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Dependence of photoabsorption spectra on long-range fields

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Strongly energy-dependent photoabsorption cross sections near excitation thresholds have been parametrized in terms of separate short- and long-range field contributions. The largest portion of this energy dependence results from standard parameters characterizing the long-range field effects; these parameters are known analytically for the most common outer fields, and can be calculated for others independently of the complicated short-range dynamics. The approach is illustrated in the Appendix by using a semiempirical fit to the *total* H^- photodetachment cross section to predict *partial* cross sections.

I. INTRODUCTION

Photoabsorption cross sections often vary rapidly with photon energy, particularly near the threshold for a new excitation process. This report develops a parametrization of these strong energy dependences using the methods of multichannel quantum defect theory (MQDT).[1,2] But whereas the original MQDT applied to photoelectrons escaping in a long-range Coulomb field, the present approach treats particle escape in an arbitrary long-range field. This formalism should then describe such diverse processes as negative-ion photodetachment, molecular photodissociation, and nuclear photodisintegration, in addition to atomic and molecular photoionization.

The most complete previous formulation of MQDT was the study of atomic photoabsorption by Lee and Lu.[3] They expressed cross sections in the discrete, autoionizing, and open portions of the spectrum in terms of two sets of parameters. The first set consists of rapidly varying but simple parameters which summarize the effect of the long-range Coulomb field. The second set compactly characterizes the short-range many-electron dynamics, and accordingly this set varies slowly with energy. The MQDT analysis was later extended by Lee[4] to treat negative-ion photodetachment, allowing for the energy dependence characterizing the long-range centrifugal field alone rather than the Coulomb field. Together, Refs. 1–4 have been instrumental in interpreting a large number of experimental photoabsorption measurements.[5]

More recently it became apparent that Seaton's classification of Coulomb field parameters[1] and Lee's classification of centrifugal field parameters[4] could be extended to arbitrary long-range fields. The article referred to below as Greene, Fano, and Strinati (GFS)[6] demonstrated this generality of MQDT and showed that the essential properties of any long-range field can be summarized by six basic parameters. In the present article, I will show how these parameters affect photoabsorption by different systems. The incorporation of the technology of GFS into the formulation of Lee and Lu is straightforward, though somewhat laborious. I present these results here to streamline applications in a broad class of systems, and also to introduce a matrix notation that may simplify future numerical implementations of MQDT. The advantages of such an analysis can be summarized as follows:

(a) The strongest contributions to the energy dependence of cross sections—namely, long-range field effects—are automatically built into the formulation. Thus experimental data near excitation thresholds can often be fitted in terms of a small number of constant or slowly varying short-range parameters.

(b) *Ab initio* calculations need to be performed only within a short-range "reaction zone" ($r<r_0$), since the outer field properties are already parametrized. Consequently, the calculation needs to be performed only over a coarse mesh of energies $\Delta\epsilon \gtrsim r_0^{-2}m^{-1}$ a.u., where m is the mass of the escaping particle in a.u.

These two advantages are illustrated in two recent articles: The semiempirical use (a) of the formalism of this paper (I) is demonstrated in a study of H^- photodetachment[7]; and the simplification of an *ab initio* calculation[8] (b) of K^- photodetachment is demonstrated in the paper (II) following this one.[9]

The parametrization of photoabsorption cross sections developed below (Sec. II) has distinct limitations which I will take care to point out. First, this formulation is not meant to include the photoeffect with more than a single escaping particle. The extension to multiple ionization processes is nontrivial and is a subject of current interest.[10] Second, only those single-particle ejection processes are treated for which the long-range potential $v(r)$ (between the particle and the residual aggregate) has certain properties. The potential must be local and central at sufficiently large radii $r > r_0$. At first sight this might seem to exclude the dipole polarization potential $-\alpha/2r^4$, which results from an off-diagonal r^{-2} potential in the close-coupling equations. The Appendix of the following paper[9] shows, however, that an MQDT treatment of this potential can be justified at sufficiently large radii by an adiabatic diagonalization. Finally, the potential $v(r)$ is assumed to become constant at $r \to \infty$, which excludes photoabsorption in the presence of external electric and/or magnetic fields. Yet some adaptation of the present MQDT procedures might prove useful for these problems as well.

