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Theory of Electron Impact Excitation and Ionization of Atoms and Ions*

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A theory of inelastic processes of electron-hydrogen and electron-ion collisions is formulated along the Gell-Mann-Goldberger approach describing all electrons by the eigenstates of the same Hamiltonian and satisfying the Pauli principle. It is found that this approach is satisfactory conceptually in that orthogonality between the initial and the final states is preserved, the boundary condition is met, the completeness relation for the unperturbed wave functions exists, and the unitarity of the scattering matrix is preserved. The conventional formalisms are also discussed with respect to these matters. Two consequences of the formulation—a finite-threshold law for excitations and the linear-threshold law, in energy, for ionization—are derived. It is shown that also obtaining are an Ochkur-like relation for excitation and the Peterkop relation for ionization. Furthermore, the theory is extended to cases of many-electron atoms and ions for which the same threshold laws are obtained. Finally, a theorem which is an essential assumption in the impulse approximation is proved, and the validity of the present formalism is noted.

I. INTRODUCTION

THE problem of the theoretical treatment of the excitation and ionization of atomic hydrogen by electron impact is a fundamental problem dealing with the simplest kind of charged, three-body system. For this reason it attracts theoretical interest. It also attracts interest because of the potential usefulness of quantitative predictions which can come out of the study. There are in such astrophysical studies as those of auroras, corona, and gaseous nebulas numerous problems arising for which one needs to have quantitative information on the cross sections associated with excitation and ionization of atoms and ions by electron impact. In recent years, the development of techniques for obtaining better elastic, as well as inelastic cross sections has led to added interest in the theoretical side of the problem.

Because, as is well known, an exact quantum-mechanical determination of the inelastic cross sections is not possible, various approximations have been introduced. Among the well-known approximations are the Born, Born-Oppenheimer, Coulomb-Born, Born-exchange, close-coupling, and effective-charge approximations.

It should be noted that in most theoretical studies the wave-function approximation method is employed. In this method, one approximates the total wave function of the system, utilizing all available properties of exact wave functions of single particles. Then one extracts the scattering amplitudes from its asymptotic behavior in the region far away from the scattering region.

On the other hand, it is known[1] that the time-dependent scattering theory is equivalent to the time-independent theory when the stationary states are involved. One can use this equivalence to formulate a scattering theory by use of the definition of the scattering matrix and of the time-independent "in"- and "out"-state wave functions. This formulation, in fact, was used by Watson[2] in 1952 in discussing the final interaction in reactions. Subsequently, Gell-Mann and Goldberger[3] in 1953, took this approach to discuss scattering from two potentials as an example of their formal scattering theory. Again in 1960, Bassel and Gerjuoy[4] took the same approach in discussing electron capture processes from atomic hydrogen.

For the excitation and the ionization of atoms and ions by electron impact, one deals with a system of electrons. Consequently, one has to take the Pauli principle into account in the theory. This was done by Kang and Sucher[5] in 1966 for the excitation process of hydrogenlike atoms by electron impact.

In this paper, the scattering matrix approach is taken to study the inelastic processes of electron-atom and electron-ion collisions. All electrons are treated on the same footing—i.e., subject to the same Hamiltonian.

As we shall see below, this formalism is advantageous in that (1) in the lowest-order perturbation, the direct and exchange amplitudes are treated to the same accuracy; (2) the resulting expressions for the scattering matrix elements exhibit symmetry among electrons; (3) the effect of the core potential is fully taken into account, and the mutual interactions of electrons are the only perturbations. The fact that this last point obtains assures us that the theory can be easily extended to the case of many-electron atoms and ions.

In Sec. II, a formulation of the theory for hydrogen atoms is presented. In Sec. III, various conventional formalisms are compared with the present formalism. Next, in Sec. IV the immediate consequences of this

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[1] B. Lippmann and J. Schwinger, Phys. Rev. 79, 469 (1950).

[2] K. Watson, Phys. Rev. 88, 1163 (1952).

[3] M. Gell-Mann and M. L. Goldberger, Phys. Rev. 91, 398 (1953).

[4] R. H. Bassel and E. Gerjuoy, Phys. Rev. 117, 749 (1960).

[5] I. J. Kang and J. Sucher, Phys. Letters 20, 22 (1966).

theory are discussed and compared with the experimental results. Finally in Sec. V, the theory is extended to treat the excitation and the ionization of many-electron atoms and ions.

The Coulomb units are used throughout. The atomic nucleus is assumed to be infinitely heavy and at the origin of the reference frame.

II. FORMULATION OF THE THEORY

We now proceed to a general formulation for the desired matrix elements. The assumptions used in the customary treatment of the problem are compared and contrasted with the ones adopted here. After getting the expressions for the matrix elements, we prove the mathematical equality of the results of the two treatments of excitation provided the exact wave function is used for the "in" state. The changes necessary for obtaining the matrix elements for ionization are noted; and lastly, we note the problem involved in obtaining higher orders of approximation in our formalism.

Consider the system consisting of an electron and a hydrogen atom. Neglecting the spin-dependent interaction, one has for the total Hamiltonian H

$$H=K_a+V_a+K_b+V_b+V_{ab}\,, \tag{1}$$

where K_a denotes the kinetic-energy operator of the a electron, V_b the potential energy of the b electron in the field of the atomic nucleus, and V_{ab} the mutual interaction energy of the two electrons. By the assumption, the spin-dependent interaction is absent, and the total spin is a good quantum number with which one can classify the states of the system.

Denoting the total, spatial wave function in which the a electron is in the continuum state by Ψ_a, one finds for the symmetrized, total wave function:

$$\Psi_{\rm tot}=\frac{1}{\sqrt{2}}(\Psi_a\pm\Psi_b)\qquad \begin{array}{l} +\text{ for spin singlet state}\\ -\text{ for spin triplet states.}\end{array} \tag{2}$$

One can denote the quantum-number set for the total system by i and write $\Psi_{i;a}$ instead of Ψ_a. The $\Psi_{i;a}$ satisfies the Schrödinger equation

$$(H-E_i)\Psi_{i;a}=0\,.$$

If there exists $\Phi_{i;a}$ such that

$$(H_{0a}-E_i)\Phi_{i;a}=0\quad\text{with}\quad H=H_{0a}+H_a'\,, \tag{3}$$

then the "in"-state (+) and "out"-state (−) wave functions $\Psi_{i;a}{}^{(\pm)}$ are given by the Lippmann-Schwinger equation[1];

$$\Psi_{i;a}{}^{(\pm)}=\Phi_{i;a}{}^{(\pm)}+\lim_{\epsilon\to0+}\frac{1}{E_i-H_{0a}\pm i\epsilon}H_a'\Psi_{i;a}{}^{(\pm)}\,. \tag{4}$$

If one now proceeds according to the formal scattering theory, the scattering matrix is defined as

$$S_{fi}=\langle\Psi_{\text{tot }f}{}^{(-)},\Psi_{\text{tot }i}{}^{(+)}\rangle\,. \tag{5}$$

