where we have made the substitution $v=\frac{1}{2}(zZe^2/E)u$ and are using the dimensionless constants

$$t=[2E/(zZe^2)]s=\tan(\tfrac{1}{2}\Phi_0), \quad (15)$$

$$\beta=\alpha 8(\hbar c/e^2)z^{-4}Z^{-2}(E/\hbar c)^3 = 2.68\times 10^{39}\alpha z^{-4}Z^{-2}E_{\mathrm{Mev}}^3, \quad (16)$$

where α is in cm^3.

Hardmeier[7] has given a formula for δ at small scattering angles and has evaluated it explicitly for large scattering angles for $\beta=1, 2, 4, 6$. We have evaluated δ at large scattering angles for $\beta=0.2$ by numerically integrating the difference of the integrals appearing in Eq. (4) except near the ends of the region of integration. At the ends, the difference was approximated by expressions that could be integrated directly. $d\delta/d\Phi_0$ was then obtained by numerical differentiation. The results for σ_p/σ_c are given in Fig. 1 using also Hardmeier's[7] results for small scattering angles.

In the case of head on collisions, σ_p/σ_c reduces to $[1+(d\delta/d\Phi_0)]^{-2}$; also, as $t\to 0$, we have

$$\lim_{t\to 0}\frac{d\delta}{d\Phi_0}=\lim_{t\to 0}\frac{\delta}{\Phi_0}=\lim_{t\to 0}\frac{\delta}{2t}=\int_0^{v_1}\frac{dv}{[1-2v+\beta v^4]^{\frac{1}{2}}}-\int_0^{v_0}\frac{dv}{[1-2v]^{\frac{1}{2}}}. \quad (17)$$

If we evaluate this as a power series in β, we obtain for backward scattering

$$\frac{\sigma_p}{\sigma_c}(0)=1-0.229\beta-0.0354\beta^2. \quad (18)$$

For $\beta=0.2$, this gives us a 4.7 percent deviation from pure Coulomb scattering in the backward direction. For the deuteron $z=1$ and from reference 1, we have[8] $\alpha=0.56\times 10^{-39}$ cm^3. Then, applying Eqs. (16) and (18) to some examples where the nuclear effects should be comparatively small[2,9] and hence our treatment be valid, we find for 8-Mev deuterons scattered by $_{83}$Bi where $\beta=0.112$ a deviation of 2.7 percent in the backward direction, and for 10-Mev deuterons scattered by $_{92}$U where $\beta=0.177$ a deviation of 4.2 percent in the backward direction.

[8] The value of α is taken from Eqs. (13) and (21) of reference 1 by noting that for the scattering problem, we must average over the magnetic quantum number so that $\langle\alpha\rangle_{\mathrm{Av}}=\alpha_{SS}+2\alpha_{DD}\approx\alpha_{SS}=0.56\times 10^{-39}$ cm^3.

[9] D. C. Peaslee, Phys. Rev. 74, 1001 (1948); C. J. Mullin and E. Guth, Phys. Rev. 82, 141 (1951).

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Exchange Scattering of an Electron by the Hydrogen Atom*

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The theory of scattering of electrons by hydrogen has been re-examined with the objective of identifying the matrix element for the exchange scattered amplitude from the same integral equation which provides direct scattered amplitudes. The theory of Mott and Massey is verified, but it is demonstrated that their result contains contributions from the incident wave which must be removed before computing exchange amplitudes. The result is a theoretical justification for the Oppenheimer (prior) matrix element.

THE analysis of exchange scattering was originally made by Oppenheimer,[1] and an entirely different treatment of this problem which has become standard was given by Mott and Massey.[2] The reason for the superiority of the latter method is that the general matrix element for the exchange scattered amplitude is identified, while Oppenheimer's solution is an approximate one from the outset so that the possibility for improved estimates is automatically ruled out. However, the method of Mott and Massey involves the assumption that the usual stationary state solution from which the direct scattered amplitude is derived has the asymptotic form

$$\operatorname*{Lim}_{r_2\to\infty}\psi(\mathbf{r}_1,\mathbf{r}_2)=\sum_\alpha\frac{e^{ik_\alpha r_2}}{r_2}\cdot g_\alpha\cdot\varphi_\alpha(\mathbf{r}_1), \quad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ refer to the primary and hydrogenic electrons, respectively. (This labeling will prevail throughout the present paper.) The φ's are Coulomb functions; the sum includes integration over continuum states. Mott and Massey point out that no proof of this assumption has been given but that one should be possible. It is the purpose of this paper to provide such

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[1] J. R. Oppenheimer, Phys. Rev. 32, 361 (1928).

