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UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

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Per-Olov Löwdin

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1. INTRODUCTION

In science one of the most important goals is to explain all the numerous phenomena in nature of varying character by means of a few basic principles, i.e. to reduce complexity to simplicity. Several times in history, the development of science has reached such stages that one has believed that the highest degree of simplicity has actually been achieved. Two important examples are provided by Aristotle's philosophy and Newton's mechanics, but the further development has shown that these epochs did not represent final stages but essential "plateaus" in the development of science. The natural sciences of today are essentially built on modern quantum theory and, even if the basic principles have now a higher degree of simplicity than even before, there are no real reasons for believing that one has actually reached the "final" stage. Keeping this important fact in mind, one may still find it very interesting to investigate the present "plateau" and to study how far modern quantum theory is able to explain the basic phenomena in nature.

Classical mechanics. - In order to understand the principles of modern quantum theory, it may be worthwhile to study the breakdown of classical physics and the development of the new ideas. At the end of last century, the mechanical model of the world was dominating physics, and the universe was assumed to consist of a number of particles moving with respect to each other in accordance with the laws of Newton's dynamics:

$$m_k \frac{d^2 \mathbf{r}_k}{dt^2} = \mathbf{K}_k , \tag{1}$$

where t is the time, m_k and $\mathbf{r}_k = (x_k, y_k, z_k)$ are the mass and position of particle k, respectively, whereas $\mathbf{K}_k$ is the force on this particle. The basic laws are hence second-order differential equations in time. Introducing the velocity $\mathbf{v}_k = d\mathbf{r}_k/dt$ and the momentum $\mathbf{p}_k = m_k \mathbf{v}_k$, one can also write (1) in the form:

$$\mathbf{p}_k = m_k \frac{d\mathbf{r}_k}{dt} , \qquad \frac{d\mathbf{p}_k}{dt} = \mathbf{K}_k ; \tag{2}$$

i.e. as a system of first-order equations in time. If in a given moment $t = t_0$, one knew the position and the momentum of each one of the particles :

$$\mathbf{r}_k = \mathbf{r}_k(0) \quad , \qquad \mathbf{p}_k = \mathbf{p}_k(0) \quad , \tag{3}$$

it would be possible to predict the future of the entire universe as well as its past history. This is the basis for the completely deterministic mechanical model of the physical world, which left a very small margin for man and his free will - if any margin at all.

If the system has a potential $U = U(\mathbf{r}_1, \mathbf{r}_2, \ldots)$ from which the forces may be derived so that $\mathbf{K}_k = -\operatorname{grad}_k U = -\nabla_k U$, the classical Hamiltonian takes the form

$$\mathcal{H} = \sum_k \frac{\mathbf{p}_k^2}{2m_k} + U \quad , \tag{4}$$

and the equations of motion (2) may then be written in the form

$$\frac{d\mathbf{r}_k}{dt} = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_k} \quad , \qquad \frac{d\mathbf{p}_k}{dt} = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_k} \quad , \tag{5}$$

which may be extended also to more general coordinates. The Hamiltonian $H = H(\mathbf{r}_k, \mathbf{p}_k)$ satisfies the relation $dH/dt = 0$ and is hence a constant of motion representing the total energy E of the system :

$$H = E \ . \tag{6}$$

Maxwell's equations. - During the nineteenth century, the theory of electricity and magnetism went through a rapid development leading to the establishment of Maxwell's equations:

$$\left\{ \begin{array}{ll} \operatorname{div} \mathbf{E} = 4\pi\rho \ ; & \operatorname{div} \mathbf{H} = 0 \ ; \\ \operatorname{curl} \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t} \ ; & \operatorname{curl} \mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t} \ , \end{array} \right. \tag{7}$$

where ρ and $\mathbf{j}$ are the charge and current density, respectively The force on a volume element exerted by the electromagnetic field is given by the force density:

$$k = \rho E + \frac{1}{c} j \times H \quad , \tag{8}$$

and the behaviour of a system of charged particles is then regulated by a combination of Maxwell's equations and the classical laws of motion.

The quantum postulate. - The success of this electrodynamics was enormous and of essential importance not only for the scientific but also the technical development. During these circumstances, it was rather remarkable that, at the end of the century, there was still a rather simple phenomenon to be explained, namely the temperature radiation from an ordinary black body. It was shown by Max Planck in 1900 that all the various experimental experiences could be explained from one and the same formula, if one made the rather drastic assumption that the energy of an oscillating electric particle had to be an integer multiple of a "quantum of energy" $h\nu$ proportional to the frequency ν of the particle. The proportionality factor h has been called Planck's constant and has the value $h = 6.625_2 \times 10^{-27}$ ergsec, which is an exceedingly small number from the macroscopic point of view. Planck soon realized that the quantum postulate would lead to a new way of thinking in physics and that a complete reformulation of the basic laws would be needed.

The next step in the development followed when Albert Einstein in 1905 in one and the same volume of "Annalen der Physik" published three papers in three different fields which each one represented a more or less complete turning-point in its area. The papers treated the special theory of relativity including the law of the equivalence between mass and energy, $E = mc^2$, the photoelectric effect, and the Brownian motion. In connection with the explanation of the threshold phenomenon in the photoelectric effect, Einstein assumed that the electromagnetic field was quantized and occured in the form of "wave packets" or photons having the energy $E = h\nu$, where ν is the frequency of the radiation.

Bohr's atomic model. - The success of these ideas made it likely that the quantum postulate would be of importance also in many other phenomena associated with the atomic structure of matter. It should be remembered that, for both chemists and physicists, the atom had until the end of the nineteenth century been "undividable" by definition. However, after the discovery of the radioactive decay and the transformation of one atom into another, the circumstances were changed. Thomson's discovery of the electron cathode rays in 1897 and Rutherford's results as to the scattering of alpha-particles in matter in 1911 led the latter to propose a model in which an atom consists of electrons moving around a small positively charged "nucleus" carrying the main part of the atomic mass.

The quantum postulate was introduced into this atomic model by Niels Bohr in 1913. He had discovered that an angular momentum has the same dimensions ML^2T^{-1} as Planck's quantum of action h, and he introduced the postulate that the electrons in an atom could move only in certain selected circles around the nucleus fulfilling the condition:

$$pa = n\frac{h}{2\pi}, \qquad (9)$$

where p is the momentum of the electron, a is the radius of the circle, and n = 1,2,3,... Bohr assumed that each such circle represents a "stationary state", with a specific energy, in which the electron does not emit any electromagnetic radiation and further that, if the electron jumps from one circle to another, the atom emits radiation with a frequency ν determined by Planck's law, i.e. $h\nu = E_1 - E_2$. This simple picture combined with the laws of classical mechanics:

$$\frac{e^2}{a^2} = \frac{p^2}{ma}, \qquad E = \frac{p^2}{2m} - \frac{e^2}{a}, \qquad (10)$$

where e is the fundamental charge. leads immediately to an explanation of the spectrum of the hydrogen atom, to a derivation of the famous Rydberg constant in spectroscopy, and to an understanding of many related phenomena. Bohr's discovery opened the new field of atomic structure, and its importance for the development of modern science can hardly be overestimated.

Bohr generalized later his atomic model so that it became similar to a planetary system in miniature with the electrons moving in ellipses characterized by three quantum numbers (n,l,m). In 1918 Sommerfeld studied the corrections in this model required by the special theory of relativity and could explain also the fine-structure of the hydrogen spectrum. This is a good example of a "perfect model" which still has only limited validity.

Using the three quantum numbers (n,l,m), the rules

$$\begin{aligned} n &= 1, 2, 3, 4, \ldots \\ l &= 0, 1, 2, \ldots n-1, \\ m &= l, l-1, l-2, \ldots -l+1, -l, \end{aligned} \tag{11}$$

and Pauli's exclusion principle saying that each ellips (n,l,m) could contain maximum two electrons, Bohr and his Copenhagen school reached in the beginning of the 1920's a new understanding of the periodic system of the elements which led, among other things, to the discovery of a new element (Hf). Using the simple rules that, with increasing atomic number, the ellipses are filled by one and two electrons after increasing values of first $(n + l)$ and then n, one could also explain the occurence of the groups of the transition metals and the rare earth metals which differ only in so-called "inner shells".

Bohr's atomic model was constructed for the hydrogen atom and, even if all attempts to generalize it to give a reasonable quantitative treatment of even the helium atom so far have failed, it gives apparently a good qualitative understanding of the entire periodic system.

Matter waves. - A second epoch in quantum mechanics started in 1924 with the introduction of the "matter waves" by Louis de Broglie. In his theory of the photoelectric effect, Einstein had in 1905 assumed that the electromagnetic waves were quantized in form of "wave packets" or photon having the energy $E = h\nu$, so that there existed a wave-corpuscle parallellism. Each photon has a vanishing rest mass and a relativistic mass m determined by Einstein's relation $E = mc^2$, where c is the velocity of light. Since $c = \nu\lambda$ is also the velocity of the wave packet, the photon has a momentum $p = mc$, for which one obtains the transformation

$$p = mc = \frac{mc^2}{c} = \frac{E}{c} = \frac{h\nu}{\lambda\nu} = \frac{h}{\lambda}, \tag{12}$$

where λ is the wave length of the radiation. Generalizing this idea, de Broglie assumed that the wave-corpuscle parallellism was universal, and that the frequency ν and the wave length λ of the "matter waves" were given by the same relations:

$$E = h\nu , \qquad p = h/\lambda \tag{13}$$

He showed that these relations are relativistically invariant and further that they lead to a new understanding of Bohr's quantum condition (9), since substitution of $p = h/\lambda$ into (9) gives $2\pi a = n\lambda$, i.e. a circle will be associated with a stationary state if and only if it contains an integer number of waves, so that the wave pattern is unique. In this way, de Broglie obtained an explanation of Bohr's otherwise rather arbitrary "quantum rule".

Introducing the relativistic mass m and the velocity v of the particle and using the relations $E = mc^2$ and $p = mv$, one finds that matter waves have a phase velocity $\omega = \nu\lambda = E/p = c^2/v$, which must necessarily exceed the speed of light. The phase α of a de Broglie wave travelling along an x-axis at the time t is given by the expression

$$\alpha = 2\pi \left(\frac{x}{\lambda} - \nu t \right) \tag{14}$$

For a wave packet having reciprocal wave lengths or wave numbers $k = 1/\lambda$ in the interval (k; k + dk) and frequencies in the interval $(\nu; \nu + d\nu)$, the phases are situated in the interval $(\alpha; \alpha + d\alpha)$ with $d\alpha = 2\pi (x\, dk - t\, d\nu)$. A "group" of waves is essentially characterized by the relation $d\alpha = 0$, i.e. it travels along the x-axis with a constant phase. For the "group velocity" $g = x/t$, one obtains directly

$$g = \frac{d\nu}{dk} = \frac{d(\omega/\lambda)}{d(1/\lambda)} = \omega - \lambda \frac{d\omega}{d\lambda} , \tag{15}$$

which is a classical formula used also in e.g. hydrodynamics in studying ocean waves. Using (13), one can also write it in the simple form $g = dE/dp$. From the relation $m = m_0 (1 - v^2/c^2)^{-1/2}$, where m_0 is the rest mass of the particle, follows the relativistic identity $(E/c)^2 - p^2 = m_0 c^2$ and further

$$g = \frac{dE}{dp} = \frac{pc^2}{E} = \frac{mvc^2}{mc^2} = v. \tag{16}$$

Hence the group velocity of the de Broglie waves is identical with the velocity of the particle.

Wave mechanics. In 1925 modern quantum theory was introduced independently in three different ways by Schrödinger, Heisenberg, and Dirac, respectively. In generalizing de Broglie's ideas, Schrödinger pointed out that the behaviour of waves is usually regulated by a wave equation. According to (14) and (13), the phase of a matter wave is given by the expression

$$\alpha = 2\pi(px - Et)/h \tag{17}$$

The physicists and engineers had previously been interested essentially in "real waves" of the type $\cos\alpha$ or $\sin\alpha$, but, in many fields e.g. the theory of alternating currents, it had turned out to be mathematically convenient to deal with "complex waves" according to Euler's formula $e^{i\alpha} = \cos\alpha + i\sin\alpha$ and to take the real component only at the end. Anyway, Schrödinger started his work by considering the complex wave:

$$\psi(x,t) = Ae^{i\alpha} = Ae^{\frac{2\pi i}{h}(px - Et)} \tag{18}$$

Taking the partial derivatives with respect to x and t, he obtained the relations

$$\frac{\partial\psi}{\partial x} = \frac{2\pi i}{h}p\psi, \quad \frac{\partial\psi}{\partial t} = -\frac{2\pi i}{h}E\psi, \tag{19}$$

which led him to postulate the connections

$$p \rightarrow \frac{h}{2\pi i}\frac{\partial}{\partial x}, \quad E \rightarrow -\frac{h}{2\pi i}\frac{\partial}{\partial t}, \tag{20}$$

representing physical quantities by linear operators. In order to proceed, Schrödinger started from the classical laws of motion in the Hamiltonian form (6) or (H - E) = 0 and postulated the existence of a wave equation of the form $(H - E)\psi = 0$, where the classical quantities are replaced by operators according to (20). The basic Schrödinger equation has hence the form

$$\boxed{\mathcal{H}_{op}\Psi = -\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} ,} \tag{21}$$

where H_{op} is the Hamiltonian operator obtained from the classical Hamiltonian by means of (20) or the more general relation:

$$\mathbf{p} \longrightarrow \frac{h}{2\pi i}\left(\frac{\partial}{\partial x_k}, \frac{\partial}{\partial y_k}, \frac{\partial}{\partial z_k}\right) = \frac{h}{2\pi i}\,\nabla_k , \tag{22}$$

and Ψ is the "wave function" in the configuration space $(\mathbf{r}_1, \mathbf{r}_2, \ldots)$. From (4) one obtains hence the following operator

$$\mathcal{H}_{op} = \sum_k \frac{1}{2m_k}\nabla_k^2 + U \tag{23}$$

where $\nabla_k^2 = \partial^2/\partial x_k^2 + \partial^2/\partial y_k^2 + \partial^2/\partial z_k^2$ is the Laplace operator for the particle k .

The Schrödinger equation (21) is a "diffusion equation" of a type studied also for a long time in classical physics, and it permits separation of the coordinates $\mathbf{r}_1, \mathbf{r}_2, \ldots$ from the time variable t . Putting $\Psi = \Psi(r_1, r_2, \ldots; t) = \Phi(r_1, r_2, \ldots)\, g(t)$, one obtains $[\mathcal{H}\Phi]\, g = \Phi\left[-\frac{h}{2\pi i}\partial g/\partial t\right]$ and, after division by Ψ :

$$\frac{\mathcal{H}\Phi}{\Phi} = -\frac{\frac{h}{2\pi i}\frac{dg}{dt}}{g} , \tag{24}$$

where the left-hand member depends only on the coordinates and the right-hand member only on the time variable t ; both must hence be equal to a constant E'. The function g has consequently the form $g(t) = g_0 \exp\left(-2\pi i E' t/h\right)$, whereas Φ must satisfy the differential equation

$$\mathcal{H}\Phi = E'\Phi \, , \tag{25}$$

which has the form of an eigenvalue problem. The intensity $|\Psi|^2$ of the wave was intepreted by Schrödinger as proportional to the particle density of the system in the configuration space $(x_1, x_2, x_3, \ldots)$ at the time t, and this quantity should hence be integrable over the entire space or, at least, stay finite even at infinity The differential equation (25) has certainly solutions for all values of E´ but, of all these solutions, only a few satisfy the physical boundary conditions associated with Schrödinger's interpretation of Ψ This leads to a natural quantization of the energy E´ without any integer-rules.

The solutions connected with the separability condition have the form :

$$\Psi(x_1, x_2, \ldots ; t) = \Phi(x_1, x_2, \ldots)\, g_0\, e^{-\frac{2\pi i}{h}E' t} \, , \tag{26}$$

and, for the associated intensity, one obtains

$$|\Psi(x_1, x_2, \ldots ; t)|^2 = |g_0|^2 \, |\Phi(x_1, x_2, \ldots)|^2 \, , \tag{27}$$

which implies that the particle density is independent of time and that the solutions correspond to "stationary states" in the sense of Bohr. From the Schrödinger equation (21) follows hence the existence of the stationary states provided that the eigenvalue problem (25) has solutions corresponding to the proper physical boundary conditions which apparently replace the previous "quantum conditions"

One of the most interesting aspects of the Schrödinger equation (21) is the fact that it is of first-order in the time variable t in contrast to the second-order Newton equation (1). In some way, it must instead be analogous to the classical first-order system (2) in the variables $x_1, x_2, \ldots$ and $p_1, p_2, \ldots$, and it seems likely that the complex wave function $\Psi = \Psi(x_1, x_2, \ldots ; t)$, which consists of a pair of real functions, will give information about the physical situation not only in the coordinate space $(x_1, x_2, \ldots)$ but also in the momentum space $(p_1, p_2, \ldots)$. This problem will be discussed in greater detail in the following section.

