Digital Computer Laboratory
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SUBJECT: GROUP 63 SEMINAR ON MAGNETISM, XX

To: Group 63 Staff

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Date: December 18, 1952

As Newton's laws were found insufficient to explain the motion of atomic particles, a more general law was needed. At the previous meeting we attempted to describe the steps that led to the formulation of this "new" more fundamental mechanics as introduced by Schroedinger.

We noted previously that Schroedinger used the notation of Hamilton, namely

$$H(p,q) = E \qquad\qquad (XX-1)$$

where p = generalized momentum
      q = generalized coordinate

Schroedinger started with equation XX-1, but he had the quantities operate on a function Ψ, which we shall define later. Then

$$H\,\Psi = \varepsilon\,\Psi \qquad\qquad (XX-2)$$

The script letter will be used throughout these notes to denote a mathematical operator.

From classical mechanics we recall

$$H = \sum_i \frac{p_i^2}{2m_i} + V\,(x_1\text{---},\ y_1\text{---},\ z_1\text{---}).$$

Schroedinger used this equation, but he equated the momentum p to the mathematical operator

$$p = -i\hbar\,\nabla \qquad\qquad (XX-3)$$

where $\hbar = \frac{h}{2\pi}$ ($\frac{1}{2\pi}$ x Planck's Constant)

∇ is the gradient

Then $$p^2 = -\hbar^2\nabla^2$$

where ∇^2 = Laplacian

$$\left(= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\ \text{ in Cartesian Coordinates}\right)$$

Substituting XX-3 into XX-1 for a system of one particle,

$$\mathcal{H} \quad -\frac{\hbar^2}{2m} \nabla^2 + v \tag{XX-4}$$

Schroedinger further defined the energy operator

$$\mathcal{E} = i\hbar \frac{\partial}{\partial t} \tag{XX-5}$$

Therefore, since

$$\mathcal{H}\Psi = \mathcal{E}\Psi$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v \right]\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{XX-6}$$

This is Schroedinger's equation with the terms $\mathcal{H}$ and $\mathcal{E}$ expressed in terms of the operators they represent. We see it is a partial differential equation involving a time derivative and a second space derivative of the function Ψ.

The function Ψ represents the state of a system, and if it is known, the various properties of the system may be determined. In the ideal case, the Schroedinger equation can be solved to yield the exact form of Ψ, and all properties of the system are then determinable. However, the equation usually cannot be solved exactly, and approximation methods must be used.

The location of a particle can be denoted by a position vector $\vec{r}$. In general, for three dimensional space, three independent coordinates are needed to define the vector. For example:

In cartesian coordinates

$$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}s$$

In spherical coordinates

$$\vec{r} = \hat{r}|r| + \hat{\sigma}\sigma + \hat{\varphi}\varphi$$

If a system consists of two independent particles, 6 quantities are required to determine their positions. We can use two position vectors ($\vec{r_1}$ and $\vec{r_2}$) or a single six-coordinate vector. In general, for a system of N independent particles, 3N coordinates are needed to define their positions. One can use a 3N-coordinate vector

$$\vec{r} = \vec{r}(x_1 \text{---} x_N, y_1 \text{---} y_N, s_1 \text{---} s_N)$$

We call this type of vector a configuration vector since it gives us the configuration of the total system. In our work in quantum mechanics we will be dealing with configurations.

Schroedinger's hypotheses regarding Ψ are as follows:

We know that the state of a system is dependent upon the spin vector of the system as well as the coordinates and time. Thus, if we denote $\vec{s}$ as the spin vector of the configuration,

$$\Psi = \Psi_{(\vec{r};\ \vec{s};\ t)}$$

From equation XX-6 we see that Ψ can be a complex quantity. If Ψ is multiplied by its complex conjugate Ψ^* we have the probability density of the system. It has the property that $\Psi^* \Psi \, d\tau$ is the probability that the system is in the configuration represented by the volume $d\tau$.