[2] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1949), second edition.

a proof[3] and to discuss other consequences arising from the analysis. Unless the validity of Eq. (1) is demonstrated, it is impossible to guarantee that the usual solution, which is conveniently outgoing in the coordinate of the primary particle, is indeed capable of describing a bound hydrogenic state in the coordinate of the primary electron together with a free wave in the coordinate of the target electron.

We begin with the Schrödinger equation,

$$(-\nabla_1^2-\nabla_2^2+v(r_1)+v(r_2)+V(|\mathbf{r}_1-\mathbf{r}_2|))\psi(\mathbf{r}_1,\mathbf{r}_2)=E\psi(\mathbf{r}_1,\mathbf{r}_2), \quad (2)$$

where the v's are the potentials between the particles, and the nucleus is presumed at rest. The Hamiltonian is split into two unsymmetrical terms so that the unperturbed states describe a freely moving primary electron in the presence of the hydrogen atom. That is,

$$\begin{aligned} H&=H_0(\mathbf{r}_1,\mathbf{r}_2)+V(\mathbf{r}_1,\mathbf{r}_2),\\ H_0&=-\nabla_1^2-\nabla_2^2+v(r_2),\\ V(\mathbf{r}_1,\mathbf{r}_2)&=v(r_1)+V(|\mathbf{r}_1-\mathbf{r}_2|). \end{aligned} \quad (3)$$

In order to incorporate the boundary conditions required in a collision problem, that of an incident wave in the coordinate $\mathbf{r}_1$ with the hydrogen atom in, say, the ground state together with outgoing waves in either coordinate, we introduce the Green's function for the operator $(E-H_0(\mathbf{r}_1,\mathbf{r}_2))$ which satisfies the equation

$$(E-H_0(\mathbf{r}_1,\mathbf{r}_2))(r_1r_2|G|r_1'r_2')=\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2'). \quad (4)$$

Here

$$(r_1r_2|G|r_1'r_2')=\lim_{\epsilon\to 0}\sum_\alpha\int\frac{d\mathbf{k}e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_1')}}{(2\pi)^3(E-\epsilon_\alpha-k^2+\epsilon i)}\times\varphi_\alpha(\mathbf{r}_2)\varphi_\alpha^*(\mathbf{r}_2'), \quad (5)$$

with $\epsilon>0$. The positive imaginary addition to the energy establishes the appropriate boundary conditions upon the scattered wave. If the integral over $\mathbf{k}$ is performed, then (5) becomes

$$(r_1r_2|G|r_1'r_2')=\sum_\alpha\frac{e^{ik_\alpha|\mathbf{r}_1-\mathbf{r}_1'|}}{-4\pi|\mathbf{r}_1-\mathbf{r}_1'|}\varphi_\alpha(\mathbf{r}_2)\varphi_\alpha^*(\mathbf{r}_2'), \quad (6)$$

$$k_\alpha=(E-\epsilon_\alpha)^{\frac{1}{2}}.$$

We now replace (2) by the following integral equation:

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\int\int(r_1r_2|G|r_1'r_2')V(\mathbf{r}_1',\mathbf{r}_2')\psi(\mathbf{r}_1',\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2. \quad (7)$$

[3] Private communication with H. E. Moses reveals that he has substantially verified the Mott-Massey conjecture using the Schwartz distribution analysis. This work appears in Research Report No. CX-5 and is issued by New York University, Washington Square College of Arts and Science Mathematics Research Group.

It is an elementary calculation to show that the asymptotic behavior of (7) as $r_1\to\infty$ is given by

$$\lim_{r_1\to\infty}\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\sum_\alpha\frac{e^{ik_\alpha r_1}}{r_1}f_\alpha(\mathbf{k}_\alpha)\varphi_\alpha(\mathbf{r}_2). \quad (8)$$

The coefficient $f_n(\mathbf{k}_n)$ is then the direct scattered amplitude corresponding to excitation of the hydrogen atom into it's nth state.

