Multichannel Photo-Ionization of Atomic Systems

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Expressions for multichannel photo-ionization are obtained with the dipole approximation assuming LS coupling; while including the effects of coupling between channels, these expressions give separate contributions for each channel. The explicit form of the cross sections for atomic systems with configurations $1s^2 2s^2 2p^q$ is obtained, assuming superpositions of determinantal wave functions (Hartree-Fock) for initial and final states. The effects of core relaxation are considered. The formalism is applied to the photo-ionization of neon, with the result that coupling between channels and core relaxation have a larger effect on the individual channel cross sections than on the total cross section. Both effects tend to bring the dipole velocity and length forms of the cross section into closer agreement with each other, but the improvement is appreciable only near threshold.

I. INTRODUCTION

THE photo-ionization of atoms in the region from threshold to a few hundred electron volts above it has been the subject of a number of recent theoretical and experimental investigations.[1-12] Quantum mechanics provides an explicit formulation of the problem in terms of initial and final wave functions which can be applied exactly (within the limits of the dipole approximation) only to atomic hydrogen. Calculations for heavier atoms require estimates of the atomic wave functions describing the system before and after ionization takes place which are accurate in the regions of electron configuration space relevant to the calculations.

Most of the theoretical work to date has been done on the lightest elements (He and Li) where accurate wave functions of the ground state are available.[1-3] For heavier atoms all of the work to date has been done within the framework described by Bates[12] which assumes that the ground state of the system for any given configuration (LS coupling is assumed) may be represented by a superposition of Slater determinants and the final state may be represented as a sum of such determinantal wave functions, each of which describes a particular channel; i.e., a particular state of the ion and a definite angular momentum of the outgoing electron coupled together to a specific total L and S of the final system.

Within this framework Bates makes two further approximations, namely:

(A) The coupling between final-state channels is negligible.

(B) The core relaxation that results from ionization is taken into account as follows. The dipole matrix elements are calculated first by assuming that the radial wave functions of the final ion state are the same as for the initial state. A multiplication factor is then added which represents the incomplete overlap of the radial wave functions of the core before and after ionization.

It is the purpose of this paper to develop a formalism within the general framework outlined by Bates which does not include these two approximations. It is now becoming feasible to perform experiments which can measure the individual channel cross sections.[13] Since one would expect the coupling between final state channels to have an appreciable effect on the calculation of these cross sections (although not necessarily on the total cross section), and since methods are now available by which one can perform calculations of final-state wave functions which explicitly include the effect of the coupling,[14] it is desirable to drop assumption (A). Recent work on atomic transition probabilities

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[2] J. H. Tait, *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 586.

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[12] D. R. Bates, Monthly Notices Roy. Astron Soc. 106, 432 (1946).

[13] For example, one might measure the photo-ionization of atomic oxygen in its ground state by counting the number of ions produced in each of the 3 ground-state configurations $(2p)^3$ ^4S, ^2D, ^2P; or, one might photo-ionize neon and measure the angular distribution of emitted electrons. The decomposition of the angular distribution into sums of Legendre polynomials would yield numbers which are related to the s- and d-wave channel cross sections.

[14] K. Smith, R. J. W. Henry, and P. G. Burke, Phys. Rev. 147, 21 (1966).

has shown that, at least for inner shell excitations, assumption B may not be valid.[15] In particular, for neon, B neglects the process by which a $2p$ electron absorbs a photon and makes a virtual transition to a $2s$ state, with a $2s$ electron being ejected into the s-wave continuum. Hence it is of interest to investigate the effects of dropping this assumption in calculations of photoionization.

The outline of the rest of the paper is as follows: In Sec. II we will consider the formal expression for photoionization cross sections and demonstrate what must be done so that standing wave functions can be used. In Sec. III these formulas are applied to atoms and ions with configurations $1s^2 2s^2 2p^q$ $(q=1,2,\cdots,6)$ for the case where initial and final states are represented by sums of Slater determinants. Finally, in Sec. IV, the quantitative effects of relaxing assumptions (A) and (B) above are investigated by considering numerical calculations of the photo-ionization of neon.

