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Double Excitation of Atoms by Electron Impact*

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The electron-impact double-excitation cross sections for several states of lithium, beryllium, magnesium, and calcium are calculated using the Born–Oppenheimer scattering approximation. The energy dependence of the total cross sections and the angular dependence of the differential cross sections for these parity-unfavored transitions are reported. The maximum values of the total cross sections for excitation of the lowest states $(np)^2\,{}^3P_g$ of beryllium, magnesium and calcium are found to be comparable in magnitude to those for single excitations in the same energy range ($\sim \pi a_0^2$). Those for the $(np)(3d)\,{}^1D_u$ and ${}^3D_u$ excitations are found to be of the order of $10^{-1}\pi a_0^2$ for magnesium and $10^{-2}\pi a_0^2$ for beryllium. The highly excited $(1s)\,(2p)^2\,{}^4P_g$ state of lithium has a maximum cross section of $4\times10^{-5}\pi a_0^2$. The highly excited $(1s)(2p)^2\,{}^4P_g$ for all these transitions are proportional to $\sin^2\theta$ and so they vanish in the forward and backward directions. The polarization of the dipole radiation emitted by these doubly excited states is described. Target wave functions are constructed using the Hartree–Fock method. For the ${}^1S_g \rightarrow {}^3P_g$ transition in magnesium and calcium, pseudopotential methods were also used to construct the target wave functions. The resulting cross sections agree closely with those computed with Hartree–Fock orbitals.

I. INTRODUCTION

The existence of doubly excited atomic configurations was established several decades ago by experimental observations of their characteristic emission spectra. Selection rules prevent direct photoexcitation from the ground state to these excited states. However, their production by electron impact is possible and has been studied both theoretically[1,2] and experimentally.[3] Indeed, it is because of the recent experimental activity in this area that we have decided to proceed beyond the previous theoretical studies which pertained to helium and construct theoretical estimates for the excitation cross sections of other atomic species. In their study of the doubly excited states of helium, Becker and Dahler[2] discovered that the magnitudes of the cross sections generated by the simple Born–Oppenheimer (BO) approximation were in substantial agreement with those gotten from more sophisticated and presumably more reliable distorted-wave (with exchange) and close-coupling (two-state) calculations. The angular dependence of the differential cross sections was found to depend only weakly upon the quality of the wave functions for the target atom and not at all upon which of these scattering approximations was employed. Therefore, in this extension of previous investigation we rely exclusively upon the BO approximation. In a subsequent communication these results will be compared with close-coupling calculations.

We first derive a formula for the amplitude of scattering to a doubly excited state of an N-electron atom. This is used to compute the cross section (in BO approximation) for one doubly excited state of lithium ($N=3$). We also examine in considerable detail target atoms (the alkaline earths) which consist of two valence electrons plus an inner core of electrons which do not participate directly in the excitation process. Under these circumstances the scattering process reduces, at least approximately, to a three-electron problem. In the examples studies here—several doubly excited states of beryllium, magnesium, and calcium—we generally have used Hartree–Fock orbitals for the initial and final states of the target atoms. However, for the ${}^1S_g \rightarrow {}^3P_g$ transitions of Be and Mg we have also made use of pseudopotential methods to construct approximate orbitals.

Finally, we have investigated the rather peculiar threshold behaviors of certain double excitations and examined the polarization of radiation emitted from these states.

A. Double-Excited Atomic States

Some atoms possess *bound* doubly excited states with energies which lie below the first ionization threshold. Much more common, however, are quasibound doubly excited states which have energies in excess of this threshold. In this case the atom may autoionize, that is, it may spontaneously emit an electron because of coupling between the excited (discrete) state and the adjacent continuum (corresponding to the free electron plus ion). The rate of this autoionization process depends upon that portion of the total Hamiltonian which couples the quasibound state to the continuum. According to first-order perturbation theory this rate is given by[4] $4\pi|V_{fi}|^2\rho_f$, with

$$V_{fi} = \langle \Psi_f | H - H_0 | \Psi_i \rangle ,$$

and where ρ_f is the density of final states. Here, H_0 is the largest part of the Hamiltonian H of which the quasibound state Ψ_i is an eigenfunction. Ψ_f is the wave function for the ion-plus-free-electron state to which the quasibound state decays. In general, $V = H - H_0$ is some part of the interelectronic repulsive term plus the spin-orbit coupling terms. If the interelectronic repulsive term couples the quasibound state to the continuum, the autoionization lifetime is found to be on the order of the collision time, 10^{-14} sec, for the excitation process. These we classify as true autoionizing doubly excited states. The calculation of the corresponding cross sections is somewhat complicated by interference between the scattered and ejected electrons. If the interelectronic repulsion term does not couple the quasibound state to the continuum, then the spin-orbit terms of the total Hamiltonian provide the only means for autoionization. The autoionization lifetime for this spin-orbit mechanism is on the order of a microsecond.[4] Quasibound states which are able to autoionize only by this second path will usually decay more readily by electric-dipole photoemission for which the lifetimes typically vary from 1 to 10 nsec. Since this is several orders of magnitude longer than the collision time for the excitation process, we can treat double excitations to these "nonautoionizing" states to be transitions from one bound state to another.

The selection rules for the dominant mode of autoionization will be those associated with a scalar interaction such as the Coulomb repulsion between two atomic electrons. If Russell–Saunders (LS) coupling is assumed, one then finds that a doubly excited state will be subject to autoionization only if it has the same parity, spin, and orbital angular momentum as the adjacent continuum. If there are no adjacent continuum states which satisfy all three of these selection rules, the state can be called nonautoionizing. The states we investigate here are all either bound or nonautoionizing.

B. Parity-Unfavored Transitions

The theory of electron-impact excitation predicts that for certain doubly excited states the forward-scattering amplitude will be identically zero.[2,5] These transitions are called "parity unfavored." Within the Russell–Saunders coupling scheme, parity-unfavored transitions are those for which $\Delta J + \Delta\Pi$ is an odd integer. Here ΔJ is the total orbital angular momentum transferred from the scattering electron to the target atom and $\Delta\Pi$ is the change of parity of the target. For transitions in which neither the initial nor final target state is an S state, the value of ΔJ will not be unique. In these cases there are both parity-favored and parity-unfavored contributions to the cross section. For transitions into or from a target S state, ΔJ will equal the change in total orbital angular momentum of the target, that is, $\Delta J = \Delta L$. For example, the helium $(1s)^2\,{}^1S_g \rightarrow (2p)^2\,{}^3P_g$ transition is parity unfavored with

$$\Delta J + \Delta\Pi = \Delta L + \Delta\Pi = 1 + 0 \ .$$

Simpson, Mielczarek, and Cooper[6] were unable to detect excitation of this state in forward-scattering experiments but they did observe parity-favored double excitations within the same range of energies. This is the only experimental information which exists concerning the angular dependence of the cross sections for parity-unfavored atomic transitions. However, the *total* inelastic cross section for this particular transition of helium has been measured by the trapped-electron method.[3]

The differential cross section for this parity-unfavored transition was calculated by Becker and Dahler who found it to be proportional to the square of the sine of the scattering angle θ. The cross sections for all of the parity-unfavored transitions considered here also contain a factor of $\sin^2\theta$ and so vanish in the forward and backward directions. Finally, we have verified for several cases the conclusions of Becker and Dahler that within the two-state approximations very few partial waves are involved in parity-unfavored transitions (e.g., only $l' = 1 \rightarrow l = 1$ for ${}^1S_g \rightarrow {}^3P_g$ transitions) and that for parity-unfavored processes the change of the projection quantum number for orbital angular momentum must be nonzero.

II. BO CROSS SECTIONS FOR IMPACT EXCITATION OF *N*-ELECTRON ATOMS

We neglect the dependence of energy upon spin so that the Hamiltonian for a projectile electron together with an N-electron target atom is given by

$$H = H_N + H'_{N+1} + T_{N+1} \ . \tag{1}$$

Here T_{N+1} denotes the kinetic-energy operator for the $(N+1)$th electron and

$$H'_{N+1} = \frac{-2N}{r_{N+1}} + \sum_{i=1}^{N} \frac{2}{r_{i,N+1}} \ . \tag{2}$$

To this approximation, solutions of the Schrödinger equation $(H - E)\,\Psi^{SM_S}(1, \ldots, N+1) = 0$ can be labeled with the good quantum numbers S and M_S pertaining to total spin and to its projection.

The characteristic functions and associated eigenvalues of the atomic-energy operator H_N are denoted by $\Phi_\nu^{s_\nu m_\nu}(1, \ldots, N)$ and E_ν, respectively. These unit normalized functions can be written in the form

$$\Phi_\nu^{s_\nu m_\nu}(1, \ldots, N) = \mathfrak{A}\{\phi_\nu(1, \ldots, N)$$

$$\times \eta_\nu^{s_\nu m_\nu}(1, \ldots, N)\} , \qquad (3)$$

where $\mathfrak{A}$ is the antisymmetrizer, $\phi_\nu(1, \ldots, N)$ an energy eigenfunction defined on the space of the electronic position coordinates, and $\eta_\nu^{s_\nu m_\nu}(1, \ldots, N)$ the appropriate eigenfunction of electron spin. The functions $\Phi_\nu^{s_\nu m_\nu}$ may be used as a basis for the expansion

$$\Psi^{SM_S}(1, \ldots, N+1) = \mathfrak{A}\{ \sum_\nu \sum_{mm_\nu} C^{s_\nu sS}_{m_\nu m M_S} \times \Phi_\nu^{s_\nu m_\nu}(1, \ldots, N)\, \phi^{sm}(N+1) F_\nu(N+1)\} \qquad (4)$$

of the wave function for the entire system of $N+1$ electrons. In (4) the sum on the index ν includes the continuum as well as the discrete states of the target. The symbols $F_\nu(i)$ and $\phi^{sm}(i)$ refer to space and spin functions of a single electron and $C^{s_\nu sS}_{m_\nu m M_S}$ is a vector-coupling coefficient.