Since (7) contains a complete statement of the boundary conditions, it is desirable to isolate the functional for the exchange scattered amplitude from this same integral equation. It is, however, inconvenient, if at all possible, to attack this problem directly by performing the sum on α involving the Coulomb functions in (5) in order, subsequently, to find the asymptotic behavior in the coordinate $\mathbf{r}_2$. Such a procedure is the analog to that carried out conveniently in the derivation of (6). Consequently, we proceed by rewriting (7) as follows:

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\int\int\int\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1''d\mathbf{r}_2''\delta(\mathbf{r}_1-\mathbf{r}_1')\times\delta(\mathbf{r}_2-\mathbf{r}_2')(r_1'r_2'|G|r_1''r_2'')\times V(\mathbf{r}_1'',\mathbf{r}_2'')\psi(\mathbf{r}_1'',\mathbf{r}_2''). \quad (9)$$

We now interchange primed and unprimed coordinates separately in (4), and obtain

$$(E-H_0(\mathbf{r}_2,\mathbf{r}_1))(r_2r_1|G|r_2'r_1')=\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2'), \quad (10)$$

which is the same as

$$(E-H_0(\mathbf{r}_2',\mathbf{r}_1'))(r_2r_1|G|r_2'r_1')=\delta(\mathbf{r}_1-\mathbf{r}_1')\delta(\mathbf{r}_2-\mathbf{r}_2'), \quad (11)$$

since the Green's function is a symmetric operator with respect to an interchange of primed with unprimed coordinates. Upon substituting into (9), we have

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\int\int\int\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1''d\mathbf{r}_2''\times[(E-H_0(\mathbf{r}_2',\mathbf{r}_1'))(r_2r_1|G|r_2'r_1')]\times(r_1'r_2'|G|r_1''r_2'')V(\mathbf{r}_1'',\mathbf{r}_2'')\psi(\mathbf{r}_1'',\mathbf{r}_2''). \quad (12)$$

It is demonstrated in Appendix I that $H_0(\mathbf{r}_2',\mathbf{r}_1')$ is Hermitian with respect to the functions $(r_2r_1|G|r_2'r_1')$ and $(r_1'r_2'|G|r_1''r_2'')$. Therefore, (12) may be written

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\int\int\int\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1''d\mathbf{r}_2''(r_2r_1|G|r_2'r_1')\times\{[E-H_0(\mathbf{r}_2',\mathbf{r}_1')](r_1'r_2'|G|r_1''r_2'')\}\times V(\mathbf{r}_1'',\mathbf{r}_2'')\psi(\mathbf{r}_1'',\mathbf{r}_2''). \quad (13)$$

We now make use of the identity,

$$H_0(\mathbf{r}_2,\mathbf{r}_1)=H_0(\mathbf{r}_1,\mathbf{r}_2)+v(r_1)-v(r_2),$$

and Eq. (4), in order to rewrite Eq. (13) as follows:

$$\begin{aligned}\psi(\mathbf{r}_1,\mathbf{r}_2)&=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)\\&+\int\int\int\int d\mathbf{r}_1'd\mathbf{r}_2'd\mathbf{r}_1''d\mathbf{r}_2''(r_2r_1|G|r_2'r_1')\\&\times\{\delta(\mathbf{r}_1'-\mathbf{r}_1'')\delta(\mathbf{r}_2'-\mathbf{r}_2'')V(\mathbf{r}_1'',\mathbf{r}_2'')\psi(\mathbf{r}_1'',\mathbf{r}_2'')\\&+[v(r_2')-v(r_1')](r_1'r_2'|G|r_1''r_2'')\\&\times V(\mathbf{r}_1'',\mathbf{r}_2'')\psi(\mathbf{r}_1'',\mathbf{r}_2'')\},\end{aligned}\qquad(14)$$

and after employment of the original integral, Eq. (7), Eq. (14) becomes

$$\begin{aligned}\psi(\mathbf{r}_1,\mathbf{r}_2)&=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)\\&+\int\int d\mathbf{r}_1'd\mathbf{r}_2'(r_2r_1|G|r_2'r_1')\cdot V(\mathbf{r}_1',\mathbf{r}_2')\psi(\mathbf{r}_1',\mathbf{r}_2')\\&+\int\int d\mathbf{r}_1'd\mathbf{r}_2'(r_2r_1|G|r_2'r_1')[v(r_2')-v(r_1')]\\&\times[\psi(\mathbf{r}_1',\mathbf{r}_2')-e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')].\end{aligned}\qquad(15)$$