II. PARAMETRIZATION OF THE PHOTOABSORPTION PROCESS

The key conclusion of GFS to be used below is that relationships between three alternative pairs of independent solutions determine the energy dependences induced by the outer field. One pair of solutions (f^0, g^0) is independent of the energy ϵ at small radii $r \sim 0$, and is analytic in ϵ at all finite r. A second pair of solutions (f, g) oscillate 90° out of phase at large r, each with the energy-normalized amplitude $(2m/\pi k)^{1/2}$. The reduced mass m of the escaping particle was set equal to unity in GFS; by including it explicitly, I allow for the escape of particles with different masses. Finally, the third pair of solutions (f^-, f^+) are incoming (outgoing) waves at $\epsilon > 0$ and rising (falling) exponentials at $\epsilon < 0$. The relationships between these three pairs of solutions were written formally in Table I of GFS in terms of six energy-dependent parameters: $\{\beta(\nu, l),\ D(\nu, l),\ A(\nu, l)$ and $\mathcal{G}(\epsilon, l)\}$ occur at $\epsilon = -1/2m\nu^2 < 0$, and $\{\eta(k, l),\ B(k, l)$ and $\mathcal{G}(\epsilon, l)\}$ occur at $\epsilon = k^2/2m \geq 0$.

To summarize briefly, the connection between the three alternative base pairs can be parametrized in general as

$$\begin{bmatrix} f \\ g \end{bmatrix} = \begin{cases} -\left(\dfrac{m}{2\pi k}\right)^{1/2} \begin{bmatrix} ie^{i\eta} & -ie^{-i\eta} \\ e^{i\eta} & e^{-i\eta} \end{bmatrix} \begin{bmatrix} f^+ \\ f^- \end{bmatrix}, & \epsilon > 0 \qquad (2.1a) \\ -\left(\dfrac{m\nu}{\pi}\right)^{1/2} \begin{bmatrix} D\cos\beta & -D^{-1}\sin\beta \\ D\sin\beta & D^{-1}\cos\beta \end{bmatrix} \begin{bmatrix} f^+ \\ f^- \end{bmatrix}, & \epsilon < 0 \qquad (2.1b) \end{cases}$$

$$\begin{bmatrix} f \\ g \end{bmatrix} = \begin{cases} \begin{bmatrix} B^{1/2} & 0 \\ B^{-1/2}\mathcal{G} & B^{-1/2} \end{bmatrix} \begin{bmatrix} f^0 \\ g^0 \end{bmatrix}, & \epsilon > 0 \qquad (2.2a) \\ \begin{bmatrix} A^{1/2} & 0 \\ A^{-1/2}\mathcal{G} & A^{-1/2} \end{bmatrix} \begin{bmatrix} f^0 \\ g^0 \end{bmatrix}, & \epsilon < 0 . \qquad (2.2b) \end{cases}$$

The parameters η and β are thus interpreted as long-range field contributions to the phase shift, while B and A are amplitude parameters which relate f and f^0. The mixing parameter $\mathcal{G}$ was introduced by Seaton for the long-range Coulomb field, and has an analog for all other fields, as discussed in GFS. Finally, the parameter D rescales the falling and rising exponentials (f^+, f^-) for negative energies. These parameters are tabulated in Table I of GFS for the attractive Coulomb field, zero field, and for the dipole field. [Note, however, that the expression for the Coulomb field amplitude parameter B, given in Table I of GFS, should actually contain an additional factor $e^{\pi/k}$, as in Eq. (2.25) of that reference.] Next, I will show how these parameters enter the photoabsorption cross section.

A. Dissociation and eigenchannel representations

As in Ref. 3, I consider N dissociation channels i characterized in jj coupling by the energy ϵ_i and angular momenta $(s_i l_i) j_i$ of an escaping photoparticle with reduced mass m_i, and by a residual aggregate of particles (e.g., an atom) in a discrete state with energy E_i and angular momentum J_i. If the escaping photoparticle has internal degrees of freedom, then corresponding quantum numbers must also be specified in addition to the internal angular momentum s_i of the photoparticle and the orbital angular momentum l_i of the photoparticle-aggregate compound. Conservation of the total energy E requires

$$E = E_i + \epsilon_i ,$$

where

$$\epsilon_i = \begin{cases} k_i^2/2m_i , & \epsilon_i \geq 0 \\ -1/2m_i\nu_i^2 , & \epsilon_i < 0 . \end{cases} \qquad (2.3)$$

The amplitude for the photoabsorption is proportional to the dipole matrix element $(\psi_f | \sum_q z_q | \psi_0)$, where ψ_0 is the initial state of the compound, where the summation includes the z coordinates of all particles, and where ψ_f is a final-state wave function satisfying appropriate boundary conditions at $r \to \infty$. MQDT postpones the application of this boundary condition,[2] and instead considers a set of N independent, unnormalized solutions of the Schrödinger equation in the outer field:

$$\psi_i' = r^{-1}\mathcal{A} \sum_{j=1}^{N} \phi_j [f_j(r)\delta_{ji} - g_j(r)K_{ji}] , \quad r \geq r_0 . \qquad (2.4)$$

