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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XXI

To: Group 63 Staff

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A list of symbols which will be used extensively during the discussion on quantum mechanics is defined as follows:

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \quad = \text{Hamiltonian operator}$$

$$\mathcal{E} = i\hbar \frac{\partial}{\partial t} \quad = \text{Energy operator}$$

$$E \quad = \text{Energy}$$

$$\mathcal{P} = -i\hbar \nabla \quad = \text{Momentum operator}$$

$$p \quad = \text{Momentum}$$

$$\Psi = \Psi(\vec{r}, \vec{s}, t) \quad = \text{Wave function (involving time)}$$

$$\psi = \psi(\vec{r}, \vec{s}) \quad = \text{Time independent wave function}$$

Let us investigate the possibility of Ψ simultaneously being an eigenfunction of more than one operator. If Ψ is simultaneously an eigenfunction of energy and momentum, it must satisfy the two equations

$$i\hbar \frac{\partial \Psi}{\partial t} = E \Psi \quad (\text{XXI-1})$$

$$\text{and } -i\hbar \frac{\partial \Psi}{\partial x} = p \Psi \quad (\text{XXI-2})$$

as well as Schroedinger's equation.

For simplicity, we are considering only one space dimension. A solution of Ψ , satisfying XXI-1 and XXI-2 is

$$\Psi = c e^{\frac{i}{\hbar}(px - Et)} \quad (\text{XXI-3})$$

This leads to the now familiar relationships

$$\frac{p}{\hbar} = \frac{2\pi}{\lambda} \quad \text{and} \quad \frac{E}{\hbar} = 2\pi \nu$$

Equation XXI-3 gives us an eigenfunction of both energy and momentum. However, to be a suitable wave function, Ψ must also satisfy the Schrodinger equation

$$\nabla^2 \Psi = \epsilon \Psi \tag{XXI-4}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{XXI-4a}$$

$$\left. \begin{aligned} \text{where } \frac{\partial^2}{\partial x^2} \left(e^{i \frac{1}{\hbar} (px - Et)} \right) &= -\frac{p^2}{\hbar^2} \Psi \\ \text{and } \frac{\partial}{\partial t} \left(e^{i \frac{1}{\hbar} (px - Et)} \right) &= -\frac{iE}{\hbar} \Psi \end{aligned} \right\} \tag{XXI-5}$$

Substituting XXI-5 into XXI-4 gives, as a solution of the Schrodinger equation

$$\frac{p^2}{2m} \Psi + V\Psi = E \Psi$$

$$\text{or } \frac{p^2}{2m} + V = E. \tag{XXI-6}$$

Since our initial condition meant that both the momentum p and the total energy E are constants, equation XXI-5 states that the potential energy V must also be constant if Ψ is a suitable wave function satisfying the Schrodinger equation. This is the solution of a free particle only, and cannot be used when V varies with x .

The conditions imposed were very stringent in the above example. In general, Ψ will not simultaneously be an eigenfunction of momentum and energy. We will not necessarily be dealing with conservative systems as we shall also consider interactions involving radiation.

In a system it is possible to have different eigenfunctions yielding the same eigenvalue. For example, n different states of the hydrogen atom may have the same energy eigenvalue. In that case, the eigenvalue energy level is said to be degenerate, with an n -fold degeneracy.

Consider a system with n eigenfunctions $\Psi_1, \Psi_2, \dots, \Psi_n$ with corresponding eigenvalues E_1, E_2, \dots, E_n , all of which are solutions of the equation

$$i\hbar \frac{\partial \Psi_n}{\partial t} = E_n \Psi_n$$

The most general solution is a combination of all the functions, that is

$$\Psi = \sum_n C_n \Psi_n$$

XXI-7

where

$$\Psi_n = \psi_n e^{-i \frac{E_n t}{\hbar}}$$

$$\Psi = \sum_n C_n \psi_n e^{-i \frac{E_n t}{\hbar}}$$

The approach to this problem is not very different from that of the vibrating string. In that case the various modes of vibration must be superposed. In addition, the boundary conditions must be known as well as the starting conditions. Similarly in quantum mechanics, we must know the state of the system at some time $t = t_0$. If this is known, then

$$\Psi(t = t_0) = \sum_n C_n \psi_n e^{-i \frac{E_n t_0}{\hbar}} = \sum_n C'_n \psi_n$$

where $C'_n = C_n e^{-i \frac{E_n t_0}{\hbar}}$

We would not have changed the form of the equation for Ψ if we had arbitrarily set $t_0 = 0$, because the C_n 's are still arbitrary. Therefore, without loss of generality, we may say

$$\Psi(t = 0) = \sum_n C_n \psi_n$$

XXI-9

This expression resembles expansion in a Fourier series. Fourier series are particularly useful when dealing with the vibrating string or membrane. In quantum mechanics we have ψ_n instead of sine or cosine functions. The method we will use to evaluate C_n , however, is the same as that used in a Fourier expansion.

From XXI-9 we see

$$\mathcal{H}\Psi = \sum_n c_n e^{\frac{-iE_n t}{\hbar}} \mathcal{H}\psi_n \quad \text{XXI-10}$$

$$E\Psi = \sum_n c_n \psi_n E_n e^{\frac{-iE_n t}{\hbar}} \quad \text{XXI-11}$$

Since equations XXI-10 and XXI-11 are identical for all values of t , the coefficients of identical functions of t $\left(e^{\frac{-iE_n t}{\hbar}} \right)$ must be equal.