II. THE PHOTO-IONIZATION CROSS SECTION

We consider the following process: An unpolarized beam of photons of energy $h\nu \ll mc^2$ moves in the z direction through a gas containing atoms or ions of nuclear charge Z and $N+1$ electrons. We describe the initial state of the atom by a wave function $\Phi_{LS}{}^{M_L M_S}$ $\times (r_1, \cdots, r_{N+1})$ depending on the $N+1$ electron coordinates r_i and with quantum numbers L, S, M_L, M_S. If $h\nu$ is greater than the lowest ionization potential of the atom, ionization can take place and final states can be described by wave functions $^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma}(r_1, \cdots, r_{N+1}; E)$ where Γ is a channel index which distinguishes different states (L_Γ, S_Γ), of the residual ion [with eigenfunctions $\Phi_{L_\Gamma S_\Gamma}{}^{M\mu}(r_1 \cdots r_N)$] and different angular-momentum states (l_Γ) of the outgoing electron of en-

ergy E. $\mathcal{L}_\Gamma$ and S_Γ are the total angular momentum and spin quantum numbers of channel Γ.

With these definitions (plus the conventions described below) the cross section for photo-absorption with electron ejection in the Γ channel is,[16] in the dipole-velocity form,

$$^\Gamma\sigma_v(E) = \frac{2\pi e^2 \hbar^2}{m^2 c \nu \omega}$$

$$\times \sum_{\substack{M_L M_S \mathfrak{M}\Gamma\mu\Gamma \\ m_1 = \pm 1}} |\langle {}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma}(r_1, \cdots, r_{N+1}; E)|$$

$$\times \sum_{i=1}^{N+1} \nabla_i{}^{m_1} | \Phi_{LS}{}^{M_L M_S}(r_1, \cdots; r_{N+1})\rangle|^2. \quad (1)$$

where

$$\nabla_i{}^{\pm 1} = \frac{1}{\sqrt{2}}\left(\mp\frac{\partial}{\partial x_i} + \frac{\partial}{\partial y_i}\right)$$

is the dipole velocity operator.

Here e, $\hbar$, m, and c are fundamental constants and the result is obtained by summing over all final spin and angular momentum directions and averaging over initial spin, angular momentum, and polarization of the photon, which accounts for the statistical weight $\omega = 2(2L+1)(2S+1)$.

The target function Φ satisfies the normalization condition,[17]

$$\int \Phi^*\Phi \, d\tau = 1, \quad (2)$$

while $^\Gamma\Psi$ represents an outgoing spherical wave in channel Γ plus incoming spherical waves in all channels, normalized per unit energy range.[16] This condition will be met if the asymptotic form of $^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}$ is taken to be

$$\lim_{r_{N+1}\to\infty} {}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma} = (2\pi\kappa_\Gamma)^{-1/2}\, {}^\Gamma\Phi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma}(r_1,\cdots r_N; r_{N+1})\exp[i\theta_\Gamma(\kappa_\Gamma, r_{N+1})]/r_{N+1}$$

$$-\sum_{\Gamma'} S_{\Gamma\Gamma'}{}^\dagger (2\pi\kappa_{\Gamma'})^{-1/2}\, {}^{\Gamma'}\bar\Phi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma}(r_1,\cdots r_N; r_{N+1})\exp[-i\theta_{\Gamma'}(\kappa_{\Gamma'}, r_{N+1})]/r_{N+1}, \quad (3)$$

where

$$^\Gamma\Phi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma\mu\Gamma}(r_1,\cdots r_N; r_{N+1}) = \sum_{M m \mu m_s} C(L_\Gamma, l_\Gamma, \mathcal{L}_\Gamma; M, m, \mathfrak{M}_\Gamma)C(S_\Gamma, \tfrac{1}{2}, S_\Gamma; \mu, m_s, \mu_\Gamma)$$

$$\times \Phi_{L_\Gamma S_\Gamma}{}^{M\mu}(r_1\cdots r_N)Y_{l_\Gamma}{}^m(r_{N+1})\sigma^{m_s}(N+1). \quad (4)$$

Here κ_Γ is the wave number of an electron ejected in the Γ channel and is related to the incident frequency and the Γth ionization potential I_Γ by the Einstein relation

$$(\tfrac{1}{2})_m \hbar^2 \kappa_\Gamma{}^2 = E = h\nu - I_\Gamma. \quad (5)$$

$\sigma(N+1)$ is a spin wave function of the $(N+1)$th electron and $Y_{l_\Gamma}(r_{N+1})$ is the usual spherical harmonic describing the angular motion of the outgoing electron having angular-momentum quantum number l_Γ. Equation (4) represents the coupling of the angular and spin

parts of $\bar\Phi$ to the outgoing electron via the Clebsch-Gordan coefficients $C(L_\Gamma, l_\Gamma, \mathcal{L}_\Gamma; M, m, \mathfrak{M}_\Gamma)$ and $C(S_\Gamma, \tfrac{1}{2}, S_\Gamma; \mu, m_s, \mu_\Gamma)$ to form a final state with quantum numbers $\mathcal{L}_\Gamma$ and S_Γ. $^\Gamma\Phi(r_1\cdots r_N, r_{N+1})$ represents the dependence of the final-state wave function on all coordinates except the radial coordinate r_{N+1}. The matrix, $S_{\Gamma\Gamma'}{}^\dagger$, is the adjoint of the scattering matrix in the angular-momentum

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[15] P. Bagus, thesis, University of Chicago, 1964 (unpublished).