It is shown in Appendix II that the following identity holds:

$$\int\int(r_2r_1|G|r_2'r_1')(v(r_2')-v(r_1'))e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\times\varphi_0(\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2'=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2).\qquad(16)$$

On using this relation, (15) reduces to

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\int\int d\mathbf{r}_1'd\mathbf{r}_2'(r_2r_1|G|r_2'r_1')\times[V(\mathbf{r}_1',\mathbf{r}_2')+v(r_2')-v(r_1')]\psi(\mathbf{r}_1',\mathbf{r}_2')\qquad(17)$$

or

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\int\int d\mathbf{r}_1'd\mathbf{r}_2'(r_2r_1|G|r_2'r_1')\times V(\mathbf{r}_2',\mathbf{r}_1')\psi(\mathbf{r}_1',\mathbf{r}_2').\qquad(18)$$

On evaluating the asymptotic behavior in the coordinate $\mathbf{r}_2$, we find precisely the form in (1). Therefore, we have succeeded in demonstrating that the same wave function satisfying the condition (8) behaves according to the assumption of Mott and Massey.

DISCUSSION

It is now possible to understand how the homogeneous integral Eq. (18) can satisfy the boundary conditions which characterize scattering problems. For example, if we replace $\psi(\mathbf{r}_1',\mathbf{r}_2')$ by the undisturbed wave, $e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')$, under the integral in (17), and utilize (16), the result is

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\int\int d\mathbf{r}_1'd\mathbf{r}_2'(r_2r_1|G|r_2'r_1')V(\mathbf{r}_1',\mathbf{r}_2')\times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2');\qquad(19)$$

or more generally, if any approximation to the scattered wave, $\psi(\mathbf{r}_1',\mathbf{r}_2')-e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')$, is inserted into the second integral in (15), it is clear that the incident as well as the scattered wave is present. In other words, Eq. (18) can be considered as an integral equation for $\psi(\mathbf{r}_1,\mathbf{r}_2)$ with the proviso that the form $\psi=e^{i\mathbf{k}r_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)+\psi_{\mathrm{scatt}}$ obtains.

That Oppenheimer's and Mott-Massey's exchange amplitudes in Born approximation are in fact identical follows by comparing (19), which yields Oppenheimers' result, with (18) after replacing $\psi(\mathbf{r}_1',\mathbf{r}_2')$ by $e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')$ in the integral, with the result

$$\psi(\mathbf{r}_1,\mathbf{r}_2)=\int\int d\mathbf{r}_1'd\mathbf{r}'(r_2r_1|G|r_2'r_1')V(\mathbf{r}_2',\mathbf{r}_1')\times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2').\qquad(20)$$

This equivalence is apparent from the vanishing as $r_2\rightarrow\infty$ of the quantity appearing on the left side of (16). A difference does exist, however, if inexact target wave functions are employed. This is necessarily the case in scattering from atoms other than the hydrogen atom, and the consequent ambiguity has been labeled "post-prior discrepancy."[4] But, since the scattering events derive from the scattered part of the wave function, it is evidenced in (19) that the Oppenheimer amplitudes are, in principle, the correct ones. These are the quantities referred[4] to as "prior" matrix elements. Furthermore, as Borowitz and Friedman[5] have discovered, the Born exchange amplitude for excitation to a continuum state fails to converge when calculated from (20). Verification is to be found in connection with the proof of (16), which appears in Appendix II. To be more specific, let us write the asymptotic form of the left side of (16), namely,

$$\sum_\alpha\frac{e^{ik_\alpha r_2}}{r_2}\varphi_\alpha(\mathbf{r}_1)\int\int\varphi_\alpha^*(\mathbf{r}_1')e^{-i\mathbf{k}_\alpha\cdot\mathbf{r}_2'}[v(r_2')-v(r_1')]\times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2'.$$

Although the integral in this expression does not converge for a particular continuum state α, the sum over the continuum values converges to zero. That this lack of convergence raises no difficulty is clear from what has already been said concerning the necessity of computing all scattering amplitudes from the scattered part of the wave in (19) which does provide continuum

[4] Bates, Fundaminsky, Leech, and Massey, Trans. Roy. Soc. (London) **A243**, 117 (1950).

