

$f(\Delta)$ plotted against $(\tau_i/2t_x)^2\Delta$ for two values of t_x/τ_i . Starting from $f(0)=0.25$ the curves go through a maximum which rapidly increases with increasing t_x/τ_i . Differentiating $f(\Delta)$, we find that at the maximum

$$(\sqrt{\Delta})I_1(\sqrt{\Delta})/I_2(\sqrt{\Delta})=2t_x/\tau_i.$$

The function on the left-hand side increases with Δ . It approaches 4 as $\Delta \rightarrow 0$. Therefore, $f(\Delta)$ has no maximum for $t_x/\tau_i < 2$. On the other hand, for large t_x/τ_i the value of Δ corresponding to the maximum of $f(\Delta)$ will be large and we have approximately

$$I_2(\sqrt{\Delta}) \sim I_1(\sqrt{\Delta}) \sim e^{\sqrt{\Delta}}/(2\pi\sqrt{\Delta})^{1/2}.$$

Therefore, the maximum of $f(\Delta)$ corresponds to

$$\sqrt{\Delta} \sim 2t_x/\tau_i. \quad (35)$$

Δ being related to t by (30), we find that the peak of pulse of excess free holes at distance x from the injection point occurs at

$$t = t_x(\tau_g + \tau_i)/\tau_i \quad (36)$$

and that the magnitude of the peak is

$$\Delta\phi_{\max} = [P_x/(4\pi)^{1/2}](T/\tau_g)(\tau_i/t_x)^{1/2}e^{t_x/\tau_i}. \quad (37)$$

For sufficiently large t_x/τ_i , the initial step in $\Delta\phi$, equal to P_x , will be negligible compared to the peak. $\Delta\phi$ will appear to rise gradually; and it will, therefore, be impractical to determine t_x from the first arrival of the pulse. The time corresponding to the easily observable maximum is given by (36). This result is easily understood. As τ_g is the average time required for releasing a trapped hole and τ_i is the average time required for trapping a free hole, $\tau_i/(\tau_i + \tau_g)$ is the fraction of time during which the hole remains free. Therefore, the time required for most of the holes to reach the collector is $(\tau_i + \tau_g)/\tau_i$ times longer than the transit time t_x in the absence of traps. The apparent drift mobility will be $\tau_i/(\tau_i + \tau_g)$ times the true mobility. Small apparent drift mobility has been reported for silicon³ and for germanium at low temperatures.⁵

Generalized Variational Equations for the Scattering of Electrons by Hydrogen Atoms*

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Generalized variational equations are derived for calculating the elastic and inelastic scattering amplitudes associated with the scattering of electrons by hydrogen atoms. The derivation of these equations is such that no unnecessary restrictions are imposed on possible trial wave functions. Two equivalent formulations are given: one involving the use of symmetrized wave functions; the other involving wave functions of the conventional (Mott and Massey) type. For trial wave functions consisting of only the incident wave (multiplied by a hydrogen eigenfunction), these variational equations yield the same results as are obtained by the approximations of Born and Oppenheimer. Various calculation procedures are discussed.

In an appendix, it is shown that the Hulthén variational equation for the scattering phases is a special case of the Kohn variational equation for the scattering amplitude.

I. INTRODUCTION

THE first development of a variational procedure for dealing with the scattering of electrons by hydrogen atoms was carried out by Huang.¹ His method is based on two assumptions: the wave function's asymptotic value contains only the incident and elastically scattered waves; only S -wave scattering takes place. By an extension of Hulthén's one-body scattering variational procedure, Huang thereby obtains a variational equation for determining the S -wave phase shifts. The calculation procedure based on the Hulthén-Huang variational equation was improved and extended

by Massey and Moiseiwitsch who carried out detailed calculations for the S -wave phases.² Where a comparison was possible, they found that the results of their variational methods, even for very simple trial functions, are in very good agreement with the results obtained previously by direct numerical integration of the wave equation. Erskine and Massey extended this work still further by calculating variationally the $1s \rightarrow 2s$ excitation cross section at low energies.³ Their method assumes that only S -wave scattering takes place and that a "distorted wave" approximation is valid. Moiseiwitsch has improved the variational method for dealing with the inelastic scattering processes.⁴ His procedure is based on two variational equations whose

* A brief report of this work and that of reference 8 was presented at the 1952 Thanksgiving Meeting of the American Physical Society [see Phys. Rev. **89**, 913 (1953)].