The existence of the 'matter waves" was shown experimentally in 1926 by Davison and Germer. Schrödinger showed further that his momentum operator $p = \frac{h}{2\pi i} \partial / \partial x$ satisfied the commutation relation

$$p x - x p = \frac{h}{2\pi i} , \tag{28}$$

which had basic importance in the matrix mechanics developed by Heisenberg, Born, and Jordan and in the q-number theory developed by Dirac, and that the three formulations of the new quantum theory were essentially equivalent. The time had now come for a complete reformation of the basic laws of physics and chemistry.

2. COORDINATE SPACE AND MOMENTUM SPACE; PHASE PROBLEM IN QUANTUM MECHANICS.

Fourier-transformation. - Let us start by considering a single particle in a one-dimensional space with the coordinate x. The physical situation is characterized by a complex wave function $\psi = \psi(x, t)$, in which the variable t will be temporarily supressed. Such a wave function may be resolved into harmonic waves with the wave number $k = 1/\lambda$ by means of the formulas:

$$\begin{aligned} \psi(x) &= \int_{-\infty}^{+\infty} \eta(k)\, e^{2\pi i k x}\, dk , \\ \eta(k) &= \int_{-\infty}^{+\infty} \psi(x)\, e^{-2\pi i k x}\, dx , \end{aligned} \tag{29}$$

and the functions $\psi(x)$ and $\eta(k)$ are said to be related by a Fourier transformation. According to the de Broglie relations (13), one may introduce the momentum p by the formula $p = h/\lambda = hk$ and, putting $\varphi(p) = h^{-1/2} \eta(k)$, one obtains

$$\begin{aligned} \psi(x) &= h^{-1/2} \int_{-\infty}^{+\infty} \varphi(p)\, e^{\frac{2\pi i}{h} p x}\, dp , \\ \varphi(p) &= h^{-1/2} \int_{-\infty}^{+\infty} \psi(x)\, e^{-\frac{2\pi i}{h} p x}\, dx \end{aligned} \tag{30}$$

It is evident that $\psi(x)$ and $\varphi(p)$ in these reciprocal formulas are completely equivalent and, since $|\psi(x)|^2$ is assumed to be proportional to the particle or "probability" density in the x-space, it seems natural to interpret $|\varphi(p)|^2$ as proportional to the probability density in the p-space.

From the Fourier transformation (30) follows immediately

$$\int_{-\infty}^{+\infty} |\varphi(p)|^2 dp = \int_{-\infty}^{+\infty} |\psi(x)|^2 dx \,, \tag{31}$$

i.e. the normalization integrals in the x-space and the p-space are the same. In the following, we will assume that these quantities are equal to unity. The average position x of the particle is then given by the expression

$$\overline{x} = \int_{-\infty}^{+\infty} x\, |\psi|^2 dx = \int_{-\infty}^{+\infty} \psi^* x\, \psi \, dx \,, \tag{32}$$

and, for an arbitrary function f(x), one has similarly

$$\overline{f(x)} = \int_{-\infty}^{+\infty} f(x) |\psi|^2 dx = \int_{-\infty}^{+\infty} \psi^* f(x) \psi \, dx \,. \tag{33}$$

The probability that the particle has a momentum in the interval (p, p + dp) is given by the quantity $|\varphi(p)|^2 dp$, and the average momentum p is defined by the relation:

$$\overline{p} = \int_{-\infty}^{+\infty} p\, |\varphi(p)|^2 dp = \int_{-\infty}^{+\infty} \varphi^* p\, \varphi \, dp \,. \tag{34}$$

From the Fourier transformation (30) follows :

$$\frac{\partial \psi(x)}{\partial x} = h^{-1/2} \int_{-\infty}^{+\infty} \frac{2\pi i}{h}\, p\, \varphi(p)\, e^{\frac{2\pi i}{h} px} \, dp \,, \tag{35}$$

and further

$$\int_{-\infty}^{+\infty} \psi^*(x) \frac{h}{2\pi i} \frac{\partial \psi(x)}{\partial x}\, dx = h^{-1/2} \int_{-\infty}^{+\infty} p\, \varphi(p)\, dp \int_{-\infty}^{+\infty} \psi^*(x)\, e^{\frac{2\pi i}{h} px}\, dx =$$

$$= \int_{-\infty}^{+\infty} \varphi^*(p)\, p\, \varphi(p)\, dp = \overline{p} . \qquad (36)$$

This gives the formula:

$$\overline{p} = \int_{-\infty}^{+\infty} \psi^* \left(\frac{h}{2\pi i} \frac{\partial}{\partial x} \right) \psi \, dx , \qquad (37)$$

which implies that p may be calculated as an average value in the x-space according to (33), provided that p is replaced by an operator $(h/2\pi i)\, \partial/\partial x$ in agreement with (20). For any polynomial function f (p) , one finds similarly

$$\overline{f(p)} = \int_{-\infty}^{+\infty} \psi^* f\left(\frac{h}{2\pi i} \frac{\partial}{\partial x} \right) \psi \, dx , \qquad (38)$$

By using the same technique, one can further show that any average value $\overline{f(x)}$ in the x-space may be evaluated in the p-space by using the formula

$$\overline{f(x)} = \int_{-\infty}^{+\infty} \varphi^*(p)\, f\left(-\frac{h}{2\pi i} \frac{\partial}{\partial p} \right) \varphi(p)\, dp , \qquad (39)$$

which implies that the coordinate x in the momentum space may be represented by the operator

$$x \longrightarrow -\frac{h}{2\pi i} \frac{\partial}{\partial p} \qquad (40)$$

in analogy to the first relation in (20).

Using the operator relations, one may finally define the average value of a polynomial function f (x; p) of both variables x and p , and it turns out that it is irrelevant if the evaluation is carried out in the x-space or in the p-space as long as one strictly observes the order of all factors and the validity of the commutation relation (28).

Scalar products and adjoint operators. - If F is a linear operator in the symbols x and p , one defines finally its expectation value in the physical situation characterized by the normalized wave function ψ by the relation

$$\overline{F} = \int_{-\infty}^{+\infty} \psi^* F_{op} \psi \, dx , \tag{41}$$

For the sake of brevity, we will in the following use the Dirac bracket symbol for the "scalar product" of two wave functions ψ_1 and ψ_2 considered as "vectors":

$$\langle \psi_1 | \psi_2 \rangle = \int_{-\infty}^{+\infty} \psi_1^* \psi_2 \, dx , \tag{42}$$

and remember that the same quantity by the mathematicians are denoted by (ψ_2, ψ_1), so that one has the translation $(\psi_2, \psi_1) = \langle \psi_1 | \psi_2 \rangle$.

The quantity $\| \psi \| = \langle \psi | \psi \rangle^{1/2}$ is said to represent the length of the vector ψ , and one has $\| \psi \| \geq 0$. The normalization implies $\| \psi \| = 1$. By considering the discriminant of the quadratic form $\| \psi_1 + \mu \psi_2 \|^2 \geq 0$ in the real variable μ , one can easily prove Schwarz's inequality

$$| \langle \psi_1 | \psi_2 \rangle |^2 \leq \langle \psi_1 | \psi_1 \rangle \langle \psi_2 | \psi_2 \rangle , \tag{43}$$

Instead of (41) , one can now write

$$\overline{F} = \langle \psi | F \psi \rangle = \langle \psi | F | \psi \rangle , \tag{44}$$

where , in the last form, one has introduced a " dummy" bar for the sake of symmetry. A wave function ψ for which $\| F\psi \|$ exists is said to belong to the domain D_F of the operator F.

Expectation values are in general complex quantities. Two operators F and $F^\dagger$ with the same domain which always have complex conjugate expectation values, so that

$$\langle \psi | F^\dagger | \psi \rangle = \langle \psi | F | \psi \rangle^* \tag{45}$$

for all ψ in D_F , are said to form a pair of adjoint operators. From the definition (45) , one obtains after some simple algebraic manipulations the "turn-over rule"

$$\langle \psi_1 | F^\dagger | \psi_2 \rangle = \langle \psi_2 | F | \psi_1 \rangle^* = \\ = \langle F \psi_1 | \psi_2 \rangle \quad , \tag{46}$$

provided that both ψ_1 and ψ_2 belong to the domain of F. By means of (46), it is then easy to prove the two basic rules $(F_1 + F_2)^\dagger = F_1^\dagger + F_2^\dagger$ and $(F_1 F_2)^\dagger = F_2^\dagger F_1^\dagger$.

Of particular importance in physics are such operators A as always have real expectation values. In such a case, the operator is identical with its adjoint so that $A^\dagger = A$, and such an operator is said to be self-adjoint or hermitean. It is easily shown that both the position x and the momentum p are represented by hermitean operators and, by using the rules for forming the adjoint, one can then test whether an operator $F = F(x,p)$ is self-adjoint or not.

The properties of the scalar product and the concept of adjoint and self-adjoint operators are here only briefly reviewed, and for a more complete treatment we will instead refer to the many special papers on these subjects.$^{1)}$

Uncertainty relations. - The accuracy of a simultaneous measurement of the position x and the momentum p of a particle in a physical situation characterized by the wave function $\psi(x)$ in x-space or its analog $\varphi(p)$ in p-space may be characterized by the two quantities Δx and Δp defined by the relations

$$(\Delta x)^2 = \int_{-\infty}^{+\infty} (x - \bar{x})^2 |\psi|^2 dx \, , \tag{47}$$

$$(\Delta p)^2 = \int_{-\infty}^{+\infty} (p - \bar{p})^2 |\varphi|^2 dx \tag{48}$$

They give a measure of the quadratic deviation of x and p from the average values $\bar{x}$ and $\bar{p}$, respectively.

Let us now consider the integral

$$I \equiv \int_{-\infty}^{+\infty} |(x-\bar{x})\psi + i\mu(p_{op}-\bar{p})\psi|^2 dx \geq 0 , \qquad (49)$$

which is positive for any value of the real parameter μ By using (20), partial integration, and the commutation relation (28), one finds the transformation

$$I = (\Delta x)^2 - \frac{h}{2\pi}\mu + \mu^2(\Delta p)^2 \geq 0 , \qquad (50)$$

This is a quadratic form in μ which is never negative, and its discriminant $D = (h/2\pi)^2 - 4(\Delta x)^2(\Delta p)^2$ is hence always negative: $D \leq 0$. This gives the inequality

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} \qquad (51)$$

which is the famous Heisenberg's uncertainty relation for the simultaneous measurement of the position x and the momentum p of a particle.

Let us now consider two general physical quantities represented by the self-adjoint operators A and B having the expectation values $\bar{A} = \langle\psi|A|\psi\rangle$ and $\bar{B} = \langle\psi|B|\psi\rangle$, and the "uncertainties" or widths

$$\begin{aligned} \Delta A &= \|(A-\bar{A})\psi\| , \\ \Delta B &= \|(B-\bar{B})\psi\| , \end{aligned} \qquad (52)$$

respectively. We note that $\Delta A = 0$, if and only if $(A - \bar{A})\psi = 0$,i.e. if ψ is a proper eigenfunction to the operator A. By using Schwarz's inequality (43) and the turn-over rule (46), one obtains directly

$$\begin{aligned} \Delta A \cdot \Delta B &\doteq \|(A-\bar{A})\psi\| \cdot \|(B-\bar{B})\psi\| \geq \\ &\geq |\langle (A-\bar{A})\psi | (B-\bar{B})\psi\rangle| \geq \\ &\geq |\Im\langle (A-\bar{A})\psi | (B-\bar{B})\psi\rangle| = \\ &= \frac{1}{2}|\langle (A-\bar{A})\psi|(B-\bar{B})\psi\rangle - \langle (B-\bar{B})\psi|(A-\bar{A})\psi\rangle| = \\ &= \frac{1}{2}|\langle A\psi|B\psi\rangle - \langle B\psi|A\psi\rangle| = \\ &= \frac{1}{2}|\langle\psi|AB-BA|\psi\rangle| , \end{aligned} \qquad (53)$$

which leads to the general uncertainty relation for any pair of operators A and B:

$$\Delta A \cdot \Delta B \geq \frac{1}{2} \left| \overline{(AB-BA)} \right| , \tag{54}$$

of which (51) is a special case. In quantum mechanics, one can hence not expect that two quantities should be simultaneously measurable unless the associated operators commute, so that AB = BA. However, even if the operators do not commute, there may exist special situations in which A and B are simultaneously measurable, provided that the expectation value of the commutator (AB-BA) vanishes in these situations.

Generalizations to several variables. - In this section, we have so far considered only a one-dimensional system, but it is now easy to generalize the results to three-dimensional systems and to several variables to treat a many-particle system in a configuration space having the composite position vector $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N)$ and the composite momentum vector $\mathbf{P} = (\mathbf{p}_1, \mathbf{p}_2, \dots \mathbf{p}_N)$. The Fourier transformation of the wave function $\Psi = \Psi(\mathbf{R}, t)$ is obtained by repeated use of (30) for each one of the $3N$ variables leading to the formula :

$$\begin{aligned} \Psi(\mathbf{R},t) &= h^{-3N/2} \int_{-\infty}^{+\infty} \Phi(\mathbf{P},t)\, e^{\frac{2\pi i}{h}\mathbf{R}\cdot\mathbf{P}} (d\mathbf{P}) \\ \Phi(\mathbf{P},t) &= h^{-3N/2} \int_{-\infty}^{+\infty} \Psi(\mathbf{R},t)\, e^{-\frac{2\pi i}{h}\mathbf{R}\cdot\mathbf{P}} (d\mathbf{R}) \end{aligned} \tag{55}$$

where

$$\begin{aligned} \mathbf{R}\cdot\mathbf{P} &= \sum_{k=1}^{N} \mathbf{r}_k \cdot \mathbf{p}_k , \\ (d\mathbf{R}) &= (d\mathbf{r}_1)(d\mathbf{r}_2)\dots(d\mathbf{r}_N) . \\ (d\mathbf{P}) &= (d\mathbf{p}_1)(d\mathbf{p}_2)\dots(d\mathbf{p}_N) . \end{aligned} \tag{56}$$

In analogy to (42), the scalar product is now defined by the relation

$$\langle \Psi_1 | \Psi_2 \rangle = \int_{-\infty}^{+\infty} \Psi_1^*(\mathbf{R},t)\, \Psi_2(\mathbf{R},t)\, (d\mathbf{R}) \tag{57}$$

where the single integral sign indicates a $3N$-dimensional integration over the entire position space. All the previous results about expectation values are now easily generalized to many-particle systems.

Phase problem in quantum mechanics. - After this preliminary discussion of the relation between the position space and momentum space, it is easier to compare the bases for classical physics and quantum mechanics. It has previously been pointed out that the Schrödinger equation (21) is a first-order differential equation in time for a complex function $\Psi = \Psi(\mathbf{R}, t)$ which depends on the position coordinate $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ alone and the time t, whereas the classical analog (2) or (5) is a system of first-order equations dealing with both $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ and $\mathbf{P} = (\mathbf{p}_1, \mathbf{p}_2, \cdots \mathbf{p}_N)$. The physical situation in the position space is fully characterized by the probability density $|\Psi(\mathbf{R}, t)|^2$, but it is clear that, at the same time, the wave function $\Psi(\mathbf{R}, t)$ must contain information about the physical situation in the momentum space. This is apparently achieved by the complex character of Ψ, i.e. by the fact that it contains two real functions, for instance, the absolute value $|\Psi|$ and the "phase" arg Ψ. This "pair" character of the wave function permits transformations between different reference scheme, and a typical example is provided by the Fourier transformation (55) which connects the $\mathbf{R}$-space with the $\mathbf{P}$-space according to the following diagram

$$\begin{tikzcd}
& \text{Position space} & & \text{Momentum space} \\
\text{Wave functions:} & \Psi(\mathbf{R},t) \arrow[rr, leftrightarrow, "\text{Fourier transformation}"] \arrow[d] & & \Phi(\mathbf{P},t) \arrow[d] \\
\text{Probabilities:} & |\Psi(\mathbf{R},t)|^2 \arrow[rr, dash, "\text{Inequalities}"'] & & |\Phi(\mathbf{P},t)|^2
\end{tikzcd} \qquad (58)$$

It should be observed that, even if the wave functions Ψ and Φ are directly and uniquely connected, this is not true for the corresponding probability densities, $|\Psi|^2$ and $|\Phi|^2$, which are interrelated only through certain inequalities of the type Heisenberg's uncertainty relation (51). Since one can only measure probability distributions, one has the fundamental problem how wave functions can be determined experimentally, i.e. how one can calculate the wave function $\Psi(\mathbf{R},t)$ - or the equivalent function $\Phi(\mathbf{P},t)$ - from two compatible distributions $|\Psi(\mathbf{R},t)|^2$ and $|\Phi(\mathbf{P},t)|^2$. This important problem was once stated by Pauli$^{2)}$, but it does not seem to have been fully solved. One can also ask how one can measure the "phase" of the wave function, i.e. the quantity arg Ψ, in a uniquely defined physical situation? We note that the classical initial condition (3), i.e. $\mathbf{R}=\mathbf{R}(0)$, $\mathbf{P}=\mathbf{P}(0)$, for $t = t_0$, in quantum mechanics correspond to the knowledge of the complex wave function $\Psi=\Psi_0(\mathbf{R})$ for $t = t_0$.