In this expression (f_j, g_j) are the energy normalized solutions appropriate to the long-range field at $r \geq r_0$ in channel j. The quantity ϕ_j includes the wave function of the residual aggregate, any internal wave function of the photoparticle, and the orbital and spin-wave functions of the compound. The calculation can be performed separately for each value of the total angular momentum J, so ϕ_j also includes the angular momentum coupling in the scheme $[(s_i l_i) j_i J_i]J$. While ϕ_j is usually independent of r, it may include an adiabatic dependence on r, such as that described in the Appendix of paper II. Finally, in Eq. (2.4), $\mathcal{A}$ is an antisymmetrization operator and K_{ij} is the symmetric "smoothed" reaction matrix which was denoted $-\pi K^{(s)}$ in GFS.

The solutions (2.4) can be written in a matrix notation similar to that used by Seaton[1]:

$$\underline{\psi}' = \underline{\phi f} - \underline{\phi g}\,\underline{K}\,, \quad r \geq r_0\,, \tag{2.5}$$

where ψ'_{ij} is an $N \times N$ matrix representation of N independent solutions ($j = 1, 2, \ldots N$). Thus each column of $\underline{\psi}'$ is a separate solution, while the ith row of that column is its component in channel i. Both $\underline{\phi f}$ and $\underline{\phi g}$ are diagonal matrices where, for example, the jth element of $\underline{\phi f}$ is $r^{-1}\mathcal{A}\phi_j f_j$. As in Ref. 3, I shall represent the "smooth" reaction matrix $\underline{K}$ in terms of its eigenvalues $\tan\pi\mu_\alpha$ and its eigenvectors $U_{i\alpha}$ by formally solving

$$\underline{K}\,\underline{U} = \underline{U}\tan\pi\underline{\mu}\,. \tag{2.6}$$

The set of solutions ψ'_{ij} is then transformed into a new representation $\psi_{i\alpha}$ in which $\underline{K}$ is diagonal:

$$\underline{\psi} = \underline{\psi}'\,\underline{U}\cos\pi\underline{\mu}\,,$$

or

$$\underline{\psi} = \underline{\phi f}\,\underline{U}\cos\pi\underline{\mu} - \underline{\phi g}\,\underline{U}\sin\pi\underline{\mu}\,, \quad r \geq r_0\,. \tag{2.7}$$

A solution satisfying particular boundary conditions at $r \to \infty$ will be written as a column vector Ψ_i and is specified by a superposition of the N columns of $\psi_{i\alpha}$ with coefficients a_α:

$$\vec{\Psi} = \underline{\psi}\,\vec{a}\,. \tag{2.8}$$

B. Boundary conditions

The boundary conditions differ for the open and closed dissociation channels. Accordingly, I will adopt the notation of Lee and subdivide the N dissociation channels i into a set P_J of N_P open channels, and a set Q_J of $N_Q = N - N_P$ closed channels at a given energy E. Though I deal with specified values of the parity π and total angular momentum J, the labels J^π will be suppressed unless necessary.

(i). Closed channels ($i \in Q_J$). The component of the wave function in each closed channel must vanish exponentially as $r \to \infty$. This condition on channel i can be expressed in terms of a Wronskian[11] as

$$W(f_i^+, r\Psi_i) = 0\,, \quad i \in Q_J\,, \tag{2.9}$$

where f_i^+ is the falling exponential solution in the outer field of channel i. This Wronskian can be evaluated using Eqs. (2.1), (2.7), and (2.8). This gives

$$\sum_{\alpha=1}^{N} F_{i\alpha} a_\alpha = 0\,, \tag{2.10}$$

where

$$F_{i\alpha} = U_{i\alpha}\sin(\beta_i + \pi\mu_\alpha)\,, \quad i \in Q_J\,. \tag{2.11}$$

[Here β_i has been introduced as a shorthand for $\beta(\nu_i, l_i)$.]

(ii). Open channels ($i \in P_J$). The open dissociation channels must satisfy the complex incoming wave boundary condition. But before applying this boundary condition I will adopt the usual MQDT approach, and first identify an intermediate set of N_P real solutions, the collision eigenchannels ρ. These diagonalize the open channel portion of the short-range scattering matrix (which was denoted $\underline{S}_{00}$ by Seaton[1]). The ρth collision eigenchannel wave function $(\vec{\Psi})_\rho = \Psi_{i\rho}$ has a common phase shift δ_ρ in each dissociation channel i at $r \to \infty$:

$$\Psi_{i\rho} \xrightarrow[r \to \infty]{} r^{-1}\mathcal{A}\phi_i (2m_i/\pi k_i)^{1/2} \times \sin(k_i r - i\zeta_i \ln r + \eta_i + \delta_\rho) T_{i\rho}\,. \tag{2.12}$$