¹ S. S. Huang, Phys. Rev. **76**, 477 (1949). A variational procedure for the analogous nuclear problem, $n-d$ scattering, was developed by: W. Kohn, Phys. Rev. **74**, 1763 (1948), and M. Verde, Helv. Phys. Acta **22**, 339 (1949).

² H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951).

³ G. A. Erskine and H. S. W. Massey, Proc. Roy. Soc. (London) **A212**, 521 (1952).

⁴ B. L. Moiseiwitsch, Phys. Rev. **82**, 753 (1951).

development involves the following assumptions: a partial wave type of wave function must be used whose asymptotic value contains the incident wave, elastically scattered wave, and only one inelastically scattered wave (the one of particular interest).

In the present paper, we shall develop generalized variational equations for dealing with the scattering of electrons by hydrogen atoms. These variational equations are such that no unnecessary restrictions are imposed on possible trial wave functions other than that they exhibit the proper asymptotic form. Our development is based on the "spatial orientation degeneracy" of the wave function and the availability of a complete set of ortho-normal eigenfunctions of the hydrogen atom. This development of the variational equations is an extension of a method devised by Kohn for a one-body scattering problem.⁵ The result is a set of simultaneous variational equations for the elastic and inelastic scattering amplitudes.⁶ For calculation purposes, these variational equations can be considered to displace the equivalent set of simultaneous integro-differential equations in terms of which the theory is usually formulated.⁷

Two equivalent formulations of the variational equations are presented. The first is a "symmetrized formulation" in which the wave functions display their proper symmetry character throughout. The second is a "conventional formulation" in which the asymptotic wave functions exhibit separately what might be called an "ordinary" and "exchange" type of collision.

For trial wave functions which consist of the incident wave (multiplied by a hydrogen eigenfunction) alone, our variational equations give for the scattering amplitudes the same expressions as are obtained with the usual approximation of Born and Oppenheimer.⁷ Calculations have been carried out to obtain a variational improvement of the Born approximation for the elastic scattering of fast electrons by taking into account effects due to "distortion" and "polarization."⁸ The results of these calculations will be presented for publication shortly.

We might note here that the existence of two separate variational equations for describing a scattering situation (e.g., our Eqs. (8) and (11)) is directly traceable to the existence of the "reciprocity" and "unitarity" properties of the S matrix. More will be said about this at some later date.

II. SYMMETRIZED FORMULATION

We consider first the eigenfunctions for both the bound and continuum states of the isolated hydrogen

⁵ See W. Kohn, reference 1.

⁶ It is not difficult to show that Kohn's variational equation for the scattering amplitude is equivalent, for a partial wave type of trial function, to Hulthén's variational equation for the scattering phases. The proof of this is given in the Appendix.

⁷ N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, Chap. VIII.

⁸ J. G. Jones, thesis, University of Florida, 1953 (unpublished).

atom. The wave equation is taken in the form (we use Hartree atomic units throughout),

$$(\Delta + E_o + 2/r)\psi_o(\mathbf{r}) = 0. \quad (1)$$

We designate the state o of the atom as that having the particular eigenfunction ψ_o and, incidentally, the eigenvalue E_o . We shall require here that the eigenfunctions are so chosen as to form a normalized, orthogonal set; that is, such that

$$\sum_a A_a \int \psi_p^*(\mathbf{r})\psi_q(\mathbf{r})d\tau = A_p, \quad (1a)$$

where the summation sign is used throughout to signify a sum over the discrete and integral over the continuous parts of the spectrum. For this purpose, we can consider the state o as specified entirely by E_o and the particular angular momentum quantum numbers (l_o, m_o) . Now the alternative set of eigenfunctions ψ_o^* also satisfy (1) and (1a). We shall find it convenient to designate separately the state o^* of the atom as that state having the particular eigenfunction ψ_o^* . The state o^* can be entirely specified then by E_o and the particular angular momentum quantum numbers $(l_o, -m_o)$. It should be evident, then, that the two alternative sets of states, o and o^* , are merely rearrangements of each other.