The equations satisfied by the functions F_ν are constructed according to the prescription

$$\langle \sum_{mm_\nu} C^{s_\nu sS}_{m_\nu m M_S} \Phi_\nu^{s_\nu m_\nu}(1, \ldots, N)\, \phi^{sm}(N+1) \,| \times (H-E) |\, \Psi^{SM_S}(1, \ldots, N+1)\rangle_{N+1} = 0 , \qquad (5)$$

where $\langle\ \rangle_{N+1}$ indicates summation over all spin variables and integration over the spatial coordinates of all but electron $N+1$. These equations may be rewritten in the form

$$(T_{N+1} - k_\nu^2)\, F_\nu(N+1) = (N+1)^{1/2} G_\nu(N+1) , \qquad (6)$$

with $k_\nu{}^2 = E - E_\nu$ and

$$(N+1)^{1/2} G_\nu(N+1) = -(N+1)^{1/2} \sum_{mm_\nu} C^{s_\nu sS}_{m_\nu m M_S} \langle \Phi_\nu^{s_\nu m_\nu}(1, \ldots, N)\, \phi^{sm}(N+1) \,|\, H'_{N+1} \,|\, \Psi^{SM_S}(1, \ldots, N+1)\rangle_{N+1}$$

$$- N \sum_\mu \sum_{mm_\nu} \sum_{m' m_\mu} C^{s_\mu sS}_{m_\mu m' M_S}\, C^{s_\nu sS}_{m_\nu m M_S} \langle \Phi_\nu^{s_\nu m}(1, \ldots, N)\phi^{sm}(N+1) |$$

$$\times (T_{N+1} + H_N - E)\, | \Phi_\mu^{s_\mu m_\mu}(2, \ldots, N+1)\; \phi^{sm'}(1) F_\mu(1)\rangle_{N+1} . \qquad (7)$$

The solutions of (6) which we desire are those appropriate to scattering by the atomic ground state ($\nu = 0$) of an incident electron with momentum $\vec{k}_0$. These boundary conditions stipulate that the functions F_ν be solutions of the integral equations

$$F_\nu(\vec{r}) = \delta_{\nu 0}\, e^{i\vec{k}_0 \cdot \vec{r}} + F_\nu{}^{sc}(\vec{r}) , \qquad (8)$$

with

$$F_\nu{}^{sc}(\vec{r}) = -\frac{(N+1)^{1/2}}{4\pi} \times \int d^3 r' \left(\frac{\exp(ik_\nu |\vec{r} - \vec{r}'|)}{|\vec{r} - \vec{r}'|} \right) G_\nu(\vec{r}')$$

$$\sim -\left(\frac{e^{ik_\nu r}}{r} \right) f_{\nu 0}(\vec{k}_\nu, \vec{k}_0) , \qquad (9)$$

and where

$$f_{\nu 0}(\vec{k}_\nu, \vec{k}_0) = -\frac{(N+1)^{1/2}}{4\pi} \int d^3 r'\, e^{-i\vec{k}_\nu \cdot \vec{r}'}\, G_\nu(\vec{r}') \qquad (10)$$

is the amplitude for scattering into the final state $(\nu, \vec{k}_\nu)$. It follows from (7) that this amplitude consists of a contribution

$$f'_{\nu 0}(\vec{k}_\nu, \vec{k}_0) = \frac{(N+1)^{1/2}}{4\pi} \langle \sum_{m_\nu m} C^{s_\nu sS}_{m_\nu m M_S}\, \Phi_\nu^{s_\nu m_\nu}(1, \ldots, N)\phi^{sm}(N+1) e^{i\vec{k}_\nu \cdot \vec{r}_{N+1}} \,|\, H'_{N+1} \,|\, \Psi^{SM_S}\rangle \qquad (11)$$

together with a sum of terms each of which is proportional to a matrix element of the form

$$t_{\nu\mu} = \langle e^{i\vec{k}_\nu \cdot \vec{r}_{N+1}} \phi_\nu(1, \ldots, N) |\; T_{N+1} + H_N - E \;|\; F_\mu(1)\phi_\mu(2, \ldots, N+1)\rangle$$

$$= \langle F_\mu(1)\phi_\mu(2, \ldots, N+1) \,|\, T_{N+1} + H_N - E \,|\, e^{i\vec{k}_\nu \cdot \vec{r}_{N+1}} \phi_\nu(1, \ldots, N)\rangle^* - T_{\nu\mu} . \qquad (12)$$

The first of these two terms vanishes identically so that

$$-t_{\nu\mu} = T_{\nu\mu} = \sum_{p=1}^{N+1} \langle \vec{\nabla}_p \cdot \{ [e^{i\vec{k}_\nu \cdot \vec{r}_{N+1}} \phi_\nu(1, \ldots, N)]^* \vec{\nabla}_p [F_\mu(1)\phi_\mu(2, \ldots, N+1)]$$

$$- [F_\mu(1)\phi_\mu(2, \ldots, N+1)] \vec{\nabla}_p [e^{i\vec{k}_\nu \cdot \vec{r}_{N+1}} \phi_\nu(1, \ldots, N)]^* \}\rangle . \qquad (13)$$

The multiply excited final states (ν) of interest to us here are either truly bound or are nonautoionizing states embedded within a continuum. In either event the corresponding wave functions are square integrable so that each term in (13) with $p \leq N$ integrates to zero. A similar argument applies to the contribution from $p = N+1$ provided that the state ϕ_μ is square integrable. The only contributions to $T_{\nu\mu}$ which one cannot immediately conclude will vanish are those coming from the portion of $F_\mu(1)\phi_\mu(2, \ldots, N+1)$ for which the state of electron $N+1$ is unbound. The way in which we have (arbitrarily) separated the total Hamiltonian into an unperturbed part and a perturbation has led us to select for an initial state the product of a bound atomic-state function and a plane wave representative of the incident electron. Because of the indistinguishability of the electrons, it is then consistent to express an ionic term as a superposition,

$$F_{\mu,\vec{k}_\mu}(1) \int d^3\kappa\, h_{\vec{k}_\mu}(\vec{\kappa}) \phi_\mu^{\text{ion}}(2, \ldots, N) e^{i\vec{\kappa}\cdot\vec{r}_{N+1}} , \tag{14}$$

of plane waves. Here μ now refers to some particular discrete state of the product ion and the variable $\vec{k}_\mu$ to the momentum of the ionized electron. We therefore conclude that for a continuum state, $T_{\mu\nu}$ is given by

$$\begin{aligned} T_{\mu\nu}^{\text{ion}} = \int d^3\kappa\, h_{\vec{k}_\mu}(\vec{\kappa}) \langle \vec{\nabla}_{N+1} \cdot \{ [e^{i\vec{k}_\nu\cdot\vec{r}_{N+1}} \phi_\nu(1, \ldots, N)]^* \vec{\nabla}_{N+1}[F_{\mu,\vec{k}_\mu}(1)\phi_\mu^{\text{ion}}(2, \ldots, N) e^{i\vec{\kappa}\cdot\vec{r}_{N+1}}] \\ - [F_{\mu,\vec{k}_\mu}(1)\phi_\mu^{\text{ion}}(2, \ldots, N) e^{i\vec{\kappa}\cdot\vec{r}_{N+1}}] \vec{\nabla}_{N+1}[e^{i\vec{k}_\nu\cdot\vec{r}_{N+1}} \phi_\nu(1, \ldots, N)]^* \} \rangle \\ = \int d^3\kappa\, h_{\vec{k}_\mu}(\vec{\kappa}) \langle \phi_\nu(1, \ldots, N) \,|\, F_{\mu,\vec{k}_\mu}(1)\phi_\mu^{\text{ion}}(2, \ldots, N) \rangle_{N+1} (\kappa^2 - k_\nu^2) \delta(\vec{\kappa} - \vec{k}_\nu) , \end{aligned} \tag{15}$$

and so it vanishes.

An alternative to the procedure adopted here is to include in the "unperturbed Hamiltonian" the Coulomb interaction between the incident electron and the atomic nucleus. This results in conclusions and formulas, the details of which are given in the Appendix, similar to those presented above.

The BO approximation is obtained from (11) by replacing the exact wave function Ψ^{SM_S} with a (totally antisymmetric) function which represents the asymptotic form of the initial state. This is accomplished by restricting the summation in (4) to the single term with $\nu = 0$ and by selecting for $F_0(\vec{r})$ the plane wave $e^{i\vec{k}_0\cdot\vec{r}}$. The resulting formula,

$$\begin{aligned} f_{\nu 0}^{\text{BO}}(\vec{k}_\nu, \vec{k}_0) = \frac{1}{4\pi} \langle \sum_{m_\nu m} C_{m_\nu m M_S}^{s_\nu s S} \Phi_\nu^{s_\nu m_\nu}(1, \ldots, N) \phi^{sm}(N+1) e^{i\vec{k}_\nu\cdot\vec{r}_{N+1}} \,|\, H'_{N+1} \,| \\ \times \sum_{m_0 m'} C_{m_0 m' M_S}^{s_0 s S} [\Phi_0^{s_0 m_0}(1, \ldots, N) \phi^{sm'}(N+1) e^{i\vec{k}_0\cdot\vec{r}_{N+1}} + N\Phi_0^{s_0 m_0}(2, \ldots, N+1) \phi^{sm'}(1) e^{i\vec{k}_0\cdot\vec{r}_1}] \rangle , \end{aligned} \tag{16}$$

includes as special cases BO scattering amplitudes which have appeared in the literature.[7]

For single excitations and especially for $S \to S$ transitions, the BO approximation often grossly overestimates the effects of exchange and generates unreliable predictions for the angular dependence of the differential cross section.[8] This usually is attributed to complications arising from the core interactions $2N/r_{N+1}$. In fact, it is possible to obtain nonzero contributions to the scattering amplitude simply by adding a constant to the potential of interaction. This undesirable feature is absent for double excitations where the only contributions to the scattering amplitude arise from electron-electron interactions. It is reasonable to surmise that it is the absence of these troublesome core-scattering terms which is responsible for the past success of the BO theory in correctly accounting for the magnitude and angular dependence of the cross sections for double excitations.

Calculations based upon the first BO approximation, (16), can account for the simultaneous excitation of three or more electrons only if the target wave function specifically includes spatial correlations among the electrons. However, even in the absence of such correlations, the second BO approximation (or a close-coupling calculation which includes one or more intermediate states) will produce nonzero estimates of the cross sections for these multiple excitations. Similarly, the second BO approximation provides for the production of final doubly excited states by means of two sequential single-excitation processes. For example, these second-order contributions to the scattering amplitude for the ${}^1S_g \to {}^3P_g(2p)^2$ transition of helium are given by

$$\begin{aligned} f_{n0}^{2\text{BO}}(\vec{k}_n, \vec{k}_0) = (3^{1/2}/4\pi) [(V_{np0} - V'_{np0}) \\ + (U'_{nq0} - V'_{nq0})] , \end{aligned} \tag{17}$$

where p and q refer to the triplet and singlet states ${}^3P_u(1s)(2p)$ and ${}^1P_u(1s)(2p)$, respectively. The terms appearing in this formula are defined as follows:

$$V_{np0}=\int\int\int d1\,d1'\,d2'\,e^{-i\vec{k}_n\cdot\vec{r}_1}\langle\phi_n(23)|H'_{1(23)}|\phi_p(23)\rangle_1\,\mathcal{G}^*_p(1-1')\langle\phi_p(2'3')|H'_{1'(2'3')}|\phi_0(3'1')\rangle_{1'2'}\,e^{i\vec{k}_0\cdot\vec{r}'_2}\,,$$

$$V'_{np0}=\int\int\int\int d1\,d1'd2\,d2'\,e^{-i\vec{k}_n\cdot\vec{r}_1}\langle\phi_n(23)|H'_{1(23)}|\phi_p(31)\rangle_{12'}\,\mathcal{G}^*_p(2-1')\langle\phi_p(2'3')|H'_{1'(2'3')}|\phi_0(3'1')\rangle_{1'2'}\,e^{i\vec{k}_0\cdot\vec{r}'_2}\,, \tag{18}$$

$$U'_{np0}=\int\int\int d1\,d1'\,d2\,e^{-i\vec{k}_n\cdot\vec{r}_1}\langle\phi_n(23)|H'_{1(23)}|\phi_p(31)\rangle_{12}\,\mathcal{G}^*_p(2-1')\langle\phi_p(2'3')|H'_{1'(2'3')}|\phi_0(2'3')\rangle_{1'}\,e^{i\vec{k}_0\cdot\vec{r}'_1}\,,$$

where subscripts on the matrix elements $\langle\;|\;|\;\rangle$ indicate upon which variables the resulting function depends (that is, over which variables integrations are not to be performed) and where

$$di=d^3r_i\,,\quad H'_{i(jk)}=2(r_{ij}^{-1}+r_{ik}^{-1}-2r_k^{-1})\,,$$

and

$$\mathcal{G}_p(m-n)=r_{mn}^{-1}\,e^{ik_pr_{mn}}\,.$$

We expect these contributions to be small compared to the first BO approximation but there may be situations for which this is not so. In either event calculations based upon formula (17) are likely to be unreliable because it is for single-electron transitions of the sort involved here that BO approximation is known to be inadequate. We have not succeeded in evaluating the complicated integrals appearing in $f^{2\mathrm{BO}}_{n0}$ but partial results which were obtained gave evidence of unsatisfactory angular dependence. Close-coupling calculations should be performed since they would permit one to obtain a more accurate picture of the importance of intermediate-state contributions to cross sections for double excitation.