[16] H. Bethe and E. Salpeter *Quantum Mechanics of One and Two Electron Systems*, (Academic Press Inc., New York, 1957), Sec. 69.

[17] Explicit dependence on quantum numbers and independent variables will be dropped whenever, as here, no confusion will result and the end result is a simplification of notation.

representation, and for a spin-independent Hamiltonian (which we assume) it is diagonal in $\mathcal{L}_\Gamma$ and $\mathcal{S}_\Gamma$.

The factor $(2\pi\kappa_\Gamma)^{1/2}\exp(i\theta_\Gamma)/r_{N+1}$ represents an outgoing spherical wave and θ_Γ is given by

$$\theta_\Gamma(\kappa_\Gamma,r)=\kappa_\Gamma r-\tfrac{1}{2}l_\Gamma\pi-\frac{Z-N}{\kappa_\Gamma}\ln(2\kappa_\Gamma r)$$

$$+\arg[\Gamma(l_\Gamma+1-i(Z-N)/\kappa_\Gamma)]. \quad (6)$$

The asymptotic form, (3), assures the usual normalization per unit energy range with different channel wave functions being orthogonal, i.e.,

$$\int{}^\Gamma\Psi^*(r_i; E){}^{\Gamma'}\Psi(r_i; E)d\tau_i=\delta(E-E')\delta_{\Gamma\Gamma'} \quad (7)$$

Application of the commutation relation, $[r,H]=(i\hbar/m)p$, to (1) yields the dipole-length form of the cross section:

$${}^\Gamma\sigma_L=\frac{8\pi^3\nu e^2}{c\omega}\sum_{\substack{M_LM_S\mathfrak{M}\Gamma_\mu\Gamma\\m_1=\pm1}}|\langle\Phi_{LS}{}^{M_LM_S}(r_1\cdots r_{N+1})|$$

$$\times\sum_{i=1}^{N+1}r_iY_1{}^{m_1}(r_i)|\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}(r_1\cdots r_{N+1})\rangle|^2. \quad (8)$$

The total cross section will be

$$\sigma_{\text{tot}}=\overset{\text{open channels}}{\sum_\Gamma}{}^\Gamma\sigma_v=\overset{\text{open channels}}{\sum_\Gamma}{}^\Gamma\sigma_L. \quad (9)$$

The wave functions which have asymptotic form (3) are inconvenient for numerical applications since they are complex. We define a standing-wave solution for the final state satisfying the boundary condition

$$\lim_{r_{N+1}\to\infty}{}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}=\left(\frac{2}{\pi\kappa_\Gamma}\right)^{+1/2}{}^\Gamma\bar{\Phi}_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}$$

$$\times\sin\theta_\Gamma+\sum_{\Gamma'}R_{\Gamma\Gamma'}{}^{\Gamma'}\bar{\Phi}_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}\cos\theta_{\Gamma'}\left(\frac{2}{\pi\kappa_{\Gamma'}}\right)^{1/2}. \quad (10)$$

Wave functions defined in this way are real everywhere. It can easily be shown by comparison of Eqs. (3) and (10) that the matrices R and S are related by

$$R_{\Gamma\Gamma'}=i\left[\frac{1-S}{1+S}\right]_{\Gamma\Gamma'} \quad (11)$$

and the wave function ${}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}$ may be expressed in terms of the standing wave solutions as

$${}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}=i\sum_{\Gamma'}(1-iR)_{\Gamma\Gamma'}{}^{-1}{}^{\Gamma'}\Psi_{\mathcal{L}_\Gamma S_\Gamma}. \quad (12)$$

One can see from Eq. (12) that the ${}^\Gamma\Psi$'s are neither orthogonal nor normalized per unit energy range, but

rather, satisfy the conditions[18]

$$\int{}^\Gamma\Psi^*(E){}^{\Gamma'}\Psi(E')=(1+R^2)_{\Gamma\Gamma'}{}^{-1}\delta(E-E').$$