(The parameter ζ_i equals i/k_i for an attractive Coulomb field, and vanishes otherwise.[6]) Here the collision eigenphase shift δ_ρ and the real orthogonal matrix $T_{i\rho}$, remain to be determined. Note also that each solution vector $(\vec{\Psi})_\rho (\rho = 1, \ldots N_P)$ is a superposition with a different coefficient vector $(\vec{a})_\rho \equiv a_{\alpha\rho}$, where now $\underline{a}$ is an $N \times N_P$ matrix. Thus Eq. (2.8) is generalized in the presence of more than one open channel to the form

$$\underline{\Psi} = \underline{\psi}\,\underline{a}\,. \tag{2.13}$$

The boundary condition (2.12) can also be expressed as a pair of Wronskian conditions,[11]

$$\left.\begin{aligned} &W(f_i\cos\delta_\rho - g_i\sin\delta_\rho, r\Psi_{i\rho}) = 0\,, \\ &W(f_i\sin\delta_\rho + g_i\cos\delta_\rho\,, r\Psi_{i\rho}) = T_{i\rho}(2/\pi)\,, \end{aligned}\right. \quad i \in P_J\,. \tag{2.14}$$

The first of these two equations, when combined with Eq. (2.1), gives a joint condition on $\delta_\rho(E)$ and $a_{\alpha\rho}(E)$:

$$\sum_\alpha F_{i\alpha}(E, \delta_\rho) a_{\alpha\rho}(E) = 0\,, \tag{2.15}$$

where

$$F_{i\alpha}(E,\delta_\rho)=\begin{cases} U_{i\alpha}\sin(-\delta_\rho+\pi\mu_\alpha)\,, & i\in P_J \\ U_{i\alpha}\sin(\beta_i+\pi\mu_\alpha)\,, & i\in Q_J\,. \end{cases} \tag{2.16}$$

C. Solution of the homogeneous system

The homogeneous system, Eqs. (2.15) and (2.16), reflects the quite different physics in different portions of the spectrum.

(i) Discrete spectrum (all channels closed). In this energy range there are no undetermined parameters in the matrix $F_{i\alpha}(E)$ of (2.15). Thus, at an arbitrary energy E the determinant of coefficients $\det \underline{F}$ will usually fail to vanish and no solution will exist. However, β_i is usually a rapidly varying function of the energy, and at certain energies the determinant may vanish $\det \underline{F}=0$. This implies the existence of a bound state of the compound system at energy E_n. An unnormalized solution vector $\vec{a}(E_n)$ of the system (2.15) is then given by

$$a_\alpha(E_n)=C_{i\alpha}(E_n)\bigg/\left(\sum_i C_{i\alpha}^2(E_n)\right)^{1/2}, \tag{2.17}$$

where $C_{i\alpha}$ is the $i\alpha$th cofactor of the matrix $\underline{F}$. [Note that different choices of the index i on the right-hand side of (2.17) yield equal results.] This solution determines the final-state wave function (2.8) at energy E_n to within its normalization integral, given by GFS Eq. (2.53) to be

$$N_n^2=\pi^{-1}\sum_{i,\alpha}\left[a_\alpha U_{i\alpha}\cos(\beta_i+\pi\mu_\alpha)\right] \times\frac{d}{d\epsilon_i}\left(\sum_{\alpha'}a_{\alpha'}U_{i\alpha'}\sin(\beta_i+\pi\mu_{\alpha'})\right). \tag{2.18}$$

(ii) Autoionizing spectrum (some channels open, some closed). In contrast to the discrete spectrum, there are now N_P allowed solutions to the Schrödinger equation at *all* energies. This is reflected in Eq. (2.15) by the presence of an unknown parameter δ_ρ in the matrix $F_{i\alpha}(E,\,\delta_\rho)$. Its determinant $\det \underline{F}$ must be *forced* to vanish by varying δ_ρ. The value of δ_ρ at a zero of $\det \underline{F}$ is then the desired collision eigenphase shift. The unnormalized coefficients entering Eq. (2.13) are then

$$a_{\alpha\rho}(E)=C_{i\alpha}(E,\delta_\rho)\bigg/\left(\sum_i C_{i\alpha}^2(E,\delta_\rho)\right)^{1/2}, \tag{2.19}$$

where again $C_{i\alpha}$ is the cofactor of $F_{i\alpha}$. The orthogonal matrix $T_{i\rho}$ (denoted $\langle i\,|\rho\rangle$ by Lee[4]) is now constructed by evaluating the second Wronskian of (2.14),

$$T_{i\rho}=\sum_\alpha U_{i\alpha}\cos(-\delta_\rho+\pi\mu_\alpha)a_{\alpha\rho}(E)/N_\rho\,, \tag{2.20}$$

where

$$N_\rho^2=\sum_{i\in P_J}\left(\sum_\alpha U_{i\alpha}\cos(-\delta_\rho+\pi\mu_\alpha)a_{\alpha\rho}(E)\right)^2. \tag{2.21}$$

The element $T_{i\rho}$ is the amplitude of the ith dissociation channel contained in the collision eigenchannel ρ.