From Eqs. (2) through (5), the scattering matrix can be rewritten as

$$S_{fi}=\delta_{fi}-2\pi i\delta(E_f-E_i)(M_D\pm M_E)\,,\qquad \begin{array}{l} +\text{ for spin singlet state}\\ -\text{ for spin triplet states}\end{array} \tag{6}$$

with

$$M_D=\langle\Phi_{f;a}{}^{(-)}H_a'\Psi_{i;a}{}^{(+)}\rangle\,, \tag{7}$$

and

$$M_E=\langle\Phi_{f;b}{}^{(-)}H_b'\Psi_{i;a}{}^{(+)}\rangle\,. \tag{8}$$

In the conventional formalism for the excitation of hydrogen atoms the unperturbed final-state function $\Phi_{f;a}{}^{(-)}$ is taken as

$$\Phi_{f;a}{}^{(-)}=\phi_a(\mathbf{k}_1)\eta_b(n)\,, \tag{9}$$

where $\phi_a(\mathbf{k}_1)$ and $\eta_b(n)$ refer, respectively, to a plane wave of the a electron with momentum $\mathbf{k}_1$ and to a hydrogenic wave function of the b electron with a set of quantum numbers $n(=\{n,l,m\})$.

$$K_a\phi_a(\mathbf{k}_1)=\tfrac{1}{2}k_1{}^2\phi_a(\mathbf{k}_1)$$

and

$$(K_b+V_b)\eta_b(n)=-|\epsilon_n|\eta_b(n)\,. \tag{10}$$

Carrying out these operations one obtains the expressions for the direct and exchange M-matrix elements in the conventional formalism

$$M_D=\langle\phi_a(\mathbf{k}_1)\eta_b(n)|V_a+V_{ab}|\Psi_a{}^{(+)}\rangle\,, \tag{11}$$

and

$$M_E=\langle\phi_b(\mathbf{k}_1)\eta_a(n)|V_b+V_{ab}|\Psi_a{}^{(+)}\rangle\,. \tag{12}$$

Let us now consider the present approach. We denote the continuum-state wave functions of the a atomic electron with momentum $\mathbf{k}$ by $\chi_a(\mathbf{k})$;

$$(K_a+V_a)\chi_a(\mathbf{k})=\tfrac{1}{2}k^2\chi_a(\mathbf{k})\,. \tag{13}$$

Expressing $\phi_b{}^{(-)}(\mathbf{k})$ in terms of $\chi_b{}^{(-)}(\mathbf{k})$ via the equation[6]

$$\chi_b{}^{(-)}(\mathbf{k})=\phi_b{}^{(-)}(\mathbf{k})+\lim_{\epsilon\to0+}[k^2/2-(K_b+V_b)-i\epsilon]^{-1}V_b\phi_b{}^{(-)}(\mathbf{k})\,, \tag{14}$$

we can rewrite M_E in Eq. (12) as

$$M_E=\langle\chi_b{}^{(-)}(\mathbf{k}_1)\eta_a(n)|V_{ab}|\Psi_{i;a}{}^{(+)}\rangle \tag{15}$$

as was shown explicitly by Day *et al.*[6]

By recognizing that V_a commutes with K_b+V_b and by following a procedure similar to one which leads to Eq. (15) for M_E, one finds for M_D in Eq. (11)

$$M_D=\langle\phi_a{}^{(-)}(\mathbf{k}_1)\eta_b(n)|V_a|\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle+\langle\chi_a{}^{(-)}(\mathbf{k}_1)\eta_b(n)|V_{ab}|\Psi_{i;a}{}^{(+)}\rangle\,. \tag{16}$$

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[6] While Eq. (14) is written here symbolically as in a paper by T. B. Day, L. S. Rodberg, G. A. Snow, and J. Sucher [Phys. Rev. **123**, 1051 (1961)], actual evaluation of the right-hand side of the equation requires special care as was emphasized in the works of R. A. Mapleton [J. Math. Phys. **2**, 482 (1961); **3**, 297 (1962)], and of S. Okuko and D. Feldman [Phys. Rev. **117**, 292 (1960)]. For the case of time-dependent theory, see J. D. Dollard, J. Math. Phys. **5**, 729 (1964).

In obtaining Eq. (16) we have used for $\Psi_{i;a}^{(+)}$

$$\Psi_{i;a}^{(+)}=\chi_a^{(+)}(\mathbf{k}_0)\eta_b(n_0)+\lim_{\epsilon\to0+}[E_i-(K_a+V_a+K_b+V_b)+i\epsilon]^{-1}\times V_{ab}\Psi_{i;a}^{(+)}. \tag{17}$$

Now the first term in Eq. (16) can be written as

$$\langle\phi_a^{(-)}(\mathbf{k}_1)\eta_b(n)|V_a|\chi_a^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle =\delta_{fi}(b)\cdot(E_f-E_i)\langle\phi_a^{(-)}(\mathbf{k}_1)|\chi_a^{(+)}(\mathbf{k}_0)\rangle.$$

We see that this term contributes nothing to the scattering matrix due to the presence of the Dirac delta function $\delta(E_f-E_i)$ in Eq. (6). Therefore, one can express M_D in Eq. (16) as

$$M_D=\langle\chi_a^{(-)}(\mathbf{k}_1)\eta_b(n)|V_{ab}|\Psi_{i;a}^{(+)}\rangle. \tag{18}$$

It is remarked that the expressions in Eqs. (15) and (18) could be obtained equally well if one chose to express $\Psi_{f;a}^{(-)}$ as

$$\Psi_{f;a}^{(-)}=\chi_a^{(-)}(\mathbf{k}_1)\eta_b(n)+\lim_{\epsilon\to0+}[E_f-(K_a+V_a+K_b+V_b)-i\epsilon]^{-1}\times V_{ab}\Psi_{f;a}^{(-)} \tag{19}$$

for then, from comparison of Eq. (4) with Eqs. (17) and (19), one notes that $\Phi_{f;a,b}^{(-)}$ and $H'_{a,b}$ in Eqs. (7) and (8) are identified as

$$\Phi_{f;a,b}^{(-)}=\chi_{a,b}^{(-)}(\mathbf{k}_1)\eta_{b,a}(n), \qquad H_a'=H_b'=V_{ab}. \tag{20}$$

Thus it is proved that the conventional expressions for the matrix elements in Eqs. (11) and (12) are *mathematically* equal to those of the present formalism in Eqs. (15) and (18) as long as the exact "in"-state wave functions $\Psi_{i;a}^{(+)}$ are used.

For the case of ionization of the hydrogen atom it is evident that the expressions for M_D and M_E become in the conventional formalism

$$M_D=\langle\phi_a(\mathbf{k}_1)\chi_b^{(-)}(\mathbf{k}_2)|V_a+V_{ab}|\Psi_{i;a}^{(+)}\rangle \tag{21}$$

and

$$M_E=\langle\phi_b(\mathbf{k}_1)\chi_a^{(-)}(\mathbf{k}_2)|V_b+V_{ab}|\Psi_{i;a}^{(+)}\rangle; \tag{22}$$

and in the present formalism

$$M_D=\langle\chi_a^{(-)}(\mathbf{k}_1)\chi_b^{(-)}(\mathbf{k}_2)|V_{ab}|\Psi_{i;a}^{(+)}\rangle, \tag{23}$$

and

$$M_E=\langle\chi_b^{(-)}(\mathbf{k}_1)\chi_a^{(-)}(\mathbf{k}_2)|V_{ab}|\Psi_{i;a}^{(+)}\rangle. \tag{24}$$

It is herein emphasized that the final state of a particle in the continuum state can be described either by a plane wave interacting with the nucleus and the other electron or by a Coulomb wave interacting with the other electron.