Inserting (12) in (1) we have

$${}^\Gamma\sigma_v(E)=\frac{2\pi e^2\hbar^2}{m^2c\nu\omega}$$

$$\sum_{\substack{M_LM_S\mathfrak{M}\Gamma_\mu\Gamma\\m_1=\pm1}}\sum_{\Gamma'\Gamma''}\langle{}^{\Gamma'}\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}|\sum_i\nabla_i{}^{m_1}|\Phi_{LS}\rangle$$

$$\times\langle\Phi_{LS}|\sum_i\nabla_i{}^{m_1*}|{}^{\Gamma''}\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}\rangle{}^\Gamma A_{\Gamma'\Gamma''} \quad (13)$$

where

$${}^\Gamma A_{\Gamma'\Gamma''}=(1-iR)_{\Gamma\Gamma'}(1+iR)_{\Gamma''\Gamma}{}^{-1}. \quad (14)$$

Note that $\sum_\Gamma{}^\Gamma A_{\Gamma'\Gamma''}=(1+R^2)_{\Gamma''\Gamma'}{}^{-1}$, hence the total photo-ionization cross section can be obtained from Eq. (9) by substituting $(1+R^2)_{\Gamma''\Gamma'}{}^{-1}$ for ${}^\Gamma A_{\Gamma''\Gamma'}$ in Eq. (13).

If R (and therefore S) is diagonal in Γ and Γ', R and S may be represented as

$$R_{\Gamma\Gamma'}=\delta_{\Gamma\Gamma'}\tan\eta_\Gamma \quad (15)$$

$$S_{\Gamma\Gamma'}=\delta_{\Gamma\Gamma'}\exp(2i\eta_\Gamma). \quad (16)$$

From (3) and (16) we have

$$\lim_{r_{N+1}\to\infty}{}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}=2i$$

$$\times\exp(-i\eta_\Gamma)(2\pi\kappa_\Gamma)^{-1/2}{}^\Gamma\bar{\Phi}_{\mathcal{L}_\Gamma S_\Gamma}{}^{\mathfrak{M}\Gamma_\mu\Gamma}$$

$$\times\sin(\theta_\Gamma+\eta_\Gamma). \quad (17)$$

Equation (17) is just a standing wave representation of the final-state wave function and is valid as shown here only when S is diagonal in Γ and Γ', i.e., when the final-state channels are decoupled (or when there is only one open channel). The whole purpose of our writing down Eqs. (3)–(9) here was to provide a correct representation when coupling between channels is included. All calculations to date have used a standing wave representation for the final state. This is perfectly correct when coupling between channels is not included or when only one channel is open as in Refs. 1 and 3. With coupling, standing waves may still be used to represent the final state but then Eq. (13) must be used to evaluate the cross section in terms of the standing wave solutions ${}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}$.

III. THE HARTREE-FOCK AND CLOSE-COUPLING APPROXIMATIONS

The preceding section provides an exact formulation of the photoionization process within the framework of the dipole approximation with spin-independent forces. In order to perform calculations, further approximations

[18] The problem of normalization is discussed by U. Fano and F. Prats, Proceedings of the Symposium on Collisional Processes, Dehradun, India, published as Proc. of the Natl. Acad. Sci., India Sec. A, **33**, (1963) Part IV, pp. 553–562.

must be made. The basic approximations which we wish to consider here are the following:

1. The initial state of the system Φ_{LS} $(r_1,\cdots,r_{N+1})$ is represented by the Hartree-Fock solution for the term LS.

2. The final state ${}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}$ is represented by the solution of the close coupling equations which are obtained by applying the Kohn variational principle to a total wave function (diagonal in $\mathcal{L}_\Gamma$ and S_Γ) of the form

$$r_{N+1}{}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}\mathfrak{M}_{r^\mu r}(r_1\cdots r_{N+1})$$

$$=\frac{1}{(N+1)^{1/2}}\left(1-\sum_{i=1}^{N}P_{iN+1}\right)\left\{\left(\frac{2}{\pi\kappa_\Gamma}\right)^{1/2}r\bar\Phi_{\mathcal{L}_\Gamma S_\Gamma}\mathfrak{M}_{r^\mu r}\right.$$

$$\times(r_1\cdots r_N,r_{N+1}){}^\Gamma F_\Gamma(r_{N+1})+\sum_{\Gamma'}{}^{\Gamma'}\bar\Phi_{\mathcal{L}_\Gamma S_\Gamma}$$

$$\left.\times(r_1\cdots r_N;r_{N+1})\left(\frac{2}{\pi\kappa_{\Gamma'}}\right)^{1/2}{}^\Gamma F_{\Gamma'}(r_{N+1})\right\}. \quad (18)$$