In many situations in physics, e.g. in the treatment of stationary states with real Hamiltonians, the eigenfunctions Ψ turn out to be real, and the question is whether this means any loss of information. The answer is no, since the Fourier transformation (55) is still valid and leads to uniquely defined momentum functions Φ. However, since $\Psi^*=\Psi$, the second relation (55) gives $\Phi^*(\mathbf{P})=\Phi(-\mathbf{P})$, and vice versa :

$$\Psi^*(\mathbf{R}) = \Psi(\mathbf{R}) \tag{59}$$

$$\Phi^*(\mathbf{P}) = \Phi(-\mathbf{P}) , \tag{60}$$

These relations show that, for real wave functions, the probability distribution in momentum space is necessarily inversion symmetric around origin, i.e. $|\Phi(-\mathbf{P})|^2 = |\Phi(\mathbf{P})|^2$. One immediate consequence of this is, of course,

$$\overline{\mathbf{P}} = 0 , \tag{61}$$

showing that the average momentum is vanishing. The use of real wave functions has thus important physical consequences and should, by no means, be considered as a matter of convenience. In connection with scattering problems and particle beams, one should observe the importance of the plane wave (18) and the de Broglie phase (17).

The phase problem is well known from many experimental fields involving radiation, as e.g. x-ray crystallography or laser and maser technique, and it is probably of still greater importance than is now realized. In this connection, it is often convenient to distinguish between coherent and incoherent phenomena, depending on whether the relative phase differences involved are essential or not.

Let us consider a wave function $\Psi = \Psi_1 + \Psi_2$ which is a superposition of two terms, Ψ_1 and Ψ_2. For the associated probability density, one has

$$|\Psi|^2 = |\Psi_1|^2 + |\Psi_2|^2 + 2\,\mathrm{Re}\{\Psi_1^* \Psi_2\}, \qquad (62)$$

which means that, in coherent phenomena, the probabilities are usually not additive. The last term is called the interference term and, as a typical example of coherent superposition, one can mention the diffraction patterns of electromagnetic waves in gratings etc. In quantum chemistry, a typical example of coherent superposition of wave patterns is offered by the molecular-orbital theory of the homopolar bond (e.g. the H_2-molecule) in which the bonding orbital (a + b) is the sum of the atomic orbitals involved, whereas the antibonding orbital has the form (a - b). Even the change of sign of the π -orbital in conjugated systems under reflection in the molecular plane is a typical phase effect.

As a contrast to the coherent phenomena, one may consider an assembly of similar systems having different phases. If the average value of the interference term in (62) vanishes over the assembly, one obtains

$$\widetilde{|\Psi|^2} = \widetilde{|\Psi_1|^2} + \widetilde{|\Psi_2|^2}, \qquad (63)$$

showing that even the probabilities in such a case become additive. Here the symbol $\sim$ indicates the formation of an average over the entire assembly. The assumption of "random phases" is of particular importance in treating the so-called transition probabilities, and we will return to these problems below.

3. SCHRÖDINGER EQUATION

Superposition Principle. - A basic assumption about the Hamiltonian H in the Schrödinger equation (21) is that it is a linear operator satisfying the relations

$$\mathcal{H}(\Psi_1+\Psi_2)=\mathcal{H}\Psi_1+\mathcal{H}\Psi_2,$$
$$\mathcal{H}(\alpha\Psi)=\alpha\mathcal{H}\Psi, \tag{64}$$

where α is a complex constant. This leads to an important consequence for the solutions to (21) known as the superposition principle, which says that if $\Psi_1(t)$ and $\Psi_2(t)$ are two solutions corresponding to the initial function $\Psi_1(0)$ and $\Psi_2(0)$ at $t = 0$, then

$$\Psi(t)=\Psi_1(t)+\Psi_2(t) \tag{65}$$

is another solution corresponding to the initial function $\Psi(0)=\Psi_1(0)+\Psi_2(0)$. The proof follows immediately from (21) and (64). The superposition principle emphasizes a very important aspect of modern quantum mechanics, and Dirac[3)] has chosen it as the fundamental introductory principle in his book. It is essential for the interference phenomena connected with the basic properties of the "matter waves", and it will be further discussed below.

Continuity equation. - Let us start by considering a single particle with the charge e in a physical situation characterized by the wave function $\Psi=\Psi(\mathbf{r},t)$. In Schrödinger's interpretation of quantum mechanics, the quantity $\rho=e|\Psi|^2$ represents the charge density, whereas, in Born's interpretation, the quantity $|\psi|^2$ represents the probability density. In both interpretations, it seems natural to require that the quantity $|\Psi(\mathbf{r},t)|^2$ varies continuously with position and time and that, in analogy with hydrodynamics, there exists a continuity equation of the form :

$$\frac{\partial|\Psi|^2}{\partial t}+\operatorname{div}\mathbf{s}=0, \tag{66}$$

where $\mathbf{s}$ is said to be the probability density current. From the

Schrödinger equation and its complex conjugate:

$$\begin{aligned} -\frac{h}{2\pi i}\frac{\partial\Psi}{\partial t} &= \mathcal{H}\Psi, \\ +\frac{h}{2\pi i}\frac{\partial\Psi^*}{\partial t} &= (\mathcal{H}\Psi)^* \end{aligned} \tag{67}$$

follows immediately

$$\begin{aligned} \frac{\partial|\Psi|^2}{\partial t} &= \frac{\partial\Psi^*}{\partial t}\Psi + \Psi^*\frac{\partial\Psi}{\partial t} = \\ &= \frac{2\pi i}{h}\left\{\Psi(\mathcal{H}\Psi)^* - \Psi^*(\mathcal{H}\Psi)\right\}, \end{aligned} \tag{68}$$

and the condition that the right-hand member should be a " divergence" puts a rather severe constraint on the form of the Hamiltonian H.

In the case when the particle moves under the influence of a potential $U = U(\mathbf{r})$, the Hamiltonian has the form $H = (p^2/2m) + U$ and, from (68), one obtains particularly

$$\frac{\partial|\Psi|^2}{\partial t} = -\frac{h}{4\pi i m}\,\mathrm{div}\,(\Psi^*\,\mathrm{grad}\,\Psi - \Psi\,\mathrm{grad}\,\Psi^*), \tag{69}$$

showing that the continuity requirement is fulfilled and that the probability density current $\mathbf{s}$ has the form

$$\begin{aligned} \mathbf{s} &= \frac{h}{4\pi i m}(\Psi^*\,\mathrm{grad}\,\Psi - \Psi\,\mathrm{grad}\,\Psi^*) = \\ &= \frac{1}{2m}\left\{\Psi^*\mathbf{p}_{op}\Psi + \Psi(\mathbf{p}_{op}\Psi)^*\right\}. \end{aligned} \tag{70}$$

If one instead uses Schrödinger's interpretation, the quantity $\mathbf{j} = e\mathbf{s}$ represents the charge density current. In both cases, the continuity equation is interpreted in the same way as in hydrodynamics, and we note particularly the relation:

$$\frac{\partial}{\partial t}\int_V |\Psi|^2 dv = -\int_F \mathbf{s}\cdot\mathbf{n}\, dF, \tag{71}$$

where V is an arbitrary volume enclosed within the surface F with the outer normal $\mathbf{n}$. If the surface is put at infinity, one obtains

$$\frac{\partial}{\partial t}\int |\Psi|^2 \, d\omega = 0 \quad , \tag{72}$$

showing that the normalization integral $\langle\psi|\psi\rangle$ over the entire volume is independent of time. Analogous discussions may also be carried out for many-particle systems.

Heisenberg's equation of motion. - Let us now consider an arbitrary many-particle system having the wave function $\Psi = \Psi(\mathbf{R}, t)$, where $\mathbf{R} = (r_1, r_2, \ldots r_N)$, and let F be a linear operator representing a physical or chemical quantity. Using the notations (42) and (44) , we will now study the quantity

$$\langle \Psi_1 | F | \Psi_2 \rangle = \int \Psi_1^* F \Psi_2 \, (d\mathbf{R}) \ , \tag{73}$$

where Ψ_1 and Ψ_2 are wave functions taken at the same time The "matrix element" (73) is hence also a function of time, and, by using the Schrödinger equation (21) and its complex conjugate together with the "turn-over rule" (46) , one obtains

$$\begin{aligned} \frac{d}{dt}\langle \Psi_1 | F | \Psi_2 \rangle &= \\ &= \left\langle \frac{\partial \Psi_1}{\partial t} \right| F \left| \Psi_2 \right\rangle + \left\langle \Psi_1 \right| F \left| \frac{\partial \Psi_2}{\partial t} \right\rangle + \left\langle \Psi_1 \left| \frac{\partial F}{\partial t} \right| \Psi_2 \right\rangle = \\ &= \frac{2\pi i}{h} \langle \mathcal{H}\Psi_1 | F | \Psi_2 \rangle - \frac{2\pi i}{h} \langle \Psi_1 | F | \mathcal{H}\Psi_2 \rangle + \left\langle \Psi_1 \left| \frac{\partial F}{\partial t} \right| \Psi_2 \right\rangle = \\ &= \left\langle \Psi_1 \left| \frac{2\pi i}{h}(\mathcal{H}^\dagger F - F\mathcal{H}) + \frac{\partial F}{\partial t} \right| \Psi_2 \right\rangle \ , \end{aligned} \tag{74}$$

which is often called Heisenberg's law of motion. Putting F = 1 , one gets the special result that all scalar products $\langle \Psi_1 | \Psi_2 \rangle$ are independent of time, if and only if $H^\dagger = H$, i.e. H is self-adjoint or hermitean:

$$\frac{d}{dt}\langle \Psi_1 | \Psi_2 \rangle = \frac{2\pi i}{h} \langle \Psi_1 | \mathcal{H}^\dagger - \mathcal{H} | \Psi_2 \rangle \tag{75}$$

We note that the condition $H^{\dagger}=H$ is related to but somewhat weaker than the continuity requirement discussed in the previous section. In the following , we will always assume that the Hamiltonian is self-adjoint:

$$H^{\dagger} = H \tag{76}$$

This is also consistent with the requirement that H is the "energy operator" and that $\overline{H}$ always should be real.

Assuming the normalization $\langle \Psi | \Psi \rangle = 1$, we will now study the time variation of the expectation value F of the operator F in the physical situation characterized by the wave function Ψ :

$$\overline{F} = \langle \Psi | F | \Psi \rangle , \tag{77}$$

Putting $\Psi_1 = \Psi_2 = \Psi$ into (74), one obtains particularly

$$\frac{d\overline{F}}{dt} = \frac{2\pi i}{h} \overline{(\mathcal{H}F - F\mathcal{H})} + \overline{\frac{\partial F}{\partial t}} , \tag{78}$$

which is the law of motion in Heisenberg's matrix mechanics.

Ehrenfest's relations. - Let us now assume that the system has a potential $U = U(r_1, r_2, \ldots r_N)$ and a Hamiltonian of the form (23):

$$\mathcal{H} = \sum_k \frac{p_k^2}{2m_k} + U \tag{79}$$

The operator $\mathbf{K}_k = -\operatorname{grad}_k U = -\nabla_k U$ corresponds to the classical force on particle k and is called the "force operator" . From commutation relations of the type (28) follows further:

$$\begin{aligned} \mathcal{H} r_k - r_k \mathcal{H} &= \frac{h}{2\pi i} \frac{p_k}{m_k} , \\ \mathcal{H} p_k - p_k \mathcal{H} &= \frac{h}{2\pi i} \mathbf{K}_k \end{aligned} \tag{80}$$

Putting $F = r_k$ and $F = p_k$ into (78) and using (80), one obtains

$$\left\{ \begin{aligned} \frac{d\overline{r}_k}{dt} &= \frac{1}{m_k} \overline{p}_k , \\ \frac{d\overline{p}_k}{dt} &= \overline{\mathbf{K}}_k , \end{aligned} \right. \tag{81}$$

which are known as Ehrenfest's relations. The formulas for the expectation values are closely analogous to the classical laws of motion (2), and one may wonder whether the "center" of a wave packet moves like a classical particle. Substitution of the first relation (81) into the second gives

$$m_k \frac{d^2 \overline{r_k}}{dt^2} = \overline{\mathbf{K}_k} \tag{82}$$

in close analogy to (1), but we note that the "center" represented by the average position vector $\overline{r_k}$ moves like a classical particle, if and only if

$$\overline{\mathbf{K}}_k = \mathbf{K}_k(\overline{r}_k) \tag{83}$$

This occurs only for forces which are linear in the positions, i.e. for potentials U which are quadratic in the same quantities. This implies that, in a harmonic oscillator field, the center of a quantum-mechanical wave packet moves as a classical particle. However, in general, one has $\overline{\mathbf{K}_k} \neq \mathbf{K}_k(\overline{r_k})$, and the center of the wave packet moves in a way which is characteristic for the quantum-mechanical problem.

We note particularly that, for the <u>stationary states</u> defined by the relations (25) and (26), all expectation values $\overline{r_k}$ and $\overline{\mathbf{p}_k}$ are independent of time. Since the associated time derivatives are vanishing, one obtains from (81) the relations

$$\overline{\mathbf{p}_k} = 0\,, \qquad \overline{\mathbf{K}_k} = 0\,, \tag{84}$$

showing that the average momentum and the average force are zero for these states. Such general relations are often very useful.

As an example, we will consider a single particle in one dimension with the position coordinate x. The kinetic energy has the form $T = p^2/2m$ and, according to (48), one obtains for the square of the width Δp in a stationary state :

$$(\Delta p)^2 = \overline{p^2} - (\overline{p})^2 = \overline{p^2} = 2m\overline{T}\,. \tag{85}$$

The uncertainty relation (51) takes then the form $\Delta x \cdot (2m\overline{T})^{1/2} \geq h/4\pi$ or :

$$\overline{T} \geq \frac{h^2}{32\pi^2 m (\Delta x)^2} , \tag{86}$$

showing an important connection between the kinetic energy and the linear dimension Δx of the system. Since the kinetic energy is related to the total energy through the virial theorem 4), one obtains information about the system as to important orders of magnitude which sometimes are remarkably exact. For a three-dimensional isotropic system, one has instead $(\Delta p)^2 = 2m\,\overline{T}/3$ and

$$\overline{T} \geq \frac{9h^2}{32\pi^2 m \overline{r^2}} , \tag{87}$$

etc. It is interesting to study how close these relations are fulfilled for the ground state of simple quantum-mechanical systems, as the harmonic oscillator or the hydrogen atom, and to investigate the modifications required to treat also excited states.

Let finally F be an arbitrary linear operator which does not contain the time t explicitly. For a stationary state, the expectation value F is then independent of time and, according to (78) , one has the relation

$$\overline{(\mathcal{H}F - F\mathcal{H})} = 0 , \tag{88}$$

which is a generalization of (84) . For, convenient choices of F, one obtains the virial theorem and many other interesting consequences. 5)

Time-reversal. - It is a characteristic feature of the classical law of motion (1) in Newton's mechanics that it is invariant against reversal of the time axis:

$$t' = -t \tag{89}$$

If one takes a movie of a system of classical particles and later runs the movie "backwards", the motions of the particles are still in accordance with the laws of dynamics and make sense. This does not apply to movies in general which usually become absurd when run backwards, since everything seems to be in conflict with both "common sense" and the laws of nature. Physical laws which are invariant against time-reversal are often called primary laws, in contrast to such laws as require a definite time direction which are called secondary laws.

Let us consider the classical laws of motion in greater detail in the form (2) or

$$\mathbf{p}_k = m_k \frac{d\mathbf{r}_k}{dt}, \quad \frac{d\mathbf{p}_k}{dt} = - \operatorname{grad}_k U, \tag{90}$$

with the initial condition $\mathbf{r}_k = \mathbf{r}_k(0)$, $\mathbf{p}_k = \mathbf{p}_k(0)$ for $t = 0$. Putting t' = -t, one finds that one has also the reverse solution:

$$\mathbf{r}'_k(t') = \mathbf{r}_k(-t), \qquad \mathbf{p}'_k(t') = -\mathbf{p}_k(-t) \tag{91}$$

corresponding to the initial condition $\mathbf{r}'_k = \mathbf{r}_k(0)$, $\mathbf{p}'_k(0) = -\mathbf{p}_k(0)$ for $t = 0$. We note particularly that all the momenta have reverse direction after the time-reversal, but the energy (4) of the system stays the same.