Thus when we integrate over all possible configurations the total probability must equal unity, so

$$\int_\tau \Psi^* \ \Psi \ d\tau = 1 \qquad\qquad\qquad (XX-7)$$

Now suppose we have a function **F**, where F represents some property of the system (e.g., momentum, position, etc.). We replace the function **F** by the proper operator $\mathcal{F}$ (e.g. momentum $\rightarrow -i\hbar\nabla$) and have the operator operate on Ψ. We then multiply by Ψ^* and integrate over the configuration space. According to Schroedinger, this yields the average value of the function **F** in the system. Expressed mathematically,

$$\bar{F} = \int \Psi^* \ \mathcal{F} \ \Psi \ dt \qquad\qquad\qquad (XX-8)$$

Depending upon the form of the operator $\mathcal{F}$ and the function Ψ, the operation of $\mathcal{F}$ on Ψ may prove to have the same effect as a multiplication. For example, if $\mathcal{F} = \dfrac{d}{dx}$ and $\Psi = e^{-mx}$

then

$$\mathcal{F}\Psi = \frac{d}{dx}\ e^{-mx} = -me^{-mx} = -m\Psi \qquad (a)$$

so that operating on Ψ with $\mathcal{F}$ only multiplied it by $-\underline{m}$. However, for the same $\mathcal{F}$ but $\Psi = \cos mx$, we see

$$\mathcal{F}\Psi = \frac{d}{dx}(\cos mx) = -m\sin mx \qquad\qquad (b)$$

and this operation is not a simple multiplication. On the other hand, if Ψ remains $\cos mx$, and $\mathcal{F}$ becomes $\dfrac{d^2}{dx^2}$,

$$\mathcal{F}\Psi = \frac{d^2}{dx^2}(\cos mx) = -m^2 \cos mx; \qquad\qquad (c)$$

thus the operator $\mathcal{F}$ has the effect on Ψ of multiplication by $-m^2$.

When the operation produces a multiplication as in examples (a) and (c) above, ψ is called an eigenfunction of the operator $\mathscr{F}$; and the value by which it is multiplied is called an eigenvalue.

In that case, on determining the average value of F, we may bring the eigenvalue outside the integral since

$$\mathscr{F}\,\Psi = F\,\Psi$$

hence
$$\bar{F} = \int \Psi^* \mathscr{F}\,\Psi\, dt$$
$$= \int \Psi^* F\,\Psi\, dt$$
$$= F\int \Psi^*\,\Psi\, dt$$
$$\bar{F} = F$$

Here the average value $\bar{F}$ is the true value. However, if ψ is not an eigenfunction of $\mathscr{F}$, we can only obtain average values.

In order to be an acceptable function, ψ must satisfy certain conditions. It must be a single valued continuous function (except at a finite number of points) and it must go to zero as the coordinates go to infinity. A more rigorous mathematical statement of the requirements is given in Eyring, Walter, and Kimball.*

In a conservative system (energy constant) ψ must be an eigenfunction of the energy operator $\mathscr{E}$:

$$\mathscr{E}\,\Psi = i\hbar\, \frac{\partial \Psi}{\partial t}$$

Solving this:

$$\frac{d\Psi}{\Psi} = \frac{-iE}{\hbar}\ dt$$

$$\ln \Psi = -\frac{iE}{\hbar}\ t + \text{Constant}$$

Therefore

$$\Psi = \psi\, e^{-\frac{iEt}{\hbar}}$$

(XX-9)

The function ψ is introduced above as a constant of integration. It must, therefore, be independent of time. However, ψ need not be a constant in space.

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* Eyring, Walter, and Kimball, Quantum Chemistry, Wiley and Sons, New York 1944 P. 26.

We see the time variation is $e^{-\frac{iE}{\hbar}t}$

$$e^{-\frac{iE}{\hbar}t} = \cos\frac{Et}{\hbar} - i\,\sin\frac{E}{\hbar}t$$

$$\frac{E}{\hbar} = \omega, \qquad \frac{2\pi E}{h} = 2\pi \nu$$

$$E = h\nu \qquad\qquad (XX-10)$$

We have thus independently arrived at Einstein's relationship of energy and frequency.

The function given in XX-9 must satisfy Schroedinger's equation; substituting the relationship XX-9 into the Schroedinger equation XX-2, we find

$$e^{-\frac{iE}{\hbar}t}\, \mathcal{H}\psi = \psi\, i\hbar \frac{\partial}{\partial t} e^{-\frac{iE}{\hbar}t}$$

$$e^{-\frac{iE}{\hbar}t}\, \mathcal{H}\psi = E\,\psi\, e^{-\frac{iE}{\hbar}t}$$

Therefore

$$\mathcal{H}\psi = E\psi \qquad\qquad (XX-11)$$

This is the time-independent Schroedinger equation. This form of the equation is of interest in conservative systems. However, it should be stressed that equation XX-11 was derived with the assumption that ψ is an eigenfunction of the operator $\mathcal{E}$, which is only true of conservative systems. Therefore, in systems in which the energy is a function of time (e.g. radiation problems) this equation cannot be used.

Signed _____
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