Here, P_{ij} is the permutation operator which exchanges coordinates i and j:

$$P_{ij}\Psi(\cdots i,\cdots j,\cdots)=\Psi(\cdots j,\cdots i,\cdots).$$

The ion-core wave functions, $\bar\Phi_{L_\Gamma S_\Gamma}{}^{M\mu}(r_1,\cdots,r_N)$, are represented by Hartree-Fock solutions of the N-electron system corresponding to the term $L_\Gamma S_\Gamma$.

The Hartree-Fock method for bound states has been discussed by Hartree.[19] Basically what is involved is representing the wave function corresponding to a term LS as a superposition of determinantal wave functions, each element of which is represented by a one-particle wave function of the form

$$\Phi(r_i)=r_i^{-1}P_{nl}(r_i)Y_l^m(r_i)\sigma(i)$$

where $r_i^{-1}P_{nl}(r_i)$, $Y_l^m(r_i)$, and $\sigma(i)$ describe the radial, angular and spin dependence, respectively. Application of the Ritz variational principle to a wave function of this form results in a set of coupled integro-differential equations for the $P_{nl}(r_i)$ (which are assumed independent of M_L,M_S) which must be solved numerically, subject to the boundary conditions $P_{nl}(r_i)\xrightarrow{r\to0}r^{l+1}$ and $\int P_{nl}(r)P_{n'l}(r)dr=\delta_{nn'}$.

The close-coupling method for continuum states when Hartree-Fock solutions are used to represent the core wave functions has been outlined by Seaton.[20] The explicit formulation applicable to final states where the core consists of only closed subshells and a single (closed or open) subshell containing p electrons has been given by Smith, Henry, and Burke.[14] The method is similar to the Hartree-Fock method for bound states in that the total wave function of the system is diagonal in $\mathcal{L}_\Gamma$ and S_Γ and is represented by a sum of Slater determinants. Here, however, the wave functions for the core electrons are assumed given, and only the radial functions ${}^\Gamma F_{\Gamma'}$ for the continuum electron are varied.

[19] D. R. Hartree *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).
[20] M. J. Seaton, Phil. Trans. Roy. Soc. **A245**, 469 (1953).

If the ${}^\Gamma F_{\Gamma'}$ are subject to the boundary conditions

$$ {}^\Gamma F_{\Gamma'}(r)\xrightarrow{r\to0}r^{l_{\Gamma'}+1} \quad (19a)$$

and

$$ {}^\Gamma F_{\Gamma'}(r)\,\delta_{\Gamma\Gamma'}\xrightarrow{r\to\infty}\sin\theta_\Gamma+R_{\Gamma\Gamma'}\cos\theta_{\Gamma'} \quad (19b)$$

for open channels, and

$$ {}^\Gamma F_{\Gamma'}(r)\xrightarrow{r\to\infty}\exp(-|\kappa_\Gamma|r) \quad (19c)$$

for closed channels, then application of Kohn's variational principle leads to a set of coupled integro-differential equations for the ${}^\Gamma F_{\Gamma'}$ which are analogous to the Hartree-Fock equations for bound states. There are as many linearly independent solutions of these equations as there are open channels. Each solution (labeled by the superscript Γ) is specified by a row of the R matrix, and a set of ${}^\Gamma F_{\Gamma'}$, one F for each channel included (subscript Γ'), closed as well as open. The detailed form of these equations and a method for solving them is discussed by Smith *et al.*[14]

Using wave functions of this form, it is possible to write the expression for the photo-absorption cross section given by Eq. (13) in the form

$$ {}^\Gamma\sigma_v(E)=(2\pi e^2\hbar^2/m^2cv\omega)B(LS\mathcal{L}_\Gamma S_\Gamma)$$

$$\times\sum_{\Gamma'\Gamma''}{}^Vg_{\Gamma'}(E){}^\Gamma A_{\Gamma'\Gamma''}{}^Vg_{\Gamma''}(E). \quad (20a)$$

If we start from Eq. (8) rather than Eq. (2) we obtain the dipole length form of the cross section as

$$ {}^\Gamma\sigma_L(E)=(8\pi^3ve^2/c\omega)B(LS\mathcal{L}_\Gamma S_\Gamma)$$

$$\times\sum_{\Gamma'\Gamma''}{}^Lg_{\Gamma'}(E){}^\Gamma A_{\Gamma'\Gamma''}{}^Lg_{\Gamma''}(E). \quad (20b)$$

Here $B(LS\mathcal{L}_\Gamma S_\Gamma)$ is just a number which is determined from the angular-momentum coupling coefficients of the initial and final states, ${}^\Gamma A_{\Gamma'\Gamma''}$ may be determined from the R matrix by Eq. (14) and $g_\Gamma(E)$ is a function which depends only on the radial parts of the wave functions of the initial and final states and will differ in the length and velocity formulation.