The wave equation for the electron plus hydrogen atom system, with total energy E , is taken in the following form:⁷

$$[E - H(1, 2)]\Psi(1, 2) \\ = [\Delta_1 + \Delta_2 + E + 2/r_1 + 2/r_2 - 2/r_{12}]\Psi(1, 2) = 0, \quad (2)$$

and

$$\Psi^{(\pm)}(1, 2) = \pm \Psi^{(\pm)}(2, 1) \quad (2a)$$

are the two solutions; one (+) symmetric, the other (−) antisymmetric in the space coordinates of the two electrons, corresponding, respectively, to their antisymmetric ($S=0$) and symmetric ($S=1$) spin states.

Solutions of Eq. (2) are desired which represent the situation in which an electron is scattered by an atom initially in some state o (not necessarily the ground state). Hence, by way of defining this situation, these solutions must satisfy the following boundary condition:

$$\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) \rightarrow \psi_o(2) \exp(ik_o \mathbf{n}_a \cdot \mathbf{r}_1) \\ + (1/r_1) \sum_q \psi_q(2) \mathcal{F}_{qo}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_1) \exp(ik_q r_1), \\ \text{as } r_1 \rightarrow \infty; \quad (3)$$

where

$$k_q^2 = E - E_q, \quad (3a)$$

and the sum in (3) extends over all energetically accessible final states q of the atom (i.e., such that $k_q^2 > 0$). \mathbf{n}_a is a unit vector in the direction of the incident electron's momentum, and is of unspecified orientation—hence the "spatial orientation degeneracy" of the wave functions.⁵ \mathbf{n}_1 is a unit vector in the direction

of \mathbf{r}_1 . $\mathfrak{F}_{qo}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_1)$ is the singlet/triplet amplitude of the scattered wave (in a direction specified by the orientation of \mathbf{n}_1 relative to \mathbf{n}_a) corresponding to the $\sigma \rightarrow q$ transition of the atom. The value of the wave function as $r_2 \rightarrow \infty$ is obtained from (3) via the symmetry requirement (2a). The set of wave functions having the property (3), for all possible initial states $\sigma (k_\sigma^2 > 0)$ and all possible \mathbf{n}_a , form the total set of possible scattering solutions of (2) for a given total energy E .

We assume that the complete set of hydrogen eigenfunctions satisfying Eqs. (1), (1a) is given so that the only parts of (3) which must be determined from a solution of (2) are the scattered wave amplitudes. We now proceed to develop generalized variational equations which can be used to determine these $\mathfrak{F}_{qo}^{(\pm)}$.

For the first of these variational equations, we introduce an alternative set of scattering solutions of Eq. (2) for the same total energy E . These solutions represent the situation in which the electron is scattered from an atom initially in some state p^* and have then the following asymptotic form analogous to (3):

$$\Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b) \rightarrow \psi_{p^*}(2) \exp(ik_p \mathbf{n}_b \cdot \mathbf{r}_1) + (1/r_1) \sum_q \psi_q^*(2) \mathfrak{F}_{qp^*}^{(\pm)}(\mathbf{n}_b; \mathbf{n}_1) \exp(ik_q r_1) \quad \text{as } r_1 \rightarrow \infty; \quad (4)$$

where \mathbf{n}_b has the same significance as \mathbf{n}_a of (3), and $\mathfrak{F}_{qp^*}^{(\pm)}$, analogous to $\mathfrak{F}_{qo}^{(\pm)}$ of (3), is the amplitude of the scattered wave corresponding to the $p^* \rightarrow q^*$ transition of the atom. Referring to the remarks following (1a), it should be apparent that the two alternative complete sets of scattering solutions, $\Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b)$ and $\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a)$, are merely rearrangements of each other.

We now define the following variational integral:

$$\mathcal{J}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b) = \left(\frac{1}{2}\right) \int \Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b) [E - H] \times \Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) d\tau_1 d\tau_2, \quad (5)$$

which is zero for $\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a)$ satisfying Eq. (2). Consider possible (physically admissible) trial wave functions, $\Psi + \delta\Psi$, which are restricted only in that their asymptotic forms differ from (3) or (4) by the replacement therein of each \mathfrak{F} by $\mathfrak{F} + \delta\mathfrak{F}$; e.g.,

$$\delta\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) \rightarrow (1/r_1) \sum_q \psi_q(2) \delta\mathfrak{F}_{qo}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_1) \times \exp(ik_q r_1), \quad (6)$$

as $r_1 \rightarrow \infty$. Then, if such trial wave functions are inserted into the integral (5), its resultant first-order variation is

$$\delta\mathcal{J}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b) = \frac{1}{2} \int \Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b) [E - H] \times \delta\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) d\tau_1 d\tau_2. \quad (7a)$$