By iteration, $\Psi_{i;a}^{(+)}$ in Eq. (17) can be expressed as

$$\Psi_{i;a}^{(+)}=(1+G^{(+)}V_{ab}+G^{(+)}V_{ab}G^{(+)}V_{ab}+\cdots)\times\chi_a^{(+)}(\mathbf{k}_0)\eta_b(n_0) \tag{25}$$

with

$$G^{(+)}=\lim_{\epsilon\to0+}[E_i-(K_a+V_a+K_b+V_b)+i\epsilon]^{-1}$$

and, in principle, one knows how to obtain the exact wave function $\Psi_{i;a}^{(+)}$. In practice it is impossible to obtain the exact "in"-state wave function of the system $\Psi_{i;a}^{(+)}$; therefore it becomes necessary to approximate $\Psi_{i;a}^{(+)}$ in some reasonable way so that the scattering matrix elements can be expressed as integrals of known functions.

III. COMPARISONS OF FORMALISMS

There are a number of aspects in which the theory being presented here has formal advantages over previous ones. We now consider some of the ways in which other theories fail to meet fundamental requirements of scattering theory; we point out, of course, that the current one meets these requirements. Three such fundamental requirements are: the two electrons are equivalent (in accordance with the Pauli principle); the transition probability is zero for a constant potential; and the scattering matrix is unitary.

A final item in this section considers a limiting behavior of the Coulomb wave.

A. The Born-Oppenheimer Approximation

In Eqs. (11) and (12) one should approximate $\Psi_{i;a}^{(+)}$ in such a way that the formalism is self-consistent. The lowest-order approximation (in the sense of perturbation) for $\Psi_{i;a}^{(+)}$ may be identified as the first term of the Lippmann-Schwinger equation in Eq. (4); that is

$$\Psi_{i;a}^{(+)}\cong\phi_a(\mathbf{k}_0)\eta_b(n_0). \tag{26}$$

It should be remarked that the Kronecker delta in Eq. (6) was due to the orthonormality of the initial and final unperturbed wave functions. Thus from Eqs. (11) and (12) one obtains in the Born-Oppenheimer[7] approximation the familiar expressions for M_D and M_E

$$M_D^{\mathrm{exe}}(\mathrm{BO})=\langle\phi_a(\mathbf{k}_1)\eta_b(n)|V_a+V_{ab}|\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle, \tag{27}$$

and

$$M_E^{\mathrm{exe}}(\mathrm{BO})=\langle\phi_b(\mathbf{k}_1)\eta_a(n)|V_b+V_{ab}|\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle. \tag{28}$$

Similarly, one finds for the ionization of hydrogen atoms, though use of Eq. (21), that to the lowest order of the perturbation

$$M_D^{\mathrm{ion}}(\mathrm{BO})=\langle\phi_a(\mathbf{k}_1)\chi_b^{(-)}(\mathbf{k}_2)|V_a+V_{ab}|\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle, \tag{29}$$

and

$$M_E^{\mathrm{ion}}(\mathrm{BO})=\langle\phi_b(\mathbf{k}_1)\chi_a^{(-)}(\mathbf{k}_2)|V_b+V_{ab}|\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle. \tag{30}$$

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[7] M. Born, Z. Physik **37**, 863 (1926); **38**, 803 (1926); J. R. Oppenheimer, Phys. Rev. **32**, 361 (1928).

In this formalism the matrix elements for the direct scattering, $M_D{}^{\text{exc}}(\text{BO})$ and $M_D{}^{\text{ion}}(\text{BO})$, satisfy the boundary condition that any constant potential (i.e., no interacting force) should lead to no transition. However, the matrix elements for the exchange scattering, $M_E{}^{\text{exc}}(\text{BO})$ and $M_E{}^{\text{ion}}(\text{BO})$, do not satisfy this boundary condition, simply because the initial and the final states are not orthogonal. The root of this discrepancy can be found in the fact that the indistinguishable electrons are described by the eigenstates of two different Hamiltonians. This discrepancy and the "post and prior" discrepancy have been known for some time, and many authors[8] tried to remedy the situation without much success.

A further fault exists in this approximation: in the sense of perturbations the direct scattering is treated to the accuracy of $(V_a+V_{ab})/(K_a+K_b+V_b)$, whereas the exchange scattering is treated to the different accuracy of $(V_b+V_{ab})/(K_a+K_b+V_a)$, as was pointed out earlier.[9]

B. The Coulomb Wave Approximation: Present Theory

By now it is obvious how one should approximate $\Psi_{i;a}{}^{(+)}$ in Eqs. (15), (18), (23), and (24) in order to have a self-consistent theory. The choice is clearly the first term of the Lippmann-Schwinger equation given in Eq. (17):

$$\Psi_{i;a}{}^{(+)}\cong\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0) \tag{31}$$

(this is the unperturbed wave function). With this choice one obtains for the excitation processes

$$M_D{}^{(0)\text{exc}}=\langle\chi_a{}^{(-)}(\mathbf{k}_1)\eta_b(n)\,|\,V_{ab}\,|\,\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle \tag{32}$$

and

$$M_E{}^{(0)\text{exc}}=\langle\chi_b{}^{(-)}(\mathbf{k}_1)\eta_a(n)\,|\,V_{ab}\,|\,\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle; \tag{33}$$

and for the ionization processes

$$M_D{}^{(0)\text{ion}}=\langle\chi_a{}^{(-)}(\mathbf{k}_1)\chi_b{}^{(-)}(\mathbf{k}_2)\,|\,V_{ab}\,|\,\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle \tag{34}$$

and

$$M_E{}^{(0)\text{ion}}=\langle\chi_b{}^{(-)}(\mathbf{k}_1)\chi_a{}^{(-)}(\mathbf{k}_2)\,|\,V_{ab}\,|\,\chi_a{}^{(+)}(\mathbf{k}_0)\eta_b(n_0)\rangle. \tag{35}$$

Thus, by describing the two identical, indistinguishable electrons as eigenstates of the same Hamiltonian, one recovers the orthogonality between the initial and final states. Now, we see that no constant potential can lead to a transition, and in this regard the formalism satisfies the boundary condition. Both the direct and exchange scatterings are dealt with to the same accuracy: $V_{ab}/(K_a+K_b+V_a+V_b)$. The expressions for the matrix elements exhibit symmetry over the two electron coordinates as they should.[10]

Another important point which should also be noted is that in the present formalism the unitarity of the scattering matrix is preserved to the lowest order of the perturbation, whereas such is not the case for the Born-Oppenheimer approximation. Let us recall that the "in"-state, total wave function in the remote past was an unperturbed, initial, total wave function and that hermiticity of the Hamiltonian of the system implies conservation of probability. Therefore, the inner product of two quasistationary (time-dependent) stationary solutions is independent of time, and

$$\begin{aligned}\lim_{t\to\infty}\langle\Psi_{\text{tot},i}{}^{(+)}\Psi_{\text{tot},j}{}^{(+)}\rangle&=\lim_{t\to-\infty}\langle\Psi_{\text{tot},i}{}^{(+)}\Psi_{\text{tot},j}{}^{(+)}\rangle\\&=\langle\Phi_{\text{tot},i}{}^{(\pm)}\Phi_{\text{tot},j}{}^{(\pm)}\rangle.\end{aligned} \tag{36}$$