A. Formulas for BO Scattering Amplitudes

In the calculations which follow we approximate the energy eigenfunctions $\phi_\nu(1,\ldots,N)$ by products of one-electron orbitals. The kth member of the orthonormal set of one-electron orbitals associated with the state ν is denoted by $\psi_{\nu k}(j)$, where the argument j refers to the position coordinates of electron j.

1. Two-Electron Targets

The singlet and triplet wave functions for a two-electron target may be written in the forms

$$\Phi^{00}_\nu(12)=\psi^+_{\nu1\nu2}(12)\eta^{00}_\nu(12)$$

and $\qquad$ (19)

$$\Phi^{1m_\nu}_\nu(12)=\psi^-_{\nu1\nu2}(12)\eta^{1m_\nu}_\nu(12)\,,$$

respectively, with

$$\psi^\pm_{\nu1\nu2}(ij)=2^{-1/2}\{\psi_{\nu1}(i)\psi_{\nu2}(j)\pm\psi_{\nu2}(i)\psi_{\nu1}(j)\}\,,$$

and where

$$\eta^{00}_\nu(12)=2^{-1/2}(\alpha_1\beta_2-\alpha_2\beta_1),\ \text{etc.},$$

denote the familiar two-electron spin eigenfunctions. By substituting into (16), we obtain the formula

$$f^{\mathrm{BO}}_{\nu0}(\vec{k}_\nu,\vec{k}_0)_{S\to S}=\frac{1}{4\pi}\langle\psi^+_{\nu1\nu2}(12)e^{i\vec{k}_\nu\cdot\vec{r}_3}|\times H'_3|\psi^+_{0102}(12)\,e^{i\vec{k}_0\cdot\vec{r}_3}-\psi^+_{0102}(23)e^{i\vec{k}_0\cdot\vec{r}_1}\rangle \tag{20}$$

for a singlet → singlet transition. In the case of a double excitation there is no contribution to this amplitude from the first term to the right of H'_3.

The amplitude for a singlet → triplet transition is given by

$$f^{\mathrm{BO}}_{\nu0}(\vec{k}_\nu,\vec{k}_0)_{S\to T}=(3^{1/2}/4\pi)\times\langle\psi^-_{\nu1\nu2}(12)e^{i\vec{k}_\nu\cdot\vec{r}_3}|H'_3|\psi^+_{0102}(23)\,e^{i\vec{k}_0\cdot\vec{r}_1}\rangle\,. \tag{21}$$

By expanding the plane waves of Eqs. (20) and (21) in spherical harmonics, we find that (i) the amplitude for transition from the configuration $(ns)^2$ to $(n'p)^2$ involves only initial and final p waves and (ii) that the amplitude for $(ns)^2\to(n'p)(n''d)$ depends upon cross couplings between incident and final p and d waves. When configuration interaction is included the situation becomes slightly more complicated.

2. Three-Electron Targets

The wave function for a quartet ($s_\nu=\frac{3}{2}$) state may be written as the product

$$\Phi^{(3/2)m_\nu}_\nu(123)=3^{-1/2}[\psi^-_{\nu1\nu2}(12)\psi_{\nu3}(3)+\psi^-_{\nu1\nu2}(23)\psi_{\nu3}(1)+\psi^-_{\nu1\nu2}(31)\psi_{\nu3}(2)]\eta^{(3/2)m_\nu}_\nu(123) \tag{22}$$

of a completely antisymmetric spatial function with one of the completely symmetric spin functions $\eta^{(3/2)m_\nu}_\nu$.

To obtain wave functions for the doublet states of three electrons we begin with three-electron spin functions, $\eta^{(1/2)m_\nu}_\nu(ij|k)$, which are antisymmetric in their first pair of arguments. Next, one of these is multiplied by a spatial function which is symmetric in the same pair of position coordinates. The associated completely antisymmetric function then can be expressed as a linear combination of these product functions. Proceeding in this fashion we obtain the doublet functions

$$\begin{aligned}\Phi_\nu^{(1/2)m_\nu}(123) = 3^{-1/2}\,[&\psi^{+}{}_{\nu1\nu2}(12)\,\psi_{\nu3}(3)\,\eta_\nu^{(1/2)m_\nu}(12\,|\,3)\\ &+\psi^{+}{}_{\nu1\nu2}(23)\psi_{\nu3}(1)\eta_\nu^{(1/2)m_\nu}(23\,|\,1)+\psi^{+}{}_{\nu1\nu2}(31)\,\psi_{\nu3}(2)\,\eta_\nu^{(1/2)m_\nu}(31\,|\,2)]\;.\end{aligned}\tag{23}$$

The scattering amplitudes for doublet → doublet and doublet → quartet transitions are found to be

$$f_{\nu0}^{\,\mathrm{BO}}(\vec{k}_\nu,\vec{k}_0)_{D\text{-}D}=\frac{2^{1/2}}{4\pi}\,\langle\psi^{+}{}_{\nu1\nu2}(12)\,\psi_{\nu3}(3)\,e^{i\vec{k}_\nu\cdot\vec{r}_4}\,|H_4'|\,[\psi^{+}{}_{01\,02}(12)\,\psi^{+}{}_{03\,\vec{k}_0}(34)+\psi^{+}{}_{01\,02}(42)\,\psi^{-}{}_{03\,\vec{k}_0}(31)-\psi^{+}{}_{01\,02}(23)\,\psi^{+}{}_{03\,\vec{k}_0}(14)]\rangle \tag{24}$$

and

$$\begin{aligned}f_{\nu0}^{\,\mathrm{BO}}(\vec{k}_\nu,\vec{k}_0)_{D\text{-}Q}=\frac{6^{-1/2}}{4\pi}\langle e^{i\vec{k}_\nu\cdot\vec{r}_4}\,[&\psi^{-}{}_{\nu1\nu2}(12)\psi_{\nu3}(3)+\psi^{-}{}_{\nu1\nu2}(23)\psi_{\nu3}(1)\\ &+\psi^{-}{}_{\nu1\nu2}(31)\,\psi_{\nu3}(2)]\,|H_4'|\,e^{i\vec{k}_0\cdot\vec{r}_1}\,[\,\psi^{+}{}_{01\,02}(34)\,\psi_{03}(2)-\psi^{+}{}_{01\,02}(24)\,\psi_{03}(4)]\rangle\;.\end{aligned}\tag{25}$$

with

$$\psi^{\pm}{}_{\nu1\,\vec{k}_0}(ij)=2^{-1/2}\,[\psi_{\nu1}(i)\,e^{i\vec{k}_0\cdot\vec{r}_j}\pm\psi_{\nu1}(j)\,e^{i\vec{k}_0\cdot\vec{r}_i}\,]\;.$$

When $\psi_{\nu1}=\psi_{\nu2}$ the functions $\Phi_\nu^{00}(12)$ and $\Phi_\nu^{(1/2)m_\nu}(123)$ given by (19) and (23) must be multiplied by $2^{-1/2}$. Corresponding alterations must then be made in the formulas for the scattering amplitudes. Furthermore, depending upon the angular-momentum coupling scheme which is chosen to represent the state ν, the two- and three-electron functions displayed above may include implicit summations (weighted by vector-coupling coefficients) over projection quantum numbers.

III. APPLICATIONS TO SPECIFIC ATOMS

A. Lithium

Here the process of special interest is the parity-unfavored doublet to quartet transition from the ground state ${}^2S_g(1s)^2(2s)$ to the excited state ${}^4P_g(1s)(2p)^2$. The ground-state wave function

$$\begin{aligned}\Phi_0^{(1/2)m_0}(123)=3^{-1/2}\,[&\phi_{1s}(1)\phi_{1s}(2)\phi_{2s}(3)\,\eta_0^{(1/2)m_0}(12\,|\,3)+\phi_{1s}(2)\phi_{1s}(3)\phi_{2s}(1)\,\eta_0^{(1/2)m_0}(23\,|\,1)\\ &+\phi_{1s}(3)\phi_{1s}(1)\phi_{2s}(2)\,\eta_0^{(1/2)m_0}(31\,|\,2)]\,Y_{00}(\hat{1})\,Y_{00}(\hat{2})\,Y_{00}(\hat{3})\end{aligned}\tag{26}$$

is obtained from (23) by setting

$$\psi_{\nu1}(\vec{r})=\psi_{\nu2}(\vec{r})\equiv\phi_{1s}(r)\,Y_{00}(\hat{r})\equiv(4\alpha^3)^{1/2}e^{-\alpha r}\,Y_{00}(\hat{r})$$

and (27)

$$\begin{aligned}\psi_{\nu3}(\vec{r})&\equiv\phi_{2s}(r)\,Y_{00}(\hat{r})\\ &\equiv(4\mu^5/3N)^{1/2}[r e^{-\mu r}-(3A/\mu)e^{-\mu b r}]\,Y_{00}(\hat{r}).\end{aligned}$$

In order that these orbitals be orthonormal, one must select A and N equal to $(\alpha+\mu b)^3/(\mu+\alpha)^4$ and $1-48A(1+b)^{-4}+3A^2b^{-3}$, respectively.

The parameters of $\Phi_0^{(1/2)m_0}$ are chosen so that the expectation value of the energy is a minimum. This criterion results in a value of $E_0=-14.80$ Ry (0.12 Ry above the experimental energy) and the parameter values $\alpha=2.69$, $b=3.19$, and $\mu=0.67$.

The wave functions for the final state may be written

$$\begin{aligned}\Phi_{\nu,M_L}^{(3/2)m_\nu}(123)=3^{-1/2}\sum_{m_1m_2}C^{111}_{m_1m_2M_L}\;[&\phi_{2p}(1)\,Y_{1m_1}(\hat{1})\,\phi_{2p}(2)\,Y_{1m_2}(\hat{2})\,\phi_{1s}(3)\,Y_{00}(\hat{3})\\ &+\text{two cyclic permutations of electron labels}]\,\eta_\nu^{(3/2)m_\nu}(123)\;,\end{aligned}\tag{28}$$

with $\phi_{2p}(r)=(\frac{4}{3}\gamma^5)^{1/2}re^{-\gamma r}$ and where $M_L=(0,\pm1)$ is the projection quantum number for orbital angular momentum. For convenience we select for α in ϕ_1 the same value of 2.69 as was used for the 1s orbital of the ground state. Then, with γ taken equal to 0. 90 we obtain an upper bound of $E_\nu = -10.36$ Ry (0. 07 Ry above the experimental value) for the energy of this excited state.