[5] S. Borowitz and B. Friedman, Phys. Rev. **89**, 441 (1953).

exchange amplitudes in Born approximation that converge.

CONCLUDING REMARKS

The theory of exchange scattering has been examined without developing two solutions based upon the separate expansions $\psi=\sum_\alpha F_\alpha(\mathbf{r}_1)\varphi_\alpha(\mathbf{r}_2)$ and $\psi'=\sum_\alpha G_\alpha(\mathbf{r}_2)d_\alpha(\mathbf{r}_1)$ which require the imposition of separate sets of boundary conditions on $F_n(\mathbf{r}_1)$ and $G_n(\mathbf{r}_2)$. This lack of symmetry for the enforcement of the boundary conditions is objectionable since there is no assurance that the two solutions are the same. To assume this equivalence is precisely the assumption in (1), the validity of which is now confirmed. Such a difficulty does not arise if the perturbation is taken to be the symmetrical one, $V(|\mathbf{r}_1-\mathbf{r}_2|)$, for the Green's function for the problem becomes correspondingly symmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$. However, this procedure possesses the disadvantage of mathematical intractibility since the Green's function is now constructed of Coulomb functions in the coordinates of both particles.

Finally, it must be pointed out that the present analysis may be extended to scattering from arbitrary atomic targets with the result that the "prior" matrix element is in principle the correct one for Born exchange scattered amplitudes.

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APPENDIX I

We consider the expression

$$\int\int d\mathbf{r}_1'd\mathbf{r}_2'\{[E-H_0(\mathbf{r}_2',\mathbf{r}_1')](r_2r_1|G|r_2'r_1')\}\times(r_1'r_2'|G|r_1''r_2'')\equiv\int\int d\mathbf{r}_1'd\mathbf{r}_2'\{[E+\nabla_1'^2+\nabla_2'^2-v(r_1')](r_2r_1|G|r_2'r_1')\}(r_1'r_2'|G|r_1''r_2''). \quad (1)$$

The theorem to be proved is that the Laplacians are Hermitian with respect to the functions $(r_2r_1|G|r_2'r_1')$ and $(r_1'r_2'|G|r_1''r_2'')$. Therefore, treating the term in $\nabla_1'^2$ alone, we apply Green's theorem and prove that the resulting surface integral vanishes. The proof for the operator $\nabla_2'^2$ is identical. The surface integral† in question is

$$\lim_{r_1'\to\infty}\int_{S_1'}dS_1'\left\{(r_1'r_2'|G|r_1''r_2'')\frac{\partial}{\partial r_1'}(r_2r_1|G|r_2'r_1')-(r_2r_1|G|r_2'r_1')\frac{\partial}{\partial r_1'}(r_1'r_2'|G|r_1''r_2'')\right\}. \quad (2)$$

† Contributions of the pole in $(r_2r_1|G|r_2'r_1')$ are automatically accounted for by the use of delta functions.

Upon inserting specific expressions for the Green's functions, we obtain

$$\lim_{r_1'\to\infty}\sum_{\alpha,\gamma}\frac{\varphi_\alpha(\mathbf{r}_2')\varphi_\alpha^*(\mathbf{r}_2'')}{-4\pi|\mathbf{r}_2-\mathbf{r}_2'|}\int_{S_1'}e^{ik_\gamma|\mathbf{r}_2-\mathbf{r}_2'|}\varphi_\gamma(\mathbf{r}_1)\times\left\{\frac{e^{ik_\alpha|\mathbf{r}_1'-\mathbf{r}_1''|}}{-4\pi|\mathbf{r}_1'-\mathbf{r}_1''|}\frac{\partial}{\partial r_1'}\varphi_\gamma^*(\mathbf{r}_1')-\varphi_\gamma^*(\mathbf{r}_1')\frac{\partial}{\partial r_1'}\frac{e^{ik_\alpha|\mathbf{r}_1'-\mathbf{r}_1''|}}{-4\pi|\mathbf{r}_1'-\mathbf{r}_1''|}\right\}ds_1'. \quad (3)$$