(iii) Open continuum (all channels open). In this portion of the spectrum, the system (2.15) is solved by inspection,

$$\begin{aligned} a_{\alpha\rho}&=\delta_{\alpha\rho}=\begin{cases}1, & \alpha=\rho\\ 0, & \alpha\neq\rho\end{cases}\\ \delta_\rho&=\sum_\alpha \pi\mu_\alpha\delta_{\alpha\rho}=\pi\mu_\rho\,,\\ T_{i\rho}&=\sum_\alpha U_{i\alpha}\delta_{\alpha\rho}=U_{i\rho}\,,\\ N_\rho&=1\,. \end{aligned} \tag{2.22}$$

D. Reduced dipole matrix element

Calculation of the cross section for photoionization into a specified open channel j, requires the final-state wave function Ψ^f to satisfy the "incoming-wave boundary condition" specifying that the outgoing wave $(2i)^{-1}(2m_j/\pi k_j)^{1/2}\phi_j f_j^+$, *has nonzero amplitude in the* jth *channel alone*. I indicate this final-state wave function by $(\vec{\Psi}^-)_j$; its ith component Ψ_{ij}^- must satisfy

$$W(f_i^-,r\Psi_{ij}^-)=\delta_{ij}(2k_jm_j/\pi)^{1/2}\,. \tag{2.23}$$

These functions Ψ_{ij}^- can be constructed by superposing the collision eigenchannels in the form

$$\Psi_{ij}^-=\sum_\rho \Psi_{i\rho}b_{\rho j}^-=(\underline{\Psi}\,\underline{b}^-)_{ij}=(\underline{\psi}\,\underline{a}\,\underline{b}^-)_{ij}\,, \tag{2.24}$$

where

$$b_{\rho j}^-=e^{-i(\eta_j+\delta_\rho)}T_{j\rho}\,. \tag{2.25}$$

That (2.25) satisfies (2.23), follows from the orthogonality of $T_{j\rho}$ and from the large-r form (2.12) of $\Psi_{i\rho}$. Then the reduced dipole matrix element is, in the notation of Lee,[12]

$$D(j,J)=\sum_{\rho=1}^{N_P}e^{i(\eta_j+\delta_\rho)}T_{j\rho}\left(\sum_\alpha D_\alpha a_{\alpha\rho}/N_\rho\right). \tag{2.26}$$

Here, D_α is the matrix element $(\psi_\alpha\,|\sum_q z_q|\,\psi_0)$, where ψ_α is the αth eigenchannel solution whose asymptotic form contains components $\psi_{i\alpha}$ in each dissociation channel i. The ground-state wave function of the compound system is written as ψ_0. The photoabsorption cross section corresponding to channel j and angular momentum J is then (in a.u.),

$$\sigma(j,J)=(4\pi^2\omega/137)\,|D(j,J)\,|^2\,, \tag{2.27}$$

where ω is the photon energy in a.u. The total cross section instead is given by

$$\sigma=\left(\frac{4\pi^2\omega}{137}\right)\sum_{J,\rho}N_\rho^{-2}\left(\sum_\alpha D_\alpha a_{\alpha\rho}\right)^2 . \tag{2.28}$$

The angular distributions and spin polarizations of ejected particles can be calculated by directly inserting the calculated dipole matrix element $D(j,J)$ into the formulas of Lee.[12]

Finally, I note that the formulas of this section also provide a parametrization of the full scattering matrix, given by

$$\begin{aligned}S_{ij}={}&\exp[i(\eta_i+\tfrac{1}{2}l_i\pi+i\zeta_i\ln 2k_i)]\\&\times\left(\sum_\rho T_{i\rho}e^{2i\delta_\rho}T_{j\rho}\right)\exp[i(\eta_j+\tfrac{1}{2}l_j\pi+i\zeta_j\ln 2k_j)],\end{aligned} \tag{2.29}$$

where the quantity in large parentheses is usually called the "short-range scattering matrix."