With these approximate wave functions we obtain from (25) the scattering amplitudes

$$f^{\mathrm{BO}}_{\mathrm{M}_L}(\vec{\mathrm{k}}_\nu, \vec{\mathrm{k}}_0) = -(\tfrac{8}{3})^{1/2} J_1(2p\,; k_0) J_{11}(1s\,; 2s, 2p; k_\nu) \times \Gamma^1_{\mathrm{M}_L}(\phi)\sin\theta$$

$$= -\tfrac{512}{9}\gamma^6 k_0(\gamma^2 + k_0^2)^{-3}(\alpha^3\mu^5/2N)^{1/2} I(k_\nu) \times \Gamma^1_{\mathrm{M}_L}(\phi)\sin\theta\,, \qquad (29)$$

where $\theta = \arccos(\hat{k}_\nu \cdot \hat{k}_0)$,

$$\Gamma^{|\mathrm{M}|}_{\mathrm{M}_L}(\phi) = e^{-i\mathrm{M}\phi}\,\delta_{\mathrm{M}_L,\mathrm{M}} + e^{+i\mathrm{M}\phi}\,\delta_{\mathrm{M}_L,-\mathrm{M}}\,,$$

and

$$J_{\mathrm{M}}(nl\,; k) = \int_0^\infty dr\, r^2 j_{\mathrm{m}}(kr)\phi_{nl}(r)\,,$$

$$J_{\mathrm{mm}'}(nl\,; n'l', n''l''\,; k) = \int_0^\infty dr\, r j_{\mathrm{m}}(kr) \times \phi_{nl}(r)\, Y_{\mathrm{m}'}(n'l', n''l''\,; r)$$

$$Y_{\mathrm{m}'}(n'l', n''l''\,; r) = r^{-\mathrm{m}'}\int_0^r dr'\, r'^{(\mathrm{m}'+2)}\,\phi_{n'l'}(r') \times \phi_{n''l''}(r') + r^{\mathrm{m}'+1}\int_r^\infty dr' r'^{(-\mathrm{m}'+1)}\phi_{n'l'}(r')\phi_{n''l''}(r')\,. \qquad (30)$$

Finally, the function

$$I(k) = \int_0^\infty dr\, j_1(kr)e^{-\alpha r}\{40\delta^{-6} - e^{-\delta r}(r^4\delta^{-2} + 6r^3\delta^{-3} + 20r^2\delta^{-4} + 40r\delta^{-5} + 40\delta^{-6}) - (3A/\mu) \times [8\rho^{-5} - e^{-\rho r}(r^3\rho^{-2} + 4r^2\rho^{-3} + 8r\rho^{-4} + 8\rho^{-5})]\} \qquad (31)$$

has been evaluated numerically for different values of $k_\nu = (E - E_\nu)^{1/2}$, the momentum of the scattered electron. In these formulas, $\delta = \gamma + \mu$, $\rho = \gamma + \mu b$, and $k_0 = (E - E_0)^{1/2}$.

It follows from (29) that the differential cross section is given by

$$\sigma(\theta) = 2(k_\nu/k_0)\,|f^{\mathrm{BO}}_1(\vec{\mathrm{k}}_\nu, \vec{\mathrm{k}}_0)|^2 = (3/8\pi)\sigma_T \sin^2\theta\,, \qquad (32)$$

where σ_T refers to the total cross section, the maximum value of which is $3.7\times10^{-5}\ \pi a_0^2$. Although this cross section is small, it is only one order of magnitude less than that for the helium ${}^1S_g(1s)^2 \to {}^3P_g(2p)^2$ transition which already has been observed by Schultz and Burrow[3] and to which it is compared in Fig. 1. The angular dependence of the scattering is identical for these two parity-unfavored processes.

B. Beryllium, Magnesium, and Calcium

In each of the alkaline earths two valence electrons lie outside a spherically symmetric core. The most important parity-unfavored transitions are those which connect the $(ns)^2\,{}^1S_g$ ground states of these atoms to the excited states $(np)^2\,{}^3P_g$, $(np)(3d)\,{}^1D_u$, and $(np)(3d)\,{}^3D_u$; here $n = 2$, 3, and 4 for Be, Mg, and Ca, respectively. To calculate the cross sections for these processes we could use the general N-electron target formulas given in Sec. II. However, because the atomic core is so weakly coupled to the valence electrons, its states will be virtually unaltered by these transitions. Therefore, it should be an excellent approximation to treat these dynamical events as if only the two valence electrons were involved. To test the validity of this assumption we have used Froese's Hartree–Fock program.[9] In every case the core orbitals for the ground and doubly excited states were found to be substantially the same. Therefore, we are justified in treating the alkaline earths as two-electron targets with cores which may be ignored except for the roles they play in shaping the valence orbitals.

We were unable to construct the singlet and triplet D states of calcium with the Froese Hartree–Fock program. To use this program it generally is necessary to begin with fairly accurate initial estimates for the orbitals. Where self-consistency is difficult to achieve these original estimates are especially crucial for success. The valence d orbital of calcium is bound to the atom by a small and slowly varying potential because of almost perfect cancellation of the screened nuclear attraction by the centrifugal potential. This is particularly significant in the vicinity of the maximum of the orbital because the d orbital will then exhibit very little curvature and a correspondingly low kinetic energy. Consequently, the orbital will extend far out from the nucleus. The long-range and relatively low binding energy of the orbital makes self-consistency extraordinar-

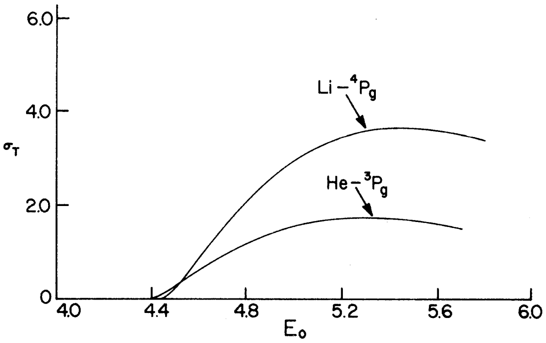

FIG. 1. Total BO cross sections for the (a) He $(1s)^2\,{}^1S_g \to (2p)^2\,{}^3p_g$ and (b) Li $(1s)^2(2s)\,{}^2S_g \to (1s)(2p)^2\,{}^4P_g$ transition plotted vs energy (in Ry) of the incident electron. Cross sections are in units of $10^{-4}\pi a_0^2$ for He and $10^{-5}\pi a_0^2$ for Li.

ily difficult to attain. Since the Froese program presumably is capable of generating exact orbitals we conclude that our failure to obtain satisfactory results for these D states is due to the inadequacy of our original orbital estimates.

The energies of the states for which we are able to generate Hartree–Fock wave functions appear in Table I. The ground-state energies agree to several decimal places with those reported by Clementi.[10] Where comparisons are possible the Hartree–Fock excitation energies can be seen to agree moderately well with experiment.

The antisymmetrized two-electron target wave functions are obtained by substituting appropriate self-consistent field (SCF) orbitals into (19), multiplying by an appropriate vector-coupling coefficient, and then summing over the projection quantum numbers for the individual electronic orbital angular momenta in order to generate eigenfunctions of the total orbital angular momentum and of its projection. This results in the set of functions

$$\begin{aligned}
{}^1S_g &: \Phi_0^{00}(12) = \phi_{ns}(1)\,\phi_{ns}(2)\,Y_{00}(\hat{1})\,Y_{00}(\hat{2})\,\eta^{00}(12) \;,\\
{}^3P_g &: \Phi^{1\mathrm{m}}_{1,\mathrm{M}_L}(12) = \sum_{\mathrm{m_1 m_2}} C^{111}_{\mathrm{m_1 m_2 M}_L}\,\phi_{np}(1)\,\phi_{np}(2)\,Y_{1\mathrm{m}_1}(\hat{1})\,Y_{1\mathrm{m}_2}(\hat{2})\,\eta^{1\mathrm{m}}(12) \;,\\
{}^1D_u &: \Phi^{00}_{2,\mathrm{M}_L}(12) = 2^{-1/2} \sum_{\mathrm{m_1 m_2}} C^{212}_{\mathrm{m_1 m_2 M}_L}\,[\phi_{3d}(1)\,\phi_{np}(2)\,Y_{2\mathrm{m}_1}(\hat{1})\,Y_{1\mathrm{m}_2}(\hat{2}) + \phi_{np}(1)\phi_{3d}(2)\,Y_{1\mathrm{m}_2}(\hat{1})\,Y_{2\mathrm{m}_1}(\hat{2})\,]\,\eta^{00}(12) \;,\\
{}^3D_u &: \Phi^{1\mathrm{m}}_{2,\mathrm{M}_L}(12) = 2^{-1/2} \sum_{\mathrm{m_1 m_2}} C^{212}_{\mathrm{m_1 m_2 M}_L}\,[\phi_{3d}(1)\,\phi_{np}(2)\,Y_{2\mathrm{m}_1}(\hat{1})\,Y_{1\mathrm{m}_2}(\hat{2}) - \phi_{np}(1)\,\phi_{3d}(2)\,Y_{1\mathrm{m}_2}(\hat{1})\,Y_{2\mathrm{m}_1}(\hat{2})]\,\eta^{1\mathrm{m}}(12) \;.
\end{aligned} \tag{33}$$

By inserting these functions into formulas (20) and (21) we obtain the scattering amplitudes and differential cross sections:

$$\begin{aligned}
{}^1S_g \to {}^3P_g &: \begin{cases} f^{\mathrm{BO}}_{ML} = -3^{1/2} A\,\Gamma^1_{ML}(\phi)\sin\theta \\ \sigma(\theta) = 3(2k_\nu/k_0)A^2\sin^2\theta \;, \end{cases}\\
{}^1S_g \to {}^1D_u &: \begin{cases} f^{\mathrm{BO}}_{ML} = -[(B\cos\theta + C)\,\Gamma^1_{ML}(\phi) \\ \qquad + B\sin\theta\,\Gamma^2_{ML}(\phi)]\sin\theta \\ \sigma(\theta) = (2k_\nu/k_0)(B^2 + C^2 \\ \qquad + 2BC\cos\theta)\sin^2\theta \;, \end{cases}\\
{}^1S_g \to {}^3D_u &: \begin{cases} f^{\mathrm{BO}}_{ML} = -3^{1/2}[(B\cos\theta - C)\,\Gamma^1_{ML}(\phi) \\ \qquad + B\sin\theta\,\Gamma^2_{ML}(\phi)]\sin\theta \\ \sigma(\theta) = 3(2k_\nu/k_0)(B^2 + C^2 \\ \qquad - 2BC\cos\theta)\sin^2\theta \;, \end{cases}
\end{aligned} \tag{34}$$

where the functions A, B, and C are defined by the formulas

$$\begin{aligned}
A &= J_1(np;k_0)\,J_{11}(ns;ns,np;k_\nu) \;,\\
B &= (\tfrac{3}{10})^{1/2} J_1(np;k_0)\,J_{22}(ns;ns;3d;k_\nu) \;,\\
C &= (\tfrac{5}{3})(\tfrac{3}{10})^{1/2} J_2(3d;k_0)\,J_{11}(ns;ns;np;k_\nu) \;.
\end{aligned} \tag{35}$$

The precise forms of the valence orbitals associated with a particular electron configuration depend upon the value of the total spin. For example, the $2p$ and $3d$ SCF orbitals for the singlet and triplet $(2p)(3d)$ D-states of beryllium will not be quite the same. Comparisons between the singlet and triplet orbitals of helium have been reported by Trefftz, Schlüter, Dettmar, and Jörgens.[11] The radial dependences of some singlet and triplet orbitals of Be and Mg are displayed in Fig. 2. Because of the differences between singlet and triplet orbitals, the values of the B and C integrals appearing in (34) will not be equal for the singlet → singlet and singlet → triplet transitions. However, were it not for these differences the differential cross sections for the transitions associated with specific initial and final configurations would be related in the manner

$$\sigma({}^1S_g \to {}^3D_u;\theta) = 3\sigma({}^1S_g \to {}^1D_u;\pi - \theta) \;.$$

Furthermore, if these differences were to be neglected, then the total cross section

$$\sigma_T({}^1S_g \to {}^3D_u) = 8\pi(2k_\nu/k_0)(B^2 + C^2)$$

for the singlet → triplet transition would be precisely three times greater than that for the singlet → singlet process (although, of course, the thresholds for the two will differ).