Inserting the explicit value of $(E - H)$ from (2), applying Green's Theorem, and combining the two

resultant surface integrals [which are equal due to the symmetry requirement (2a)], one obtains

$$\begin{aligned} \delta\mathcal{J}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b) &= \int [\Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b) \nabla_1 \delta\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) \\ &\quad - \delta\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) \nabla_1 \Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b)] \cdot d\sigma_1 d\tau_2. \quad (7b) \end{aligned}$$

Inserting into this expression the asymptotic values of Ψ and $\delta\Psi$ from (4) and (6), carrying out first the integral over $d\tau_2$ via (1a), then the surface integral over a sphere at $r_1 \rightarrow \infty$, one obtains [see Eq. (3.7) of reference 5]

$$\delta\mathcal{J}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b) = -4\pi \delta\mathfrak{F}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b), \quad (7c)$$

or

$$\delta[\mathcal{J}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b) + 4\pi \mathfrak{F}_{po}^{(\pm)}(\mathbf{n}_a; -\mathbf{n}_b)] = 0; \quad (8)$$

that is, the quantity in the brackets is stationary.

By the same procedure as above, one also finds

$$\delta[\mathcal{J}_{op^*}^{(\pm)}(\mathbf{n}_b; -\mathbf{n}_a) + 4\pi \mathfrak{F}_{op^*}^{(\pm)}(\mathbf{n}_b; -\mathbf{n}_a)] = 0, \quad (9)$$

where the roles of $\Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b)$ and $\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a)$ in (5) are interchanged to give

$$\begin{aligned} \mathcal{J}_{op^*}^{(\pm)}(\mathbf{n}_b; -\mathbf{n}_a) &= \frac{1}{2} \int \Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) [E - H] \\ &\quad \times \Psi_{p^*}^{(\pm)}(1, 2; \mathbf{n}_b) d\tau_1 d\tau_2. \quad (9a) \end{aligned}$$

Equations (8) and (9) represent the first of the generalized variational equations for $\mathfrak{F}_{po}^{(\pm)}$.

We consider next a companion form of the above variational equations. We define as the variational integral here:

$$\begin{aligned} \mathcal{K}_{po}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_b) &= \frac{1}{2} \int \Psi_p^{(\pm)*}(1, 2; \mathbf{n}_b) [E - H] \\ &\quad \times \Psi_o^{(\pm)}(1, 2; \mathbf{n}_a) d\tau_1 d\tau_2, \quad (10) \end{aligned}$$

where the left-hand wave function in the integrand differs from the corresponding member of (5) in that it is the actual complex conjugate of the appropriate member of the set of wave functions $\Psi_o^{(\pm)}(1, 2; \mathbf{n}_a)$. Applying to this integral the same considerations which led from (5) above to the variational Eq. (8), one finds

$$\begin{aligned} \delta[\mathcal{K}_{po}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_b) + 4\pi \mathfrak{F}_{po}^{(\pm)}(\mathbf{n}_a; \mathbf{n}_b)] &= 2i \sum_q k_q \int \mathfrak{F}_{qp}^{(\pm)*}(\mathbf{n}_b; \mathbf{n}) \delta\mathfrak{F}_{qo}^{(\pm)}(\mathbf{n}_a; \mathbf{n}) d\Omega, \quad (11) \end{aligned}$$

where the solid angle integration is over all orientations of \mathbf{n} . Equation (11) is the second of the generalized variational equations for determining the $\mathfrak{F}_{po}^{(\pm)}$.

In either of the above formulations, (8)–(9) or (11), one has available a set (generally infinite) of simultaneous variational equations for determining the required $\mathcal{F}_{p_0}^{(\pm)}$. These equations can be considered to replace the equivalent set of simultaneous integro-differential equations in terms of which the theory is usually formulated.⁷

In the particular case where one uses as trial wave functions merely the first terms of (3) and (4), one obtains values for $\mathcal{F}_{p_0}^{(\pm)}$ which are the same as those obtained via the Born-Oppenheimer approximation, as might be expected (see below).