This quantity vanishes at once for the discrete γ's, or for the states for which k_α is imaginary. For the remaining case involving real k_α and the continuum γ, we rewrite (3) after introducing asymptotic forms given by

$$\lim_{r_1'\to\infty}\frac{e^{ik_\alpha|\mathbf{r}_1'-\mathbf{r}_1''|}}{|\mathbf{r}_1-\mathbf{r}_1''|}=\frac{e^{ik_\alpha r_1'}}{r_1'}e^{-ik_\alpha\mathbf{r}_0\cdot\mathbf{r}_1''}, \quad (4)$$

where $\mathbf{r}_0$ is a unit vector in the direction of $\mathbf{r}_1'$, and

$$\lim_{r_1'\to\infty}\varphi_\gamma^*(\mathbf{r}_1')=(2/\pi k)^{\frac{1}{2}}\frac{\sin(kr_1'+\delta_l)}{r_1'}Y_l^{m*}(\theta_1',\varphi_1'),$$
$$\delta_l=\ln(2kr)/k-\arg\Gamma(l+1+i/k). \quad (5)$$

Here the Coulomb function is normalized on the energy scale, $\epsilon=k^2$. We now consider the first of the two terms in the surface integral. After incorporating (4) and (5), the following result is obtained:

$$\lim_{r_1'\to\infty}\int_{S_1'}\sum_{l,m}\int_0^\infty d\epsilon\exp[i(E-k^2)^{\frac{1}{2}}|\mathbf{r}_2-\mathbf{r}_2'|]\times Y_l^m(\theta_1,\varphi_1)R_{k,l}(r_1)\left\{\frac{e^{ik_\alpha r_1'}}{r_1'\sqrt{k}}e^{-ik_\alpha\mathbf{r}_0\cdot\mathbf{r}_1''}\times\frac{k\cos(kr_1'+\delta_l)}{r_1'}Y_l^{m*}(\theta_1',\varphi_1')\right\}r_1'^2\sin\theta_1'd\theta_1'd\varphi_1'. \quad (6)$$

Here, we have dropped the term in $1/r_1'^2$ which arises from differentiating with respect to r_1'. Clearly the angular integration does not affect the k or r_1' dependence. Consequently, the integration over the energy may be examined directly. This integral is

$$\lim_{r_1'\to\infty}\int_0^\infty k^{\frac{1}{2}}dk\exp[i(E-k^2)^{\frac{1}{2}}|\mathbf{r}_2-\mathbf{r}_2'|]R_{k,l}(r_1)\times\cos(kr_1'+\delta_l),$$

apart from irrelevant factors. It is not difficult to show the convergence of this integral. Consequently, the entire quantity vanishes in the limit $r_1'\to\infty$. The second term in (3) may be handled in the same way. Thus the vanishing of (3) completes the proof.

APPENDIX II

By using the Schrödinger equation defining the ground state of the hydrogen atom we can rewrite the expression on the left in (16) as

$$\int\int (r_2r_1|G|r_2'r_1')[\nabla_2'^2+\epsilon_0-v(r_1')] \times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2'. \quad (1)$$

On adding and subtracting k_0^2, the energy of the incident electron, (1) becomes

$$\int\int (r_2r_1|G|r_2'r_1')[E+\nabla_2'^2+\nabla_1'^2-v(r_1')] \times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2'. \quad (2)$$

Here $E=k_0^2+\epsilon_0$, the total energy of the system, and $-k_0^2$ has been replaced by $\nabla_1'^2$. On using (2), we observe that the difference,

$$e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)-\int\int (r_2r_1|G|r_2'r_1')[E-H_0(\mathbf{r}_2',\mathbf{r}_1')] \times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2'), \quad (3)$$

is an eigenfunction of the operator $H_0(\mathbf{r}_2,\mathbf{r}_1)$. Verification is immediate by operating from the left with $[E-H_0(\mathbf{r}_2,\mathbf{r}_1)]$. This result is the physical basis for the vanishing of (3), for $H_0(\mathbf{r}_2,\mathbf{r}_1)$ contains no coupling between electronic coordinates and thus cannot represent an incident and scattered wave as (3) appears to suggest; nor can (3) describe a bound state in $\mathbf{r}_2$. To proceed with the demonstration that (3) vanishes, we first observe that $\nabla_2'^2$ behaves as a Hermitian operator in the presence of the ground state $\varphi_0(\mathbf{r}_2')$. Therefore, we rewrite the second term in (3) as