III. FURTHER REDUCTION OF PARAMETERS

A. Removal of strong energy dependences

The short-range parameters μ_α, $U_{i\alpha}$, and D_α discussed above, were defined with reference to the energy-normalized pair of long-range field solutions (f_i, g_i). These solutions are nonanalytic functions of ϵ_i and may have a strong energy dependence near an excitation threshold, where $\epsilon_i \sim 0$. This nonanalyticity is very weak for the attractive Coulomb field and has been justifiably ignored in usual quantum defect theory (QDT) applications, though it did prove important in a study of neon photoabsorption.[13] The energy dependence of (f_i, g_i) for other fields is essential, e.g., giving rise to the Wigner threshold laws in a purely centrifugal outer field. In the following, I will further parametrize the energy dependence of μ_α, $U_{i\alpha}$, and D_α resulting from that of (f_i, g_i); it involves the long-range QDT parameters $A(\nu,l)$, $B(k,l)$, and $\mathcal{G}(\epsilon,l)$ which relate (f_i,g_i) to the analytic base pair (f_i^0, g_i^0) through Table I of GFS or Eq. (2.2) above.

The most general possible form of the transformation will be considered initially, written for the ith channel as

$$\begin{aligned}f_i&=\Gamma^i_{ff}f_i^0+\Gamma^i_{fg}g_i^0,\\ g_i&=\Gamma^i_{gf}f_i^0+\Gamma^i_{gg}g_i^0.\end{aligned} \tag{3.1}$$

Since the Wronskian $W(f_i,g_i)=2/\pi$ is independent of energy, it is conventional to normalize $W(f_i^0,g_i^0)$ to $2/\pi$ as well, which implies that $\Gamma^i_{ff}\Gamma^i_{gg}-\Gamma^i_{fg}\Gamma^i_{gf}=1$ for all channels. The set (2.5) of N independent solutions $\underline{\psi}'$ to the outer field multichannel Schrödinger equation can be replaced by a new smoother set $\underline{\psi}'^0$ defined by its large r form

$$\underline{\psi}'^0=\underline{\phi f}^0-\underline{\phi g}^0\underline{K}^0 . \tag{3.2}$$

This implies that the energy dependences of $\underline{K}$ and $\underline{\psi}'$ are given by

$$\begin{aligned}\underline{K}&=(\underline{\Gamma}_{fg}+\underline{\Gamma}_{ff}\underline{K}^0)(\underline{\Gamma}_{gg}+\underline{\Gamma}_{gf}\underline{K}^0)^{-1},\\ \underline{\psi}'&=\underline{\psi}'^0(\underline{\Gamma}_{gg}+\underline{\Gamma}_{gf}\underline{K}^0)^{-1},\end{aligned} \tag{3.3}$$

where the matrices $\underline{\Gamma}_{ff}$, $\underline{\Gamma}_{fg}$, etc. are diagonal in ij. The eigenchannel representation in the transformed basis (f_i^0, g_i^0) is given explicitly by (2.6) and (2.7), provided $\underline{\psi}$, $\underline{K}$, $\underline{U}$, and $\underline{\mu}$ are replaced by $\underline{\psi}^0$, $\underline{K}^0$, $\underline{U}^0$, and $\underline{\mu}^0$. The two sets of eigenchannel solutions are then related by

$$\underline{\psi}=\underline{\psi}^0[(\underline{\Gamma}_{gg}\underline{U}^0\cos\pi\underline{\mu}^0+\underline{\Gamma}_{gf}\underline{U}^0\sin\pi\underline{\mu}^0)^{-1}\underline{U}\cos\pi\underline{\mu}] . \tag{3.4}$$

This same matrix in (3.4) also relates the D_α to the smoother D_α^0:

$$\underline{D}=\underline{D}^0(\ldots) . \tag{3.5}$$

For those dissociation channels i strongly open (i.e., $\epsilon_i \gg r_0^{-2}m_i^{-1}$), the threshold nonanalyticity has no consequence, and the transformation matrices should be taken as $\Gamma^i_{gg}=\Gamma^i_{ff}=1$, $\Gamma_{fg}=\Gamma_{gf}=0$. For other channels with $\epsilon_i \approx 0$, the strong energy dependence should be explicitly removed by setting

$$\left.\begin{aligned}\Gamma^i_{ff}&=A^{1/2}(\nu_i,l_i),\\ \Gamma^i_{fg}&=0,\\ \Gamma^i_{gf}&=A^{-1/2}(\nu_i,l_i)\mathcal{G}(\epsilon_i,l_i),\\ \Gamma^i_{gg}&=A^{-1/2}(\nu_i,l_i),\end{aligned}\quad\right.\epsilon_i\leqslant 0 \tag{3.6}$$

and identical expressions with $A(\nu_i,l_i)$ replaced by $B(k_i,l_i)$ for channels with $\epsilon_i \geqslant 0$. See Table I of GFS for a tabulation of these parameters for different long-range fields.

