[7]The ratio ρ/ξ is strictly less than unity, if $Z' \geq 1$. From Eq. (6) we see that $\xi \geq r_A$, so that $U\xi \geq Ur_A = (Z'+1)/2$. Thus

$$\rho/\xi \leq U\rho/Ur_A = [2/(Z'+1)]\,(U^2\sigma'_{\text{ion}}/\pi)^{1/2}.$$

This last factor can be shown to be less than 1 from the equations in Ref. 4.

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Asymptotic Form of the Total Wave Function for Electron-Impact Excitation of Hydrogen Atoms

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An asymptotic form of the total wave function for electron-impact excitation of hydrogen atoms is obtained by the use of the Coulomb Green function. The result is compared with the corresponding usual form, obtained through the free-particle Green function. The validity of the Coulomb wave formulation is upheld in view of the physical quantities being finite definite.

I. INTRODUCTION

In describing inelastic electron-atom collisions, the outgoing boundary conditions on the total wave function of a system of an electron and an atom are important. From the boundary conditions, one finds the scattering amplitudes for the processes; and from the amplitudes one can predict various physical properties, such as the probability of having a specific process, or specific energy and angular dependences. This asymptotic form of the wave function can be, in principle, derived from the Schrödinger equation with the use of either a plane wave or a Coulomb wave to represent a positive energy electron. These correspond to employing either a free-particle Green function or a Coulomb Green function.

In the literature, the former method of a free-particle Green function has been carried out[1,2] while the latter has not. However, when the method of a free-particle Green function is applied to the Coulomb potential scattering of a charged particle, the apparent asymptotic form of the wave function differs from that of the known exact Coulomb wave function by an indefinite phase factor whose argument diverges. Thus one is left with an inconsistency.

In this paper, the asymptotic form of the total wave function for the electron-atom inelastic collision process is obtained via the Coulomb Green function and compared with that of a free-particle Green function method. It is pointed out that the two forms of the same total wave functions are the same and unique, though they appear differently. It is also found that the scattering amplitudes for both electron-atom collisions and the Coulomb potential scattering in the plane wave formulation contain the undesirable indefinite phase factor, while those in the Coulomb wave formulation are finite and definite. Thus some doubts which were raised by some authors[3,4] about the validity of the Coulomb wave formulation by Kang and Foland[5] for the electron-atom collision process, are dispelled.

II. THE DERIVATION OF THE ASYMPTOTIC FORM

In the scattering of an electron by a hydrogen atom, the proton is assumed to be infinitely massive. The total wave function $\Psi(\vec{r}_1, \vec{r}_2)$ of the system of two electrons at positions $\vec{r}_1$ and $\vec{r}_2$ satisfies the Schrödinger equation,

$$H\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2) \ . \tag{1}$$

In the above, H and E denote the total Hamiltonian and its eigenvalue. The total Hamiltonian of the system of an electron and a hydrogen atom consists of the sum of the two hydrogenic Hamiltonians,

$$H(\vec{r}_i) = -\tfrac{1}{2}\nabla_i^2 + V_i$$

(in the atomic units), and the electronic mutual interaction V_{12}. Thus

$$H = H(\vec{r}_1) + H(\vec{r}_2) + V_{12} \ . \tag{2}$$

The bound-state wave function of a hydrogenic atom with a set of quantum numbers n is denoted by $\psi(n|\vec{r})$, and the continuum-state wave function of the atom with a wave vector $\vec{k}$ by $\psi(\vec{k}|\vec{r})$. The eigenvalue equations satisfied by them are as follows:

$$H(\vec{r})\psi(\gamma|\vec{r}) = E_\gamma \psi(\gamma|\vec{r}) \ ,$$
$$\text{with} \quad \gamma = n \ \text{ or } \ \vec{k} \ . \tag{3}$$

The E_γ in Eq. (3) refers to the energy of the hydrogenic electron.