$$\begin{aligned}&\int\int [E-H_0(\mathbf{r}_2',\mathbf{r}_1')](r_2r_1|G|r_2'r_1')\\ &\quad\times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\varphi_0(\mathbf{r}_2')d\mathbf{r}_1'd\mathbf{r}_2'\\ &+\lim_{r_1'\to\infty}\int d\mathbf{r}_2'\int_{S_1'}\varphi_0(\mathbf{r}_2')\Big\{(r_2r_1|G|r_2'r_1')\frac{\partial}{\partial r_1'}\\ &\quad\times e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}-e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\cdot\frac{\partial}{\partial r_i'}\partial r_1'(r_2r_1|G|r_2'r_1^1)\Big\}ds_1', \quad (4)\end{aligned}$$

after applying Green's theorem with respect to $\nabla_1'^2$. On referring to (11), we observe that the term on the left in (4) is just the incident wave, $e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\varphi_0(\mathbf{r}_2)$. We now show that the surface integral vanishes when S_1' is allowed to recede to infinity. Let us rewrite this expression in detail. We have, after some minor rearrangement,

$$\int\frac{d\mathbf{r}_2'\varphi_0(\mathbf{r}_2')}{-4\pi|\mathbf{r}_2-\mathbf{r}_2'|}\lim_{r_1'\to\infty}\sum_\alpha e^{ik_\alpha|\mathbf{r}_2-\mathbf{r}_2'|}\varphi_\alpha(\mathbf{r}_1) \times\int_{S_1'}\Big\{\varphi_\alpha^*(\mathbf{r}_1')\frac{\partial}{\partial r_1'}e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}-e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\frac{\partial}{\partial r_1'}\varphi_\alpha^*(\mathbf{r}_1')\Big\}ds_1'. \quad (5)$$

It is obvious that only the contribution arising from the continuum α need be investigated. It is sufficient for our purpose to examine the expression to the right of the limit symbol which is written as

$$\begin{aligned}&\lim_{r_1'\to\infty}\sum_{m,l}Y_l^m(\theta_1,\varphi_1)\\ &\quad\times\int_0^\infty kdk\exp[i(E-k^2)^{\frac{1}{2}}|r_2-r_2'|]R_{k,l}(r_1)\\ &\times\int_{S_1'}Y_l^{m*}(\theta_1',\varphi_1')\Big\{\frac{\sin(kr_1'+\delta_l)}{\sqrt{k\cdot r_1'}}\frac{\partial}{\partial r_1'}e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\\ &\quad-\frac{e^{i\mathbf{k}_0\cdot\mathbf{r}_1'}\cdot k}{\sqrt{kr_1'}}\cos(kr_1'+\delta_l)\Big\}r_1'^2\sin\theta_1'd\theta_1'd\varphi_1'. \quad (6)\end{aligned}$$

Here we have employed (4) and (5) in Appendix I. On choosing the direction of $\mathbf{k}_0$ as polar axis, the angular integrations for the first term in the curly bracket is carried out as follows:

$$\begin{aligned}&\int_{S_1'}Y_l^{m*}(\theta_1',\varphi_1')ik_0\cos\theta_1'e^{ik_0r_1'\cos\theta_1'}r_1'\sin\theta_1'd\theta_1'd\varphi_1'\\ &=2\pi ik_0r_1'\int_{-1}^1dx\cdot xP_l(x)e^{ik_0r_1'x}\\ &=2\pi[P_l(x)\cdot xe^{ik_0r_1'x}]^1_{-1}=2\pi(e^{ik_0r_1'}+(-1)^le^{-ik_0r_1'}). \quad (7)\end{aligned}$$

In the third step we have performed partial integration and retained only the leading term in $1/r_1'$. with this result the integral in (6) becomes

$$\lim_{r_1'\to\infty}\int_0^\infty k^{\frac{1}{2}}dk\cdot\exp[i(E-k^2)^{\frac{1}{2}}|\mathbf{r}_2-\mathbf{r}_2'|]R_{k,l}(r_1) \times(e^{ik_0r_1'}+(-1)^le^{-ik_0r_1'})\sin(kr_1'+\delta_l). \quad (8)$$

As in Appendix I, the integral is convergent so that (8) vanishes in the limit $r_1'\to\infty$. By an exactly analogous argument, the contribution of the second term in curly brackets vanishes. Thus, the surface term in (4) vanishes and the proof of the equality in (16) is concluded.