Even in quantum mechanics, the transformation (89) is of fundamental importance. The physical situation is now described by a wave function $\Psi = \Psi(\mathbf{R}, t)$ which is a function of t and the coordinates $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ alone. In order to study the situation in momentum space $\mathbf{P} = (\mathbf{p}_1, \mathbf{p}_2, \ldots \mathbf{p}_N)$, one should consider the Fourier-transformation (55) which defines the associated wave function $\Phi = \Phi(\mathbf{P}, t)$ in momentum space. By taking the conjugate complex, one obtains directly the connections

$$\begin{aligned} \Psi(\mathbf{R}, t) &\longleftrightarrow \Phi(\mathbf{P}, t), \\ \Psi^*(\mathbf{R}, t) &\longleftrightarrow \Phi^*(-\mathbf{P}, t), \end{aligned} \tag{92}$$

showing that this operation also leads to a reversal of the directions of all the momenta; compare (59) and (60).

Let us now consider the Hamiltonian (23) which corresponds to the classical case with a potential U. This Hamiltonian is not only self-adjoint $(\mathcal{H}^\dagger = \mathcal{H})$ but even real $(\mathcal{H}^* = \mathcal{H})$ which means that it stays the same when i is replaced by - i. From the Schrödinger equation (21) and its complex conjugate, one obtains

$$\mathcal{H}_{op}\Psi = -\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t}, \qquad (93)$$

$$\mathcal{H}_{op}\Psi^* = +\frac{h}{2\pi i}\frac{\partial \Psi^*}{\partial t}$$

If $\Psi = \Psi(\mathbf{R}, t)$ is a solution to the first equation corresponding to the initial condition $\Psi = \Psi_0$ for t = 0, one finds from the second equation by putting t' = - t that one has also the solution

$$\Psi'(\mathbf{R}, t') = \Psi^*(\mathbf{R}, -t) \qquad (94)$$

corresponding to the initial condition $\Psi' = \Psi^*_0$ for t = 0. Relation (94) is the quantum-mechanical anologue to the classical formula (91), and it shows that the Schrödinger equation for real Hamiltonians is invariant against time-reversal, i.e. it is a primary physical law.

4. SCHRÖDINGER EQUATION FOR PARTICLES IN ELECTROMAGNETIC FIELD

Electromagnetic potentials. - Maxwell's equations (7) form also in quantum mechanics the basis for the treatment of all electromagnetic phenomena. Let us start our brief review by introducing the electromagnetic potentials ϕ and $\mathbf{A}$

From the equation $\operatorname{div} \mathbf{H} = 0$ follows the existence of a vector field $\mathbf{A} = \mathbf{A}(x, y, z, t)$ such that $\mathbf{H} = \operatorname{curl} \mathbf{A}$. From the equation $\operatorname{curl} \mathbf{E} + (1/c)\partial \mathbf{H}/\partial t = \operatorname{curl}\{\mathbf{E} + (1/c)\partial \mathbf{A}/\partial t\} = 0$ follows further the existence of a scalar field $\Phi = \Phi(x, y, z, t)$ such that $\mathbf{E} + (1/c)\partial \mathbf{A}/\partial t = -\operatorname{grad} \Phi$. Hence one has the relations

$$\left\{\begin{aligned} \mathbf{H} &= \operatorname{curl} \mathbf{A}, \\ \mathbf{E} &= -\operatorname{grad} \Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \end{aligned}\right. \tag{95}$$

which define the field strengths $\mathbf{E}$ and $\mathbf{H}$ in terms of the scalar potential Φ and the vector potential $\mathbf{A}$. It should be observed that the potentials Φ and $\mathbf{A}$ are auxiliary quantities which are not directly physically measurable. For our discussion, it is convenient to introduce the notation

$$S = \operatorname{div} \mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t}, \tag{96}$$

where S is a four-dimensional scalar.

Substitution of the expressions (95) into the Maxwell equations $\operatorname{div} \mathbf{E} = 4\pi\rho$ and $\operatorname{curl} \mathbf{H} = (4\pi/c)\,\mathbf{j} + (1/c)\partial \mathbf{E}/\partial t$ and using the fact that, in cartesian coordinates, $\operatorname{div}\operatorname{grad} = \nabla^2$ and $\operatorname{curl}\operatorname{curl} = -\nabla^2 + \operatorname{grad}\operatorname{div}$, gives immediately:

$$\begin{aligned} \Box \Phi + \frac{1}{c}\frac{\partial S}{\partial t} &= -4\pi\rho; \\ \Box \mathbf{A} - \operatorname{grad} S &= -\frac{4\pi}{c}\,\mathbf{j}; \end{aligned} \tag{97}$$

where

$$\Box = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} = \sum_{k=1}^{4}\frac{\partial^2}{\partial x_k^2}. \tag{98}$$

is the four-dimensional wave operator with $x_1 = x$, $x_2 = y$, $x_3 = z$, and $x_4 = i\,c\,t$.

At this point, it is convenient to introduce the so-called gauge transformation:

$$\begin{aligned} \Phi' &= \Phi + \frac{1}{c}\frac{\partial \chi}{\partial t}, \\ \mathbf{A}' &= \mathbf{A} - \operatorname{grad}\chi, \end{aligned} \tag{99}$$

where $\chi = \chi(x, y, z, t)$ is a completely arbitrary real function. Substitution into (95) and (96) gives

$$\begin{gathered} \mathbf{H}' = \mathbf{H}, \qquad \mathbf{E}' = \mathbf{E}, \\ S' = S - \Box\chi, \end{gathered} \tag{100}$$

showing that the field strengths are gauge-invariant, whereas the scalar S undergoes a transformation. If one chooses the gauge-function χ so that $\Box\chi = S$ one obtains particularly $S' = 0$ showing that there always exists a choice of potentials for which one has

$$\operatorname{div}\mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t} = 0, \tag{101}$$

which is the so-called Lorentz condition. In the following, we will always assume that this condition is valid. We note that the gauge transformations (99) are then restricted to functions χ satisfying the relation

$$\Box\chi = 0 \tag{102}$$

The equations (97) are now simplified to the form

$$\Box\Phi = -4\pi\rho; \qquad \Box\mathbf{A} = -\frac{4\pi}{c}\mathbf{j}. \tag{103}$$

Of particular importance are the solutions known as retarded potentials:

$$\left\{ \begin{aligned} \Phi(P,t) &= \int \frac{\rho(Q, t - r_{PQ}/c)}{r_{PQ}}\, d\omega_Q, \\ \mathbf{A}(P,t) &= \frac{1}{c}\int \frac{\mathbf{j}(Q, t - r_{PQ}/c)}{r_{PQ}}\, d\omega_Q. \end{aligned} \right. \tag{104}$$

Since the wave operator $\Box$ is invariant against the transformation $c \to -c$, one has also advanced potentials containing the time-variable $(t + r_{PQ}/c)$ and "symmetric potentials" obtained by averaging over the retarded and the advanced potentials. The general solution to (103) is obtained by taking any special solution and adding solutions Φ_0 and $\mathbf{A}_0$ to the homogeneous wave equations $\Box \Phi_0 = 0$ and $\Box \mathbf{A}_0 = 0$

Single particle in an outer electromagnetic field. - Let us first consider a single particle with charge e in an outer electromagnetic field. In classical mechanics, there is a simple rule for introducing an electromagnetic field into the Hamiltonian which may be directly taken over into quantum mechanics. The rule is most easily understood by considering the relation:

$$\mathbf{p} = \boldsymbol{\pi} + \frac{e}{c}\mathbf{A} \tag{105}$$

which says that the total momentum $\mathbf{p}$ is the sum of the kinetic momentum $\boldsymbol{\pi}$ and the electromagnetic momentum $(e/c)\mathbf{A}$. Since the total energy is the sum of the kinetic energy and the electromagnetic contribution $e\Phi$, one has further

$$\begin{aligned} H &= \frac{1}{2m}\boldsymbol{\pi}^2 + e\Phi = \\ &= \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + e\Phi , \end{aligned} \tag{106}$$

which is the classical Hamiltonian desired. By putting $\mathbf{p} = (h/2\pi i)\nabla$, one obtains the quantum-mechanical analogue. We note that the Hamiltonian operator is self-adjoint $(H^\dagger = H)$, but that it is no longer real $(H^* \neq H)$, which is of importance in discussing time-reversal.

It is interesting to observe that the Schrödinger equation (21) for a Hamiltonian of the type (106) leads to a continuity equation of the form (66) having the probability density current:

$$\mathbf{s} = \frac{1}{2m}\left\{\psi^* \boldsymbol{\pi} \psi + \psi(\boldsymbol{\pi}\psi)^*\right\} , \tag{107}$$

which is obtained from (70) by replacing $\mathbf{p}$ by $\boldsymbol{\pi}$. Using Schrödinger's interpretation of quantum mechanics, one has the identifications

$$\begin{cases} \rho = e\,|\psi|^2 , \\ \mathbf{j} = \frac{e}{2m}\left(\psi^* \boldsymbol{\pi}\, \psi + \psi\, \boldsymbol{\pi}^* \psi^*\right) \end{cases} \tag{108}$$

leading to the quantum-mechanical expressions for the charge density ρ and the current density $\mathbf{j}$. By using these expressions in the wave equations (103) for the potentials, one can then derive the electromagnetic field created by the "matter wave" associated with the particle.

The operator $\boldsymbol{\pi}$ for the kinetic momentum $\boldsymbol{\pi} = \mathbf{p} - (e/c)\mathbf{A}$ is of fundamental importance in the theory, and we note that it has the commutation relations

$$\boldsymbol{\pi} \times \boldsymbol{\pi} = i\,(eh/2\pi c)\,\mathbf{H} \tag{109}$$

Using Heisenberg's law of motion (78), it is now interesting to study the time-dependence of the expectation values $\bar{\mathbf{r}}$ and $\bar{\boldsymbol{\pi}}$. One obtains

$$\begin{cases} \frac{d\bar{\mathbf{r}}}{dt} = \frac{1}{m}\bar{\boldsymbol{\pi}} , \\ \frac{d\bar{\boldsymbol{\pi}}}{dt} = e\,\bar{\mathbf{E}} + \frac{e}{2mc}\,\overline{(\boldsymbol{\pi} \times \mathbf{H} - \mathbf{H} \times \boldsymbol{\pi})} \end{cases} \tag{110}$$

where the right-hand member of the second relation is the quantum-mechanical analogue to the classical Lorentz force (8) in hermitean form:

$$\frac{d\bar{\boldsymbol{\pi}}}{dt} = \int \left[\rho \mathbf{E} + \frac{1}{2c}(\mathbf{j} \times \mathbf{H} - \mathbf{H} \times \mathbf{j}) \right] d\omega . \tag{111}$$

The equations (110) correspond to the Ehrenfest's relations (81) in the case of an outer electromagnetic field.

Let us now study the behaviour of the Schrödinger equation for a Hamiltonian of the type (106) under a gauge transformation (99) characterized by the real function $\chi = \chi(x, y, z, t)$. For the basic operators, one obtains the following transformations

$$\boldsymbol{\pi}' = \boldsymbol{\pi} + \frac{e}{c}\,\mathrm{grad}\,\chi , \quad \phi' = \phi + \frac{1}{c}\frac{\partial \chi}{\partial t} , \tag{112}$$

and for the Hamiltonian

$$\mathcal{H}' = \frac{1}{2m}(\pi')^2 + e\phi' = \qquad (113)$$
$$= \frac{1}{2m}\left(\pi + \frac{e}{c}\,\mathrm{grad}\,\chi\right)^2 + e\phi + \frac{e}{c}\frac{\partial\chi}{\partial t}$$

Let $\psi = \psi(r, t)$ be a solution to the original Schrödinger equation corresponding to the initial condition $\psi = \psi_0$ for t = 0. It is now easily shown that the function

$$\psi' = \psi\, e^{-(2\pi i e/hc)\chi} \qquad , \qquad (114)$$

is a solution to the transformed Schrödinger equation

$$\mathcal{H}'_{op}\,\psi' = -\frac{h}{2\pi i}\frac{\partial\psi'}{\partial t} \quad , \qquad (115)$$

corresponding to the initial condition $\psi'_0 = \psi_0 \exp\{-(2\pi i e/hc)\chi_0\}$ for t = 0. The proof follows from the fact that

$$\pi'\psi' = e^{-(2\pi i e/hc)\chi}\,(\pi\psi) \; ,$$
$$-\frac{h}{2\pi i}\frac{\partial\psi'}{\partial t} = e^{-(2\pi i e/hc)\chi}\left\{-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} + \frac{e}{c}\frac{\partial\chi}{\partial t}\psi\right\} \qquad (116)$$

and substitution of these relations into (113) verifies the statement.

The relation (114) is called the gauge-transformation of the wave function. It follows immediately that

$$|\psi'(r, t)|^2 = |\psi(r, t)|^2 \; , \qquad (117)$$

showing that the probability density in the coordinate space stays invariant under a gauge transformation. For the kinetic momentum one has the commutation relation

$$\pi'\, e^{-(2\pi i e/hc)\chi} = e^{-(2\pi i e/hc)\chi}\,\pi \; , \qquad (118)$$

and more generally for any polynomial function $f = f(\pi_1, \pi_2, \pi_3)$:

$$f(\pi_1', \pi_2', \pi_3')\, e^{-(2\pi i e/hc)\chi} = e^{-(2\pi i e/hc)\chi} f(\pi_1, \pi_2, \pi_3). \tag{119}$$

This leads to the relation

$$(\psi')^* f(\pi_1', \pi_2', \pi_3')\, \psi' = \psi^* f(\pi_1, \pi_2, \pi_3)\, \psi, \tag{120}$$

showing that all expectation values of the kinetic momentum will be gauge-invariant. The formulas (117) and (120) show that the quantum mechanics based on the Schrödinger equation (115) fulfils the basic requirement that all physically measurable quantities should in principle be gauge-invariant. In this connection, it should be observed that the Hamiltonian H is an auxiliary quantity which undergoes the gauge transformation (113). Using (114) and (120), one obtains further

$$(\psi')^* \mathcal{H}'_{op}\, \psi' = \psi^* \left(\mathcal{H}_{op} + \frac{e}{c}\frac{\partial \chi}{\partial t}\right) \psi \tag{121}$$

This relation implies that, in order to discuss "stationary states" and properties of energy levels etc., it is convenient to restrict the permissible gauge transformations so that χ is independent of time.

Let us now make a few comments about the effect of a time-reversal of the type (89). The equations (93) were based on the assumption that the Hamiltonian was real, i.e. $\mathcal{H}^*_{op} = \mathcal{H}_{op}$, which follows directly from (23) and the fact that $\mathbf{p}^*_{op} = -\mathbf{p}_{op}$ according to (22). This does not apply to the Hamiltonian (106), for which one obtains

$$\mathcal{H}^*_{op} = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + e\phi \tag{122}$$

Even if the outer magnetic field would be static, its presence would prevent the simple time-reversal previously discussed, unless the currents producing the vector potential $\mathbf{A}$ would also be reversed in accordance with the general rule that all momenta should change direction. The non-static case is much more cumbersome for, if one uses retarded potentials, they go under time-reversal over into advanced potentials, and vice-versa. This means that, in order to keep the primary character of the basic laws of quantum mechanics, it would be necessary to use symmetric potentials which are the average of retarded and advanced potentials. We will discuss these questions further below in connection with radiation theory.

Many-particle system in an outer electromagnetic field. - Let us now consider a system of particles having the charges e_k $(k = 1, 2, \dots N)$ under the influence of an internal potential $U = U(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N)$ and an outer electromagnetic field with the potentials $\phi = \phi(\mathbf{r}, t)$ and $\mathbf{A} = \mathbf{A}(\mathbf{r}, t)$. The Schrödinger equation for the wave function $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N; t)$ takes again the form

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = \mathcal{H}_{op}\Psi, \tag{123}$$

with the Hamiltonian

$$\mathcal{H}_{op} = U(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) + \sum_{k=1}^{N}\left\{\frac{1}{2m_k}\left(\mathbf{p}_k - \frac{e_k}{c}\mathbf{A}_k\right)^2 + e_k\phi_k\right\}, \tag{124}$$

which is formed by a generalization of the simple rule given in the previous section; here we have used the abbreviations

$$\phi_k = \phi(\mathbf{r}_k, t), \quad \mathbf{A}_k = \mathbf{A}(\mathbf{r}_k, t). \tag{125}$$

By using Heisenberg's law of motion (78), one obtains in analogy to (110) the Ehrenfest's relations:

$$\left\{\begin{aligned} \frac{d\overline{\mathbf{r}}_k}{dt} &= \frac{1}{m_k}\overline{\boldsymbol{\pi}}_k, \\ \frac{d\overline{\boldsymbol{\pi}}_k}{dt} &= -\overline{\text{grad}_k U} + \overline{e_k\mathbf{E}_k + \frac{e_k}{2m_k c}(\boldsymbol{\pi}_k \times \mathbf{H}_k - \mathbf{H}_k \times \boldsymbol{\pi}_k} \end{aligned}\right. \tag{126}$$

where $\Pi_k = p_k - (e_k/c)\, A_k$ is the kinetic momentum for particle k. It is also interesting to observe that the Schrödinger equation (123) leads to a continuity equation for the total probability density $|\Psi|^2$ of the form:

$$\left\{ \begin{aligned} & \frac{\partial |\Psi|^2}{\partial t} = - \sum_{k=1}^{N} \operatorname{div}_k s_k \, ; \\ & s_k = \frac{1}{2m_k} \left(\Psi^* \Pi_k \Psi + \Psi \Pi_k^* \Psi^* \right) , \end{aligned} \right. \tag{127}$$

in analogy to (70) and (107). This continuity equation is valid within the 3N-dimensional configuration space, but we note that there exists also a continuity equation in a 3-dimensional space for each one of the particles separately.