The detailed form of the function $g_\Gamma(E)$ must be worked out for each particular electronic configuration. The general procedure is to express Φ_{LS} and ${}^\Gamma\Psi_{\mathcal{L}_\Gamma S_\Gamma}$ as antisymmetrized wave functions. Expressing Φ_{LS} by means of a fractional parentage expression allows one to perform the summations and angular integrations in Eq. (13) and yields the form of $g_\Gamma(E)$.

We consider here only the form of Eq. (20) for ionization of an electron from the $2p^q$ subshell in the configuration $1s^2 2s^2 2p^2\ {}^{2S+1}L$. For this case $B(LS\mathcal{L}_\Gamma S_\Gamma)=3q\delta_{S_\Gamma S}$ $\times(2\mathcal{L}_\Gamma+1)$ and $g_\Gamma(E)$ is given by the expression

$$g_\Gamma(E)=\sum_{\Gamma'}C_{\Gamma'}\left\{(2p|P_\Gamma|{}^\Gamma F_{\Gamma'})-\delta_{l_\Gamma 0}\right.$$

$$\times\left[\frac{(1s2s|{}^\Gamma F_{\Gamma'}2\bar s)}{(1s2s|1\bar s2\bar s)}(2p|P_{\Gamma'}|1s)\right.$$

$$\left.\left.+\frac{(1s2s|1\bar s{}^\Gamma F_{\Gamma'})}{(1s2s|1\bar s2\bar s)}(2p|P_{\Gamma'}|2s)\right]\right\}. \quad (21)$$
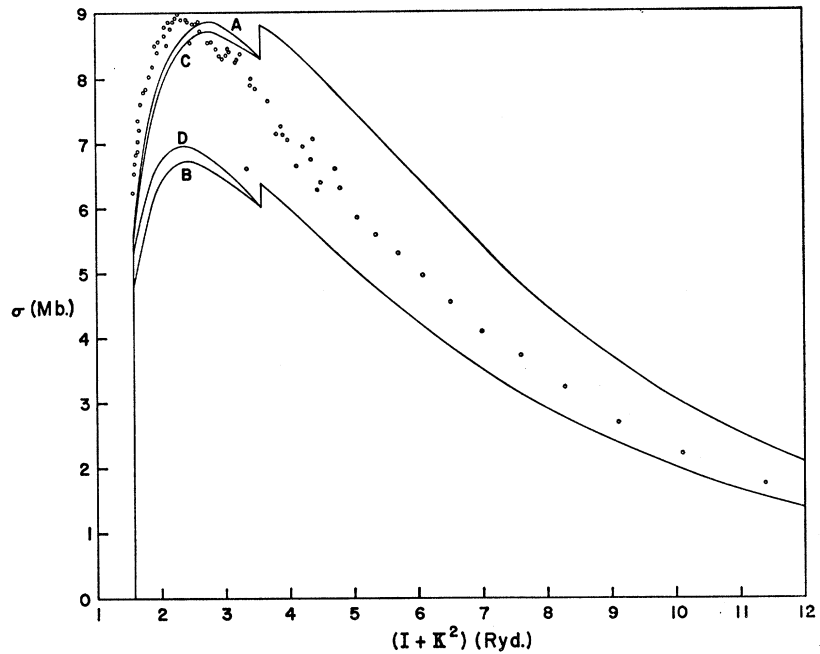
FIG. 1. Photo-ionization cross sections for neon. Curves A, C: Dipole-length approximation, using (i) and (iv), respectively; curves B, D: Dipole-velocity approximation, using (i) and (iv), respectively, O; Experimental results obtained by Samson.

