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VARIATIONAL PRINCIPLES FOR NONSTATIONARY QUANTUM MECHANICAL PROBLEMS AND PERTURBATION THEORY

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A variational principle is formulated which is invariant with respect to the normalization of the wave functions and which can be used in the case when the wave functions of the initial and final states are not orthogonal. The problem of the uniqueness of perturbation theory in this case is considered. The possibility of employing the variational principle for the solution of problems concerning the decay of stationary states and charge exchange is discussed. The basic equations for charge exchange at large impact parameters are derived from the variational principle.

1. INTRODUCTION

IT occurs frequently in the solution of nonstationary problems in quantum mechanics that the wave functions of the initial and final states are not orthogonal, becoming orthogonal only in the limit $t \rightarrow \pm\infty$. Processes of this kind are, for example, all collisions involving a redistribution and, in particular, the simplest of these collisions, the charge-exchange collision. If these problems are solved by perturbation theory, assuming that the transition probability is small, we are faced with the non-uniqueness of the basic formulas of perturbation theory. Indeed, adding an arbitrary function of time to the perturbation changes the transition probability calculated by perturbation theory. On the other hand, this addition can be eliminated from the energy operator by an elementary unitary transformation and, evidently, cannot affect the true transition probability. This fact was noted in a number of papers[1] and ways of removing this non-uniqueness were proposed.[2]

It is well known that the basic formulas of perturbation theory can be derived from a variational principle. It is therefore natural to investigate this non-uniqueness by variational methods. The usual formulation of the variational principle for nonstationary problems (see, for example, reference 3, Sec. 25) does not immediately lead to a solution of this problem. It turns out, however, that one can formulate a new variational principle, using a stationary expression for the transition probability which is invariant with respect to multiplications of the trial functions by arbitrary functions of time. This makes it possible to avoid the above-mentioned non-uniqueness.

The new variational principle is very convenient for the investigation of the decay of nonstationary states. Using it for processes of the charge exchange type, we are able to explain why the usual formulas of perturbation theory are unsatisfactory in this case and to establish which properties of the trial functions are essential for the correct formulation of the problem. By taking account of these properties we can give a more consistent derivation of Bates'[2] basic equations for charge exchange for large impact parameters from the variational principle.

2. FORMULATION OF THE PROBLEM AND THE VARIATIONAL PRINCIPLE

Consider the problem of finding that solution Ψ_1 of the Schrödinger equation

$$H\Psi = i\hbar\,\partial\Psi/\partial t, \tag{1}$$

which satisfies the initial condition

$$\Psi_1(t_1) = \varphi_1. \tag{2}$$

The quantity

$$a_{12} = \int \varphi_2^* \Psi_1(t_2)\,d\tau, \tag{3}$$

which is usually the unknown, determines the probability for the transition of the system from the state φ_1 at time t_1 to the state φ_2 at time t_2. We assume that the operator H is self-conjugate and can depend on the time. The functions φ_1 and φ_2 are in general nonorthogonal.

For the formulation of the variational principle we consider the functional

$$J(\Phi_2, \Phi_1) = \int_{t_1}^{t_2} dt \int \Phi_2^*(t)\,(H - ih\,\partial/\partial t)\,\Phi_1(t)\,d\tau, \tag{4}$$

where the functions Φ_1 and Φ_2 satisfy the conditions

$$\Phi_1(t_1) = \varphi_1, \quad \Phi_2(t_2) = \varphi_2, \tag{5}$$

and make a variation of this functional in the neighborhood of the exact solutions Ψ_1 and Ψ_2 of the Schrödinger equation (1) satisfying the condition (2) and the condition

$$\Psi_2(t_2) = \varphi_2, \tag{6}$$

respectively. Using the hermiticity of the operator H, integrating by parts, and imposing the conditions $\delta\Psi_1(t_1) = \delta\Psi_2(t_2) = 0$, we obtain

$$J(\Psi_2 + \delta\Psi_2, \Psi_1 + \delta\Psi_1) = -ih\int \Psi_2^*(t_2)\,\delta\Psi_1(t_2)\,d\tau \cdot + \int_{t_1}^{t_2} dt \int \delta\Psi_2^*\left(H - ih\frac{\partial}{\partial t}\right)\delta\Psi_1\,d\tau. \tag{7}$$