If $(dv) = dv_1\, dv_2 \ldots dv_N$, is the total volume element in the configuration space, it is convenient to introduce the notation

$$(dv_k') = dv_1\, dv_2 \ldots dv_{k-1}\, dv_{k+1} \ldots dv_N \tag{128}$$

which goes over all particles <u>except particle k</u>. The probability density for finding particle k in the point r_k at the time t, when all the other particles have arbitrary positions, is then given by the quantity

$$\rho_k(r_k, t) = \int |\Psi(r_1, r_2, \ldots r_k, \ldots r_N, t)|^2 (dv_k') , \tag{129}$$

In a similar way, one introduces the probability density current s_k' for the particle k alone when all the other particles have arbitrary motions through the relation

$$s_k'(r_k, t) = \int s_k(r_1, r_2, \ldots r_k, \ldots r_N; t)(dv_k') \tag{130}$$

Integrating the continuity equation (127) over the coordinates $r_1, r_2, \ldots r_{k-1}, r_{k+1} \ldots r_N$, one obtains

$$\frac{\partial \rho_k}{\partial t} = - \operatorname{div}_k s_k' \tag{131}$$

So far everything is simple and straightforward. The crucial problem is to find the true charge density ρ and current density j of the many-particle system to be used in evaluating the electromagnetic potentials created by the 3N-dimensional matter waves. In the historical development of quantum mechanics[6)], it seemed natural to assume that $e_k \gamma_k$ and $e_k \mathfrak{s}'_k$ would be the contributions from particle k to the charge density and current density, respectively, and to make tentatively the identifications:

$$\begin{aligned} \rho(\mathfrak{r}, \mathfrak{t}) &= \sum_{k=1}^{N} e_k \gamma_k(\mathfrak{r}, \mathfrak{t}), \\ \mathfrak{j}(\mathfrak{r}, \mathfrak{t}) &= \sum_{k=1}^{N} e_k \mathfrak{s}'_k(\mathfrak{r}, \mathfrak{t}) \end{aligned} \tag{132}$$

We note that, for $e_1 = e_2 = \cdots = e_N$, the charge density ρ is essentially identical to the diagonal element of the reduced first-order density matrix treated in modern many-particle theory.

By combination of (132) and (103), one can hence study the electromagnetic field created by a system of matter waves and, by introducing the potentials ϕ and $\mathfrak{A}$ into the Schrödinger equation (123) with the Hamiltonian (124), one can investigate the effect of the field on the matter waves. This coupling of the equations leads necessarily to a problem which is formally of a non-linear character.

So far, there are only a few many-particle systems which have been treated with sufficient accuracy to permit a real comparison between theory and experimental experience. The theoretical data for the ground state and lowest excited states of the helium atom and the hydrogen molecule obtained by Hylleraas, Kinoshita, Pekeris etc[7)] and by James and Coolodge, Kolos and Roothaan etc[8)], respectively, show that Schrödinger's idea about a wave equation in configuration space seems to lead to results in complete agreement with experimental experience. At the same time, the form of the Coulomb potential is no longer derived from the average charge density ρ defined in (132). It seems hence evident that the question of the nature of the electromagnetic field generated by the matter waves has a more complicated character than is indicated above. Using the formulism of second quantization, these problems are treated in the new field of quantum electrodynamics which deals with modern radiation theory as well as the very difficult problem of the nature of the elementary particles themselves and their "self-interaction". Even if the progress in this area has been considerable during the last two decades, there are still many fundamental problems to be solved, particularly in connection with the relativistic formulation of the theory.

In this paper, we will confine our interest to the much simpler problem of solving the Schrödinger equation for a given fixed Hamiltonian. This Hamiltonian may contain an outer magnetic field and a given interaction between the particles, and it is assumed that the problem has strictly a linear character.

5. EVOLUTION OPERATOR

The main problem in the quantum theory of a time-dependent system is to find the solution $\Psi = \Psi(\mathbf{R}, t)$ to the Schrödinger equation

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = \mathcal{H}_{op}\Psi \tag{133}$$

which corresponds to the initial condition $\Psi = \Psi_0$ at $t = t_0$. Here $\mathbf{R} = (r_1, r_2, \ldots r_N)$ is the space-coordinate of the many-particle system, but the problem can, of course, also be treated equally well in the momentum space. The space-coordinate will in the following often be surpressed, and the main emphasis is put on the time dependence of the wave function. One can write the connection between $\Psi(t)$ and Ψ_0 symbolically in the form

$$\Psi(t) = U(t, t_0)\,\Psi_0\,. \tag{134}$$

Since the Schrödinger equation (133) is linear and there exists a superposition principle (65), one can conclude that U must be a <u>linear operator</u>.

Since U describes the time dependence of the system completely, it is called the "evolution operator". From the definition follows immediately the relation

$$U(t_2; t_0) = U(t_2; t_1)\,U(t_1; t_0) \tag{135}$$

for $t_0 \leq t_1 \leq t_2$, which is the multiplication law characteristic for the evolution operator. One has further $U(t_0, t_0) = 1$, where the symbol 1 means the identity operator.

The Hamiltonian is assumed to be self-adjoint, $\mathcal{H}^\dagger = \mathcal{H}$, and this implies according to (75) that the normalization integral is independent of time. This gives

$$\begin{aligned} \langle \Psi | \Psi \rangle - \langle \Psi_0 | \Psi_0 \rangle &= \langle U\Psi_0 | U\Psi_0 \rangle - \langle \Psi_0 | \Psi_0 \rangle = \\ &= \langle \Psi_0 | U^\dagger U - 1 | \Psi_0 \rangle = 0 , \end{aligned} \tag{136}$$

for all Ψ_0, which leads to the conclusion $U^\dagger U = 1$. Letting $U^\dagger$ work on the relation $\Psi = U\Psi_0$, one obtains $\Psi_0 = U^\dagger \Psi$. We will now make the specific assumption that not only the initial state Ψ_0 but also the final state Ψ may be chosen quite arbitrarily, i.e. that there always exists a Ψ_0 so that a given Ψ may be obtained. Since one has now

$$\begin{aligned} \langle \Psi_0 | \Psi_0 \rangle - \langle \Psi | \Psi \rangle &= \langle U^\dagger \Psi | U^\dagger \Psi \rangle - \langle \Psi | \Psi \rangle = \\ &= \langle \Psi | U U^\dagger - 1 | \Psi \rangle = 0 , \end{aligned} \tag{137}$$

for all Ψ, one is lead to the conclusion $UU^\dagger = 1$. Under these assumptions, the evolution operator is hence a unitary operator:

$$U^\dagger U = U U^\dagger = 1 , \tag{138}$$

Substitution of the relation $\Psi = U\Psi_0$ into the Schrödinger equation (133) gives

$$\left(- \frac{h}{2\pi i} \frac{\partial U}{\partial t} - \mathcal{H}_{op} U \right) \Psi_0 = 0 , \tag{139}$$

for all Ψ_0, and the evolution operator fulfils hence the differential equation

$$- \frac{h}{2\pi i} \frac{\partial U}{\partial t} = \mathcal{H}_{op} U , \tag{140}$$

with the initial condition $U = 1$ for t = 0. In order to solve this equation, it is convenient to distinguish between three cases:

1) H is independent of time.
2) H depends on the time, but in a commutative way so that $\mathcal{H}(t_1)\mathcal{H}(t_2) = \mathcal{H}(t_2)\mathcal{H}(t_1)$ for all pairs (t_1, t_2) in the interval concerned.
3) H depends on the time in a non-commutative way, so that in general $\mathcal{H}(t_1)\mathcal{H}(t_2) \neq \mathcal{H}(t_2)\mathcal{H}(t_1)$.

Hamiltonian independent of time. - In the case when the Hamiltonian H does not contain the time t explicitly, one can immediately solve (140) and represent the evolution operator symbolically in the form

$$U(t; t_0) = e^{-\frac{2\pi i}{h}\mathcal{H}_{op}(t-t_0)} \tag{141}$$

In this case, the evolution operator is translationally invariant on the time axis, i.e. $U(t+\tau\,;\,t_0+\tau) = U(t; t_0)$ and it is easily shown that the reverse is also true. For the sake of simplicity, we will now put $t_0 = 0$, and the solution (134) may then be written in the form

$$\underline{\Psi}(t) = e^{-\frac{2\pi i}{h}\mathcal{H}_{op}t}\,\underline{\Psi}_0 \tag{142}$$

Introducing the normalized eigenstates $\Phi_k(\mathbf{R})$ of H satisfying the relation $\mathcal{H}\Phi_k = E_k\Phi_k$ as a basis, and assuming that this basis is complete so that one has the following resolution of the identity

$$1 = \sum_k |\Phi_k\rangle\langle\Phi_k|, \tag{143}$$

where one sums of the discrete eigenvalues and integrates over the continuous eigenvalues, one obtains the spectral resolution $\mathcal{H} = \sum_k E_k|\Phi_k\rangle\langle\Phi_k|$, and more generally for an arbitrary function f:

$$f(\mathcal{H}) = \sum_k f(E_k)|\Phi_k\rangle\langle\Phi_k|, \tag{144}$$

This gives particularly for the evolution operator (141):

$$U = \sum_{k} e^{-\frac{2\pi i}{h} E_k t} \, |\Phi_k\rangle\langle\Phi_k| \quad (145)$$

In ordinary space, one has the identifications $|\Phi_k\rangle = \Phi_k(\mathbf{R})$ and $\langle\Phi_k| = \int (dv)\, \Phi_k^*(\mathbf{R})$. Substitution of the sum (145) into (142) gives the formula

$$\Psi(\mathbf{R}, t) = \sum_{k} e^{-\frac{2\pi i}{h} E_k t} \, |\Phi_k\rangle\langle\Phi_k|\Psi_0\rangle, \quad (146)$$

which is the famous expansion of the solution into stationary states. Hence, one can determine the time dependence of a solution by a study of the stationary states, and vice versa.

<u>Hamiltonian dependent on time in a commutative way</u>. - In this case, the Hamiltonian $\mathcal{H} = \mathcal{H}(t)$ is assumed to fulfil the commutation relation

$$\mathcal{H}(t_1)\mathcal{H}(t_2) = \mathcal{H}(t_2)\mathcal{H}(t_1) \quad (147)$$

for any pair (t_1, t_2) within the time interval under consideration. Starting from (140), it is easily shown that the evolution operator may be written symbolically in the form

$$U(t; t_0) = e^{-\frac{2\pi i}{h} \int_{t_0}^{t} \mathcal{H}(t_1)\, dt_1} \quad (148)$$

The operator is no longer translationally invariant. However, since all the operators H(t) commute, it is possible to introduce the normalized eigenstates $\Phi_k(\mathbf{R})$ of the operator H(0) in such a way that they become simultaneous eigenstates to all the operators H(t) satisfying the relations:

$$\mathcal{H}(t)\,\Phi_k(\mathbf{R}) = E_k(t)\,\Phi_k(\mathbf{R}), \quad (149)$$

where the eigenvalues $E_k = E_k(t)$ are now functions of time t. From the resolution of identity $1 = \Sigma_k |\Phi_k\rangle\langle\Phi_k|$, one obtains according to (148) the following spectral resolution of the evolution operator:

$$U(t;0) = \sum_k e^{-\frac{2\pi i}{h}\int_0^t E_k(t_1)dt_1} |\Phi_k\rangle\langle\Phi_k| , \qquad (150)$$

which gives the following solution to the Schrödinger equation:

$$\Psi(\mathbf{R};t) = \sum_k e^{-\frac{2\pi i}{h}\int_0^t E_k(t_1)dt_1} \Phi_k(\mathbf{R})\langle\Phi_k|\Psi_0\rangle . \qquad (151)$$

This is a trivial extension of formula (146). We note that there still exist "stationary states" associated with the eigenfunctions $\Phi_k(\mathbf{R})$ but that the energy values are now functions of time.

Hamiltonian dependent on time in a general way. - In this case, the Hamiltonian H = H(t) is assumed to be of such a general character that the commutation relation (147) is no longer valid, i.e.

$$\mathcal{H}(t_1)\mathcal{H}(t_2) \neq \mathcal{H}(t_2)\mathcal{H}(t_1) , \qquad (152)$$

In order to treat this case, it is convenient to transform the differential-equation (140) into the associated integral equation:

$$U(t) = 1 - \frac{2\pi i}{h}\int_0^t \mathcal{H}(t_1)U(t_1)\,dt_1 , \qquad (153)$$

where we have used the abbreviation $U(t;0) = U(t)$ and the initial condition $U(0) = 1$. This is a "Volterra-equation of the second kind", except that the kernel $\mathcal{H}(t_1)$ is not a simple function of t but a linear operator acting on functions of the space-coordinates $\mathbf{R} = (r_1, r_2, \dots r_N)$. By substituting the left-hand member of (153) for t = t$_1$ into the right-hand member, one obtains by iteration:

$$U(t) = 1 - \frac{2\pi i}{h}\int_0^t \mathcal{H}(t_1)dt_1 + \left(-\frac{2\pi i}{h}\right)^2\int_0^t \mathcal{H}(t_1)dt_1\int_0^{t_1}\mathcal{H}(t_2)U(t_2)dt_2$$

$$= \sum_{n=0}^{\infty}\left(-\frac{2\pi i}{h}\right)^n\int_0^t dt_1\int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n\, \mathcal{H}(t_1)\mathcal{H}(t_2)\dots\mathcal{H}(t_n)$$

In the integrand of each term in this formal series, one has the condition $t \geq t_1 \geq t_2 \geq \ldots \geq t_n$, and one says the factors in the product $\mathcal{H}(t_1)\mathcal{H}(t_2)\ldots\mathcal{H}(t_n)$ are arranged in "chronological order".

Let us now study the connection between the series (154) and the expression (148) which is obtained under the special assumption (147). For a series of symmetrical terms $u_{ij}, u_{ijk}, \ldots$ one has the general transformation formulas

$$\sum_{i<j} u_{ij} = \frac{1}{2!}\sum_{i,j}{}' u_{ij}, \qquad \sum_{i<j<k} u_{ijk} = \frac{1}{3!}\sum_{i,j,k}{}' u_{ijk}, \tag{155}$$

and similar relations are also valid for integrals. If P is the "Dyson chronological-order operator" which has the property that it permutes the time-variables in any product $\mathcal{H}(t_1')\mathcal{H}(t_2')\ldots\mathcal{H}(t_n')$ so that they occur in chronological sequence after decreasing order, one has

$$\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \ldots \int_0^{t_{n-1}} dt_n \, \mathcal{H}(t_1)\mathcal{H}(t_2)\mathcal{H}(t_3)\ldots\mathcal{H}(t_n) = \tag{156}$$

$$= \frac{1}{n!}\int_0^t dt_1 \int_0^t dt_2 \ldots \int_0^t dt_n \, P\left\{\mathcal{H}(t_1)\mathcal{H}(t_2)\ldots\mathcal{H}(t_n)\right\}$$

According to (154), this gives

$$U(t) = P\sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 \mathcal{H}(t_1)\int_0^t dt_2 \mathcal{H}(t_2) \ldots \int_0^t dt_n \mathcal{H}(t_n)$$

$$= P e^{-\frac{2\pi i}{h}\int_0^t dt_1 \mathcal{H}(t_1)} \tag{157}$$

in analogy to (148), which gives the connection desired. It is evident that the series (154) is convergent only under rather limited conditions, and it will now be transformed into more useful forms.