III. CONVENTIONAL FORMULATION

We consider, now, the formulation of the above variational equations in their nonsymmetrized forms. These are related more directly with the conventional integro-differential equation formulation of the electron-hydrogen scattering problem as presented by Mott and Massey.⁷ It must be emphasized here that this relationship is not a perfect analogy, however, since the Mott and Massey formulation is based *ab initio* on certain assumed expansions for the total wave function whose validity has recently been questioned.^{9–11} The formulations of the variational equations given in this section follow directly from those of the previous section and are, therefore, free of the questionable expansions used by Mott and Massey. For purposes of comparison, however, we adopt a notation which directly parallels that of Mott and Massey. The present section introduces nothing essentially new, but serves to formulate the results of the previous section in conventional form.

If $\Psi^{(+)}(1, 2)$ and $\Psi^{(-)}(1, 2)$ are each solutions of Eq. (2), it then follows that

$$\Psi(1, 2) = \frac{1}{2}[\Psi^{(+)}(1, 2) + \Psi^{(-)}(1, 2)], \quad (13a)$$

$$\Psi(2, 1) = \frac{1}{2}[\Psi^{(+)}(1, 2) - \Psi^{(-)}(1, 2)], \quad (13b)$$

are also solutions. From this, one may write

$$\Psi^{(\pm)}(1, 2) = (1 \pm X)\Psi(1, 2), \quad (13c)$$

where X is an operator which interchanges the position coordinates of the two electrons. We recognize that X is hermitian and commutes with $(E-H)$ of (2), and also that

$$(1 \pm X)^2 = 2(1 \pm X). \quad (13d)$$

We define

$$f = \frac{1}{2}[\mathcal{F}^{(+)} + \mathcal{F}^{(-)}], \quad (14a)$$

$$g = \frac{1}{2}[\mathcal{F}^{(+)} - \mathcal{F}^{(-)}], \quad (14b)$$

so that

$$\mathcal{F}^{(\pm)} = f \pm g. \quad (14c)$$

The f and g are usually thought of as the scattering amplitudes corresponding to an “ordinary” and “exchange” type of collision, respectively.⁷

Corresponding to the asymptotic forms (3) and (4) of the two sets of wave functions considered in the previous section, we now have the following asymptotic forms of the nonsymmetrized wave function (13a):

$$\begin{aligned} \Psi_o^{(a)}(1, 2) \rightarrow & \psi_o(2) \exp(ik_o \mathbf{n}_a \cdot \mathbf{r}_1) \\ & + (1/r_1) \sum_q \psi_q(2) f_{qo}(\mathbf{n}_a; \mathbf{n}_1) \exp(ik_q r_1), \\ & \text{as } r_1 \rightarrow \infty; \end{aligned} \quad (15)$$

$$\Psi_o^{(a)}(1, 2) \rightarrow (1/r_2) \sum_q \psi_q(1) g_{qo}(\mathbf{n}_a; \mathbf{n}_2) \exp(ik_q r_2), \quad \text{as } r_2 \rightarrow \infty;$$

which follows directly from (3), (13a), (14); and

$$\begin{aligned} \Psi_p^{*(b)}(1, 2) \rightarrow & \psi_p^*(2) \exp(ik_p \mathbf{n}_b \cdot \mathbf{r}_1) \\ & + (1/r_1) \sum_q \psi_q^*(2) f_{qp}^*(\mathbf{n}_b; \mathbf{n}_1) \exp(ik_q r_1), \\ & \text{as } r_1 \rightarrow \infty; \end{aligned} \quad (16)$$

$$\Psi_p^{*(b)}(1, 2) \rightarrow (1/r_2) \sum_q \psi_q^*(1) g_{qp}^*(\mathbf{n}_b; \mathbf{n}_2) \exp(ik_q r_2), \quad \text{as } r_2 \rightarrow \infty;$$

which follows directly from (4), (13a), (14).

We define now the following two variational integrals, which are equivalent to (5):

$$\begin{aligned} I_{p_0}(\mathbf{n}_a; -\mathbf{n}_b) \\ = \int \Psi_p^{*(b)}(1, 2) [E-H] \Psi_o^{(a)}(1, 2) d\tau_1 d\tau_2, \end{aligned} \quad (17a)$$

$$\begin{aligned} J_{p_0}(\mathbf{n}_a; -\mathbf{n}_b) \\ = \int \Psi_p^{*(b)}(2, 1) [E-H] \Psi_o^{(a)}(1, 2) d\tau_1 d\tau_2. \end{aligned} \quad (17b)$$

One then finds, corresponding to (8),

$$\delta[I_{p_0}(\mathbf{n}_a; -\mathbf{n}_b) + 4\pi f_{p_0}(\mathbf{n}_a; -\mathbf{n}_b)] = 0, \quad (18a)$$

$$\delta[J_{p_0}(\mathbf{n}_a; -\mathbf{n}_b) + 4\pi g_{p_0}(\mathbf{n}_a; -\mathbf{n}_b)] = 0, \quad (18b)$$

which follows from (5), (8), (13c, d), (14c). The variational equations which correspond to (9) follow in similar fashion.