From this we immediately find the stationary expression for a_{12}:

$$a_{12} = \mathrm{St}\left\{\int \Phi_2(t_2)\,\Phi_1(t_2)\,d\tau + \frac{1}{ih}\int_{t_1}^{t_2} dt \int \Phi_2^*\left(H - ih\frac{\partial}{\partial t}\right)\Phi_1\,d\tau\right\}. \tag{8}$$

Substituting in this formula functions Φ_1 and Φ_2 which are close to the exact wave functions Ψ_1 and Ψ_2, we obtain an approximate value for a_{12}, which differs from the exact value only in second order of smallness.

The first term on the right hand side of (8) represents the value of a_{12} as computed directly by (3) with the help of the approximate function Φ_1. In cases when the second term does not vanish we can improve the value of a_{12} by using (8); this improvement is often quite essential.

It is seen from (7) that (8) gives the exact value for a_{12} also if only one of the functions Φ_1, Φ_2 is replaced by the exact wave function, assuming that the other is arbitrary, satisfying only condition (5).

The asymmetry of (8) with respect to t_1 and t_2 is only seeming, for the same formula can be written in the form

$$a_{12} = \mathrm{St}\left\{\int \Phi_2^*(t_1)\,\Phi_1(t_1)\,d\tau + \frac{1}{ih}\int_{t_1}^{t_2} dt \int \left[\left(H - ih\frac{\partial}{\partial t}\right)\Phi_2\right]^* \Phi_1\,d\tau\right\}. \tag{9}$$

By going to the limit of the stationary problem we can obtain the usual formulation of the variational principle[3] for the scattering phases and amplitudes in perturbation theory.

3. PERTURBATION THEORY. NON-UNIQUENESS OF THE BASIC FORMULAS

Let us now consider the case when the energy operator can be split up into a perturbation and an unperturbed part in two ways:

$$H = H_1 + V_1 = H_2 + V_2. \tag{10}$$

We assume that the solutions of the Schrödinger equations for the unperturbed operators are known:

$$H_1\psi_1 = ih\,\partial\psi_1/\partial t, \quad \psi_1(t_1) = \varphi_1, \tag{11}$$

$$H_2\psi_2 = ih\,\partial\psi_2/\partial t, \quad \psi_2(t_2) = \varphi_2. \tag{12}$$

Regarding the perturbation as small, we can then assume that the functions ψ_1 and ψ_2 are close to the corresponding solutions Ψ_1 and Ψ_2 of equation (1). Substituting the functions ψ_1 and ψ_2 in the functional (8), we obtain an expression for a_{12} in the first order of perturbation theory:[*]

$$a_{12} = \int \varphi_2^*\psi_1(t_2)\,d\tau + \frac{1}{ih}\int_{t_1}^{t_2} dt \int \psi_2^* V_1 \psi_1\,d\tau. \tag{13}$$

In order that this expression be invariant with respect to the addition of an arbitrary function of time to the perturbation V_1, it is necessary that the functions ψ_1 and ψ_2 are orthogonal for all times between t_1 and t_2. This condition is satisfied in the usual case, when $V_1 = V_2$, and ψ_1 and ψ_2 are functions corresponding to different stationary states of a system with the energy operator $H_1 = H_2$. However, this orthogonality requirement is evidently not fulfilled in this case if $\varphi_1 = \varphi_2$, i.e., if we ask for the probability that the system remains in its previous state. It is true that the quantity a_{12} is then not necessarily small, but in contrast to the usual formulation of perturbation theory, the use of the variational principle is not based on the assumption that a_{12} is small.