From Fig. 2 we see that there is little difference between the radial p functions for the singlet and triplet states. However, in both cases the singlet d function is substantially larger than the triplet near the nucleus. Figure 3 reveals that the cross sections for the Be and Mg singlet → singlet processes are larger than for the corresponding singlet → triplet transitions. This is a consequence of the very considerable differences in the values of the B and C integrals for the two types of transitions. The large amplitude of the singlet d orbital in the vicinity of the nucleus enhances its

TABLE I. Hartree – Fock energies for several states of Be, Mg, and Ca. The excitation energies which appear in parentheses in the "experimental" column are estimates (not experimentally available) we have used in subsequent calculations of the cross sections.

State	HF Energy	Excitation energy	
		Calc.	Expt.
Be ^1S_g $(1s)^2(2s)^2$	−29.146		
Be ^3P_g $(1s)^2(2p)^2$	−28.673	0.473	0.543
Be ^1D_u $(1s)^2(2p)\,(3d)$	−28.384	0.762	(0.847)
Be ^3D_u $(1s)^2(2p)\,(3d)$	−28.377	0.769	0.853
Mg ^1S_g $KL\,(3s)^2$	−399.229		
Mg ^3P_g $KL\,(3p)^2$	−398.769	0.460	0.527
Mg ^1D_u $KL\,(3p)\,(3d)$	−398.576	0.653	(0.745)
Mg ^3D_u $KL\,(3p)\,(3d)$	−398.551	0.678	0.760
Ca ^1S_g $KL(3s)^2(3p)^6$ $(4s)^2$	−1343.516		
Ca ^3P_g $KL(3s)^2(3p)^6$ $(4p)^2$	−1343.214	0.302	0.351

overlap with the s orbital of the ground state and so results in a large transition probability. This effect is much more pronounced for magnesium than for beryllium. In Fig. 4 the differential cross sections are plotted for the singlet → singlet and singlet → triplet transitions of magnesium at 0.91 Ry above their respective threshold energies. Both cross sections are zero in the forward and backward directions as is expected for these parity-unfavored transitions. The singlet → singlet and singlet → triplet cross sections peak at angles which are, respectively, somewhat less and somewhat greater than 90°. If the cross term $2BC$ had been negative this angular dependence would have been reversed.

The maximum values of the total cross sections are listed in Table II. For the ^3P_g states of the alkaline earths these cross sections are roughly as large as the cross sections for single excitations which fall within the same range of energies. The cross sections for excitation of the magnesium D states are greater by almost an order of magnitude than for the corresponding transitions of beryllium. This is easy to understand because the first involves the orbital excitation $3s \rightarrow 3d$ whereas in the case of beryllium the relevant transition $2s \rightarrow 3d$ involves a change of principal quantum number.

C. Target Wave Functions Generated by Pseudopotential Method

It is possible to approximately account for the effect of the core upon a valence electron by introducing a spherically symmetric effective potential, called a pseudopotential, the functional form of which depends only upon the orbital angular momentum of that particular electron. This pseudopotential not only represents the effective shielding of the nuclear charge by the core electrons but also must account for the orthogonality constraints imposed by the Pauli principle.

Using the methods of Szasz and McGinn[12] we have constructed Hellmann-type pseudopotentials for the s and p valence orbitals of magnesium and calcium. [Unfortunately, this method is not immediately adaptable to the valence d orbitals of magnesium and calcium because there are no core electrons of this same (d) symmetry type to provide the necessary repulsive forces.] We found that for the accuracy desired in the present calculations (see subsequent results) it was unnecessary to use separate pseudopotentials for the s and p orbitals. Once the potentials for a particular atom (Mg or Ca) had been determined it was then a simple task to construct approximate wave functions (from Slater-type orbitals) for the ground ^1S_g and doubly excited ^3P_g states. The BO cross

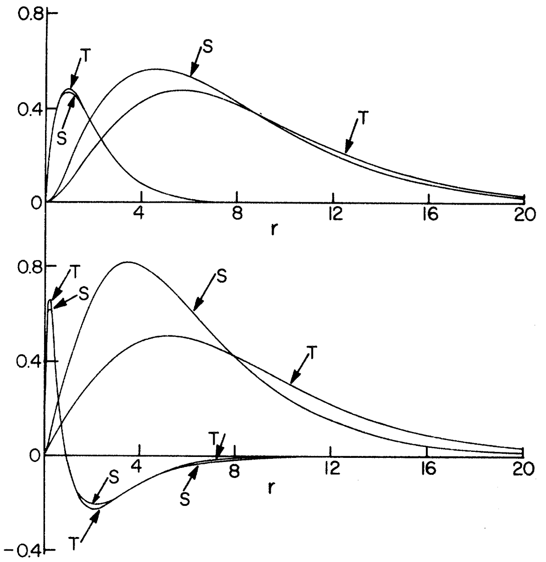

FIG. 2. Comparison of the radial dependence (in units of a_0) of the Hartree–Fock p and d orbitals for the ^1D_u and ^3D_u states of beryllium (upper figure) and magnesium. The d orbitials which have significant amplitude quite far out are multiplied by a factor of 10.

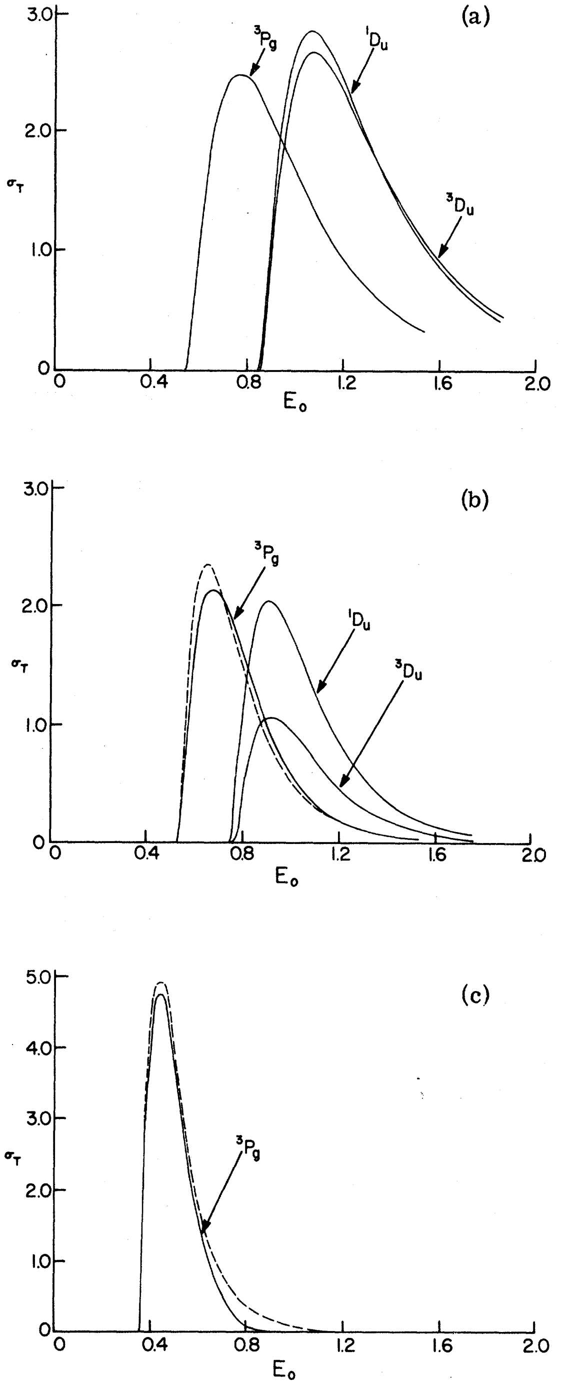

FIG. 3. Total BO cross sections (in units of πa_0^2) for the (i) $(ns)^2\,{}^1S_g \rightarrow (np)^2\,{}^3P_g$, (ii) $(ns)^2\,{}^1S_g \rightarrow (np)(3d)\,{}^1D_u$, and (iii) $(ns)^2\,{}^1S_g \rightarrow (np)(3d)\,{}^3D_u$ transitions plotted vs the energy of the incident electron (in Ry). (a) is for beryllium ($n = 2$) where the D cross sections have been multiplied by a factor of 10^2; (b) is magnesium ($n = 3$) where the D cross sections have been multiplied by a factor of 10; and (c) is for calcium. The dashed lines in (b) and (c) denote the cross sections for transition (i) with pseudo-wave-functions used in place of the Hartree–Fock orbitals.

sections computed from these target wave functions were found to be in excellent agreement with those based upon the Hartree–Fock functions. Let us now consider these calculations in somewhat greater detail.