We define now the following two variational integrals, which correspond to (10):

$$\begin{aligned} K_{p_0}(\mathbf{n}_a; \mathbf{n}_b) \\ = \int \Psi_p^{(b)*}(1, 2) [E-H] \Psi_o^{(a)}(1, 2) d\tau_1 d\tau_2, \end{aligned} \quad (19a)$$

$$\begin{aligned} L_{p_0}(\mathbf{n}_a; \mathbf{n}_b) \\ = \int \Psi_p^{(b)*}(2, 1) [E-H] \Psi_o^{(a)}(1, 2) d\tau_1 d\tau_2. \end{aligned} \quad (19b)$$

⁹ T. Y. Wu, Phys. Rev. **87**, 1012 (1952).

¹⁰ S. Borowitz and B. Friedman, Phys. Rev. **89**, 441 (1953).

¹¹ It is not difficult to show, however, that the final results obtained by Mott and Massey from these expansions are quite valid as far as the discrete spectrum of states (excitation, but not ionization) is concerned.

One then finds, corresponding to (11),

$$\begin{aligned} & \delta[K_{po}(\mathbf{n}_a; \mathbf{n}_b) + 4\pi f_{po}(\mathbf{n}_a; \mathbf{n}_b)] \\ &= 2i \sum_q k_q \int [f_{qp}^*(\mathbf{n}_b; \mathbf{n}) \delta f_{qo}(\mathbf{n}_a; \mathbf{n}) \\ & \quad + g_{qp}^*(\mathbf{n}_b; \mathbf{n}) \delta g_{qo}(\mathbf{n}_a; \mathbf{n})] d\Omega; \quad (20a) \end{aligned}$$

$$\begin{aligned} & \delta[L_{po}(\mathbf{n}_a; \mathbf{n}_b) + 4\pi g_{po}(\mathbf{n}_a; \mathbf{n}_b)] \\ &= 2i \sum_q k_q \int [f_{qp}^*(\mathbf{n}_b; \mathbf{n}) \delta g_{qo}(\mathbf{n}_a; \mathbf{n}) \\ & \quad + g_{qp}^*(\mathbf{n}_b; \mathbf{n}) \delta f_{qo}(\mathbf{n}_a; \mathbf{n})] d\Omega. \quad (20b) \end{aligned}$$

We now consider the results that are obtained when one uses as trial wave functions merely the first terms of (15) and (16); i.e.,

$$\Psi_o^{(a)}(1, 2) = \psi_o(2) \exp(ik_o \mathbf{n}_a \cdot \mathbf{r}_1), \quad (21a)$$

$$\Psi_p^{*(b)}(1, 2) = \psi_p^*(2) \exp(ik_p \mathbf{n}_b \cdot \mathbf{r}_1). \quad (21b)$$

Substituting these trial wave functions into (18a, b) or (20a, b), one finds

$$\begin{aligned} 4\pi f_{po}(\mathbf{n}_a; \mathbf{n}_b) &= \int [2/r_1 - 2/r_{12}] \psi_p^*(2) \psi_o(2) \\ & \quad \times \exp(ik_o \mathbf{n}_a \cdot \mathbf{r}_1 - ik_p \mathbf{n}_b \cdot \mathbf{r}_1) d\tau_1 d\tau_2; \quad (22a) \end{aligned}$$

$$\begin{aligned} 4\pi g_{po}(\mathbf{n}_a; \mathbf{n}_b) &= \int [2/r_1 - 2/r_{12}] \psi_p^*(1) \psi_o(2) \\ & \quad \times \exp(ik_o \mathbf{n}_a \cdot \mathbf{r}_1 - ik_p \mathbf{n}_b \cdot \mathbf{r}_2) d\tau_1 d\tau_2. \quad (22b) \end{aligned}$$