Hence
$$\mathcal{H}\psi_n = E_n \psi_n \quad \text{XXI-12}$$

From equation XXI-12 and a knowledge of the boundary conditions, ψ_n and E_n may be determined. This will be done quantitatively for a specific example at our next meeting.

In order to evaluate the c 's, we must show a fundamental property of the eigenfunctions, their orthogonality.

Consider the $n = l$ and $n = j$ in equation XXI-12;

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_j + v \psi_j = E_j \psi_j \quad \text{XXI-13}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_l^* + v \psi_l^* = E_l \psi_l^* \quad \text{XXI-14}$$

Equation XXI-14 holds because the complex conjugate of the eigenfunctions are also solutions of Schrodinger's equation, and because E_j and E_l are real. Multiplying XXI-13 by ψ_l^* and XXI-14 by ψ_j

$$-\frac{\hbar^2}{2m} \psi_l^* \nabla^2 \psi_j + v \psi_j \psi_l^* + E_j \psi_j \psi_l^*$$

$$-\frac{\hbar^2}{2m} \psi_j \nabla^2 \psi_l^* + v \psi_l^* \psi_j = E_l \psi_l^* \psi_j$$

Subtracting,

$$\frac{\hbar^2}{2m} (\psi_l^* \nabla^2 \psi_j - \psi_j \nabla^2 \psi_l^*) = (E_l - E_j) \psi_l^* \psi_j$$

Integrating over configuration space

$$\frac{\hbar^2}{2m} \int_{\tau} (\psi_i^* \nabla^2 \psi_j - \psi_j \nabla^2 \psi_i^*) d\tau = (E_i - E_j) \int_{\tau} \psi_i^* \psi_j d\tau$$

Applying Green's theorem* which states

$$\int_{\tau} (\psi_i^* \nabla^2 \psi_j - \psi_j \nabla^2 \psi_i^*) d\tau = \int_{\mathfrak{s}} (\psi_i^* \nabla \psi_j - \psi_j \nabla \psi_i^*) ds$$

where \mathfrak{s} is the surface bounding the volume τ .

Therefore

$$\frac{\hbar^2}{2m} \int_{\mathfrak{s}} (\psi_i^* \nabla \psi_j - \psi_j \nabla \psi_i^*) ds = (E_i - E_j) \int_{\tau} \psi_i^* \psi_j d\tau \quad \text{XXI-15}$$

Here \mathfrak{s} is an infinite surface, surrounding the entire configuration space τ . One of the conditions placed upon the eigenfunction ψ is that it go to 0 as configuration space goes to infinity with such rapidity that the left hand side of XXI-15 be identically zero. Then,

$$(E_i - E_j) \int_{\tau} \psi_i^* \psi_j d\tau = 0 \quad \text{XXI-16}$$

Since, in general, $E_i \neq E_j$ if $i \neq j$

$$\int_{\tau} \psi_i^* \psi_j d\tau = 0 \quad \text{XXI-17}$$

for $i \neq j$

This is known as the orthogonality condition, which states that all wave functions corresponding to different states are orthogonal.

The orthogonality condition XXI-17 and the normalization condition can be combined by the equation

$$\int_{\tau} \psi_i^* \psi_j d\tau = \delta_{ij} \quad \text{XXI-18}$$

where $\delta_{ij} = 0$ when $i \neq j$
 $\delta_{ij} = 1$ when $i = j$

* Stratton, J. A. Electromagnetic Theory, McGraw-Hill Co., New York, 1941 P. 165.

Functions which are both normalized and orthogonal are known as orthonormal functions.

To find the value of the C's, making use of the orthonormality of the eigenfunctions, we have

$$\Psi(t = 0) = \sum_n c_n \psi_n$$

Multiplying by ψ_m^* and integrating over configuration space,

$$\int \psi_m^* \Psi(t = 0) dt = \sum_n c_n \int \psi_m^* \psi_n dt \quad \text{XXI-19}$$

$$\text{But } \int \psi_m^* \psi_n dt = \delta_{nm}$$

Therefore all terms except the one with $n = m$ vanish on the right hand side of XXI-19, so that

$$c_m = \int \psi_m^* \Psi(t = 0) dt \quad \text{XXI-20}$$

An additional property of the C's is derived as follows:

$$\Psi^*(t = 0) = \sum_m c_m^* \psi_m^*$$

$$\Psi^*(t = 0) \Psi(t = 0) = \sum_m \sum_n c_m^* c_n \psi_m^* \psi_n = \sum_n c_n^* c_n$$

But

$$\int_{\tau} \Psi^*(t = 0) \Psi(t = 0) d\tau = 1$$

Therefore

$$1 = \sum_n c_n^* c_n = \sum_n |c_n|^2 \quad \text{XXI-21}$$

The steps involved in determining the properties of a system in quantum mechanics are:

- 1 - Require a knowledge of system at time $t = 0$
- 2 - From (1) can find $\Psi(t = 0)$
- 3 - Solve equation $\mathcal{H} \psi_n = E_n \psi_n$
- 4 - Find c_n ($= \int \psi_n^*(t = 0) \Psi(t = 0) dt$)

5 - Find $\Psi(t)$ ($= \sum_n c_n \psi_n e^{-\frac{iE_n t}{\hbar}}$)

6 - Find properties desired at time t from $\Psi(t)$.

Signed Arthur L. Loeb
~~Arthur L. Loeb~~

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