Assuming the completeness relation for the Φ's, one can expand $\lim_{t\to\infty}\Psi_{\text{tot},i}{}^{(+)}$ in terms of unperturbed states with the S-matrix elements as expansion coefficients

$$\lim_{t\to\infty}\Psi_i{}^{(+)}=\sum_n\Phi_n{}^{(-)}S_{ni}. \tag{37}$$

When one carries out the calculation for both sides of Eq. (36) using Eq. (37) and

$$\Phi_n{}^{(\pm)}=\frac{1}{\sqrt{2}}[\chi_a{}^{(\pm)}(\mathbf{k}_0)\eta_b(n_0)\pm\chi_b{}^{(\pm)}(\mathbf{k}_0)\eta_a(n_0)],$$

$+$ for spin-singlet state

$-$ for spin-triplet states,

one obtains the unitarity of the scattering matrix. On the other hand the Born-Oppenheimer (BO) approximation uses for the unperturbed wave function

$$\Phi_n{}^{(+)}(\text{BO})=\frac{1}{\sqrt{2}}[\phi_a(\mathbf{k}_0)\eta_b(n_0)\pm\eta_a(n_0)\phi_b(\mathbf{k}_0)],\quad\begin{matrix}+\text{ singlet}\\-\text{ triplet}\end{matrix}$$

and due to the lack of orthogonality mentioned earlier the set of $\Phi_n{}^{(+)}(\text{BO})$'s does not satisfy the completeness relation. In consequence, an expansion in the form of Eq. (37) is not possible. If the expansion of Eq. (37) is assumed, the equation corresponding to that of unitarity of the S matrix becomes, in matrix form,

$$I+A=S^\dagger S+S^\dagger AS,$$

with

$$A_{ij}=\langle\phi_b(\mathbf{k}_i)\eta_a(n_i),\phi_a(\mathbf{k}_j)\eta_b(n_j)\rangle. \tag{38}$$

The matrix A is neither I nor 0. In order for Eq. (38)

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[8] See for the lack of orthogonality, L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 239, and for a remedial attempt, see Ref. 6 and K. L. Bell and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A276**, 346 (1963).

[9] T. Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), Sec. L, p. 192.

[10] Although a different approach is used, Borowitz and Friedman in 1953 obtained matrix elements identical to those in Eqs. (32) through (35) from their so-called "symmetric perturbation" scheme. Later Borowitz and Klein in 1956 calculated the first Born amplitudes for 2*s*- and 2*p*-excitations of hydrogen atoms by electron impact. For details, see S. Borowitz and B. Friedman, Phys. Rev. **89**, 441 (1953); S. Borowitz and M. M. Klein, *ibid.* **103**, 612 (1956).

to be consistent with the unitarity of the S matrix, one must have $SA=AS$, which is not true unless A is either I or 0. Thus the choice for $\Psi_{i;a}^{(+)}$ in Eq. (31) is the only choice which has all the required properties.

At this point it may be worthwhile to point out that Geltman's work[11] of 1956 employed the same formalism as we use in Eqs. (23) and (24) but approximated $\Psi_{i;a}^{(+)}$ by $\phi_a(\mathbf{k}_0)\eta_b(n_0)$. Thus his work suffers inconsistency of the theory and nonorthogonality between the initial and the final states with consequent violation of the boundary condition and of the requirement of unitarity of the scattering matrix. Note, however, that prediction of linear ionization threshold law is the same as ours.

C. Other Approximations

The so-called Born-exchange approximation[12] is often used to determine the ionization cross sections. This approximation is defined by

$$M_D^{\text{ion}}(\text{BE})=\langle\phi_a(\mathbf{k}_1)\chi_b^{(-)}(\mathbf{k}_2)\,|\,V_a+V_{ab}\,|\,\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle\,,$$

and

$$M_E^{\text{ion}}(\text{BE})=\langle\phi_a(\mathbf{k}_2)\chi_b^{(-)}(\mathbf{k}_1)\,|\,V_a+V_{ab}\,|\,\phi_a(\mathbf{k}_0)\eta_b(n_0)\rangle \neq M_E^{\text{ion}}(\text{BO})\,,$$

and is not in accordance with the Pauli principle. We note that it does maintain the proper orthogonality between initial and final states.

Next let us discuss the effective-charge approximation which was introduced by Vainshtein *et al.*,[13] in 1964 and studied subsequently by Crothers and McCarroll[14] and more recently by Omidvar.[15] This formalism lacks self-consistency, in the sense of the perturbation theory, and orthogonality, not only for the direct scattering but also for the exchange scattering. Therefore this formalism leads to nonvanishing transition amplitudes even when there is no interacting force (viz., a nonzero, constant potential).

Finally let us discuss the Coulomb-Born-Oppenheimer approximation.[16] This formalism was outlined by Seaton[17] in 1962 for the case of collisions of electrons with positive ions. According to his article, the plane waves in the Born-Oppenheimer approximation are simply replaced by the attractive Coulomb wave with a strength of $Z-1$ (Z=atomic number). No other changes are made. Obviously, one cannot just transform the state vector and ignore accounting for the resulting effects of the transformation on the interaction Hamiltonian.

In summary, it is remarked that one can find numerous faults with the conventional formalisms which are all associated with the wave-function approximation method. We are accustomed to describing an incoming particle in the region far from the scattering region. Often we are apt to forget that this incoming, plane wave interacts with a certain field whose potential falls off at large distances. What is proven in the present formalism is that (using the prior form instead of the post form) the incoming plane wave being attracted by the nucleus and at the same time being repulsed by the residual atomic electron is equivalent to an attractive, incoming Coulomb wave being repulsed by the other electron. In order to be consistent—a requirement noted particularly in the case of ionization processes—one must avoid discriminating between electrons, as is done, for example, by saying that one outgoing electron should be described by a Coulomb wave while the second electron—which is indistinguishable from the first—should be described by a plane wave. The behavior of the Coulomb wave in the high-energy limit is that of the plane wave. Therefore the Coulomb wave approximation has a region of validity which includes that of the Born approximation. In the threshold regions of inelastic collisions the intuitive argument for the validity of the Coulomb-wave, perturbation theory may be given as follows: when the total energy of the system of colliding electron and target, $E_{\text{tot}}[=\frac{1}{2}k_0^2-\frac{1}{2}(1/n_0^2)]$, approaches zero, a consequence of the Coulomb repulsion between the two electrons is that the time average of their spatial separation can not be of the order of the Bohr radius but must be much larger than this; then the average of the perturbation interaction, say $\langle 1/r_{ab}\rangle$ is quite small compared to the total energy of the system.