An example of the type of problem that can be treated in this way is the charge exchange problem, i.e., the transition of an electron from one atomic system to another in the collision of the two. In the simplest approximation we can assume that the atomic systems move along classical trajectories (for sufficiently large impact parameters, simply along a straight line) and describe the interaction with the electron by the effective potentials U_1 and U_2. Then the energy operator has the form

$$H = -\tfrac{1}{2}\nabla^2 + U_1(\mathrm{r} - \mathbf{R}/2) + U_2(\mathrm{r} + \mathbf{R}/2), \tag{14}$$

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[*] If the wave functions ψ_1 and ψ_2 are substituted in the functional (9), this quantity will be expressed in terms of the matrix element of the operator V_2.

$$\mathbf{R} = \boldsymbol{\rho} + \mathbf{v}t, \quad \boldsymbol{\rho}\mathbf{v} = 0. \tag{15}$$

The potentials U_1 and U_2 play the role of the perturbations V_1 and V_2, and the functions ψ_1 and ψ_2 have the form

$$\psi_1 = \chi_1(\mathbf{r} + \mathbf{R}/2)\exp\{-\tfrac{1}{2}i\mathbf{v}\mathbf{r} - i(E_1 + v^2/8)t\},$$

$$\psi_2 = \chi_2(\mathbf{r} - \mathbf{R}/2)\exp\{\tfrac{1}{2}i\mathbf{v}\mathbf{r} - i(E_2 + v^2/8)t\}, \tag{16}$$

where χ_1 and χ_2 satisfy the equations

$$[-\tfrac{1}{2}\nabla^2 + U_2(\mathbf{r})]\chi_1(\mathbf{r}) = E_1\chi_1(\mathbf{r}),$$

$$[-\tfrac{1}{2}\nabla^2 + U_1(\mathbf{r})]\chi_2(\mathbf{r}) = E_2\chi_2(\mathbf{r}). \tag{17}$$

Then the coefficient a_{12} which determines the probability for charge exchange in a transition from the state χ_1 to the state χ_2 has in first order perturbation theory the form

$$a_{12} = \frac{1}{ih}\int_{-\infty}^{+\infty} dt\, e^{i(E_2 - E_1)t}\int \chi_2^*\left(\mathbf{r} - \frac{\mathbf{R}}{2}\right)U_1\left(\mathbf{r} - \frac{\mathbf{R}}{2}\right)\chi_1\left(\mathbf{r} + \frac{\mathbf{R}}{2}\right)e^{-i\mathbf{v}\mathbf{r}}\,d\tau. \tag{18}$$

Since the functions χ_1 and χ_2 are nonorthogonal for finite t, this expression changes if a function of time is added to U_1. The problem of how to choose this function has been discussed by Bates.[2]

4. INVARIANT VARIATIONAL PRINCIPLE

We now discuss how the formulation of the variational principle must be modified in order that the substitution of arbitrary trial functions should not lead to the above-mentioned non-uniqueness and that the expression for the transition probability be automatically invariant with respect to addition of an arbitrary function of time to the energy operator.

Let us assume that we know functions Φ_1 and Φ_2 which are close to the exact wave functions Ψ_1 and Ψ_2. Substituting these functions in (8) we obtain an approximate value for a_{12}. Then we multiply the function Φ_1 by f_1 and Φ_2 by f_2, where f_1 and f_2 are some functions of time which satisfy the conditions

$$f_1(t_1) = f_2(t_2) = 1. \tag{19}$$

We require that the functional be stationary with respect to arbitrary variations δf_1 and δf_2 with the condition

$$\delta f_1(t_1) = \delta f_2(t_2) = 0. \tag{20}$$

Using the expressions (8) and (9) for the functional we then obtain equations for the functions f_1 and f_2:

$$ih\dot{f}_1\int \Phi_2^*\Phi_1\,d\tau = f_1\int \Phi_2^*(H - ih\,\partial/\partial t)\,\Phi_1\,d\tau, \tag{21}$$

$$ih\dot{f}_2^*\int \Phi_2^*\Phi_1\,d\tau = f_2^*\int [(H - ih\,\partial/\partial t)\,\Phi_2]^*\,\Phi_1\,d\tau. \tag{22}$$