Interaction Representation. - Let us assume that the Hamiltonian $\mathcal{H} = \mathcal{H}(t)$ may be written in the form

$$\mathcal{H} = \mathcal{H}_0 + V(t), \tag{158}$$

where $\mathcal{H}_0$ is the "unperturbed Hamiltonian" and $V = V(t)$ is a comparatively small "perturbation". The operator $\mathcal{H}_0$ is further assumed to be independent of time t and to have well-known eigenfunctions $\Phi_k^0 = \Phi_k^0(\mathbf{R})$ and eigenvalues E_k^0. The associated evolution operator U_0 has the form

$$U_0 = e^{-\frac{2\pi i}{h}\mathcal{H}_0 t} = \tag{159}$$
$$= \sum_k e^{-\frac{2\pi i}{h} E_k^0 t} \, |\Phi_k^0\rangle\langle\Phi_k^0| \, ,$$

and satisfies the differential equation (140) for $\mathcal{H} = \mathcal{H}_0$. In order to proceed, we will now introduce the substitution

$$U = U_0 \; U_V \tag{160}$$

where U_V is a unitary operator to be determined. According to (140), one obtains the differential equation:

$$-\frac{h}{2\pi i}\frac{\partial U_0}{\partial t}\cdot U_V - \frac{h}{2\pi i} U_0 \cdot \frac{\partial U_V}{\partial t} = (\mathcal{H}_0 + V)\, U_0 \cdot U_V \, ; \tag{161}$$
$$-\frac{h}{2\pi i} U_0 \cdot \frac{\partial U_V}{\partial t} = V U_0 \cdot U_V \, ;$$
$$-\frac{h}{2\pi i}\frac{\partial U_V}{\partial t} = (U_0^\dagger V U_0)\cdot U_V$$

It is clear that U_V satisfies a differential equation of exactly the same type as U but with the Hamiltonian H replaced by the operator

$$V_H = U_0^\dagger V U_0 = \tag{162}$$
$$= e^{\frac{2\pi i}{h}\mathcal{H}_0 t}\, V \, e^{-\frac{2\pi i}{h}\mathcal{H}_0 t}$$

The operator V_H is said to represent the perturbation in the "interaction representation". Since U_V satisfies the initial condition $U_V(0) = 1$, one obtains from (161) the integral equation:

$$U_V(t) = 1 - \frac{2\pi i}{h}\int_0^t V_H(t_1)\, U_V(t_1)\, dt_1 \tag{163}$$

Iteration leads to the series expansion

$$U_V(t) = 1 - \frac{2\pi i}{h}\int_0^t V_H(t_1)\,dt_1 + \left(-\frac{2\pi i}{h}\right)^2\int_0^t V_H(t_1)\,dt_1\int_0^t V_H(t_2)\,U_V(t_2)\,dt_2$$

$$= \sum_{n=0}^{\infty}\left(-\frac{2\pi i}{h}\right)^n\int_0^t dt_1\int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n\, V_H(t_1)\,V_H(t_2)\ldots V_H(t_n)\,, \qquad (164)$$

which is fundamental for the so-called time-dependent perturbation theory. In analogy to (157), one obtains the following form for the total evolution operator:

$$U(t) = P\,e^{-\frac{2\pi i}{h}\int_0^t\{\mathcal{H}_0 + V(t_1)\}\,dt_1} =$$

$$= e^{-\frac{2\pi i}{h}\mathcal{H}_0 t}\; P\,e^{-\frac{2\pi i}{h}\int_0^t V_H(t_1)\,dt_1} = \qquad (165)$$

$$= e^{-\frac{2\pi i}{h}\mathcal{H}_0 t}\sum_{n=0}^{\infty}\left(-\frac{2\pi i}{h}\right)^n\int_0^t dt_1\int_0^{t_1} dt_2 \ldots \int_0^{t_{n-1}} dt_n\, V_H(t_1)\,V_H(t_2)\ldots V_H(t_n)$$

The various terms in this expansion will be further discussed below.

6. REFORMULATION OF QUANTUM THEORY

So far the evolution operator $\mathcal{U}$ has been expressed in terms of a given Hamiltonian H, but sometimes it seems more convenient to turn things around and reformulate the fundamentals of quantum mechanics with $\mathcal{U} = \mathcal{U}(t; t_0)$ as the basic operator. This may also be of importance from philosophical point of view, since the evolution operator $\mathcal{U}$ is defined with respect to a finite time-interval $(t_0; t)$, whereas H is associated with a differential equation of type (21).

Let us now assume that the relation

$$\underline{\Psi}(t) = \mathcal{U}(t; t_0)\,\underline{\Psi}_0 \tag{166}$$

is the fundamental law for the time-evolution of a quantum-mechanical system, and that $\mathcal{U}$ is linear and unitary:

$$\mathcal{U}^\dagger \mathcal{U} = \mathcal{U}\mathcal{U}^\dagger = 1 \tag{167}$$

The evolution operator has an eigenvalue problem of the form:

$$\mathcal{U}\eta_k = \lambda_k \eta_k , \tag{168}$$

where the eigenfunctions $\eta_k = \eta_k(\mathbf{R}, t)$ depend on $\mathbf{R} = (r_1, r_2, \dots r_N)$ and t. The eigenvalues $\lambda_k = \lambda_k(t)$ are situated on the unit circle $|\lambda_k| = 1$ and have the form $\lambda_k = \exp(i\alpha_k)$, where α_k is real. Since the operator is normal, one has also $\mathcal{U}^\dagger \eta_k = \lambda_k^* \eta_k$, and the eigenfunctions form an orthogonal system which is assumed to be normalized so that $\langle \eta_k | \eta_l \rangle = \delta_{kl}$. The system is further assumed to be complete, so that $1 = \Sigma_k |\eta_k\rangle\langle\eta_k|$. This gives the spectral resolution

$$\mathcal{U} = \sum_k \lambda_k |\eta_k\rangle\langle\eta_k| , \tag{169}$$

which substituted into (166) gives the expansion

$$\underline{\Psi}(t) = \sum_k e^{i\alpha_k} \eta_k \langle \eta_k | \underline{\Psi}_0 \rangle , \tag{170}$$

corresponding to the expansion in "stationary states" (146).

Let us now consider an operator Λ which commutes with U so that:

$$U\Lambda = \Lambda U \tag{171}$$

For the expectation value of Λ, one obtains $\langle \Psi | \Lambda | \Psi \rangle = \langle U\Psi_0 | \Lambda | U\Psi_0 \rangle = \langle \Psi_0 | U^\dagger \Lambda U | \Psi_0 \rangle = \langle \Psi_0 | \Lambda | \Psi_0 \rangle$, i.e. the expectation value $\langle \Lambda \rangle_{av}$ is the same for the times t_0 and t. Such an operator Λ will be called a "constant of evolution", and its eigenprojectors may be used to classify the degeneracies of the eigenstates of U.

If the evolution operator U exists in the interval $(t; t+dt)$ and has a first derivative, one can show the existence of a specific Hamiltonian H. Differentiating relation (166) with respect t, one obtains

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}\Psi_0 = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}U^\dagger \Psi, \tag{172}$$

i.e. the connection

$$\mathcal{H}_{op} = -\frac{h}{2\pi i}\frac{\partial U}{\partial t}U^\dagger, \tag{173}$$

which defines the Hamiltonian. Taking the time-derivative of the relation $UU^\dagger = 1$, one obtains the alternative form

$$\mathcal{H}_{op} = +\frac{h}{2\pi i} U \frac{\partial U^\dagger}{\partial t}, \tag{174}$$

and combination of (173) and (174) gives finally $H^\dagger = H$. If the evolution operator is unitary, the associated Hamiltonian is hence self-adjoint.

The eigenfunctions η_k of the evolution operator U are usually not eigenfunctions of the Hamiltonian H, and it is instructive to derive the matrix representation of H with respect to the basis η_k. From the relation $(U^\dagger - \lambda_k^*)\eta_k = 0$ follows by taking the time-derivative and using (174):

$$\left(\frac{\partial U^\dagger}{\partial t} - \frac{\partial \lambda_k^*}{\partial t}\right)\eta_k + \left(U^\dagger - \lambda_k^*\right)\frac{\partial \eta_k}{\partial t} = 0\,;$$

$$\left(\mathcal{H} - \frac{h}{2\pi i}\lambda_k \frac{\partial \lambda_k^*}{\partial t}\right)\eta_k = \frac{h}{2\pi i}\left(1 - U\lambda_k^*\right)\frac{\partial \eta_k}{\partial t}\,;$$

$$\langle \eta_k|\mathcal{H}|\eta_l\rangle = \frac{h}{2\pi i}\lambda_k \frac{\partial \lambda_k^*}{\partial t}\delta_{kl} + \frac{h}{2\pi i}\left(1-\lambda_k\lambda_l^*\right)\left\langle \eta_k \middle| \frac{\partial \eta_l}{\partial t}\right\rangle; \tag{175}$$

and further

$$\langle \eta_k|\mathcal{H}|\eta_k\rangle = -\frac{h}{2\pi}\frac{\partial \alpha_k}{\partial t}\,; \tag{176}$$

$$\langle \eta_k|\mathcal{H}|\eta_l\rangle = \frac{h}{2\pi i}\left\{1 - e^{i(\alpha_k-\alpha_l)}\right\}\left\langle \eta_k \middle| \frac{\partial \eta_l}{\partial t}\right\rangle \tag{177}$$

Hence one has

$$\alpha_k = -\frac{2\pi}{h}\int_0^t \langle \eta_k|\mathcal{H}|\eta_k\rangle\, dt_1\,; \tag{178}$$

and substitution of this expression into (170) leads to an expansion closely analogous to (151).

The matrix representation $\langle \eta_k|\mathcal{H}|\eta_l\rangle$ will be strictly diagonal, if and only if $\mathcal{H}U = U\mathcal{H}$, i.e. if H is a constant of evolution. By using (173) and (167) this condition may also be written

$$\frac{\partial U}{\partial t}\,U = U\,\frac{\partial U}{\partial t} \tag{179}$$

which implies that $U(t)$ should commute with $U(t+dt)$, i.e. the evolution operator should commute with itself in the extended interval (t; t + dt). In this latter case, H and U have simultaneous eigenfunctions at the time t, and the eigenvalues of the Hamiltonian is given by (176). The evolution operator description has many advantages but, so far, the Hamiltonian description has been dominating in quantum mechanics particularly for systems where H is easily constructed from classical analogs.

7. TRANSITION PROBABILITIES.

In order to study the probability distribution over a set of discrete states as a function of time, we will introduce a complete set of orthonormal functions $f_k = f_k(\mathbf{R})$ as a basis:

$$\langle f_k | f_l \rangle = \delta_{kl}; \qquad 1 = \sum_k |f_k\rangle\langle f_k| . \tag{180}$$

Expanding the wave function $\Psi = \Psi(\mathbf{R}, t)$ in this basis, one obtains $\Psi = \sum_k |f_k\rangle\langle f_k|\Psi\rangle$, i.e.

$$\Psi(\mathbf{R}, t) = \sum_k f_k(\mathbf{R})\, C_k(t) , \tag{181}$$

where $C_k(t) = \langle f_k | \Psi \rangle$ is a time-dependent coefficient. Introducing the relation $\Psi(t) = U\Psi_0$, the expansion $\Psi_0 = \sum_l f_l(\mathbf{R}) C_l(0)$, and the notation $U_{kl} = \langle f_k | U | f_l \rangle$, one obtains directly

$$\begin{aligned} C_k(t) &= \langle f_k | \Psi \rangle = \langle f_k | U \Psi_0 \rangle = \\ &= \langle f_k | U | \sum_l f_l C_l(0) \rangle = \\ &= \sum_l \langle f_k | U | f_l \rangle C_l(0) = \\ &= \sum_l U_{kl} C_l(0) , \end{aligned} \tag{182}$$

which formula describes the time-evolution of the coefficients. The quantities $P_k(t) = |C_k(t)|^2$ are conventionally interpreted as the probability for finding the quantum-mechanical system in the state k characterized by the wave function f_k at the time t. From (182) we get further

$$\begin{aligned} P_k(t) &= C_k^*(t) C_k(t) = \{\sum_l U_{kl} C_l(0)\}^* \{\sum_m U_{km} C_m(0)\} = \\ &= \sum_{l,m} U_{kl}^* U_{km} C_l^*(0) C_m(0) = \\ &= \sum_l |U_{kl}|^2 |C_l(0)|^2 + \sum_{l \neq m} U_{kl}^* U_{km} C_l^*(0) C_m(0) , \end{aligned} \tag{183}$$

where the last term may be characterized as an "interference term" between the various states. Using the unitary property of the operator U expressed in the relations

$$\sum_k |U_{kl}|^2 = \sum_l |U_{kl}|^2 = 1 \; ; \tag{184}$$

$$\sum_k U^*_{kl} U_{km} = \sum_k U^*_{lk} U_{mk} = 0 \; ; \; (l \neq m) \tag{185}$$

one finds that

$$\sum_k P_k(t) = \sum_l P_l(0) = 1 \, . \tag{186}$$

Transition probabilities. - Let us start the discussion of the interpretation of equation (183) by assuming that at $t = t_0$, the system is completely in the state characterized by the wave function f_m, so that $P_m(0) = 1$, whereas all other $P_l(0) = 0$. From (183), it follows that

$$P_k(t) = |U_{km}|^2 \, , \tag{187}$$

and the quantity $|U_{km}(t;t_0)|^2$ is then interpreted as the probability that the system jumps from the original state m to the state k during the time interval $(t_0; t)$. This interpretation is obtained in a very special physical situation, and it is then generalized to more complicated situations:

$$S_{m\to k}(t_0; t) = |U_{km}(t; t_0)|^2 \tag{188}$$

From the unitary properties (184) of the evolution operator follows that

$$\sum_k S_{m\to k}(t_0; t) = \sum_k |U_{km}|^2 = 1 \, , \tag{189}$$

showing that the total probability that the system either stays in the state n or leaves this state equals 1. Since all the quantities S are positive, one has further

$$0 \leq \mathcal{S}_{n \to k}(t_0; t) \leq 1, \tag{190}$$

which means that transition probabilities can never "blow up". If this is the case in an approximate treatment, e.g. in perturbation theory, the phenomenon must hence depend on a defect in the approximation itself.

One should observe that the question of the transition probabilities depends essentially on the reference system $\{f_k\}$ chosen. For instance, if one chooses the eigenfunctions η_k of the evolution operator as a basis, one has $\langle \eta_k | U | \eta_l \rangle = \lambda_l \delta_{kl}$, and

$$|\langle \eta_k | U | \eta_l \rangle|^2 = \begin{cases} 1, & \lambda_k = \lambda_l \\ 0, & \lambda_k \neq \lambda_l, \end{cases} \tag{191}$$

which relation shows that the probability distribution over this specific basis is the same at the times t_0 and t, i.e. remains stationary. However, the system as a whole is by no means stationary, and the evolution from t_0 to t is instead described by the phase changes in the coefficients C_k in (182). In general, the phases play hence a key role in the description of the time dependence as one could also expect from the discussion in Sec. 2.

Random-phase systems. - It has been emphasized in connection with the quantum-mechanical superposition principle that the interference term in (62) plays a fundamental role in many basic phenomena in physics and chemistry. However, there are also situations where it is of interest to study assemblies of systems having different phases, where probabilities are additive in accordance with (63).

Let us introduce an assembly of systems having the same probability distribution $P_l(0)$ at the time $t = t_0$, whereas the phases are distributed at random so that, in average over the assembly, one has

$$\overline{C_l^*(0)\, C_m(0)} = 0; \qquad l \neq m \tag{192}$$

By applying this averaging procedure to (183), one obtains

$$P_k(t) = \sum_l |U_{kl}|^2 P_l(0) , \tag{193}$$

which is the fundamental equation in the random-phase systems. Using the fact that U is a unitary operator and the definition (188) of the transition probabilities, one can write relation (193) in the form

$$P_k(t) = P_k(0) + \sum_{l \neq k} P_l(0) S_{l \to k}(t) - P_k(0) \sum_{l \neq k} S_{k \to l}(t) , \tag{194}$$

showing that the probability for the occurrence of the system in the state k at time t equals the probability at $t = t_o$, plus the probability that the system would jump from any other state l to the state k under the time interval $(t_o; t)$, minus the probability that the system would leave the original state k and go over to another state during the same period. In random-phase systems, the transition probabilities are hence truly additive, as one could expect in an incoherent phenomenon.

In a conventional treatment of (194), one would proceed by assuming the existence of a law of "microscopic reversibility" saying that $S_{n \to k} = S_{k \to n}$ for the time interval $(t_o; t)$. In the general case, however, one has usually for the unitary operator U :

$$|U_{km}|^2 \neq |U_{mk}|^2 , \tag{195}$$

except in special cases which will be further discussed below. Even in the general case, one can now proceed by noting the existence of the relation

$$1 - \sum_{l \neq k} S_{k \to l}(t) = |U_{kk}|^2 = 1 - \sum_{l \neq k} S_{l \to k}(t) , \tag{196}$$

which follows directly from (184). Introducing this relation into (194) we obtain

$$P_k(t) = P_k(0) + \sum_{l \neq k} \{ P_l(0) - P_k(0) \} S_{l \to k}(t) , \tag{197}$$

which is exactly the relation one usually derives by means of the law of microscopic reversibility. This equation shows that, in general, there is a flow of probability from levels of higher probability to levels of lower probability, and, since this flow is always going in one and the same direction, one can expect that the process should be irreversible. This is also the case, as we will see below.