Both the higher-order contribution to the transition probability and the convergence of the perturbation series are for this formalism subjects for future study.[18]

IV. THRESHOLD LAWS

Evaluations of the matrix elements of Eqs. (32)–(35) can only be done approximately. The approximations are straightforward and relatively simple for threshold processes. For these one can get predictions. To compare these predictions with experiment is not easy: The experimentalists have not agreed on the extrapolation to threshold for the cross sections. We now consider these matters.

A. Excitation Processes of Hydrogen Atoms

It is well-known that the Born-Oppenheimer approximation predicts the threshold law that the cross section

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[11] S. Geltman, Phys. Rev. **102**, 171 (1956).

[12] M. R. H. Rudge and M. J. Seaton, Proc. Roy. Soc. (London) **A283**, 262 (1965); M. R. H. Rudge and S. B. Schwartz, *ibid.* **88**, 563 (1966).

[13] L. Vainshtein, L. Presnyakov, and I. Sobelman, Zh. Eksperim. i Teor Fiz. **45**, 2015 (1963) [English transl.: Soviet Phys.—JETP **18**, 1383 (1964)].

[14] D. Crothers and R. McCarroll, Proc. Phys. Soc. (London) **86**, 753 (1965).

[15] K. Omidvar, Phys. Rev. Letters **18**, 153 (1967).

[16] O. Bely, J. Jully, H. Van Regemorter, Ann. Phys. (N.Y.) **8**, 303 (1963); A. Burgess, Mém. Soc. Roy. Sci. Liège **4**, 299 (1961).

[17] M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Sec. 2.9, p. 388.

[18] An approach which might be taken is the one by A. C. Zemach and A. Klein, Nuovo Cimento **10**, 1078 (1958).

is linear in the momentum of the outgoing electron k_1. This prediction was supposedly verified experimentally for $H(1s)\rightarrow H(2p)$ by Fite *et al.*,[19] in 1959. However their data did not include values close enough to the threshold to please the theorist. Furthermore, in the same year Lichten and Schultz[20] reported for $H(1s)\rightarrow H(2s)$ measurements which did not agree with those of the k^1 power law. More recently, Chamberlain *et al.*,[21] reported finite cross sections for threshold for $H(1s)\rightarrow H(2p)$, a finding in support of our prediction.

There have been a few theoretical predictions[22,23] of nonzero cross sections at threshold—all developed through use of the close-coupling approximations for $1s\rightarrow 2s$ and $1s\rightarrow 2p$ excitation processes of hydrogen atoms. These predictions of the finite threshold law were attributed to the degeneracy of hydrogen atoms in the orbital angular momentum l.[23] The explanation is not at all clear. What is agreed on between the two formalisms, which give the same finite threshold law, is that the incoming wave is not a simple plane wave but a distorted wave.

We now proceed to approximate the values of $M_D{}^{(0)\mathrm{exc}}$ and $M_E{}^{(0)\mathrm{exc}}$ in Eqs. (32) and (33). The "in"- and "out"-state, attractive, Coulomb wave functions[24] are

$$\chi_a{}^{(+)}(\mathbf{k}_0)=N_0e^{i\mathbf{k}_0\cdot\mathbf{r}_a}F(i/k_0,1,ik_0r_a-i\mathbf{k}_0\cdot\mathbf{r}_a)$$

and (39)

$$\chi_a{}^{(-)*}(\mathbf{k}_1)=N_1{}^*e^{-i\mathbf{k}_1\cdot\mathbf{r}_a}F(i/k_1,1,ik_1r_a+i\mathbf{k}_1\cdot\mathbf{r}_a)\,,$$

with

$$|N_i|^2=2\pi/[k_iV(1-(e^{-2\pi/k_i})]\,, \tag{40}$$

for a box normalization. As k_1 approaches zero, the Coulomb wave function with momentum k_1 becomes independent of $|k_1|$, apart from the normalization constant in Eq. (40).

In order to show the convergence of the integrals and to obtain the functional forms for $M_{D,E}{}^{(0)\mathrm{exc}}$ in the present formalism, we employ the so-called "peaking approximation."[25]

By defining

$$G(\mathbf{k})=\int\eta_b{}^*(n,l,m)\eta_b(n_0,l_0,m_0)e^{i\mathbf{k}\cdot\mathbf{r}}d^3r\,, \tag{41}$$

and using the identity

$$\frac{1}{r_{ab}}=\frac{1}{2\pi^2}\int\frac{e^{i\mathbf{k}\cdot(\mathbf{r}_a-\mathbf{r}_b)}}{k^2}d^3k\,, \tag{42}$$

we can rewrite the $M_D{}^{(0)\mathrm{exc}}$ in Eq. (32) as

$$M_D{}^{(0)\mathrm{exc}}=N_0N_1{}^*\int\int G(\mathbf{q}+\mathbf{k})\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{2\pi^2(\mathbf{k}+\mathbf{q})^2}\times F(\mathbf{k}_0,\mathbf{r})F^*(\mathbf{k}_2,\mathbf{r})d^3kd^3r\,. \tag{43}$$

The "peaking approximation" is the approximation

$$\int G(\mathbf{q}+\mathbf{k})\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(\mathbf{k}+\mathbf{q})^2}d^3k\cong G(\mathbf{q})\int\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(\mathbf{k}+\mathbf{q})^2}d^3k =G(\mathbf{q})\frac{2\pi^2}{r}e^{i\mathbf{q}\cdot\mathbf{r}}\,. \tag{44}$$

The remaining integral over d^3r was evaluated by Nordsieck[26] in 1953 in connection with the bremsstrahlung problem. Thus one finds for $M_D{}^{(0)\mathrm{exc}}$ that

$$M_D{}^{(0)\mathrm{exc}}=2\pi N_0N_1{}^*\frac{G(\mathbf{q})}{(q^2/2)}e^{-\pi/k_0}\left(\frac{\alpha}{\gamma}\right)^{i/k_0}\left(\frac{\alpha}{\alpha+\beta}\right)^{i/k_1}\times F(i/k_0,i/k_1,1;\chi) \tag{45}$$

with

$$\begin{aligned}\mathbf{q}&=\mathbf{k}_0-\mathbf{k}_1, & \chi&=\frac{\beta\gamma-\alpha\delta}{\gamma(\alpha+\beta)};\\ 2\alpha&=q^2, & \beta&=\mathbf{k}_1\cdot\mathbf{q};\\ \alpha+\gamma&=\mathbf{k}_0\cdot\mathbf{q}, & \delta+\beta&=k_0k_1+\mathbf{k}_0\cdot\mathbf{k}_1;\end{aligned} \tag{46}$$

$F(u,v,w;x)$ in Eq. (45) denotes the hypergeometric series.

