1.2: Extension to N-particle system

a) Consider N particles: i = 1,2,3,…,N

Now: $$\hat{H} = \hat{T} + \hat{V} = \sum_i \hat{T}_i + V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N; t)$$

$$\hat{T}_i = \frac{1}{2m_i}\vec{p}_i^{\,2} = -\frac{\hbar^2}{2m_i}\nabla_i^2 = -\frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

Solve to get $\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, t)$

b) Ψ must be bounded, continuous, single-valued, continuous derivatives with respect to all coordinates.

c) Integrals over all space: $d\tau = \mathrm{dx}_1\mathrm{dx}_2\ldots\mathrm{dx}_\mathrm{N}\mathrm{dy}_1\mathrm{dy}_2\ldots\mathrm{dy}_\mathrm{N}\mathrm{dz}_1\mathrm{dz}_2\ldots\mathrm{dz}_\mathrm{N}$

d) Operators depend on all coordinates and all momenta and time

e) $\left|\Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N, t)\right|^2 d\tau$ = probability that particle i is found between x_i and $x_i + dx_i$, y_i and $y_i + dy_i$, z_i and $z_i + dz_i$ at time t

f) $$\overline{M} = \int \Psi^*(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \hat{M} \int \Psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) d\tau$$

implies integration over all coordinates.

1.3: Stationary States

In C374 we saw several examples in which $\hat{H}$ was independent of time because both $\hat{T}$ and $\hat{V}$ were independent of time. This generated a set of stationary states

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

Solve by letting $\Psi(\vec{r},t) = \psi(\vec{r})e^{-\frac{iEt}{\hbar}}$ (comes from separation of variables)

and solving $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$

This works:

LHS

$$\hat{H}\Psi = \hat{H}\psi(\vec{r})e^{-\frac{iEt}{\hbar}} = e^{-\frac{iEt}{\hbar}}\hat{H}\psi(\vec{r}) = e^{-\frac{iEt}{\hbar}}E\psi(\vec{r}) = E\Psi$$

RHS

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = -\frac{\hbar}{i}\frac{\partial\psi(\vec{r})e^{-\frac{iEt}{\hbar}}}{\partial t} = -\frac{\hbar}{i}\psi(\vec{r})\left(-\frac{iE}{\hbar}\right)e^{-\frac{iEt}{\hbar}} = E\psi(\vec{r})e^{-\frac{iEt}{\hbar}} = E\Psi$$

Show $\overline{H} = E$ Assume Ψ is normalized.

$$\overline{H} = \int \Psi^{*}\hat{H}\Psi\, d\tau = \int\left(\psi^{*}(\vec{r})e^{\frac{iEt}{\hbar}}\right)\hat{H}\left(\psi(\vec{r})e^{-\frac{iEt}{\hbar}}\right)d\tau$$

$$= \int\left(e^{\frac{iEt}{\hbar}}e^{-\frac{iEt}{\hbar}}\right)\psi^{*}(\vec{r})\hat{H}\psi(\vec{r})d\tau \quad = E\int\psi^{*}(\vec{r})\psi(\vec{r})d\tau = E$$

Called stationary states because all expectation values of the time-independent Operators are constants with respect to time and because $|\Psi|^2$ is independent of time.

Examples covered in C374 were the particle in a box, simple harmonic oscillator The rigid rotor, and the H-atom.

1.4: Self-adjoint (Hermitian) operators

These operators are special because they have real eigenvalues and therefore, correspond to physical observables.

Designate an adjoint operator as: $\hat{M}^{+}$

This corresponds to the complex conjugate of a transposed matrix (Later)

$$\hat{M}^{+} = \left(\hat{M}^{T}\right)^{*}$$

Must satisfy the following defining equation:

$$\int \chi^{*}\left(\hat{M}\phi\right)d\tau = \int \left(\hat{M}^{+}\chi\right)^{*}\phi d\tau$$

A self-adjoint operator means $\hat{M}^{+} = \hat{M}$

Therefore: $\int \chi^{*}\left(\hat{M}\phi\right)d\tau = \int \left(\hat{M}\chi\right)^{*}\phi d\tau$

Theorem: Quantum mechanical operators corresponding to real physical properties of a system are self-adjoint.

From postulate II $\hat{M}\psi_j = m_j\psi_j$ where m_j is real.

$$\Rightarrow \langle M \rangle = \overline{M} = \int \psi^* \left(\hat{M}\psi\right) d\tau = m\int \psi^* \psi d\tau = m$$

Now: $\left(\langle M \rangle\right)^* = \left(\overline{M}\right)^* = \left[\int \psi^* \left(\hat{M}\psi\right) d\tau\right]^*$

If operator is self-adjoint $\Rightarrow \left[\int \left(\hat{M}\psi\right)^* \psi d\tau\right]^* = \left[m^* \int \psi^* \psi d\tau\right]^* = m$

$\therefore \left(\overline{M}\right)^* = \overline{M}$ as it must be since M corresponds to a physical observable.

Theorem: The eigenfunctions of a self-adjoint operator corresponding to different eigenvalues are orthogonal.

Choose Ψ_n and Ψ_m such that:

$$\hat{M}\psi_n = m_n\psi_n \quad \text{and} \quad \hat{M}\psi_m = m_m\psi_m \quad \text{and} \quad m_n \neq m_m \neq 0$$

Then: $$\int \psi_m^* \left(\hat{M}\psi_n\right) d\tau = \int \left(\hat{M}\psi_m\right)^* \psi_n d\tau$$ **M** is self-adjoint

$$\therefore m_n \int \psi_m^* \psi_n d\tau = m_m^* \int \psi_m^* \psi_n d\tau$$

$$\therefore \left(m_n - m_m^*\right) \int \psi_m^* \psi_n d\tau = 0$$

But $\left(m_n - m_m^* \neq 0\right)$ $\quad \therefore \int \psi_m^* \psi_n d\tau = 0$ unless m = n

Definition: Kronecker delta function:

$$\delta_{mn} = 1 \; if \;\; m = n$$
$$= 0 \; if \;\; m \neq n$$

$$\Rightarrow \int \psi_m^* \psi_n \, d\tau = \delta_{mn}$$

Importance of this result lies in the Expansion Theorem