For the purpose of describing excitation processes, the wave function $\Psi(\vec{r}_1, \vec{r}_2)$ is expanded in terms of the complete set of the hydrogenic wave functions as

$$\begin{aligned}\Psi(\vec{r}_1, \vec{r}_2) &= \sum_\gamma \psi(\gamma|\vec{r}_2) F(\gamma|\vec{r}_1) \\ &= \sum_{\gamma,\beta} A_{\gamma\beta}\psi(\gamma|\vec{r}_2)\psi(\beta|\vec{r}_1) \\ &= \sum_\beta G(\beta|\vec{r}_2)\psi(\beta|\vec{r}_1) \ . \end{aligned} \tag{4}$$

According to the Pauli principle, the $\Psi(\vec{r}_1, \vec{r}_2)$ must be antisymmetric in the space coordinates when the spins of the two electrons are parallel, and symmetric when antiparallel. This requirement on the $\Psi(\vec{r}_1, \vec{r}_2)$ requires that the $A_{\gamma\beta}$ must be antisymmetric for the spin triplet states and symmetric for the spin singlet state.

The asymptotic behavior of the total wave function is, then, determined by that of either $F(\gamma|\vec{r})$ or $G(\beta|\vec{r})$, which represents the projectile electron. From Eqs. (1) through (4), and the use of the orthonormality of the hydrogenic wave functions, one finds the differential equation satisfied by $F(\gamma|\vec{r}_1)$ as in the following:

$$\begin{aligned}&[\tfrac{1}{2}k_n^2 - H(\vec{r}_1)]F(n|\vec{r}_1) \\ &\quad = \int \psi^*(n|\vec{r}_2)V_{12}\Psi(\vec{r}_1, \vec{r}_2)d^3\vec{r}_2 \ , \end{aligned} \tag{5}$$

with $\tfrac{1}{2}k_n^2 = E - E_n$.

Now, using the Coulomb Green function $G_C(\vec{r}_1, \vec{r}_2; \vec{k}_n)$, obtained by Hostler[6] in (1964), one can express $F(n|\vec{r}_1)$ in the form of an integral equation as

$$\begin{aligned}F(n|\vec{r}) &= \delta_{n1}\psi(\vec{k}_n|\vec{r}) + \int G_C(\vec{r}, \vec{r}_1; \vec{k}_n) \\ &\quad \times \psi^*(n|\vec{r}_2)V_{12}\Psi(\vec{r}_1, \vec{r}_2)d^3r_1 d^3r_2 \ . \end{aligned} \tag{6}$$

The Kronecker delta δ_{n1} assures the inclusion of elastic processes (with $n = 1$). Using the available asymptotic form[6] of the Coulomb Green function, one obtains for the excitation processes, where $n \neq 1$,

$$\begin{aligned}&F(n|\vec{r}) \sim f_n^C(\theta)\exp[ik_n r + i\eta_n(r)]/r \ , \\ &\qquad\qquad r \to \infty \ , \end{aligned} \tag{7}$$

$$\begin{aligned}\text{with} \quad f_n^C(\theta) &= -(2\pi)^{-1}\int \psi(-\vec{k}_n|\vec{r}_1)\psi^*(n|\vec{r}_2) \\ &\quad \times V_{12}\Psi(\vec{r}_1, \vec{r}_2)d^3r_1 d^3r_2 \ , \end{aligned} \tag{8}$$

and

$$\eta_n(r) = (Z/k_n)\ln 2k_n r, \quad (Z = \text{atomic no.}) \ . \tag{9}$$

Similarly, through a procedure similar to one which led to the asymptotic form of the $F(n|\vec{r})$, one finds for that of the $G(n|\vec{r})$ in Eq. (4) that

$$\begin{aligned}&G(n|\vec{r}) \sim g_n^C(\theta)\exp[ik_n r + i\eta_n(r)]/r \ , \\ &\qquad\qquad r \to \infty \ , \end{aligned} \tag{10}$$

with

$$\begin{aligned}g_n^C(\theta) &= -(2\pi)^{-1}\int \psi^*(n|\vec{r}_1)\psi(-\vec{k}_n|\vec{r}_2) \\ &\quad \times V_{12}\Psi(\vec{r}_1, \vec{r}_2)d^3r_1 d^3r_2 \ . \end{aligned} \tag{11}$$