These expressions are equivalent to those obtained by the Born-Oppenheimer approximation. The expression for f_{po} agrees exactly with that given by Mott and Massey.⁷ The expression for g_{po} , however, differs from that of Mott and Massey in that the $2/r_1$ in (22b) is $2/r_2$ according to them—a difference which is significant only in the continuous spectrum. That the above expressions are correct has been pointed out by other workers using different approaches to these same results.^{9,10}

IV. CONCLUDING REMARKS

Variational equations for the scattering of electrons by hydrogen atoms which are comparable to those given above have been independently obtained by Borowitz and Friedman.¹⁰ Their development is based on a generalization of the Schwinger (integral equation) variational formulation of the one-body scattering problem. As Kohn has shown in the one-body case, his scattering amplitude variational equation (derived from the spatial orientation degeneracy of the wave function) reduces to the comparable Schwinger variational equation when use is made of the integral equation for the wave function.⁵ Hence, a similar

relationship, at least in part, undoubtedly exists between the variational equations given above and those of Borowitz and Friedman.

In the Schwinger method, the integral equation for the wave function provides for a definite iteration procedure for systematically improving the trial wave function.¹² Indeed, Kato has shown that a modification of this iteration procedure will yield upper and lower bounds for the scattering coefficients.¹³ For the scattering of electrons by hydrogen atoms, however, the appropriate integral equations given by Borowitz and Friedman are formidably complex so that there is little hope that such an iteration procedure (except for a one-body approximation, or the like) can be readily carried through.¹⁴

The procedure adopted by the London group^{2,3} for applying the variational equations is simple to carry out although there is no guaranty, in general, concerning the quality of the results. This procedure involves choosing a reasonable trial wave function which is linear in all the variational parameters (scattering amplitudes included) and for which the variational integrals can be evaluated without difficulty. Two different methods are then used to determine the variational parameters: a linear (Kohn⁵) procedure; and a quadratic (Hulthén¹⁵) procedure. The linear procedure leads to a value for the scattering amplitude and wave function which satisfy identically the integral equation which relates them; that is, the wave function so determined satisfies a necessary (but not sufficient) condition for its being an exact solution. In the quadratic procedure, the wave function is required, as an auxiliary condition to the variational equation, to satisfy the equation (quadratic in the variational parameters): variational integral = 0, which is also a necessary (but not sufficient) condition for the wave function to be an exact solution. In the limit where the trial wave function approaches the exact solution, the two procedures must give the same results. Hence, the closeness of the results obtained by the two procedures is a criterion for the reliability of the results. What is lacking, of course, is a proof, if one is possible, that this criterion is sufficient for determining the reliability of the results.¹⁶ Even so, such a criterion may be more stringent than necessary, since it serves to judge the quality of the trial wave function and one may suppose it to be possible for some relatively poor trial wave function to give fairly good results variationally for the scattering amplitudes by one or the

¹² See, e.g., J. M. Blatt and J. D. Jackson, *Phys. Rev.* **76**, 18 (1949).

¹³ T. Kato, *Progr. Theoret. Phys.* **6**, 295, 394 (1951).

¹⁴ Variational calculations for elastic electron-hydrogen scattering using the one-body approximation have been carried out by T. Kato, reference 13; L. Mower, *Phys. Rev.* **89**, 947 (1953); S. Altshuler, *Phys. Rev.* **89**, 1278 (1953).

¹⁵ See, e.g., reference 7, page 128.

¹⁶ For the elastic S-wave scattering case, the London group (reference 2) found that when the two procedures gave essentially the same results, these results agreed very well with those from direct numerical integrations of the wave equation.

other procedure, but not both, depending on certain factors as yet unknown.

APPENDIX: RELATIONSHIP BETWEEN KOHN'S VARIATIONAL EQUATION FOR THE SCATTERING AMPLITUDE AND HULTHÈN'S VARIATIONAL EQUATION FOR THE SCATTERING PHASES

We restrict our considerations here to a one-body scattering situation and a central force potential $V(r)$. The wave equation is

$$(E-H)\psi(\mathbf{r}) = [\Delta + k^2 - V(r)]\psi(\mathbf{r}) = 0; \quad (\text{A1})$$

and a solution is desired which has the asymptotic form:

$$\psi^{(a)}(\mathbf{r}) \rightarrow \exp(ik\mathbf{n}_a \cdot \mathbf{r}) + f(\mathbf{n}_a; \mathbf{n})(1/r) \exp(ikr). \quad (\text{A2})$$