Here,

$$C_\Gamma = (p^{q-1}S_\Gamma L_\Gamma p \mid \} p^q SL)C(11 l_\Gamma \mid 00)W(\mathcal{L}_\Gamma L_\Gamma 11 \mid l_\Gamma L)$$
$$\times (2p \mid 2\bar{p})^{q-1}(1s2s \mid 1\bar{s}2\bar{s})^2,$$

where $(p^{q-1}S_\Gamma L_\Gamma p \mid \} p^q SL)$ is the fractional parentage coefficient[21] and $C(abc \mid de)$ and $W(abcd; ef)$ are the Clebsch-Gordan and Racah coefficients.[21] Also, $(1s2s \mid 1\bar{s}2\bar{s}) = (1s \mid 1\bar{s})(2\bar{s} \mid 2\bar{s}) - (1s \mid 2\bar{s})(2s \mid 1\bar{s})$. The terms of the form $(a \mid b)$ are overlaps of the radial wave functions $1s$, $2s$, $2p$ of the atom and $1\bar{s}$, $2\bar{s}$, $2\bar{p}$ of the ion[22] and of the free wave orbitals $^\Gamma F_{\Gamma'}$. The radial operators are

$$P_\Gamma = \frac{d}{dr} + \left[1 + \frac{(1 - l_\Gamma)(2l_\Gamma + 1)}{2r} \right]$$

for the dipole velocity, and r for dipole length forms, respectively.

Equations (14), (20), and (21) provide a complete prescription for calculating photo-ionization cross sections given a Hartree-Fock solution for the ground state for the configuration $1s^2 2s^2 2p^q$ and a close coupling solution corresponding to the ionic core $1s^2 2s^2 2p^{q-1}$. The coupling between channels appears in the formula in two places; first in the explicit sum over channels in Eqs. (20a) and (20b) and second, implicitly due to the fact that the functions F_Γ and $F_{\Gamma'}$ will be modified by the coupling. The structure of Eq. (21) illustrates the effects of core relaxation. The term multiplying the $\delta_{l_\Gamma 0}$, apart

from the overlap integral, represents the relaxation of the ion core when photo-ionization takes place. The terms $(2p \mid P_{\Gamma'} \mid F)$ are just the radial dipole matrix elements for a single electron transition corresponding to $l \to l \pm 1$. The remainder of the expression corresponds to transitions in which the outer p electron goes to either the $1s$ or $2s$ orbital with ejection of an s electron and is nonvanishing if the ion- and atom-core orbitals are not orthogonal. This term, which represents an additional effect of core relaxation, we shall call the s-wave core-relaxation term.

The relationship between the present treatment and Bates' earlier treatment is clearly seen from Eqs. (20) and (21). If coupling between channels is ignored the sum in Eq. (20) over Γ' and Γ'' reduces to a single term for each channel Γ. Also, Bates' approximation for the squared matrix element ignores the s-wave core-relaxation term.

IV. PHOTO-IONIZATION OF NEON

Since previous calculations on neon photo-ionization (Refs. 4 and 5) performed using the methods outlined by Bates show relatively good agreement with experiment (Refs. 6–8) we expect the effects of coupling and core relaxation to be small.[23] To explore these effects we have performed calculations on neon using the methods outlined above. These calculations were performed using the Hartree-Fock wave functions of Clementi[24] for the

[21] G. Racah, Phys. Rev. 63, 367, (1943). For Clebsch-Gordon and Racah coefficients, we use the conventions of M. E. Rose, Elementary Theory of Angular Momentum (John Wiley & Sons, Inc., New York, 1957).

[22] Note that there may be different orbitals, nl for each of the channels Γ' because 2 different channels may have different ions.

[23] This is further illustrated by the calculations of J. W. Cooper [Phys. Rev. 128, 681 (1962)] who obtains moderate agreement with experiment neglecting core relaxation entirely. However, Cooper's calculations are expected to give poorer results closer to threshold than the methods used here since his method does not allow for different exchange effects in initial and final states.

[24] E. Clementi, IBM J. Res. Develop. 9, 2 (1965).

TABLE I. Photo-ionization for the outer subshell of neon. κ^2 is the energy above the ionization threshold. The various columns represent (i) uncoupled equations, no core-relaxation s-wave correction; (ii) uncoupled equations including core-relaxation s-wave corrections; (iii) coupled equations no core relaxation s wave correction; (iv) coupled equations with core relaxation s wave correction.