Thus one obtains the asymptotic form of the total wave function $\Psi(\vec{r}_1, \vec{r}_2)$ for the excitation processes as follows:

$$\begin{aligned}\Psi(\vec{r}_1, \vec{r}_2) &\sim \sum_n \psi(n|\vec{r}_2)f_n^C(\theta) \\ &\quad \times \exp[ik_n r_1 + i\eta_n(r_1)]/r_1 \ , \\ &\qquad\qquad r_1/r_2 \to \infty \ , \\ &\sim \sum_n \psi(n|\vec{r}_1)g_n^C(\theta) \\ &\quad \times \exp[ik_n r_2 + i\eta_n(r_2)]/r_2 \ , \\ &\qquad\qquad r_2/r_1 \to \infty \ . \end{aligned} \tag{12}$$

The asymptotic form for the exchange excitation processes, which is the same as in the second equation of (12), has been given by Mott and Massey[1] without giving any detailed derivation, while the asymptotic form for the direct scattering as given in the first equation of (12) has never been given in literature to the author's knowledge.[7] The asymptotic forms in (12) are contrasted with the following well accepted forms[1,2]

$$\Psi(\vec{r}_1,\vec{r}_2)\sim\sum_n \psi(n|\vec{r}_2) f_n^{\,p}(\theta)\, e^{ik_n r_1}/r_1 , \quad r_1/r_2\to\infty , \tag{13}$$

$$\sim\sum_n \psi(n|\vec{r}_1) g_n^{\,p}(\theta)\, e^{ik_n r_2}/r_2 , \quad r_2/r_1\to\infty ,$$

with

$$f_n^{\,p}(\theta) = -(2\pi)^{-1}\int \phi^*(\vec{k}_n|\vec{r}_1)\psi^*(n|\vec{r}_2) \times (V_1+V_{12})\Psi(\vec{r}_1,\vec{r}_2)\, d^3r_1 d^3r_2 , \tag{14}$$

and

$$g_n^{\,p}(\theta) = -(2\pi)^{-1}\int \phi^*(k_n|\vec{r}_2)\psi^*(n|\vec{r}_1) \times (V_2+V_{12})\Psi(\vec{r}_1,\vec{r}_2)\, d^3r_1 d^3r_2 . \tag{15}$$

The $\phi(\vec{k}_n|\vec{r})$ in the above refers to the plane wave with the wave vector $\vec{k}_n$. The conventional asymptotic form in Eq. (13) has been obtained through the use of the free-particle Green function, in place of the Coulomb Green function. It can be shown without too much difficulty that the two forms of both the direct and exchange amplitudes, f and g, respectively, are related by a phase factor, $e^{i\eta_n(r)}$, whose argument diverges logarithmically as follows:

$$f_n^{\,p}(\theta) = f_n^{\,C}(\theta)\lim_{r\to\infty} e^{i\eta_n(r)} ,$$

$$\text{and } g_n^{\,p}(\theta) = g_n^{\,C}(\theta)\lim_{r\to\infty} e^{i\eta_n(r)} . \tag{16}$$

The proof of Eq. (16) consists of expressing both $f_n^{\,p}(\theta)$ and $g_n^{\,p}(\theta)$ of Eqs. (14) and (15) as surface integrals at infinity in the $\vec{r}_1$ and the $\vec{r}_2$ space, respectively, and using the asymptotic form of the total wave function in Eq. (11). In fact, Rudge[3] recently obtained a relation similar to the second of Eq. (16), but he did not distinguish the $g_n^{\,C}(\theta)$ from the $g_n^{\,p}(\theta)$, ending up with a paradoxical relation

$$g_n = g_n \lim_{r\to\infty} e^{\pm i\eta_n(r)} , \tag{17}$$

and concluding that the Coulomb wave approximation by Kang and Foland,[5] or, the integral expressions for the direct and exchange amplitudes as in Eqs. (8) and (11), were not acceptable.