The variational integral is defined as follows (see reference 5, Sec. III):

$$I(\mathbf{n}_a; -\mathbf{n}_b) = \int \psi^{(b)} [E-H] \psi^{(a)} d\tau. \quad (\text{A3})$$

For trial functions $\psi + \delta\psi$ having the same asymptotic form as (A2), but with f replaced by $f + \delta f$, one obtains to first-order,

$$\begin{aligned} \delta I(\mathbf{n}_a; -\mathbf{n}_b) &= \int \psi^{(b)} [E-H] \delta\psi^{(a)} d\tau \\ &= -4\pi\delta f(\mathbf{n}_a; -\mathbf{n}_b), \end{aligned} \quad (\text{A4})$$

which is Kohn's variational equation for the scattering amplitude f .

The solution of (A1) having the asymptotic form (A2) can be expanded into partial waves and thereby written in terms of the scattering phases η_n as follows (see reference 7, Chap. II):

$$\psi^{(a)}(\mathbf{r}) = (1/kr) \sum_n (2n+1) i^n \times \exp(i\eta_n) G_n(r) P_n(\mathbf{n}_a \cdot \mathbf{n}); \quad (\text{A5})$$

where

$$\mathcal{L}G_n = [d^2/dr^2 - n(n+1)/r^2 + k^2 - V(r)]G_n(r) = 0, \quad (\text{A5a})$$

and

$$G_n \sim \sin(kr - \frac{1}{2}n\pi + \eta_n), \quad (\text{A5b})$$

asymptotically. Then

$$\begin{aligned} f(\mathbf{n}_a; \mathbf{n}) &= (1/2ik) \sum_n (2n+1) \\ &\times [\exp(i2\eta_n) - 1] P_n(\mathbf{n}_a \cdot \mathbf{n}). \end{aligned} \quad (\text{A6})$$

Now, we have from (A5):

$$\begin{aligned} \delta\psi^{(a)} &= (1/kr) \sum_n (2n+1) i^n \\ &\times \exp(i\eta_n) \delta G_n(r) P_n(\mathbf{n}_a \cdot \mathbf{n}), \end{aligned} \quad (\text{A7})$$

plus an additional term (from $\delta\eta_n$) which gives, because of (A5a), no contribution to the integral (A4) which becomes

$$\begin{aligned} \delta I(\mathbf{n}_a; -\mathbf{n}_b) &= (1/k^2) \sum_{n,m} (2n+1)(2m+1) (i)^{n+m} \\ &\times \exp(i\eta_n + i\eta_m) \int G_m(r) \mathcal{L}\delta G_n(r) dr \\ &\times \int P_m(\mathbf{n}_b \cdot \mathbf{n}) P_n(\mathbf{n}_a \cdot \mathbf{n}) d\Omega. \end{aligned} \quad (\text{A8})$$

Making use of the Addition Theorem for Legendre Polynomials, one obtains

$$\begin{aligned} \delta I(\mathbf{n}_a; -\mathbf{n}_b) &= (4\pi/k^2) \sum_n (2n+1) (-1)^n \\ &\times \exp(i2\eta_n) \delta L_n P_n(\mathbf{n}_a \cdot \mathbf{n}_b), \end{aligned} \quad (\text{A9})$$

where

$$\delta L_n = \int_0^\infty G_n(r) \mathcal{L}\delta G_n(r) dr. \quad (\text{A9a})$$

From (A6) one has

$$\begin{aligned} 4\pi\delta f(\mathbf{n}_a; -\mathbf{n}_b) &= (4\pi/k) \sum_n (2n+1) (-1)^n \\ &\times \exp(i2\eta_n) \delta\eta_n P_n(\mathbf{n}_a \cdot \mathbf{n}_b). \end{aligned} \quad (\text{A10})$$

Hence, from (A4), (A9), it follows that

$$\delta L_n = -k\delta\eta_n, \quad (\text{A11})$$

which is Hulthèn's variational equation for the scattering phases η_n .¹⁵ Hence, one may conclude that Hulthèn's variational equation for the phases is a particular case of Kohn's variational equation for the scattering amplitude. Kohn⁵ has already shown that his scattering amplitude variational equation reduces to the comparable Schwinger variational equation when use is made of the integral equation expression for the wave function. Hence, the above discussion serves as a further link between the various forms of the one-body scattering variational equations.¹⁷

¹⁷ See also: T. Kato, Phys. Rev. **80**, 475 (1950).