The following paper[9] discusses a different use of the "smoothing" transformation $\underline{\Gamma}$, whereby the outer region can be treated in successive stages of approximation. A sensible *first approximation* to the negative-ion photodetachment problem takes the electron-atom potential at large r to be zero field alone; this requires setting the boundary of the inner region at a large radius ($r_0 \sim 10^3$ a.u.) so that the polarization field is negligible for $r>r_0$. In such a treatment (f^0, g^0) are simply the spherical Bessel functions renormalized to be energy independent at $r=0$; effects of the polarization field must then be regarded as "short-range" dynamics. This point of view was adopted by Norcross and Taylor[8] in their close-coupling studies of the problem. They found, however, that the short-range dynamics caused a fast energy dependence of $\underline{K}^0$ and $\underline{D}^0$ *in the zero-field* *basis* (see, e.g., Figs. 5–7 of the following paper[9]). At the *second stage of approximation* the analytic base pairs (f^0, g^0) are taken to be the exact Mathieu function solutions to the polarization potential Schrödinger equation. Since much more of the long-range properties are built into the Mathieu (f^0, g^0), the inner region needs to extend only to $r_0 \sim 30$ a.u., and the $\underline{K}^0$ and $\underline{D}^0$ *in the polarization field basis* are then essentially constant over the energy range of interest. The matrices $\underline{\Gamma}$ discussed above are then regarded not as a transformation between (f, g) and (f^0, g^0), but rather as the transformation between the zero field (f^0, g^0) and the polarization field (f^0, g^0) at $r = \infty$. These details are worked out explicitly in Sec. III of the following paper.

B. Frame transformation treatment

For most atoms and negative ions the exchange energy is much larger than the spin-orbit energy when all electrons reside within $r < r_0$. To this extent the short-range α eigenchannels should be approximately LS-coupled, while the long-range dissociation channels i are jj coupled. To reflect this feature of the atomic dynamics, the orthogonal matrix $U^0_{i\alpha}$ is written as a product of two factors:

$$\underline{U}^0 = \underline{X}\,\underline{V}^0 . \tag{3.7}$$

The matrix $X_{i\bar{\alpha}}$ is the geometrical transformation from LS-coupled $\bar{\alpha}$ channels to jj-coupled i channels. The orthogonal matrix $V^0_{\bar{\alpha}\alpha}$ is then approximately block diagonal in L and S.

Two simplifications result when $V^0_{\bar{\alpha}\alpha}$ is block diagonal. Firstly, the number of independent parameters to be fitted in a semiempirical analysis of data is reduced; Lee's study of Cs$^-$ photodetachment[4] demonstrated this for a four-channel problem. Whereas a 4×4 $U^0_{i\alpha}$ would have six independent elements, each of the two submatrices $V^0_{\bar{\alpha}\alpha}$ has a single independent parameter (a mixing angle of *sp* and *ps* for the singlets and one for the triplets). Similarly, Lee had to fit only two dipole matrix elements connecting the initial and final singlet states, rather than four. Secondly, block diagonality of $\underline{V}^0$ implies a simplification of *ab initio* calculations of the photoabsorption. This results because the matrix $V^0 \tan \pi\underline{\mu}^0 V^{0T}$ can be interpreted as a set of uncoupled reaction matrices $\underline{K}^0(L,S)$. The matrices $\underline{K}^0(L,S)$ can thus be *calculated separately* for given L and S, ignoring spin-orbit terms in the Hamiltonian, and *then* transformed to jj coupling by the factor $\underline{X}$ of Eq. (3.7). The effect of spin-orbit coupling is introduced finally through the transformation (3.1) by entering in the elements of the matrices Γ electron energy values pertaining to each relevant fine-structure channel. Norcross and Taylor[8] have successfully used this approach in a recent calculation of K$^-$ photodetachment. (While the frame transformation treatment of the present subsection has utilized the short-range LS-coupling scheme, the formulation is useful whenever the short-range Hamiltonian is nearly diagonal in *any* standard representation.)

C. Numerical fitting

The multichannel parametrization of energy-dependent photoabsorption cross sections has been used in the past primarily to interpret data semiempirically. This step serves to express a large number of rapidly varying observables in terms of a few (fitted) slowly varying parameters $U^0_{i\alpha}$, D^0_{α}, and μ^0_{α}. For example, Starace predicted photoabsorption *cross sections* after fitting to the *energy-level positions* of perturbed neon Rydberg spectra.[13] In other applications, a fit to the total photoabsorption cross section has been used to predict branching ratios, angular distributions, and spin polarizations of the emitted photoelectrons.[2] Here I summarize the procedure to be followed in numerical fitting.