Reversible Processes. - The problem of time-reversal has previously been discussed in some detail, and it has been emphasized that the basic laws in classical mechanics as well as in quantum mechanics are reversible in time under certain general conditions and are hence "primary laws" of physics. According to (93), this applies in the latter case if a time-independent Hamiltonian H is not only self-adjoint ($H^\dagger = H$) but also real:

$$\mathcal{H}^* = \mathcal{H} , \tag{198}$$

in which case the process $\underline{\Psi}_0 \rightarrow \underline{\Psi}$ has the reverse process $\underline{\Psi}^* \longrightarrow \underline{\Psi}_0^*$ as outlined in (94).

This problem can now be treated by means of the evolution operator. From the definition $\underline{\Psi} = \mathcal{U} \underline{\Psi}_0$ follows directly $\underline{\Psi}_0 = \mathcal{U}^\dagger \underline{\Psi}$ and

$$\underline{\Psi}_0^* = (\mathcal{U}^\dagger)^* \underline{\Psi}^* \tag{199}$$

In the special case when the evolution operator has the simple form (141), one obtains

$$(\mathcal{U}^\dagger)^* = \mathcal{U} , \tag{200}$$

showing that the reverse process $\underline{\Psi}^* \longrightarrow \underline{\Psi}_0^*$ is associated with the same evolution operator and the same Hamiltonian as the original process $\underline{\Psi}_0 \longrightarrow \underline{\Psi}$.

This result is of interest also for studying the principle of "microscopic reversibility". If the Hamiltonian is real according to (198), its eigenfunctions may also be chosen real, and we will now choose even the basis $\{f_k\}$ to consist of only real functions. Using the relation $U^\dagger = U^*$, one obtains

$$U_{kl} = U^\dagger_{lk} = \langle f_l | U^\dagger | f_k \rangle = \langle f_l | U^* | f_k \rangle = \qquad (201)$$
$$= \langle f_l | U | f_k \rangle^* = U_{lk}^* ,$$

and

$$|U_{kl}|^2 = |U_{lk}|^2 , \qquad (202)$$

which means that, under these specific assumptions, the principle of microscopic reversibility is strictly valid.

It should be observed, however, that the wave functions themselves have in general complex character in order to describe the probability distributions in both ordinary position space and momentum space as outlined in Sec. 2. If one has insufficient information about the phases, one has also insufficient information about the physical situation in general, and any averaging procedure will then usually lead to equations which are no longer reversible in time, and which are hence characterized as "secondary laws".

Irreversible processes. - As a simple example of an irreversible process, we will study the behaviour of a random-phase system based on the assumption (192). The random-phase postulate was first clearly stated by Pauli[9)] in connection with a study of irreversible processes, but it was also used by Dirac[10)] in his formulation of the time-dependent perturbation theory.

In order to study some of the consequences of the random-phase postulate (192), we will introduce an arbitrary function L(x) which is convex in the interval $0 \leq x \leq 1$ so that $L''(x) > 0$ According to Lagrange's mean-value formula, one has

$$L(x+h) - L(x) - h L'(x) = \frac{h^2}{2!} L''(x+\theta h) \geq 0 , \qquad (203)$$

where $0 \leq \theta \leq 1$. Putting $x + h = P_l(0)$ and $x = P_k(t)$, we obtain

$$Q_{kl} \equiv L\{P_l(0)\} - L\{P_k(t)\} - \{P_l(0) - P_k(t)\} L'\{P_k(t)\} \geq 0 , \quad (204)$$

where the equality is valid only if h = 0. Using the fundamental relation (193) and the unitary properties (184) of the evolution operator, one finds

$$\begin{aligned} 0 \leq & \sum_{kl} Q_{kl} |U_{kl}|^2 = \\ = & \sum_l L\{P_l(0)\} \sum_k |U_{kl}|^2 - \sum_k L\{P_k(t)\} \sum_l |U_{kl}|^2 - \\ - & \sum_k \Big[\sum_l |U_{kl}|^2 P_l(0)\Big] L'\{P_k(t)\} + \sum_k P_k(t) L'\{P_k(t)\} \sum_l |U_{kl}|^2 = \quad (205) \\ = & \sum_l L\{P_l(0)\} - \sum_k L\{P_k(t)\} , \end{aligned}$$

$$\sum_k L\{P_k(0)\} \geq \sum_k L\{P_k(t)\} , \quad (206)$$

Here the equality sign holds only if the initial probabilities $P_k(0)$ are all the same. The relation indicates hence that, in general, the time evolution of a random-phase system from t_o to t is irreversible and that the quantity $\sum_k L\{P_k\}$ has decreased.

There are many choices of the convex function L possible, and the particular form L = x log x is characterized by the fact that $\sum_k P_k \log P_k$ is additive over independent subsystems. The quantity

$$S = -k \sum_k P_k \log P_k , \quad (207)$$

where the coefficient k is Boltzmann's constant, is such that $S(0) \leq S(t)$ and is sometimes characterized as the "microentropy" It is defined over the configuration space associated with all the particles of the system, whereas the conventional entropy refers to the ordinary space and may be obtained by a reduction procedure.

As mentioned above, the random-phase postulate has been used to a large extent in modern quantum mechanics, particularly by Dirac$^{10)}$. However, it has considerable weaknesses, since it can be valid only in a specific reference system and only at a specific time t_o. With the evolution in time, the system leaves the pure random-phase situation, and the same happens if one goes over to another basis.

In conclusion, it should be observed that the Schrödinger equation itself may contain irreversible elements in the form of time-dependent electromagnetic potentials, e.g. retarded potentials. However, even in the case when the Schrödinger equation is fully reversible in time, a study of the probability properties of assemblies may show irreversible features depending on the fact that one has not complete knowledge of the entire physical situation, i.e. the wave function including its phase. The question is how these uncertainties should be properly described. Important work on the irreversibility problem has during the last decades been carried out by Kirkwood$^{11)}$, Prigogine$^{12)}$, and Bogoliubov$^{13)}$.

Time-dependence of density matrices. - In concluding this section, it should be observed that the evolution operator formalism is particularly useful in treating statistical assemblies described by density matrices. In the terminology of von Neumann$^{14)}$, a system characterized by a wave function Ψ corresponds to a "pure state" and is associated with a homogeneous assembly which has a density matrix Γ defined by the relation $\Gamma = \Psi\Psi^\dagger$ or

$$\Gamma(\mathbf{R}, t \mid \mathbf{R}', t') = \Psi(\mathbf{R}, t)\, \Psi^\dagger(\mathbf{R}, t') \cdot \tag{208}$$

where, for the sake of simplicity, we will choose $t' = t$. Since the wave functions have a time-evolution of the type $\Psi = U\Psi_0$, $\Psi^\dagger = \Psi_0^\dagger U^\dagger$, one obtains

$$\Gamma(t) = U\,\Gamma(0)\,U^\dagger \tag{209}$$

for the density matrix of the homogeneous assembly. This relation is then generalized to define the time behaviour of density matrices in general. A density matrix $\Gamma = \Gamma(\mathbf{R}, t \mid \mathbf{R}', t)$ is essentially characterized by the following three conditions:

$$\Gamma^\dagger = \Gamma \quad , \qquad \Gamma \geq 0 \quad , \quad \mathrm{Tr}(\Gamma) = 1 \; , \tag{210}$$

and it represents usually a "mixture" of physical situations associated with wave functions.

In order to study the properties of density matrices in greater detail, it is convenient to introduce a complete orthonormal basis $\{f_k\}$ fulfilling the relations (180). In considering the initial time $t = t_0$, one obtains the expansion

$$\Gamma(\mathbf{R}, t_0 \mid \mathbf{R}', t_0) = \sum_{kl} f_k(\mathbf{R}) \, \Gamma_{kl}(0) \, f_l^*(\mathbf{R}') \; , \tag{211}$$

or, in matrix form, $\Gamma_0 = f\,\Gamma(0)\,f^\dagger$. In analogy to (210), the discrete matrix $\Gamma(0) = \{\Gamma_{kl}(0)\}$ has the properties $\Gamma^\dagger = \Gamma$, $\Gamma \geq 0$, $\mathrm{Tr}(\Gamma) = 1$. There exists hence a unitary transformation V which brings $\Gamma(0)$ to diagonal form $n(0)$:

$$V^\dagger \Gamma(0) \, V = n(0) \; , \tag{212}$$

where the eigenvalues $n(0)_k$ are real and satisfy the relations

$$n_k(0) \geq 0 \; , \qquad \sum_k n_k(0) = 1 \tag{213}$$

One has further $\Gamma(0) = V n(0) V^\dagger$ and, introducing the wave functions $\chi_k(\mathbf{R})$ through the transformation

$$\chi = f V \; , \tag{214}$$

one obtains $\Gamma_0 = f\,\Gamma(0) f^\dagger = f \, V n(0) \, V^\dagger f^\dagger = \chi \, n(0) \chi^\dagger$, i.e.

$$\Gamma(\mathbf{R}, t_0 \mid \mathbf{R}', t_0) = \sum_k \chi_k(\mathbf{R}) \, n_k(0) \, \chi_k^*(\mathbf{R}') \tag{215}$$

which relation may be considered as the "spectral resolution" of the density matrix Γ for $t = t_0$; the functions $\chi_k(\mathbf{R})$ are its eigenfunctions and the numbers $n_k(0)$ its eigenvalues, and one has $\Gamma\chi_k = n_k\chi_k$. Each one of the terms $\chi_k(\mathbf{R})\chi_k^*(\mathbf{R}')$ represents the density matrix for a "pure state" having the wave function $\chi_k(\mathbf{R})$, and the sum (215) represents hence a "mixture" of such pure states with the weights $n_k(0)$. We note the essential physical difference between the expansion (215) which is used in analyzing a general assembly and the expansion (181) which is used in studying the wave function associated with a "pure state".

The sum (215) contains usually many terms, and it is reduced to a single term if and only if $n_p(0) = 1$, $n_k(0) = 0$ for $k \neq p$, in which case one has

$$\Gamma(\mathbf{R}, t_0 | \mathbf{R}', t_0) = \chi_p(\mathbf{R})\chi_p^*(\mathbf{R}'), \qquad (216)$$

i.e. the assembly is homogeneous and corresponds to a pure state with the wave function $\chi_p(\mathbf{R})$. It is easily shown that an assembly corresponds to a pure state, if and only if the density matrix is idempotent, so that $\Gamma^2 = \Gamma$

After this analysis of the density matrix at $t = t_0$, we will now study the time-dependence defined through the relation (209). Introducing the time-dependent basis

$$\chi_k(\mathbf{R}, t) = U(t)\chi_k(\mathbf{R}), \qquad (217)$$

one obtains directly

$$\begin{aligned} \Gamma(t) &= U\Gamma(0)U^\dagger = U\chi\, n(0)\chi^\dagger U^\dagger = \\ &= \chi(t)\, n(0)\, \chi^\dagger(t), \end{aligned} \qquad (218)$$

and the spectral resolution

$$\Gamma(\mathbf{R}, t | \mathbf{R}', t) = \sum_k \chi_k(\mathbf{R}, t)\, n_k(0)\, \chi_k^*(\mathbf{R}', t), \qquad (219)$$

which shows that the weight factors n_k and hence the character of the mixture are independent of time.

For a more detailed study of the properties of the density matrices and their use in physics and chemistry, we will refer to von Neumann[14)] and to Husimi[15)].

8. TIME-DEPENDENT PERTURBATION THEORY

Let us now consider the case when the Hamiltonian $H = H(t)$ may conveniently be written in the form

$$\mathcal{H} = \mathcal{H}_0 + V(t) , \tag{220}$$

where V is a small perturbation to the unperturbed system characterized by the Hamiltonian H_0 having the normalized eigenfunctions Φ_k^0 and the eigenvalues E_k^0. In the following, we will make the choice $f_k = \Phi_k^0$ and introduce the unperturbed eigenfunctions as a basis and reference system.

The transition probabilities caused by the perturbation V are given by the general formula (188):

$$S_{m\rightarrow k}(t_0;t) = |U_{km}(t;t_0)|^2 , \tag{221}$$

and we note that, depending on the condition (190), these quantities can never "blow up". The absolute values of the unitary matrix $\mathbf{U}$ are always well-behaved, whereas the phases may turn out to be "dangerous" quantities involving some of the divergence difficulties still associated with modern quantum mechanics.

It is convenient to treat the perturbation problem in the "interaction representation" and to express the evolution operator U, in the product form $U = U_0 \cdot U_V$, where U_V is given by expansion (164):

$$U_V(t) = \sum_{n=0}^{\infty} \left(-\frac{2\pi i}{h}\right)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \, V_H(t_1) V_H(t_2) \dots V_H(t_n) , \tag{222}$$

where

$$V_H = U_0^\dagger V U_0 = e^{+\frac{2\pi i}{h}\mathcal{H}_0 t}\, V\, e^{-\frac{2\pi i}{h}\mathcal{H}_0 t} . \qquad (223)$$

For the matrix elements of U one obtains directly:

$$\langle \Phi_k^0 | U | \Phi_l^0 \rangle = e^{\frac{2\pi i}{h} E_k^0 t} \langle \Phi_k^0 | U_V | \Phi_l^0 \rangle , \qquad (224)$$

and consequently

$$S_{n\rightarrow k}(t_0 ; t) = |\langle \Phi_k^0 | U_V | \Phi_l^0 \rangle|^2 , \qquad (225)$$

which is a considerable simplification. Introducing the "Bohr frequency"

$$\nu_{kl}^0 = (E_k^0 - E_l^0)/h , \qquad (226)$$

one obtains similarly for the matrix elements of V_H :

$$\langle \Phi_k^0 | V_H | \Phi_l^0 \rangle = e^{2\pi i \nu_{kl}^0 t} \langle \Phi_k^0 | V | \Phi_l^0 \rangle . \qquad (227)$$

Using the expansion (222), we will now study the matrixelements of the operator U_V :

$$\begin{aligned} \langle \Phi_k^0 | U_V | \Phi_l^0 \rangle = {} & \delta_{kl} - \frac{2\pi i}{h} \int_0^t dt_1 \{V_H(t_1)\}_{kl} + \\ & + \sum_\alpha \left(-\frac{2\pi i}{h}\right)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \{V_H(t_1)\}_{k\alpha} \{V_H(t_2)\}_{\alpha l} + \qquad (228) \\ & + \sum_{\alpha\beta} \left(-\frac{2\pi i}{h}\right)^3 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \{V_H(t_1)\}_{k\alpha} \{V_H(t_2)\}_{\alpha\beta} \{V_H(t_3)\}_{\beta l} + \cdots , \end{aligned}$$

for various forms of the perturbation V . The indices $\alpha, \beta, \ldots$ are said to refer to so-called "intermediate states".

Time-independent perturbation. - Let us start by considering the simplest case when the perturbation is a constant in time, $V(t) = V$. Using (227) and (228), one obtains directly

$$\langle \Phi_k^0 | U_V | \Phi_l^0 \rangle = \delta_{kl} - \frac{2\pi i}{h} V_{kl} \frac{e^{2\pi i \nu_{kl}^0 t} - 1}{2\pi i \nu_{kl}^0} + \left(-\frac{2\pi i}{h}\right)^2 \sum_\alpha V_{k\alpha} V_{\alpha l} \left\{ \frac{e^{2\pi i \nu_{kl}^0 t} - 1}{2\pi i \nu_{kl}^0 \cdot 2\pi i \nu_{\alpha l}^0} - \frac{e^{2\pi i \nu_{k\alpha}^0 t} - 1}{2\pi i \nu_{k\alpha}^0 \cdot 2\pi i \nu_{\alpha l}^0} \right\} + \dots \tag{229}$$

For $\nu_{kl}^0 = 0$, one obtains so-called "resonance denominators", but we note that all terms are still regular according to formulas of the type:

$$\lim_{\nu \to 0} \frac{e^{2\pi i \nu t} - 1}{2\pi i \nu} = t \, . \tag{230}$$

In the special case when V commutes with H_0, the matrix V_{kl} is diagonal, and one has further the explicit solution

$$U_V = e^{-\frac{2\pi i}{h} V t} = 1 - \frac{2\pi i}{h} V t + \left(-\frac{2\pi i}{h} V\right)^2 \frac{t^2}{2!} + \dots , \tag{231}$$

which often serves as a convenient check.