Now let us evaluate $M_E{}^{(0)\mathrm{exc}}$, changing variables according to

$$\begin{aligned}\mathbf{R}&=\tfrac{1}{2}(\mathbf{r}_a+\mathbf{r}_b)\,,\\ \boldsymbol{\varrho}&=\tfrac{1}{2}(\mathbf{r}_a-\mathbf{r}_b)\,,\end{aligned} \tag{47}$$

and denoting the momentum representation of the hydrogenic, bound-state wave function by $\phi_n(\mathbf{q})$,

$$\phi_n(\mathbf{q})=\frac{1}{(2\pi)^3}\int\eta(n,r)e^{i\mathbf{q}\cdot\mathbf{r}}d^3r\,. \tag{48}$$

The $M_E{}^{(0)\mathrm{exc}}$ in Eq. (33) can be rewritten as

$$M_E{}^{(0)\mathrm{exc}}=4N_0N_1{}^*\int\frac{1}{\rho}\phi_n{}^*(\mathbf{s}_1)\phi_{n_0}(\mathbf{s}+\mathbf{q}+\mathbf{s}_1)\times e^{i(\mathbf{R}-\rho)\cdot\mathbf{s}}e^{-i\rho\cdot(2\mathbf{s}_1+\mathbf{q}-\mathbf{k}_0-\mathbf{k}_n)}e^{i(\mathbf{q}+\mathbf{k}_0-\mathbf{k}_n)\cdot\mathbf{R}}\times F^*(\mathbf{k}_1,\,\mathbf{R}-\boldsymbol{\varrho})F(\mathbf{k}_0,\,\mathbf{R}+\boldsymbol{\varrho})d^3Rd^3\rho d^3s_1d^3s\,.$$

Then with the additional approximations[27]

$$\int\phi(\mathbf{s}+\mathbf{q}+\mathbf{s}_1)e^{i\mathbf{s}\cdot(\mathbf{R}-\rho)}d^3s\cong\phi(\mathbf{q}+\mathbf{s}_1)(2\pi)^3\delta^3(\mathbf{R}-\boldsymbol{\varrho})\,,$$

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[19] W. L. Fite, R. F. Stebbings, and R. T. Brackmann, Phys. Rev. **116**, 356 (1959).

[20] W. Lichten and S. Schultz, Phys. Rev. **116**, 1132 (1959).

[21] G. E. Chamberlain, S. J. Smith, and D. W. O. Heddle, Phys. Rev. Letters **12**, 647 (1964).

[22] R. Damburg and M. Gailitis, Proc. Phys. Soc. (London) **82**, 1068 (1963).

[23] P. G. Burke, S. Ormonde, and W. Whitaker, Phys. Rev. Letters **17**, 800 (1966).

[24] G. Breit and H. A. Bethe, Phys. Rev. **93**, 888 (1954); H. A. Bethe, F. Low, and L. C. Maximon, *ibid.* **91**, 417 (1953).

[25] See Ref. 14 for details.

[26] A. Nordsieck, Phys. Rev. **93**, 785 (1953).

[27] Similar approximations were employed by Crothers and McCarroll in Ref. 14.

and

$$\int \phi_n{}^*(\mathbf{s}_1)\phi_{n_0}(\mathbf{q}+\mathbf{s}_1)e^{-2i\boldsymbol{\rho}\cdot\mathbf{s}_1}d^3s_1 \cong \int \phi_n{}^*(\mathbf{s}_1)\phi_{n_0}(\mathbf{q}+\mathbf{s}_1)d^3s_1 = \frac{G(\mathbf{q})}{(2\pi)^3}, \quad (49)$$

one gains

$$M_E{}^{(0)\mathrm{exc}} = 4N_0N_1{}^*G(\mathbf{q})\int \frac{d^3R}{R}e^{2i\mathbf{k}_0\cdot\mathbf{R}}F^*(\mathbf{k}_1,0)F(\mathbf{k}_0,2\mathbf{R})d^3R.$$

The integral over d^3R can be evaluated with Nordsieck's formula, and one obtains for the exchange scattering

$$M_E{}^{(0)\mathrm{exc}} = 2\pi N_0N_1{}^*\frac{G(\mathbf{q})}{(k_0{}^2/2)} \times e^{-\pi/k_0}F\left(1-i/k_0,\ 1,\ \frac{2i(k_0k_1-\mathbf{k}_0\cdot\mathbf{k}_1)}{k_0{}^2k_1}\right). \quad (50)$$

$F(u,v,x)$ above denotes the confluent hypergeometric series.

Comparison of $M_E{}^{(0)\mathrm{exc}}$ with $M_D{}^{(0)\mathrm{exc}}$ yields a relation

$$M_E{}^{(0)\mathrm{exc}} = M_D{}^{(0)\mathrm{exc}}\frac{q^2}{k_0{}^2}\left(\frac{\gamma}{\alpha}\right)^{i/k_0}\left(\frac{\gamma+\delta}{\gamma}\right)^{i/k_1} \times \frac{F[1-i/k_0,\ 1,\ 2i(k_0k_1-\mathbf{k}_0\cdot\mathbf{k}_1)/k_0{}^2k_1]}{F(i/k_0,i/k_1,1;\chi)}, \quad (51)$$

which in the high-energy limit approaches

$$M_E{}^{(0)\mathrm{exc}} = M_D{}^{(0)\mathrm{exc}}q^2/k_0{}^2. \quad (52)$$

This last relationship was derived by Ochkur[28] in 1964. From Eq. (51) one obtains $M_E{}^{(0)\mathrm{exc}} = M_D{}^{(0)\mathrm{exc}}$ at threshold. Originally Ochkur derived the relation in Eq. (52) in the Born-Oppenheimer approximation for helium excitation processes. He obtained the relation through the high-energy expansions of the scattering amplitudes. Since in our derivation, we have not used any energy-limiting procedures, the relation in Eq. (51) is valid for all energy regions.

The approximations which were employed in evaluating the $M_{D,E}{}^{(0)\mathrm{exc}}$ should be studied further for improvement. However, the ratio of $M_E{}^{(0)\mathrm{exc}}$ to $M_D{}^{(0)\mathrm{exc}}$ in Eq. (51) would seem to give promise of canceling this crudeness and appears to give a correct relation. This relation appears to be universal, independent of the species of atoms involved.

It should be remarked that in the reference frame where $k_0 = k_{0z}$, we have $G(\mathbf{q})$ behaving as $k_1{}^{|m-m_0|}$ as $k_1 \to 0$, as has been shown by one of us (I.J.K.).[29] This factor, $G(\mathbf{q})$, is present in the direct scattering amplitude in the Born approximation. The abovementioned threshold behavior of the $G(\mathbf{q})$ may be traced to the spherical harmonics, $Y_L{}^{|m_0-m|}(\theta_q,\phi_q)$ which arise from the coupling of two spherical harmonics of the initial and final hydrogenic, bound-state wave functions.

In order to get the cross section, one squares the scattering matrix element S_{fi}, then divides by the incident flux $\hbar k_0/mV$ and by the duration of the transition, $T = 2\pi\delta(0)$ to form a transition rate, and finally sums over final states $Vd^3k_1\hbar^3/(2\pi\hbar)^3$ in the observed interval of phase space. For a cross section for a process, $\mathbf{k}_0,\ (n_0,l_0) \to \mathbf{k}_1(n,l)$, with unpolarized electrons, one should sum over final electron spin and m states and average over initial electron spin and m_0 states. Thus one finds for the cross section of the process $\mathbf{k}_0,\ (n_0,l_0) \to \mathbf{k}_1,\ (n,l)$,

$$\left\langle\frac{d\sigma}{d\Omega}\right\rangle_{\mathrm{spin},m_0} \underset{k_1\to 0}{\cong} \text{a certain function of } k_0 \text{ only}, \quad (53)$$

which cross section exhibits k_1 to the zeroth power; this is the threshold law. The difference between the $k_1{}^1$ power law of the Born-Oppenheimer approximation and the present law is due to the way in which the final-state, positive-energy electron is described.