D. Construction of Pseudopotentials

We assume for the valence electron in the $(ns)\,{}^2S_g$ ground state and the $(np)\,{}^2P_u$ excited state of Mg^+ ($n = 3$) and Ca^+ ($n = 4$) an energy operator of the form

$$\tilde{H}_1 = -\Delta - 4/r + 2A_n r^{-1} e^{-2K_n r} , \tag{36}$$

where A_n and K_n are the characteristic parameters of this "Hellmann pseudo-Hamiltonian." These quantities are determined by requiring that the expectation values of the pseudo-Hamiltonian for the states with the radial wave functions

$$\phi_{ns}(r) = (4\alpha_n^3)^{1/2} e^{-\alpha_n r} \quad \text{and} \quad \phi_{np}(r) = (\tfrac{4}{3}\gamma_n^5)^{1/2} r\, e^{-\gamma_n r}$$

be equal to the experimentally observed energies for the corresponding ionic states. These expectation values can be written

$$E_{ns} = \langle \phi_{ns} Y_{00} | \tilde{H}_1 | \phi_{ns} Y_{00} \rangle$$
$$= \alpha_n^2 - 4\alpha_n + 2A_n \alpha_n [\alpha_n/(\alpha_n + K_n)]^2 ,$$
$$E_{np} = \langle \phi_{np} Y_{1m} | \tilde{H}_1 | \phi_{np} Y_{1m} \rangle$$
$$= \gamma_n^2 - 2\gamma_n + A_n \gamma_n [\gamma_n/(\gamma_n + K_n)]^4 .$$

We further require that E_{ns} and E_{np} be the variational extrema (with respect to α_n and γ_n) associated with the selected forms of the two wave functions. These four conditions permit the calculation of the parameters A_n, K_n, α_n, and γ_n. In the case of $\mathrm{Mg}^+ (n = 3)$, where $E_{3s} = -1.105$ and $E_{3p} = -0.776$, we find that $A_3 = 5.0$ and $K_3 = 0.89$. For Ca^+ ($n = 4$) where $E_{4s} = -0.873$ and $E_{4p} = -0.64$, it is found that

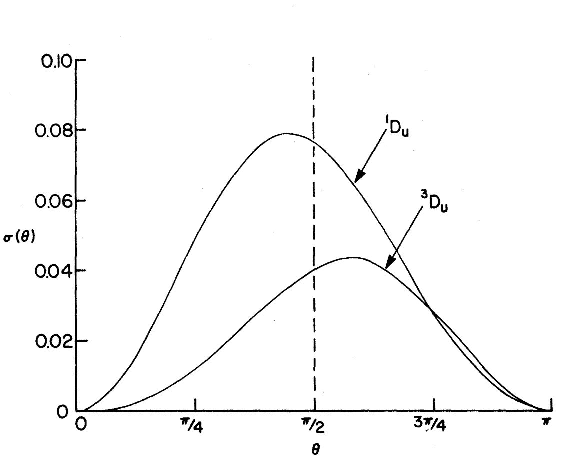

FIG. 4. Differential-scattering cross sections (in units of πa_0^2) for the (a) ^1D_u and (b) ^3D_u states of magnesium at an incident-energy electron of 0.91 Ry are plotted vs the scattering angle θ.

TABLE II. Maximum values of total cross sections (in units of πa_0^2).

	^3P_g	^1D_u	^3D_u
He	1.9×10^{-4}	1.4×10^{-7}	3.2×10^{-8}
Be	2.5	2.8×10^{-2}	2.7×10^{-2}
Mg	2.1	2.0×10^{-1}	1.1×10^{-1}
Ca	4.7		

$A_4 = 3.30$ and $K_4 = 0.46$. Our potential parameters differ from those reported by Szasz and McGinn because we use somewhat different criteria to fix the parameter values.

E. Construction of Two-Electron Target Wave Functions

The pseudo-Hamiltonian for the $(ns)^2\,{}^1S_g$ ground state and the $(np)^2\,{}^3P_g$ doubly excited state of Mg$(n=3)$ and Ca$(n=4)$ is taken to be

$$\tilde{H}_2 = -\Delta_1 - \Delta_2 - 4/r_1 - 4/r_2 + 2A_n[r_1^{-1}e^{-2K_n r_1} + r_2^{-1}e^{-2K_n r_2}] + 2/r_{12}\ , \quad (37)$$

where the values of the parameters A_n and K_n are those which we have just determined. Two-electron wave functions are constructed by inserting radial functions ϕ_{ns} and ϕ_{np} (of the forms used in the preceding subsection) into the formulas (33) for Φ_0^{00} and Φ_{1,M_L}^{1m}. The parameters in these trial orbitals are then determined by minimizing the expectation values of $\tilde{H}_2$ for the two states. The results of these simple calculations are collected in Table III.

F. BO Cross Sections from Pseudopotential Wave Functions

The two-electron variational wave functions associated with the pseudo-Hamiltonian $\tilde{H}_2$ can be used to evaluate integral A of (35). In Fig. 3 we compare cross sections (for the $^1S_g \rightarrow {}^3P_g$ transitions of Mg and Ca) computed in this manner with those based upon Hartree-Fock wave functions for the target atoms. The remarkable agreement between the two calculations demonstrates the dependability of the pseudopotential method. This is further illustrated in Figs. 5 and 6 where we see that the Hartree-Fock and pseudopotential wave functions are substantially the same outside of the atomic core. There are striking dissimilarities near the atomic nucleus because, unlike the Hartree-Fock functions, our pseudopotential wave functions are not orthogonal to the core orbitals.

We previously have observed that the scattering amplitudes for double excitations depend exclusively upon matrix elements of the Coulomb interactions among the valence electrons. Since the orbital amplitudes within the core contribute very little to integrals of this sort we expect the values of the scattering amplitudes to be the same whether calculated with the Hartree-Fock or pseudopotential wave functions. Because the simple procedure we have followed here produces pseudopotential orbitals of such high quality outside the core, this same scheme should be a valuable and easily applicable tool for investigating double excitations of other atoms. The situation for these particular transitions is peculiarly fortunate for in most problems (for example, single excitations) there generally will occur electron-nuclear interactions which cause great sensitivity to the behavior of the valence orbitals within the core. There then would be little reason to trust the reliability of calculations based upon pseudopotential wave functions, or at least upon such unsophisticated functions as those which have proved to be so satisfactory in the present application.

The choice of a different form for the d pseudopotential should make it possible to apply these same techniques to the cross sections for excitation of the ^1D_u and ^3D_u states of calcium. We tried to represent the shielded nuclear attractions upon a valence d electron by a linear combination of exponential terms in order to simulate the shell structure of the core. However, the resulting pseudopotential orbital was localized far too near the nucleus. It appears that an entirely different form for the pseudopotential may be needed to handle the calcium d orbital.

IV. FURTHER CONSIDERATIONS

A. Polarization of Impact Radiation

Doubly excited states can decay by photoemission to singly excited configurations or to other lower-lying doubly excited states. When the atoms are excited by a directed beam of electrons the subsequent radiation will be polarized. To compute the degree of this polarization we have made use of the theory of Oppenheimer and Penney as described by Percival and Seaton.[13]

Suppose that the electron beam is directed along the z axis and that we observe the radiation which is emitted from the excited gas in a direction at right angles to this beam. The intensities of

TABLE III. Characteristic parameters and expectation values for two-electron states.

	Magnesium	Calcium
ns screening parameters α	0.425	0.350
Calculated value of $E(^1S_g)$	-1.63 Ry	-1.25 Ry
Experimental value of $E(^1S_g)$	-1.67 Ry	-1.32 Ry
np screening parameter γ	0.625	0.500
Calculated value of $E(^3P_g)$	-1.17 Ry	-0.96 Ry
Experimental value of $E(^3P_g)$	-1.14 Ry	-0.97 Ry

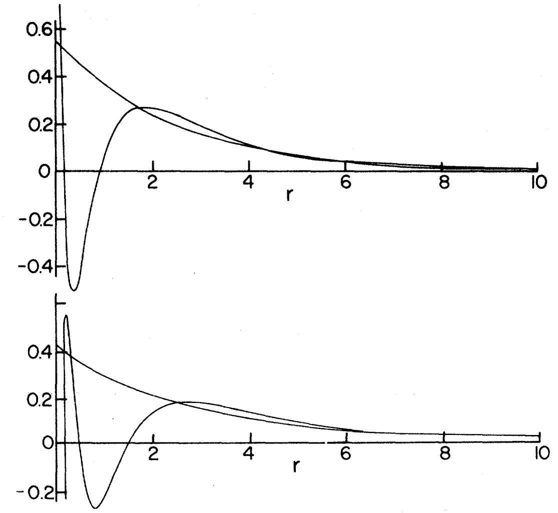

FIG. 5. Comparison of the radial dependence (in units of a_0) of the Hartree–Fock and the (nodeless) pseudo-wave-functions for the valence electrons in the ground states of magnesium (upper figure) and calcium.

emission which are polarized parallel and perpendicular to the direction of the beam will be designated as $I^{\parallel}$ and $I^{\perp}$, respectively, and the "percentage polarization" is defined by

$$P = 100\,(I^{\parallel} - I^{\perp})/(I^{\parallel} + I^{\perp}) \; . \tag{38}$$

Let it be assumed that prior to excitation the atoms are in S states and their electron spin (if any) and those of the intersecting beam electrons are randomly oriented. For these conditions, Oppenheimer[14] derived a relationship between the polarization P and the cross sections Q_{M_L} for excitation to a final state with a specific value M_L of the quantum number for the projection of atomic orbital angular momentum. In this theory of Oppenheimer and Penney the polarization is dependent upon the representations chosen for the excited state and for the final state to which it radiatively decays. In particular, the appropriate choice of angular momentum coupling scheme is governed by the relative magnitudes of the natural linewidth and of the fine- or hyperfine-structure splittings. When the magnitudes of these are approximately equal there is no unique choice of coupling scheme and the Oppenheimer–Penney theory produces ambiguous predictions for the polarization. Although Percival and Seaton[13] have developed a modified theory which is able to cope with these awkward situations, we shall have no need for it here.

For excited P and D states the percentage polarization can be expressed in the forms

$$P = 100\, g(Q_0 - Q_1)/(h_0 Q_0 + h_1 Q_1) \; , \tag{39}$$

and

$$P = 100\, g(Q_0 + Q_1 - 2Q_2)/(h_0 Q_0 + h_1 Q_1 + h_2 Q_2) \; , \tag{40}$$

respectively. In these formulas

$$Q_{M_L} = (k/k_0) \int\!\!\int d\theta\, d\phi\, \sin\theta \left| f_{M_L}(\theta, \phi) \right|^2 \tag{41}$$

and the values of g, h_0, h_1, and h_2 for the transitions of interest are collected in Table IV. These pure numbers are determined solely by requirements of angular-momentum conservation (as expressed by Wigner and Racah coefficients) and have been computed here on the assumption that the observed radiation is characteristic of emission from an experimentally unresolved multiplet-to-multiplet transition. For lithium and beryllium we have assumed the hyperfine splitting in the upper excited state to be less than the natural linewidth. In all cases the fine-structure splittings are larger than the natural linewidths.

From Eqs. (29) and (34) we see that the partial cross sections Q_0 are zero for parity-unfavored transitions. Therefore, the polarization of the radiation which accompanies the transitions $(np)^2\,{}^3P_g \rightarrow (ns)(np)\,{}^3P_u$ will be independent of beam energy and equal to − 10.06%. Specific cases to which this prediction should be applicable include the 4300-Å line of calcium, the 2780-Å line of magnesium, the 2650-Å line of beryllium, and the 320-Å line of helium (the polarization of which probably is unmeasurable). The $(1s)(2p)^2\,{}^4P_g \rightarrow (1s)^2(2p)\,{}^4P_u$ emission line of lithium likewise will exhibit an energy-independent polarization equal to 9.06%. However, just as in the case of helium the polarization of this highly energetic transition, with a wavelength of 212 Å, will be extremely difficult to measure. Polarization

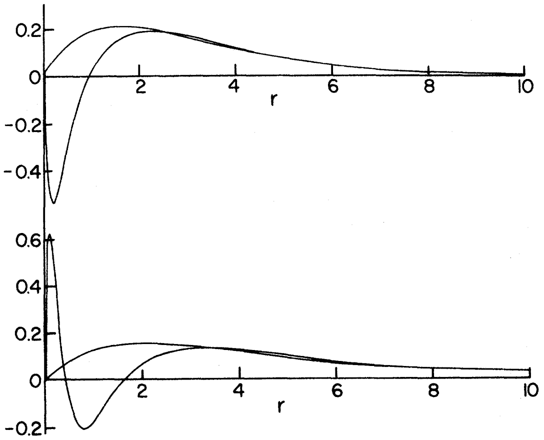

FIG. 6. Comparison of the radial dependence (in units of a_0) of the Hartree–Fock and the (nodeless) pseudo-wave-functions for the valence electrons in the doubly excited ${}^3P_g$ states of magnesium (upper figure) and calcium.