κ^2(Ry.)	Channel	Dipole length				Dipole velocity			
		(i)	(ii)	(iii)	(iv)	(i)	(ii)	(iii)	(iv)
0.1	(a)	1.72	1.55	1.97	1.79	1.25	1.45	1.69	1.92
	(b)	4.67	4.67	4.45	4.46	3.97	3.97	3.78	3.79
	Total	6.39	6.22	6.42	6.24	5.22	5.42	5.49	5.71
0.5	(a)	1.25	1.11	1.44	1.29	0.87	1.00	1.20	1.34
	(b)	6.93	6.93	6.70	6.72	5.63	5.63	5.46	5.46
	Total	8.18	8.04	8.15	8.01	6.50	6.63	6.66	6.80
1.0	(a)	0.91	0.80	1.07	0.95	0.61	0.69	0.85	0.94
	(b)	7.89	7.89	7.69	7.70	6.10	6.10	5.97	5.96
	Total	8.80	8.69	8.76	8.65	6.71	6.79	6.81	6.90
2.0	(a)	0.55	0.48	0.68	0.60	0.36	0.39	0.51	0.55
	(b)	7.83	7.83	7.66	7.67	5.65	5.65	5.49	5.49
	Total	8.38	8.31	8.34	8.26	6.01	6.04	6.00	6.04

Ne and Ne$^+$ wave functions and the methods outlined in Ref. 14 for the final state wave functions.

For neon we consider 3 final-state channels corresponding to the transitions

(a) $Ne(1s^2 2s^2 2p^6)\ ^1S_0 \rightarrow Ne^+(1s^2 2s^2 2p^5)+\epsilon s\ ^1P_e$,

(b) $Ne(1s^2 2s^2 2p^6)\ ^1S_0 \rightarrow Ne^+(1s^2 2s^2 2p^5)+\epsilon d\ ^1P_e$,

(c) $Ne(1s^2 2s^2 2p^6)\ ^1S_0 \rightarrow Ne^+(1s^2 2s\ 2p^6)+\epsilon p\ ^1P_e$.

Inner subshell ionization corresponding to (c) is expected to be small and the widths of the resonances below the $1s^2 2s 2p^6$ ionization limit indicate that channel (c) is weakly coupled to channels (a) and (b).[25] Consequently we have concentrated mainly on channels (a) and (b). A separate calculation corresponding to (c) was made using the uncoupled equation given by Dalgarno, Henry and Stewart[26] for this process and is included in the curve of the total photo-ionization Fig. 1 for completeness. The calculations were performed

[25] U. Fano and J. W. Cooper, Phys. Rev. **137**, A1364 (1965). While including the coupling with channel c is not expected to change the total cross section appreciably, such a calculation would be interesting since it would allow a detailed calculation of the cross section in the vicinity of the resonances below the $1s^2\ 2s\ 2p^6$ ionization limit.

[26] A. Dalgarno, R. J. W. Henry, and A. L. Stewart, Planetary Space Sci. **12**, 235 (1964). In this calculation the ion-core wave function of P. S. Kelly [Proc. Phys. Soc. (London) **83**, 533 (1964)] was used for Ne$^+$ ($1s^2\ 2s\ 2p^6$). The relative multiplet strengths are incorrect. For neon the value is 6 rather than unity.

both with and without coupling between channels (a) and (b) and the core relaxation s wave correction was evaluated explicitly to determine its effect. In Table I we show the results of these calculations in various stages of approximation.

The calculations show only a small change in the total photoionization cross section when the coupling is included. Using dipole length form the effect of coupling was to decrease the $p \rightarrow d$ contribution by about 5% at low energies and to increase the $p \rightarrow s$ contribution by about 14%. Since the $p \rightarrow s$ transition only contributes 25% to the total cross section in this region the net effect of coupling is a decrease of 1% in the total cross section. At higher energies the individual contributions become less affected resulting in virtually no change when coupling is included. In the dipole velocity approximation the effects were similar for the $p \rightarrow d$ and $p \rightarrow s$ transitions, except in this case there is a small net increase in the total cross section.

The allowance for the core relaxation s-wave correction term in computing the cross sections decreased the $p \rightarrow s$ contribution by about 13% in the dipole length approximation, and a similar increase in this contribution was noted in the dipole velocity cross section. The $p \rightarrow d$ contribution is naturally unchanged by this correction in the uncoupled approximation, and there was a negligible change in this contribution when coupled solutions were used. Again, since the $p \rightarrow s$ yields the minor contribution the net effect is a slight decrease in σ_L and a slight increase in σ_V.

The effects of coupling and the core-relaxation s-wave correction term, tend to bring the cross sections computed in the dipole length and dipole velocity approximations into closer agreement in the case of neon. However these effects are small except near threshold where the discrepancy between the dipole-length and dipole-velocity cross sections is halved on comparing the "full" calculation with the uncoupled one (Table I). There still remains a discrepancy between the two approximations which is probably due to the neglect of correlation and polarization.

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