It is significant that the functional form of the M-matrix, and not the absolute magnitude, is used. Because of this generality the nonzero value of the cross section at threshold is assuredly correct.

B. The Ionization Process for Hydrogen Atoms

By examination of Eqs. (23) and (24), one finds exactly the Peterkop relation[30] between the direct- and exchange-scattering matrices

$$M_E{}^{\mathrm{ion}}(\mathbf{k}_1,\mathbf{k}_2) = M_D{}^{\mathrm{ion}}(\mathbf{k}_1 \leftrightarrow \mathbf{k}_2), \quad (54)$$

without needing to make any complicated phase assignment.[31]

We proceed to the evaluation of $M_D{}^{(0)\mathrm{ion}}$ of Eq. (34) by using the peaking approximation—not because this approximation gives correct values but because it gives after manageable mathematical labor functional forms for the amplitudes.

Using the identity in Eq. (42), with a quantity $G(n_0,\mathbf{k}_2,\mathbf{k})$ which is defined as

$$G(n_0,\mathbf{k}_2,\mathbf{k}) = \int \eta(n_0)\chi^{(-)*}(\mathbf{k}_2)e^{i\mathbf{k}\cdot\mathbf{r}}d^3r, \quad (55)$$

one can rewrite the $M_D{}^{(0)\mathrm{ion}}$ in Eq. (34) as

$$M_D{}^{(0)\mathrm{ion}} = \prod_{i=0}^{2} N_i\frac{1}{2\pi^2}\int \frac{d^3kd^3r}{(\mathbf{k}+\mathbf{q})^2}e^{-i\mathbf{k}\cdot\mathbf{r}}G(n_0,\mathbf{k}_2,\ \mathbf{k}+\mathbf{q}) \times F(\mathbf{k}_0,\mathbf{r})F^*(\mathbf{k}_1,\mathbf{r}). \quad (56)$$

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[28] V. I. Ochkur, Zh. Eksperim. i Teor. Fiz. **45**, 734 (1963) [English transl.: Soviet Phys.—JETP **18**, 503 (1964)].

[29] I. J. Kang, Phys. Rev. **144**, 29 (1966).

[30] R. K. Peterkop, Proc. Phys. Soc. (London) **77**, 1220 (1961).

[31] P. G. Burke and A. J. Taylor, Proc. Roy. Soc. (London) **A287**, 105 (1965).

Using the corresponding peaking approximation,

$$\int G(n_0,\mathbf{k}_2,\ \mathbf{k}+\mathbf{q})\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(\mathbf{k}+\mathbf{q})^2}d^3k \cong G(n_0,\mathbf{k}_2,\mathbf{q})\int\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(\mathbf{k}+\mathbf{q})^2}d^3k \qquad (57)$$

and the Nordsieck's first integral formula,[26] one obtains

$$M_D{}^{(0)\,\mathrm{ion}}(\mathbf{k}_1,\mathbf{k}_2)=2\pi\prod_{i=0}^{2}N_iG(n_0,\mathbf{k}_2,\ \mathbf{k}_0-\mathbf{k}_1)\frac{e^{-\pi/k_0}}{\alpha}\left(\frac{\alpha}{\gamma}\right)^{i/k_0}\times\left(\frac{\alpha}{\alpha+\beta}\right)^{i/k_1}F(i/k_0,1/k_1,1,\chi) \qquad (58)$$

with $\alpha,\beta,\gamma,\delta,\mathbf{q}$, and χ the quantities defined in Eq. (46).

The quantity $G(n_0,\mathbf{k}_2,\ \mathbf{k}_0-\mathbf{k}_1)$ in Eq. (58) can be calculated by use of the integral representation of the confluent hypergeometric function.

For $H(1s)$ ionization, using the definition of G in Eq. (55), one finds that

$$G(1s,\mathbf{k}_2,\ \mathbf{k}_0-\mathbf{k}_1)=-4\sqrt{\pi}\frac{\partial}{\partial\lambda}\left\{\frac{1}{p^2+\lambda^2}\left[\frac{p^2+\lambda^2}{p^2+\lambda^2+2\mathbf{k}_2\cdot\mathbf{p}-2i\lambda k_2}\right]^{1/k_2}\right\}\Bigg|_{\lambda=1}$$

with

$$\mathbf{p}=\mathbf{k}_0-\mathbf{k}_1-\mathbf{k}_2. \qquad (59)$$

For a general case of $H(n_0,l_0,m_0)$ ionization, using the differential operator method,[32] one finds for $G(n,l,m;\ \mathbf{k}_2,\ \mathbf{k}_0-\mathbf{k}_1)$ that

$$G(n,l,m;\mathbf{k}_2,\ \mathbf{k}_0-\mathbf{k}_1)=-4\pi N_{n,l,m}L_{n,l}(\nabla_{k0\pm})^{|m|}P_{l-|m|}(k_{0z})\times\frac{\partial}{\partial\lambda}\frac{1}{p^2+\lambda^2}\left[\frac{p^2+\lambda^2}{p^2+\lambda^2+2\mathbf{k}_2\cdot\mathbf{p}-2i\lambda k_2}\right]^{i/k_2}\Bigg|_{\lambda=1/n}, \qquad (60)$$

where

$$N_{n,l,m}=-\left\{\left(\frac{2}{n}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}\left(\frac{2}{n}\right)^l\times\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}i^{-|m|}, \qquad (61)$$

$$\nabla_{k0\pm}=\frac{\partial}{\partial k_{0x}}\pm i\frac{\partial}{\partial k_{0y}},$$

$$L_{n,l}=\sum_{j=0}^{n-l-1}(-1)^{j+1}\frac{(n!)^2\rho^j}{(n-1-j)!(j+1)!j!}\Bigg|_{\rho=(-2/n)\partial/\partial\lambda}$$

and $P_{l-|m|}(k_{0z})$ is a polynomial differential operator obtained by substituting $(\partial/\partial ik_{0z})^t(\partial/\partial(-\lambda))^{l-|m|-t}$ for x^t in $(d/dx)^{|m|}P_l(x)$, in which $P_l(x)$ denotes the Legendre polynomial.