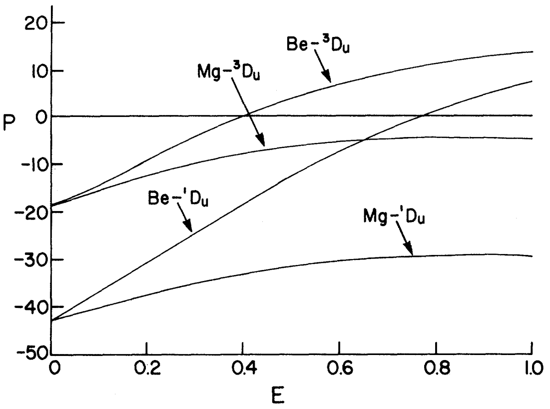

FIG. 7. Energy dependence of the calculated percentage polarization of dipole radiation emitted from the (a) Be-^3D_u, (b) Mg-^3D_u, (c) Be-^1D_u, and (b) Mg-^1D_u states. These are plotted vs the energy (in Ry) of the scattered electron.

measurements for emission from the D states of helium, which are also subject to this same difficulty, are further complicated by the very small excitation cross sections of these states.

From Eqs. (34) and (40) we find that the polarization of radiation from the singlet and triplet D states of the alkaline earths are given by

$$P=100\,\frac{21B^2-15C^2}{47B^2+35C^2}\,,\qquad (np)(3d)\,^1D_u\rightarrow(ns)(3d)\,^1D_g \tag{42}$$

and

$$P=100\,\frac{1491B^2-1065C^2}{6497B^2+5645C^2}\,,\qquad (np)(3d)\,^3D_u\rightarrow(ns)(3d)\,^3D_g\,, \tag{43}$$

respectively. Figure 7 displays our theoretical predictions for beryllium and magnesium of these energy-dependent polarizations.

A straightforward analysis based upon the definitions (35) of the integrals B and C reveals that the ratio C/B becomes unbounded at the excitation threshold $k\rightarrow 0$ and in the high-energy limit $k\rightarrow\infty$ as well. (Although these conclusions have been derived here on the basis of the Born approximation, we expect them to be valid under far less restrictive conditions.) Thus, we expect the percentage polarization for these D states to assume the same numerical values in each of these limits. For beryllium and magnesium the threshold values of P are -18.86% for the triplet state and -42.86% for the singlet. In principle, these same values should be observed at very high beam energies but in practice there will be complications due to cascading and to the very small high energies limits of the excitation cross sections.

B. Threshold Law for Parity-Unfavored Transitions

To determine the behavior of the scattering amplitude near the threshold we expand the plane wave $e^{i\vec{k}_\nu\cdot\vec{r}_{N+1}}$ appearing in Eq. (11) in spherical harmonics and obtain

$$f_{\nu0}(\vec{k}_\nu,\vec{k}_0)=\frac{(N+1)^{1/2}}{4\pi}\sum_{l'm'}\Big\langle\sum_{m_\nu m}C^{s_\nu sS}_{m_\nu mM_S}\times\Phi_\nu^{s_\nu m_\nu}(1,\ldots,N)\,\phi^{sm}(N+1)\,4\pi i^{l'}j_{l'}(k_\nu r_{N+1})\times Y^*_{l'm'}(\hat{k}_\nu)\,Y_{l'm'}(\hat{r}_{N+1})\,\Big|H'_{N+1}\Big|\,\Psi^{SM_S}\Big\rangle\,. \tag{44}$$

For parity-unfavored transitions $m'\neq 0$ and so the sum in (44) consists only of terms with $l'\geq 1$. Since Ψ^{SM_S} varies slowly with energy just above threshold, the energy dependence of $f_{\nu0}$ is due primarily to the Bessel functions $j_{l'}(k_\nu r_{N+1})$. Thus, we conclude that

$$f_{\nu0}(\vec{k}_\nu,\vec{k}_0)_{k_\nu\rightarrow0}\rightarrow\text{cons}\times k_\nu^{\tilde{l}}\,, \tag{45}$$

where $\tilde{l}$ is the lowest contributing term in the sum on the partial wave index l'. From this it follows that near threshold the total cross section will be proportional to $k_\nu^{2\tilde{l}+1}=(E-E_\nu)^{\tilde{l}+1/2}$. For the parity-unfavored transitions considered here the lowest-order contributions are due to p waves. Therefore, we expect the cross section to vary as $(E-E_\nu)^{3/2}$ for low energies and hence to exhibit a zero slope at threshold. This means that the threshold energy must be exceeded by some finite amount before any significant rate of transition can be observed. In contrast to this the cross section for a process to which there are s wave contributions has an infinite slope and a finite value at threshold.

Only the p-wave contributes to the ^3P_g excitation and we expect the k_ν^3 energy dependence to persist for quite some distance beyond threshold. Support for this expectation is provided by the BO cross section for the ^3P_g excitation of calcium, which exhibits the k_ν^3 dependence to approximately one-third of the peak height. Hopefully, this behavior might be observed experi-

TABLE IV. Polarization parameters for several optical transitions.

Excited state	Final state	g	h_0	h_1	h_2
^3P_g	^3P_u	15	67	149	
^4P_g	^4P_u	-42	211	464	
^3D_u	^3D_g	-213	529	1129	1342
^1D_u	^1D_g	-3	3	7	10

mentally.

C. Discussion of Results

The magnitudes of the BO cross sections calculated here are surely reliable to within a factor of 2 and their angular dependence is very nearly exact. Therefore, it is safe to conclude that the cross sections for doubly excited states with high threshold energies or which involve changes of principal quantum numbers will be much smaller than πa_0^2. The cross sections for doubly excited states which are bound or which at least have low excitation thresholds and do not involve changes of principal quantum number will be of the order of πa_0^2 or larger and hence comparable in magnitude to the cross sections for single-electron excitations. Processes belonging to this second category surely must contribute significantly to the measured total inelastic scattering cross sections.

We have seen that cross sections for double excitation computed from pseudopotential valence orbitals are very nearly identical to those computed from Hartree–Fock functions. This is a clear indication that the form of the valence orbitals within the core is of no consequence in double-excitation processes. This is as it should be because there are no core interaction contributions to the operators which appear in the scattering amplitudes for these transitions.

The formulas derived here could be applied to other atoms simply by altering the values of the various screening parameters and of the excitation energies. In fact, formulas (34) can be applied without change to the $(ns)^2\,{}^1S_g \to (np)^2\,{}^3P_g$ transitions for all the alkaline earths. However, for atoms heavier than calcium there are significant deviations from the LS coupling scheme. One must allow for these in the description of the target states as well as in the concept of the parity favorability of the transitions. Both boron and aluminum can undergo parity-unfavored transitions from their ground $(ns)^2(np)\,{}^2P_u$ configurations to $(np)^3\,{}^4S_u$ states which are embedded within ionic continua. The cross-section formulas for these processes are similar to those for lithium which we have considered here. The theory of the doubly excited states of zinc, cadmium, and mercury, whose ground states are of the form $(ns)^2\,{}^1S_g$, closely resembles that for the alkaline earths. The doubly excited states of the alkalis are generally to be found high in the continuum because of the combination of a low first and a high second-ionization potential. Bound doubly excited states of the transition metals are known and have been listed in tables of atomic energy levels such as those of Moore.[15] The electron-impact cross sections for excitation of these states could be calculated by using the N-electron atom theory presented here in Sec. II.

Doubly excited states of other atoms certainly exist but their descriptions vary from those discussed above not only because more electrons are involved in the transitions but, more importantly, because the concept of being parity favored becomes irrelevant for states of higher angular momentum.

We have discovered that the polarization of the impact radiation emitted from a doubly excited P state is independent of electron energy, whereas that characteristic of a D state does vary with the energy of the beam. The numerical values of the energy-independent polarizations of the P states are determined solely by considerations of angular momentum coupling and therefore are independent of our scattering theory. Deviations from these predicted values could come about only from incorrect characterizations of the states involved.

We have used our calculated cross sections Q_{M_L} to predict the energy dependence of the polarization for D states. It is, in fact, only the ratio Q_2/Q_1 whose energy dependence appears in the formula for the percentage polarization. Therefore, if our scattering theory is capable of correctly predicting the ratio of these partial cross sections, the predicted polarizations would be correct even if the absolute magnitudes of our cross sections were wrong. If the only mode of decay of these excited states is by emission of polarized photons, then the total intensity of radiation must be proportional to the total excitation cross section. By measuring the total light emitted as a function of electron energy one then could obtain the energy dependence of the total cross section provided that one accounts for cascading.

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APPENDIX

In electron-atom scattering it generally is realized that physically more appealing scattering matrix elements are obtained by expressing the scattered-electron wave functions asymptotically as Coulomb waves instead of the normally chosen plane waves.[16] The computationally more tractable plane-wave approximations suffer from post-prior discrepancies and nonvanishing contributions from constant potentials which arise from the lack of orthogonality between the symmetrized initial and final states. By including the scattered-electron–nuclear interaction in the unperturbed Hamiltonian, the initial and final states become eigenfunctions of the same operator and the undesirable features of the plane-wave approximations are avoided. In this Appendix we derive the scattering amplitude in the Coulomb-wave approximation.