Following Dirac[10), we will now study the first-order term in (229) for $k \neq 1$ in greater detail:

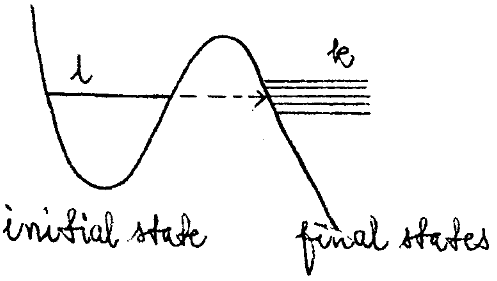
$$\langle \Phi_k^0 | U_V | \Phi_l^0 \rangle \approx - \frac{2\pi i}{h} V_{kl} \frac{e^{2\pi i \nu_{kl}^0 t} - 1}{2\pi i \nu_{kl}^0} , \tag{232}$$

Substitution into (225) gives the transition probability

$$\mathcal{P}_{l \to k}^{(1)}(t) = \frac{2}{h^2} |V_{kl}|^2 \frac{1 - \cos 2\pi \nu_{kl}^0 t}{(\nu_{kl}^0)^2} \tag{233}$$

This quantity oscillates a great deal with time and we observe that, for a small $t \approx 0$, one has a quadratic behaviour $\mathcal{P}_{l \to k}^{(1)}(t) \approx \approx (4\pi^2/h^2)|V_{kl}|^2 t^2$

Of particular importance in physics and chemistry are the time-proportional transition probabilities, and one may wonder how they are related to perturbation theory. It turns out[10) that they are characteristic for transitions from a discrete level 1 to a series of levels k which are so tight-lying that they form a continuous band. Such transitions occur e.g. in phenomena where a free particle is emitted, for instance radioactivity. Let us assume that the "band" for the final state E_k^0 covers the energy interval $(E-\Delta E;\ E+\Delta E)$ and that the density of states is given by the quantity $\rho(E)$. Assuming that the probabilities are additive, one obtains for the total transition probability:



$$S^{(1)}_{l\to \mathrm{cont}}(t) = \sum_k S^{(1)}_{l\to k}(t) = \int_{E-\Delta E}^{E+\Delta E} S^{(1)}_{l\to k}(t)\,\rho(E_k^0)\,dE_k^0 = \tag{234}$$

$$= \frac{2}{h^2}\int_{E-\Delta E}^{E+\Delta E} |\langle\Phi_k^0|V|\Phi_l^0\rangle|^2\,\frac{1-\cos 2\pi(E_k^0-E_l^0)t/h}{(E_k^0-E_l^0)^2/h^2}\,\rho(E_k^0)\,dE_k^0$$

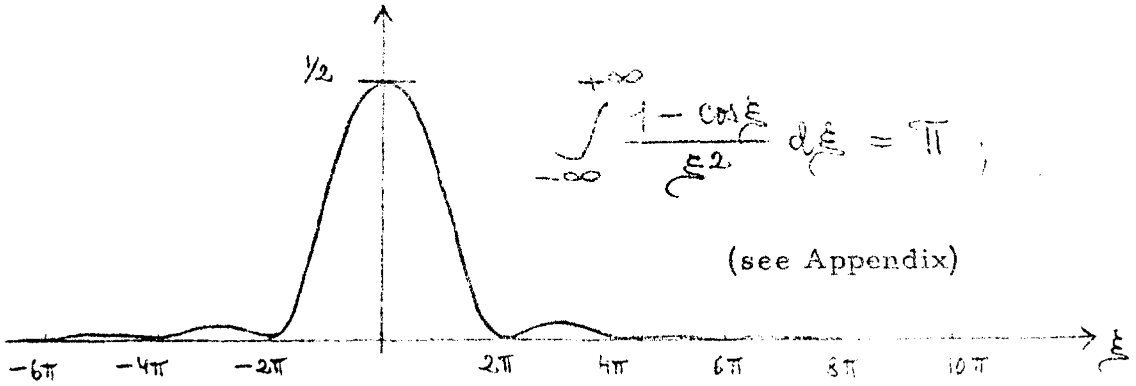
We will assume that the quantities $|\langle\Phi_k^0|V|\Phi_l^0\rangle|$ and $\rho(E_k^0)$ are slowly varying functions of E_k^0 which may be taken outside the integration. Making the substitution

$$\frac{2\pi}{h}(E_k^0-E_l^0)t = \xi, \quad \frac{2\pi}{h}t\,dE_k^0 = d\xi, \tag{235}$$

one obtains

$$S^{(1)}_{l\to \mathrm{cont}}(t) = \frac{4\pi t}{h}|V_{kl}|^2\rho(E)\int_{-2\pi t\cdot\Delta E/h}^{+2\pi t\cdot\Delta E/h}\frac{1-\cos\xi}{\xi^2}\,d\xi\,. \tag{236}$$

The integrand is plotted in the diagram below:



$$\int_{-\infty}^{+\infty} \frac{1-\cos\xi}{\xi^2}\, d\xi = \pi \; ; \qquad (237)$$

(see Appendix)

We note that the main contribution to the integral comes from the environment of the point $\xi = 0$, which corresponds to the energy resonance $E_k^0 \approx E_l^0$ between the initial and final states. This resonance is never completely sharp, however, depending on the uncertainty relation for the energy and time.

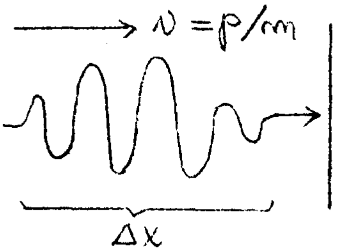
All energy measurements involve some interaction between the object and the apparaturs which is carried by at least one elementary particle in the form of a wave packet having the kinetic energy $E = p^2/2\,m$ and the extension Δx The time Δt needed for the entire wave packet to enter the measuring device is approximately the same as the time needed to pass through a plane separating the object from the apparatus, perpendicular to the motion of the wave packet. Since the velocity is p/m, one has

$$(p/m)\,\Delta t \approx \Delta x \qquad (238)$$

From $E = p^2/2\,m$ follows further $\Delta E = p\,\Delta p/m$, which gives $\Delta E \cdot \Delta t = \Delta p\,(p/m)\,\Delta t =$ $= \Delta p \;\Delta x \gtrsim h/4\pi$, and the uncertainty relation

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi} \qquad (239)$$

This implies that, in order to make a measurement of the energy with a certain accuracy ΔE , a certain minimum time interval Δt is always needed.



"Passage of wave packet through a plane".

Let us now return to relation (236). It is clear that this formula has a meaning only if the time interval t is not too short with reference to the uncertainty relation (239), i.e.

$$t \geq \frac{h}{4\pi \Delta E} , \tag{240}$$

which implies that $2\pi t \Delta E / h > +1/2$. With increasing t, the integral takes quickly its full value according to (237), and one obtains the final formula

$$P^{(1)}_{l \to cont}(t) = \frac{4\pi^2}{h} |V_{kl}|^2 \rho(E) \cdot t , \tag{241}$$

which is a time-proportional transition probability. Because of (190), it can only be valid for times t which are not too large, and formula (241) gives essentially the transition coefficient $\gamma = (4\pi^2/h)|V_{kl}|^2 \rho$, which enters the decay relation

$$\frac{dP_l}{dt} = -\gamma P_l , \tag{242}$$

with the solution $P_l(t) = P_l(0)\, e^{-\gamma t}$. The probability of the levels k in the "band" increases further according to the rule

$$P_k(t) = P_l(0) \{ 1 - e^{-\gamma t} \} , \tag{243}$$

and we note that the term γt in the right-hand member (241) may be considered as the first term in the expansion of $(1 - e^{-\gamma t})$.

The relations (242) and (243) may be obtained by considering also the higher terms in the expansion (228) but, in reality, the situation is usually more complicated than indicated here.

Oscillatory perturbation. - Let us now consider a general perturbation V, which is a function of time, and let us assume that it may expressed as a Fourier series:

$$V(t) = \sum_{\chi} e^{-2\pi i \nu_\chi t} v_\chi , \tag{244}$$

where the coefficients v_χ are linear operators working on the functions in the $\mathbf{R}$ -space. According to (227), one obtains for the matrix elements of V_H :

$$\langle \Phi_k^0 | V_H | \Phi_l^0 \rangle = \sum_\chi e^{2\pi i(\nu_{kl}^0 - \nu_\chi)t} \langle k | v_\chi | l \rangle \tag{245}$$

The matrix elements of the operator U_V are again given by formula (228), and we note that, for a perturbation of the form (244), the time integrations are of an elementary nature and are easily carried out explicitly. One obtains

$$\begin{aligned} \langle \Phi_k^0 | U_V | \Phi_l^0 \rangle = {} & \delta_{kl} - \frac{2\pi i}{h} \sum_\chi \frac{e^{2\pi i(\nu_{kl}^0 - \nu_\chi)t} - 1}{2\pi i(\nu_{kl}^0 - \nu_\chi)} \langle k | v_\chi | l \rangle + \\ & + \left(-\frac{2\pi i}{h}\right)^2 \sum_{\chi\lambda} \sum_\alpha \left\{ \frac{e^{2\pi i(\nu_{kl}^0 - \nu_\chi - \nu_\lambda)t} - 1}{2\pi i(\nu_{kl}^0 - \nu_\chi - \nu_\lambda)\, 2\pi i(\nu_{\alpha l}^0 - \nu_\lambda)} - \right. \\ & \left. - \frac{e^{2\pi i(\nu_{k\alpha}^0 - \nu_\chi)t} - 1}{2\pi i(\nu_{k\alpha}^0 - \nu_\chi)\, 2\pi i(\nu_{\alpha l}^0 - \nu_\lambda)} \right\} \langle k | v_\chi | \alpha \rangle \langle \alpha | v_\lambda | l \rangle + \cdots \end{aligned} \tag{246}$$

It is interesting to observe that "resonance denominators" occur for $\nu_\chi = \nu_{kl}^0$ and, in the second order terms, also for $\nu_\chi + \nu_\lambda = \nu_{kl}^0$ etc. , corresponding to one- and two-quantum processes etc. These terms are of essential interest in studying time-proportional transition probabilities, and the treatment follows essentially the same lines as given in the previous section.

For the sake of simplicitly, we will study a single oscillatory term in greater detail:

$$V = e^{-2\pi i \nu t}\, v \tag{247}$$

Such a perturbation is not self-adjoint, but the result is still typical for the terms occuring in this connection. Using (246), one obtains through the first order

$$\langle \Phi_k^0 | U_V | \Phi_l^0 \rangle \approx -\frac{2\pi i}{h} v_{kl} \frac{e^{2\pi i(\nu_{kl}^0 - \nu)t} - 1}{2\pi i(\nu_{kl}^0 - \nu)}, \tag{248}$$

in complete analogy to (232). This gives for the associated transition probability

$$\mathcal{P}^{(1)}_{l\to k}(t) = \frac{2}{h^2}|v_{kl}|^2 \, \frac{1-\cos 2\pi(\nu^0_{kl}-\nu)t}{(\nu^0_{kl}-\nu)^2} , \tag{249}$$

and, by studying the transitions from the discrete level l to the continuous levels **k** having the energy

$$E^0_k \approx E^0_l + h\nu , \tag{250}$$

one obtains in analogy to (241):

$$\mathcal{P}^{(1)}_{l\to \mathrm{cont}}(t) = \frac{4\pi^2}{h}|v_{kl}|^2 \rho(E^0_k)\, t , \tag{251}$$

which is the formula desired. According to (250), one finds that, from the point of view of the unperturbed system, this transition involves the absorption of the energy $h\nu$ from the oscillatory field associated with the perturbation V. By studying the self-adjoint perturbation

$$V = e^{-2\pi i\nu t}\, v + e^{+2\pi i\nu t}\, v^{\dagger} , \tag{252}$$

one finds also the transition probability for the corresponding emission process.

It is clear that, since the evolution operator in principle describes all the various time-dependent phenomena in physics and chemistry, we have here only touched a very small field of applications. The further study of the evolution operator and its matrix elements is probably one of the most important current research problems and, even if very important progress has been made during the last two decades particularly in connection with the so-called diagram technique, the study is still far from being concluded.

9. DISCUSSION

The purpose of this paper is to give a brief discussion of the treatment of time-dependent phenomena in the non-relativistic quantum theory. In many of the applications, the theory has been quite successful and has led to results in complete agreement with the experimental experience, but there are still certain difficulties connected with the concept of a complex wave function and particularly the evaluation of its phase. In the formula for time-evolution $\Psi(t) = U\Psi_0$, it may be possible to calculate the evolution operator U but considerably more difficult ot determine the wave function Ψ_0 for the initial state. The phase problem has been discussed in some detail in Sec. 2.

The problem of the behaviour of a many-particle system under the influence of an outer electromagnetic field can be treated in principle, but it is more difficult to study the interaction between a system of matter waves and their own electromagnetic field. The problem of the self-interactions leads to divergence difficulties in both the non-relativistic and relativistic formulations of quantum theory, and the nature of the elementary particles themselves is still completely unknown. For some time, one hoped that the evolution-operator formalism would be helpful in solving these problems, particularly since the absolute values of the matrix elements of U can never blow up, but it turned out that the difficulties were again connected with the phases. In scattering theory, the S-matrix given by the relation

$$S = U(+\infty, -\infty) \tag{253}$$

has been studied in many papers with interesting results, but the main problems associated with the basic divergence difficulties seem still to be unsolved.

One way out of the difficulties would be to quantize the space-time coordinates and to introduce a minimum length and a minimum time. In such a case, one would have to give up the differential form of the laws of nature which has been characteristic for classical mechanics (2) as well as wave mechanics (21). We note, however, that the evolution-operator formalism is based on the use of a <u>finite</u> time-interval $(t_0; t)$. If the Hamiltonian H is time-independent, the evolution operator takes the form:

$$U = e^{-\frac{2\pi i}{h}\mathcal{H}_{op} t} = \sum_k e^{-\frac{2\pi i}{h}E_k t} \, |\Phi_k\rangle\langle\Phi_k| , \qquad (254)$$

where Φ_k and E_k are the eigenfunctions and eigenvalues of H, respectively. The eigenvalue relation $\mathcal{H}\Phi_k = E_k \Phi_k$ is certainly a differential equation, but the quantities Φ_k and E_k entering (254) may instead be found by considering the variational integral:

$$I = \frac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \qquad (255)$$

Since the expectation value of the differential operator $\sum_k p_k^2/2m_k$ may be evaluated in momentum space according to (38), it is not necessary to use any derivatives whatsoever - all the results may be obtained by integration only. In this way, wave mechanics may be formulated entirely in terms of integral calculus. Instead of requesting the wave functions to be continuous and differentiable, it is now sufficient to require that they should be quadratically integrable. Whether this change in the character of the theory gives a better fundament for solving the basic difficulties as to the nature of the elementary particles remains to be seen.

The time-dependent Schrödinger equation (21) has deepened the understanding of physics, and it has further rendered a unification of physics and chemistry which was previously unconceivable. It has led to a new model of the inner structure of atoms, molecules, and the solid-state in excellent agreement with experience. Even of the remaining difficulties indicate that the theory is still not in its final form, it is highly useful as a tool for a unified description of numerous phenomena in nature.

APPENDIX

EVALUATION OF CERTAIN INTEGRALS.

In time-dependent perturbation theory, there are certain definite integrals which often occur and have to be evaluated. It is convenient to start from the formula

$$\int_0^{\xi} e^{-x}\cos tx\,dx = \frac{1}{1+t^2} - e^{-\xi}\,\frac{\cos t\xi - t\sin t\xi}{1+t^2}, \qquad \text{(A1)}$$

which is easily proven by differentiation. Integration over t between the limits 0 and t gives further:

$$\int_0^{\xi} e^{-x}\frac{\sin tx}{x}\,dx = \operatorname{arctg} t - e^{-\xi}\int_0^{t}\frac{\cos t\xi - t\sin t\xi}{1+t^2}\,dt \qquad \text{(A2)}$$

By letting $\xi \to +\infty$, one obtains

$$\int_0^{+\infty} e^{-x}\frac{\sin tx}{x}\,dx = \operatorname{arctg} x\,. \qquad \text{(A3)}$$

Putting x instead of $x\,t$ and $t = 1/u$, one has for $t > 0$ that

$$\int_0^{+\infty} e^{-ux}\frac{\sin x}{x}\,dx = \operatorname{arctg}\frac{1}{u}\,. \qquad \text{(A3)}$$

Because of the uniform convergence of the integral, one can easily put $u \to +0$, which gives the result

$$\int_0^{+\infty}\frac{\sin x}{x}\,dx = \frac{\pi}{2}, \qquad \text{(A4)}$$

Let us now return to the relation (A3). Integrating t over the interval between 0 and t, one obtains

$$\int_0^{+\infty} e^{-x}\frac{1-\cos tx}{x^2}\,dx = t\operatorname{arctg} t - \frac{1}{2}\log(1+t^2) \qquad \text{(A5)}$$

Putting x instead of $x\,t$ and $t = 1/u$, one gets immediately

$$\int_0^{+\infty} e^{-ux}\frac{1-\cos x}{x^2}\,dx = \operatorname{arctg}\frac{1}{u} - \frac{u}{2}\log\left(1+\frac{1}{u^2}\right) \qquad \text{(A6)}$$

which, for $u \rightarrow +0$, gives:

$$\int_0^{+\infty} \frac{1-\cos x}{x^2}\, dx = \frac{\pi}{2} \qquad \text{(A7)}$$

One has $1-\cos x = 2\sin^2 x/2$ and, substituting x instead of x/2, one obtains finally

$$\int_0^{+\infty} \left(\frac{\sin x}{x}\right)^2 = \frac{\pi}{2} \qquad \text{(A8)}$$

These examples may be sufficient to illustrate a general technique for evaluating definite integrals of this specific type.

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