The magnitude of the fourth argument χ of the hypergeometric series is less than 1, and the series converges. Furthermore, as k_1 approaches zero, the hypergeometric series becomes a confluent hypergeometric series depending only on k_0. Therefore one can conclude in the region near threshold that

$$M_D{}^{(0)\,\mathrm{ion}}(\mathbf{k}_1,\mathbf{k}_2)=f(k_0)N_1N_2. \qquad (62)$$

Following a procedure similar to the one described above to obtain the differential ionization cross section, one gets

$$\left\langle\frac{d^2\sigma}{d\Omega_1 d\Omega_2}\right\rangle_{\mathrm{spin}}^{\mathrm{ion}}=\int\int\frac{2\pi\delta(E_f-E_i)}{(\hbar k_0/mV)}\{\tfrac{1}{4}|M_D{}^{(0)}+M_E{}^{(0)}|^2+\tfrac{3}{4}|M_D{}^{(0)}-M_E{}^{(0)}|^2\}^{\mathrm{ion}}\frac{V^2k_1{}^2k_2{}^2dk_1dk_2\hbar^6}{2!h^6}. \qquad (63)$$

From Eqs. (62) and (63), one now finds that

$$\sigma_{\mathrm{tot}}=(\text{some function of }k_0\text{ only})\times E_{\mathrm{tot}}, \qquad (64)$$

which equation exhibits the linear threshold law. Geltman[11] in 1956 and Rudge and Seaton[12] in 1965 obtained the same linear threshold law by describing the outgoing electrons as Coulomb waves and the incoming electron as a plane wave. The slope of the curve of the cross section versus total energy for the $H(1s)$-ionization case as obtained in 1960 by Peterkop[33] from the s-wave contribution in Geltman's work is reported as $0.022\pi a_0{}^2/\mathrm{eV}$, and has been misquoted in the recent literature.[15] The corresponding slope by Rudge and Seaton[12] is $0.136\pi a_0{}^2/\mathrm{eV}$. The experimental values reported are: 0.078 by Fite and Brackman[34]; 0.067 by Boksenburg[35]; and 0.064 (in the region of energy 0.3 eV, and above, beyond the threshold estimated to agree with the experiment) by McGowan and Fineman[36] (all units are $\pi a_0{}^2/\mathrm{eV}$). The preliminary study shows that the "peaking approximation" gives too large a value for the slope; the reason for this has been traced to approximating an oscillatory factor $e^{i\mathbf{k}\cdot\mathbf{r}}$ by 1 for all $\mathbf{k}$ and $\mathbf{r}$. A better approximation for $M_D{}^{(0)\,\mathrm{ion}}$ has been carried out by numerical calculation for comparison with observations. The slope turns out to be $0.024\pi a_0{}^2/\mathrm{eV}$. This study will be reported later.

V. MANY- ($N>1$) ELECTRON ATOMS AND IONS

Some of the work for the case of hydrogen can be extended in a fairly general way. Let us turn to the case of the many-electron atom to see what is possible. As long as one takes a product of hydrogenic wave functions for the unperturbed atomic wave functions, the perturbation interaction Hamiltonian is

$$\sum_{i>j=1}^{N+1}V_{ij}.$$

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[32] See, for an example, Ref. 29.

[33] R. K. Peterkop, Izv. Akad. Nauk, SSSR **24**, 947 (1960).

[34] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).

[35] A. Boksenburg, thesis, University College, London, 1960 (unpublished).

[36] J. W. McGowan and M. A. Fineman, in Proceedings of the Fourth International Conference on Atomic Collisions, Quebec, Canada, 1965 (unpublished).

Then the present formalism gives the M matrix, from which one finds the scattering matrix by using linear combinations of these elements, as follows:

$$M^{(0)\text{exc ion}}=\Big\langle \chi_1^{(-)}(\mathbf{k}_1)\prod_{i=2}^{N+1}\binom{\eta_i(n_i)}{\chi_i(\mathbf{k}_i)}\Big|\sum_{i>j=1}^{N+1}V_{ij}\Big|$$

$$\times\chi_1^{(+)}(\mathbf{k}_0)\prod_{j=2}^{N+1}\eta_j(n_{0j})\Big\rangle. \quad (65)$$

Because of the nature of the two-body potential assumed and the orthogonality of the wave functions, one finds the following theorem:

To the lowest order of the mutual interaction of electrons, one incoming electron excites or ionizes one residual electron in an atom at a time.

It is remarked that the content of this theorem stated above is the first of the three assumptions on which the impulse approximation[37,38] is founded. The use of the impulse approximation has been rather extensive in inelastic, high-energy, nucleon-nuclei scattering since 1950. The second assumption of the impulse approximation is that the amplitude of the incident wave falling on each of the constituent nucleons is the same as if that constituent were alone. (We read "electrons" instead of "nucleons," of course.) The appropriateness of this second assumption is understandable in the light of this work, as one sees upon recalling the nature of the superposition principle of classical electrodynamics.

To complete our remarks on the foundation of the impulse approximation, it can be pointed out that the third assumption (that the binding forces between the constituents of the system are negligible during the decisive phase of the collision, the time during which the incident particle interacts strongly with the system) has been justified[37] for the inelastic, high-energy, nucleon-nuclei scattering and is characteristic of the short-range and the nonelectromatnetic nature of nuclear forces.

At this point, it should be pointed out that the present formalism is closely related to the impulse approximation. The validity of the latter approximation has been studied. Following the criterion of Mott and Massey[39] that

$$aE_0/hv \ll 1 \quad (66)$$

(where a is a scattering length or the range of interaction; E_0 is the bound-state energy, and v is the speed of the incident incident electron), one finds that the present formalism can be valid even at the threshold by taking a to be unity in Coulomb units.

Returning to the problem of the electron-atom or ion collisions, one finds that it follows from the theorem that the electron-impact excitation cross section for any process, $\mathbf{k}_0$, $(n_0,l_0)\rightarrow\mathbf{k}_1$, (n,l), is finite at the threshold regardless of the atomic species, whereas the linear threshold ionization law is true for all electron-atom ionization processes.

These threshold laws encompass the existing experimental results mentioned earlier in this section. Yet their far greater generality should be tested in the future. It is obvious by now that these threshold laws and the Ochkur-like relation, as well as the Peterkop relation, hold true for electron impact excitation and ionization, respectively, of positive and negative ions. According to Burgess,[40] who used the so-called Coulomb-Born-Oppenheimer approximation, the linear threshold law for ionization is valid for scattering of electrons from positive ions. Recently Bely[41] found for the scattering of electrons from positive, lithium-like ions a threshold cross section for excitation which was finite. It might well be, therefore, that an actual search for these effects might show that they have been overlooked all along.

VI. SUMMARY

The present formalism is, in summary and to the lowest order of the perturbation, satisfactory in that:

(1) No "post-prior" discrepancy exists.

(2) Orthogonality between the symmetrized initial and final state wave functions is preserved.

(3) Consequently, the boundary condition that any constant potential (no interacting force) should lead to no transition is met.

(4) Furthermore, the unitarity of the scattering matrix is preserved.

(5) The direct and exchange scattering are dealt to the same accuracy.

(6) The formalism can be applied easily to the cases of electron scattering from positive ions and from negative ions.

One inevitable difficulty with this approximation is the mathematical one. Because of the confluent hypergeometric series in the Coulomb wave functions, tediousness increases considerably. However we are hopeful that this may be overcome soon.

The argument given in Sec. III about the choice of the unperturbed wave function can be applied to the case of scattering of a particle by an identical particle in a bound state.

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[37] G. F. Chew, Phys. Rev. **80**, 196 (1950).

[38] G. F. Chew and G. C. Wick, Phys. Rev. **85**, 636 (1952); Ashkin and G. C. Wick, *ibid.* **85**, 686 (1952); G. F. Chew and M. L. Goldberger, *ibid.* **87**, 778 (1952).

[39] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (The Clarendon Press, Oxford, England, 1965), 3rd ed., p. 338.

[40] A. Burgess, Astrophys. J. **132**, 503 (1960).

[41] O. Bely, Ann. Astrophys. **29**, 683 (1966).