Solving these equations with the initial conditions (19), we find

$$f_1 = \exp\left\{-\frac{i}{h}\int_{t_1}^{t} L dt\right\}, \tag{23}$$

$$L = \int \Phi_2^*(H - ih\,\partial/\partial t)\,\Phi_1 d\tau \Big/ \int \Phi_2^*\,\Phi_1\,d\tau;$$

$$f_2^* = \exp\left\{-\frac{i}{h}\int_{t}^{t_2} L\,dt\right\}\int \Phi_2^*(t_2)\,\Phi_1(t_2)\,d\tau \Big/ \int \Phi_2^*(t)\,\Phi_1(t)\,d\tau. \tag{24}$$

Let us now substitute the "improved" functions $f_1\Phi_1$ and $f_2\Phi_2$ in the functional (8). We see immediately that the function under the time integral from t_1 to t_2 vanishes; only the first term remains, and we obtain

$$a_{12} = \mathrm{St}\left\{\int \Phi_2^*(t_2)\,\Phi_1(t_2)\ \exp\left[-\frac{i}{h}\int_{t_1}^{t_2} L\,dt\right]d\tau\right\}. \tag{25}$$

This variational principle has all the required properties. Indeed, it is easily seen that the multiplication of the functions Φ_1 and Φ_2 by the arbitrary functions f_1 and f_2, which are subject only to the conditions (19), does not alter the value of the functional. Moreover, it is apparent at once that the addition of a real function of time to the operator H changes a_{12} only by a phase factor.

In contrast to the usual variational principle, the functional takes on its stationary value not only for the exact functions Ψ_1 and Ψ_2, but also for any other functions which differ from the exact functions by a time factor. In the solution of the problem by direct methods both variational principles lead, of course, to the same results if the time factor is regarded as one of the parameters to be varied. If this condition is not satisfied, the variational principle (25) guarantees the stationary property of the functional for a wider class of functions and gives, in this sense, a more exact expression for a_{12} than the functional (8). It must be borne in mind, however, that the functional (8) does not have the extremal property, so that the agreement between the approximate and exact values of a_{12} can only be accidental; in this case the extension of the class of functions to be varied leads sometimes (as we shall see later) to a poorer approximate value for a_{12}.

The remarks made in connection with the variational principle (8) at the end of Sec. 2 also apply to the new variational principle. Thus, for example, we obtain the exact value of a_{12} if we substitute $\Phi_2 = \Psi_2$ and an arbitrary Φ_1 in the functional (25). Dividing the interval $t_1 \le t \le t_2$ into the two intervals $t_1 \le t \le t_0$ and $t_0 \le t \le t_2$, we can easily rewrite the expression (25) in a symmetric form with respect to t_1 and t_2. For the transition probability we obtain

$$w_{12} = \mathrm{St}\left\{\left|\int \Phi_2^*(t_0)\,\Phi_1(t_0)\,d\tau\right|^2 \exp\left[\frac{2}{h}\,\mathrm{Im}\int_{t_1}^{t_0} L\,dt + \frac{2}{h}\,\mathrm{Im}\int_{t_0}^{t_2} L'\,dt\right]\right\},$$

$$L' = \int\left(\left(H - ih\frac{\partial}{\partial t}\right)\Phi_2\right)^*\Phi_1\,d\tau \Big/ \int \Phi_2^*\Phi_1\,d\tau, \tag{26}$$

where the dependence on the intermediate time instant must disappear from the final result.

We note in conclusion that formula (25) leads immediately to an exponential law for the decay of a quasi-stationary state, if Φ_1 is replaced, as usual, by an approximate function which satisfies the equation

$$H\Phi_1 = (E_0 - i\Gamma)\,\Phi_1. \tag{27}$$

In this case the functions of the initial and final states coincide, which is especially convenient for the application of the variational principle.

