ it gives us a number. Thus action is a functional of $q(t)$.

Lagrange's equations are derived by demanding that if $q(t)$ is varied about its true solution then $\delta A = 0$

$$\delta A = \int_{t_0}^{t_1} L(q + \delta q, \dot{q} + \delta \dot{q}, t) dt$$

$$= \int_{t_0}^{t_1} \left\{ \frac{\partial L}{\partial q} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) \right\} \delta q(t) dt$$

+ higher order

~~In general we will have~~ We then demand that

$$\delta A = 0 \text{ to first order in } \delta q$$

This gives the equation of motion

$$\frac{\partial L}{\partial q} - \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{q}} \right) = 0$$

⑧ $\delta F = \int \left\{ \frac{\delta F}{\delta f} \delta f + \frac{\delta F}{\delta \dot{f}} \delta \dot{f} \right\} d\vec{r}$

In general

$$\delta F[F] = \int \left\{ \frac{\delta F}{\delta f} \delta f + \frac{\delta F}{\delta \dot{f}} \delta \dot{f} \right\} d\vec{r}$$

The quantity in brackets is called the functional derivative and is denoted as

$$\left(\frac{\delta F}{\delta f(\vec{r})} \right)$$

So $\delta F = 0$ (stationarity of a functional)

$$\Rightarrow \frac{\delta F}{\delta f} = 0$$

When F depends on f and ∇f

$$\frac{\delta F}{\delta f} = \frac{\partial F}{\partial f} - \nabla \cdot \left(\frac{\partial F}{\partial (\nabla f)} \right)$$

Reference: Gelfand and Fomin, Calculus of variations

Expectation value of H : (Single particle)

$$\begin{aligned} \langle \psi | H | \psi \rangle &= \int \psi^* \left(-\frac{1}{2} \nabla^2 \right) \psi d\vec{r} + \int \psi^*(\vec{r}) V(\vec{r}) \psi(\vec{r}) d\vec{r} \\ &= \frac{1}{2} \int (\nabla \psi^*) \cdot (\nabla \psi) d\vec{r} + \int \psi^*(\vec{r}) V(\vec{r}) \psi(\vec{r}) d\vec{r} \end{aligned}$$

Expectation value is a functional of $\psi(\vec{r})$

Make $\langle \psi | H | \psi \rangle$ stationary with respect to variation ψ

$$\delta \langle \psi | H | \psi \rangle = \int \frac{\delta}{\delta \psi} \langle \psi | H | \psi \rangle \delta \psi(\vec{r}) d\vec{r} + \text{High order}$$

$$\frac{\delta}{\delta \psi^*} \langle \psi | H | \psi \rangle = \frac{\partial}{\partial \psi^*} \left[\psi^* V(\vec{r}) \psi - \frac{1}{2} |\nabla \psi|^2 \right]$$

$$= \nabla \cdot \left[\frac{\partial}{\partial (\nabla \psi)} \left(\psi^* \nabla \psi - \frac{1}{2} \nabla \psi \cdot \nabla \psi \right) \right]$$

$$= V(\vec{r}) \psi(\vec{r}) - \frac{1}{2} \nabla^2 \psi = 0$$

This looks like the Schrodinger equation but is NOT quite what is missing.

The part that is missing is the normalization of $|\psi\rangle$. We want to put in the constraint that $\int \psi^* \psi d\vec{r} = 1$. This is done by the method of Lagrange multipliers. Thus we multiply the constraint by a constant λ and make

$$\{ \langle \psi | H | \psi \rangle - \lambda \langle \psi | \psi \rangle \}$$

Stationary with respect to variations in ψ . This gives

$$V(\vec{r}) \psi(\vec{r}) - \frac{1}{2} \nabla^2 \psi - \lambda \psi = 0$$

$$\text{or } -\frac{1}{2} \nabla^2 \psi + V(\vec{r}) \psi = \lambda \psi$$

λ is so chosen as to make $|\psi\rangle$ normalized. This happens only for certain values of λ which are the eigenenergies of the system.