The interelectronic repulsion operator, $\tilde{H}'_{N+1} = H'_{N+1} - V_{N+1}$, where $V_{N+1} = -2N/r_{N+1}$, is used as the perturbation. The Eq. (6) can be rewritten,

$$(T_{N+1} + V_{N+1} - k_\nu^2)\tilde{F}_\nu(N+1) = (N+1)^{1/2}\tilde{G}_\nu(N+1)\ , \tag{A1}$$

where $\tilde{G}_\nu(N+1)$ differs from $G_\nu(N+1)$ of Eq. (7) in that H'_{N+1} is replaced with $\tilde{H}'_{N+1}$ and $T_{N+1} + H_N - E$ is replaced with $T_{N+1} + V_{N+1} + H_N - E$. Boundary conditions require $\tilde{F}_\nu$ to be a solution of the integral equation:

$$\tilde{F}_\nu(\vec{r}) = \delta_{\nu 0}\psi^-_{\vec{k}_0}(\vec{r}) + \tilde{F}^{\rm sc}_\nu(\vec{r})\ , \tag{A2}$$

with

$$\psi^\pm_{\vec{k}_\nu}(\vec{r}) = (2\pi)^{-3/2} e^{N\pi/2k_\nu}\,\Gamma\left(1 \mp \frac{iN}{k_\nu}\right) \times e^{i\vec{k}_\nu\cdot\vec{r}_1}\,F_1\left(\pm\frac{iN}{k_\nu};\ 1, i(\pm k_\nu r - \vec{k}_\nu\cdot\vec{r})\right)\ , \tag{A3}$$

and where

$$\tilde{F}^{\rm sc}_\nu(r) \sim \frac{1}{r}\exp\left[i\left(k_\nu r + \frac{N\ln 2k_\nu r}{k_\nu}\right)\right]\tilde{f}_{\nu 0}(\vec{k}_\nu, \vec{k}_0)\ . \tag{A4}$$

Here

$$\tilde{f}_{\nu 0}(\vec{k}_\nu, \vec{k}_0) = -\frac{(N+1)^{1/2}}{4\pi}\int d^3\vec{r}'\,\psi^+_{\vec{k}_\nu}(\vec{r}')\,\tilde{G}_\nu(\vec{r}') \tag{A5}$$

is the amplitude for scattering into the final state $(\nu, \vec{k}_\nu)$. Again there is a contribution of the form

$$\tilde{f}'_{\nu 0}(\vec{k}_\nu, \vec{k}_0) = \frac{(N+1)^{1/2}}{4\pi}\Big\langle \sum_{m_\nu m} C^{s_\nu s S}_{m_\nu m M_S}\,\Phi^{s_\nu m}_\nu(1, \ldots, N)\,\phi^{sm}(N+1)\,\psi^+_{\vec{k}_\nu}(N+1)\,\Big|\,\tilde{H}'_{N+1}\,\Big|\,\Psi^{SM_S}\Big\rangle\ , \tag{A6}$$

where the operator $\tilde{H}'_{N+1}$ now only includes the interactions among the electrons. The remaining contributions to the scattering amplitude are from terms of the type

$$\tilde{t}_{\nu\mu} = \langle \psi^+_{\vec{k}_\nu}(N+1)\,\phi_\nu(1, \ldots, N)\ |\ T_{N+1} + V_{N+1} + H_N - E\,|\ F_\mu(1)\phi_\mu(2, \ldots, N+1)\rangle\ , \tag{A7}$$

which are again trivially zero except for the continuum target states of Eq. (14). These must now be represented by

$$\tilde{F}_{r,\vec{k}_\mu}(1)\int d^3\kappa\,\tilde{h}_{\vec{k}_\mu}(\vec{\kappa})\,\phi^{\rm ion}_\mu(2, \ldots, N)\,\psi^+_{\vec{\kappa}}(N+1)\ .$$

Then,

$$\begin{aligned}\tilde{t}_{\nu\mu} = T^{\rm ion}_{\nu\mu} &= \int d^3\vec{\kappa}\,\tilde{h}_{\vec{k}_\mu}(\vec{\kappa})\,\langle\vec{\nabla}_{N+1}\cdot\{[\psi^+_{\vec{k}_\nu}(N+1)\,\phi_\nu(1, \ldots, N)]^*\,\vec{\nabla}_{N+1}[\tilde{F}_{\mu,\vec{k}\mu}(1)\,\phi^{\rm ion}_\mu(2, \ldots, N)\,\psi^+_{\vec{\kappa}}(N+1)] \\ &\qquad - [\tilde{F}_{\mu,\vec{k}_\mu}(1)\,\phi^{\rm ion}_\mu(2, \ldots, N)\,\psi^+_{\vec{\kappa}}(N+1)]\,\vec{\nabla}_{N+1}\,[\psi^+_{\vec{k}_\nu}(N+1)\,\phi_\nu(1, \ldots, N)]^*\}\rangle \\ &= \int d^3\kappa\,\tilde{h}_{\vec{k}_\mu}(\vec{\kappa})\,\langle\phi^*_\nu(1, \ldots, N)\,\tilde{F}_{\mu,\vec{k}_\mu}(1)\,\phi^{\rm ion}_\mu(2, \ldots, N)\rangle_{N+1}(\kappa^2 - k_\nu^2)\,\delta(\vec{\kappa} - \vec{k}_\nu)\ .\end{aligned} \tag{A8}$$

Therefore, we conclude that the terms $\tilde{t}_{\nu\mu}$ contribute nothing to the scattering amplitude.

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[1] H. S. W. Massey and C. B. O. Mohr, Proc. Cambridge Phil. Soc. 31, 604 (1935).

[2] P. M. Becker and J. S. Dahler, Phys. Rev. 136, A73 (1964).

[3] G. J. Schultz, Phys. Rev. 112, 150 (1958); P. D. Burrow and G. J. Schultz, *ibid.* 187, 97 (1969); P. D. Burrow, Phys. Rev. A 2, 1774 (1970).

[4] S. T. Manson, Phys. Rev. 145, 35 (1966).

[5] U. Fano, Phys. Rev. 135, B863 (1964).

[6] J. A. Simpson, S. R. Mielczarek, and J. Cooper, J. Opt. Soc. Am. 54, 269 (1964).

[7] L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1968), p. 394.

[8] J. C. Steelhammer and S. Lipsky, J. Chem. Phys. 53, 1445 (1970).

[9] C. Froese, Phys. Rev. 137, A1644 (1965).

[10] E. Clementi, *Tables of Atomic Functions* (IBM Corp., San Jose, Calif., 1965).

[11] E. Trefftz, A. Schlüter, K.-H. Dettmar, and K. Jörgens, Z. Astrophysik 44, 1 (1957).

[12] L. Szasz and G. McGinn, J. Chem. Phys. 46, 729 (1965).

[13] I. C. Percival and M. J. Seaton, Proc. Roy. Soc. (London) A251, 113 (1958). The following errors in equations were found in this paper. Some of them evidently were made in transcription since the reported results are consistent with the correct formulas:

$$\bar{I} = \tfrac{2}{3}(I^{\parallel} + 2I^{\perp})\ ,$$

$$\bar{I} = \tfrac{2}{3}Dn(b)\,A(b)\ , \tag{2.8}$$

$$P = 100\,(6I^{\parallel} - 3\bar{I})/(2I^{\parallel} + 3\bar{I})\ , \tag{2.10}$$

$$K(SL\rightarrow SL'') = V_a \frac{A(SL\rightarrow SL'')}{A(SL)} \sum_{M_L} Q_{|M_L|}\ , \qquad (3.34)$$

$$\sum_{F,M_F} \tau(\tfrac{1}{2}1JIFM_F) = \tfrac{1}{3}(2J+1)(2I+1)\ , \qquad (3.42)$$

$$K_Z({}^2P_J\rightarrow {}^2S) = \frac{V_a}{2(2I+1)}\left(\frac{(2J+1)(2I+1)\,Q_1}{3} + \mu(\tfrac{1}{2}1JI)(Q_0-Q_1)\right), \qquad (3.43)$$

$$K({}^2P_J\rightarrow {}^2S) = \tfrac{1}{6}V_a(2J+1)(2Q_1+Q_0)\ . \qquad (3.45)$$

[14] J. R. Oppenheimer, Proc. Natl. Acad. Sci. (U.S.) 13, 800 (1927); W. G. Penney, *ibid.* 18, 231 (1932).

[15] *Atomic Energy Levels*, edited by C. Moore, Natl. Bur. Std. Circ. No. 467 (U.S. GPO, Washington, D. C. 1949), Vol. 1.

[16] T. B. Day, L. S. Rodberg, G. A. Snow, and J. Sucher, Phys. Rev. 123, 1051 (1961). I.-J. Kang and W. D. Foland, *ibid.* 164, 122 (1967).

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Glauber Cross Sections for Excitation of the $2\,^1S$ State of Helium by Electron Impact[*]

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The Glauber amplitude for describing collisions of charged particles with two-electron atoms, resulting in transitions between spherically symmetrical states, is reduced to a readily computable form. Application is then made to the $2^1S\leftarrow 1^1S$ transition in helium, for which angular distributions are determined for 26.5-, 34-, 50-, and 83-eV incident electrons. Comparison with experiment shows that the Glauber theory is capable of accurately predicting the angular distributions for even our lowest-energy calculation. In particular the theory predicts the recently observed structure in the differential cross section. The energy dependence of the "apparent" generalized oscillator strength is also demonstrated for incident energies in the range 300–1100 eV.

A number of recent papers have dealt with the applicability and usefulness of the Glauber approximation[1] with respect to collisions of charged particles with atomic systems. In particular, a fairly complete study of the approximation as applied to the elastic and inelastic (bound-state excitation) scattering of electrons and protons by hydrogen,[2–5] has shown the Glauber theory to be quite accurate in the energy range where the first Born approximation is known to fail and close-coupling theories[6] with their modifications[7] are not feasible. Additional applications have been made to helium[5,8,9] and lithium,[10] and quite recently the theory has been applied to impact ionization of hydrogen[11] by electrons, and multiple scattering effects[12] in electron-molecule collisions.

Although Thomas and Gerjuoy[4] have been able to obtain closed form expressions for the scattering amplitudes for the excitation of certain energy levels of hydrogen by electrons or protons, it is unlikely that such will be the case for many-electron atomic systems even with the simplest approximate wave functions. Using a particular form for the atomic wave function, however, Franco[13] has been successful in reducing the $(3Z+2)$-dimensional integral occurring in the amplitude expression (for scattering of charged particles by a Z-electron atom) to a one-dimensional integral involving products of the generalized ${}_1F_2(a;\ b,\ c;\ x)$ hypergeometric functions. This expression is quite appealing in its scope, but apart from $(e^-,\ \mathrm{H})$ and $(p^+,\ \mathrm{H})$ collisions, its numerical tractability has yet to be demonstrated. Thus, the essential aim of the present article is to present a simplification of the Glauber amplitude for the two-electron atom, for certain excitations by charged particles. Specifically, the amplitude for excitation by electrons, of ground state helium ($1\,^1S$), to the first metastable state ($2\,^1S$) is put in a readily computable form and evaluated. The differential cross sections for this process for selected energies in the 25–1100 eV range are presented and compared with experiment and other theoretical values.

The collision amplitude $F_{fi}(\vec{q})$, where the atom (two electrons in the field of a doubly positively charged core, e.g., He, alkaline earths, Hg, etc.) is excited from some initial state i to some final state f by an incident electron, is given according to the Glauber theory by

$$F_{fi}(\vec{q}) = \frac{ik_i}{2\pi}\int d\vec{b}\, e^{i\vec{q}\cdot\vec{b}} \langle \Psi_f(\vec{r}_1,\ \vec{r}_2)\,|\,1-\gamma(\vec{b},\ \vec{r}_1) \times \gamma(\vec{b},\ \vec{r}_2)\,|\,\Psi_i(\vec{r}_1,\ \vec{r}_2)\rangle\ , \qquad (1)$$

where

$$\gamma(\vec{b},\ \vec{r}_i) = (|\vec{b}-\vec{s}_i|/b)^{2i\eta} \qquad (2)$$

and $\eta = 1/k_i$. Here Ψ_i and Ψ_f are the wave functions representing the target state before and after collision. $\vec{k}_i$ and $\vec{k}_f$ are, respectively, the incident