III. THE COULOMB SCATTERING AMPLITUDES

If one describes the initial state of the electron by a plane wave, the Coulomb scattering amplitude contains an indefinite phase factor whose argument diverges logarithmically. Indeed, this fact can be shown with the variational method by calculating the integral of the form,

$$f^p = \int \phi^*(\vec{k}_n|\vec{r}_1)\, V_1 \psi(\vec{k}_0|\vec{r}_1)\, d^3r_1 . \tag{18}$$

The source of the phase factor in f^p in Eq. (18) can be traced to representing the initial state by the plane wave, when one observes the asymptotic behavior of the exact Coulomb wave function. It is interesting to point out that Dalitz[8] (1951), later Kacser[9] (1959), and more recently Kang and Brown[10] (1962) studied higher Born approximations for the Coulomb scattering of a charged particle. They found that while the first Born approximation gives the correct Rutherford or Mott cross sections, the higher Born scattering amplitudes which are divergent, can be grouped into a phase factor with a divergent argument, multiplied by the sum of the first Born term and some finite correction terms. These results are in accordance with the fact that f^p in Eq. (18) has an indefinite phase factor. As was pointed out by Dollard[11] in (1964), there exists no "pure" plane wave state of an electron even in the asymptotic region of a Coulomb field. This can be seen easily by transforming into a new gauge for the four-vector electromagnetic potentials,

$$A_\mu \to A_\mu' = A_\mu + \nabla_\mu \Lambda(\vec{r}) ,$$

with the gauge function $\Lambda(\vec{r})$ given by

$$\Lambda(\vec{r}) = -\eta_n(r) . \tag{19}$$

In the new gauge the scalar potential becomes zero. Thus the wave function in the new gauge of a charged particle in the Coulomb field becomes a plane wave in the asymptotic region, and the wave function in the asymptotic region of the Coulomb field is a "pseudo" plane wave which is the product of a plane wave and the phase factor, $\exp[i\eta_n(r)]$. If this "pseudo" plane wave is substituted for the ϕ in Eq. (18), then the indefinite phase factor will be cancelled out, resulting in a finite and definite amplitude. This very aspect of the Coulomb scattering has in recent years attracted attentions of many authors[12] [Mapleton (1961), (1962); Okubo and Fieldman (1960); Dollard (1964); Ford (1966); West (1967)].

IV. REMARKS ON ELECTRON-ATOM COLLISIONS

We now want to show that the $f_n^{\,p}(\theta)$ in Eq. (14), for instance, has the indefinite undesirable phase

factor $\lim_{r\to\infty} e^{+i\eta_n(r)}$,

and that the corresponding amplitude $f_n^C(\theta)$ in the Coulomb wave formulation is finite definite. According to Eq. (14) the plane wave $\phi(\vec{k}_n|\vec{r}_1)$ interacts via the V_1 with the nucleus of the atom and becomes the Coulomb wave, and then an attractive Coulomb wave electron interacts with a bound-state electron, resulting in the inelastic process. In the first stage, the bound-state electron is merely a bystander whereas the other positive energy electron undergoes a potential scattering. In the final stage, the scattered electron undergoes for the second time a potential scattering in the repulsive Coulomb field of the bound electron, averaged over the process. In Eq. (14), the exact wave function $\Psi(\vec{r}_1, \vec{r}_2)$ is used while the intermediate states are described implicitly. Thus no error is made in describing the second stage of the process. Therefore the $f_n^D(\theta)$ is a product of a finite definite quantity and the indefinite phase factor. In view of Eq. (16), one concludes that the $f_n^C(\theta)$ is finite definite.

It is emphasized that as reference states in describing the electron-atom collision processes, the Coulomb waves are preferable to the plane waves, contrary to the statements made by Rudge[3] (1968) and by Kyle and McDowell[4] (1968). It is pointed out that those equalities by Day, *et al.*,[13] and later by Kang and Foland[5] exhibiting the equivalence of the expressions for the inelastic scattering amplitudes between the plane wave and the Coulomb wave formulations are correct provided that the "pure" plane wave is replaced by the "pseudo" plane wave, as are displayed in Eq. (16).

Finally, it is remarked that the asymptotic form of the total wave function for electron-hydrogen atom collision processes is unique and the forms in Eqs. (12) and (13) are the same. It is emphasized that the expressions for the scattering amplitudes $f_n^C(\theta)$ and $g_n^C(\theta)$ in Eqs. (8) and (11) are preferable to the $f_n^D(\theta)$ and the $g_n^D(\theta)$ in Eqs. (14) and (15), because the former's being finite and definite, in addition to the reasons cited by Kang and Foland.[5]

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