5. CHOICE OF TRIAL FUNCTIONS FOR CHARGE EXCHANGE TYPE PROBLEMS

In the calculation of the charge exchange by perturbation theory it would be natural to substitute $\Phi_1 = \psi_1$ and $\Phi_2 = \psi_2$ in the functional (25), setting $t_1 = -\infty$ and $t_2 = +\infty$. The functions ψ_1 and ψ_2 become orthogonal for $t \to \pm\infty$ and in order to avoid ambiguities it is more convenient to use the equivalent formula (26), setting in it $t_0 = 0$, for example.

In order to investigate the legitimacy of such a procedure, we return to the initial formulation of the variational principle (8). We do not impose any further restrictions on the functions Φ_1 and Φ_2 except the conditions (5) for $t = t_1$ and $t = t_2$. In particular, the normalization condition and the condition $\int \Phi_2^*\Phi_1\,d\tau = \mathrm{const}$, which hold only for the exact functions Ψ_1 and Ψ_2, may not be satisfied. If we now turn to the "corrected" functions $\Phi_1 f_1$ and $\Phi_2 f_2$ and use the explicit forms of f_1 and f_2 [formulas (23) and (24)], we see that

$$\int \Phi_2^* f_2^* \Phi_1 f_1\,d\tau = \mathrm{const}$$

and, hence, the normalizing functions f_1 and f_2 are determined by the variational principle in such a way as to make the overlap integral a constant. This implies that, if ψ_1 and ψ_2 are chosen as trial functions, the normalizing functions f_1 and f_2 will increase exponentially with time and the functions Ψ_1 and Ψ_2 will cease completely to be close to the exact Ψ_1 and Ψ_2. Indeed, the corresponding calculations for the charge exchange of protons with hydrogen atoms indicate that the integrals in the denominator of formula (26) diverge in this case and that, therefore, this choice of trial functions is unsatisfactory.

We therefore require that the class of functions to be substituted in the functional is consistent with the condition that the overlap integral $\int \Phi_2^*\Phi_1\,d\tau$ be constant without any appreciable distortion of the wave functions. The simplest choice that can be made in this case is the superposition of the functions ψ_1 and ψ_2:

$$\Phi_1 = f_1^1\psi_1 + f_1^2\psi_2, \quad \Phi_2 = f_2^1\psi_1 + f_2^2\psi_2; \tag{28}$$

$$|f_1^1(-\infty)| = 1, \quad f_1^2(-\infty) = 0,$$

$$f_2^1(\infty) = 0, \quad |f_2^2(\infty)| = 1; \tag{29}$$

$$w_{12} = |f_1^2(\infty)|^2. \tag{30}$$

In this case the normalizing factor is one of the parameters to be varied, and we can require that the functional (8) or even the functional (4) be stationary in the derivation of the equations for the functions f, assuming that the variations are zero at the ends of the interval. We obtain the following equations for f_1 and f_2:

$$ih(\dot f^1 + S\dot f^2) = V_{11}f^1 + V_{12}f^2,$$

$$ih(\dot f^2 + S^*\dot f^1) = V_{21}f^1 + V_{22}f^2, \tag{31}$$

where

$$S = \int \psi_1^*\psi_2\,d\tau, \quad V_{ij} = \int \psi_i^* U_j \psi_j\,d\tau \qquad (i, j = 1, 2). \tag{32}$$

These equations were obtained directly from the Schrödinger equation by Bates.[2] Their derivation from a variational principle is more consistent and unique (see reference 3, Sec. 13). Solving these equations with the boundary conditions (29), we can determine the probability for charge exchange for different impact parameters.

It was shown in the paper of Bates[2] that this approximation is useful for fast collisions. However, the most important criterion for the applicability of this method is provided by the value of the impact parameter ρ. For sufficiently large impact parameters (in practice, at distances of the order of two to three atomic radii) the wave functions are given with sufficient accuracy by (28), so that the approximation is adequate. Arguments can also be given in favor of the assertion that the polarization has a small effect on the probability for charge exchange.[4]

It follows immediately from the variational principle that all integrals

$$\int \Phi_i^*\left(H - ih\frac{\partial}{\partial t}\right)\Phi_j\,d\tau \tag{33}$$

vanish. From this we obtain at once the normalization conditions and the condition that the over-