The basic idea is to guess trial values for the μ^0_{α}, $U^0_{i\alpha}$ (or $V^0_{\bar{\alpha}\alpha}$), and D^0_{α}, after which the algebraic manipulations of Sec. II determine corresponding trial values of the observables near threshold. (The long-range field parameters A, B, $\mathcal{G}$, η, β, and D are provided by an independent calculation.) Over an energy range of $\Delta\epsilon \lesssim r_0^{-2} m^{-1}$ near threshold, the short-range parameters can be assumed energy independent at least in a first approximation. The trial values of μ^0_{α} and $U^0_{i\alpha}$ then determine $\underline{K}^0 = \underline{U}^0 \tan \pi\underline{\mu}^0 \underline{U}^{0T}$. The energy-dependent reaction matrix $\underline{K}$ is then given by Eqs. (3.3) and (3.6) in terms of the energy-independent $\underline{K}^0$ and of the energy-dependent long-range field parameters. At each energy E for which a measurement is known, the matrix $\underline{K}$ should be diagonalized as in Eq. (2.4); this determines $U_{i\alpha}$ and μ_{α}, and also D_{α} through Eqs. (3.4) and (3.5). The matrix $F_{i\alpha}$ in (2.14) can now be constructed and solved as in Sec. II C. When all channels are closed this procedure determines trial energy levels. In the presence of N_P open channels, the procedure determines N_P values of δ_ρ and N_ρ and the $N_P \times N_P$ orthogonal matrix $T_{i\rho}$, at each energy. Finally, the observables (e.g., the total cross section) can be calculated (Sec. II D) over the experimental interval and compared with the data. Standard computer least-squares minimization programs can be used to repeat this entire procedure automatically until the values of μ^0_{α}, $U^0_{i\alpha}$, and D^0_{α} are found which best reproduce the experimental results. A further energy dependence of these parameters can be introduced if necessary.

IV. DISCUSSION

The point of view of GFS and the present paper holds that particle escape in any long-range field can be treated by MQDT methods once the long-range field parameters (A, B, $\mathcal{G}$, β, η, and D) are known for that field. These parameters have been specified for only a few potentials; this includes the attractive Coulomb ($-r^{-1}+r^{-2}$), the attractive dipole ($-r^{-2}$), and the repulsive centrifugal or zero potential ($+r^{-2}$). Paper II calculates the long-range field parameters for the polarization potential ($-r^{-4}+r^{-2}$). Long-range fields yet to be treated in this framework include the following:

(i) Combination of attractive Coulomb and polarization potential ($-r^{-1}+r^{-2}-r^{-4}$). A polarization potential induces an extra energy dependence of the Coulomb long-range field parameters; its effect could be determined by the methods of Sec. II E of GFS. The largest effect (near threshold) of the r^{-4} potential is to shift the Coulomb parameters $\beta(\nu, l)$ and $\eta(k, l)$ by a constant amount, as is known from perturbation treatments. A numerical or semianalytical method for handling effects of this outer field should simplify studies of alkaline earth atom photoionization near excited states of the residual positive ion.

(ii) Interatomic potentials. An MQDT treatment of the Morse or Lennard-Jones molecular potentials should relate high-lying vibrational states to the continuum states of the dissociating molecule. These potentials converge rapidly at $r=\infty$ and modify the parameters of zero long-range field. The Morse potential may be the simplest to treat because its radial Schrödinger equation reduces to the confluent hypergeometric equation.[14] By including photodissociation and photoionization channels simultaneously, the competition between these processes can be analyzed. Work on this general problem is currently in progress elsewhere.[15]

(iii) Repulsive Coulomb potential ($r^{-1}+r^{-2}$). Effects of the outer Coulomb field are clearly important in treating the photodissociation of positive molecular ions. A parametrization of the effects of an outer Coulomb field may also prove useful for treating photoabsorption by nuclei with ejection of protons or α particles. Adaptation of results for an attractive Coulomb field is probably straightforward, but it has not yet been investigated.

(iv) Relativistic effects. Recently Zilitis[16] and Johnson and Cheng[17] have independently extended Seaton's quantum defect theory to describe the motion of a Dirac electron in a long-range Coulomb field. With modest effort the relativistic version of MQDT could also be incorporated into the present framework. Once this work is completed it should be straightforward to parametrize the escape of a Dirac particle in any long-range field.

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APPENDIX: APPLICATION TO H$^-$ PHOTODETACHMENT

Very recently the formulation of Secs. II and III of the present article was used to fit and interpret a series of H$^-$ Feshbach resonances converging to the $n=3$ level of hydrogen.[7] Here I point out a simplified analysis using Fano profiles and some additional implications of that analysis.[7] Actually two infinite series of resonances exist, since the long-range potential has the form (in a.u.)

$$V_i(r) \xrightarrow[r\to\infty]{} a_i/2r^2\,, \tag{A1}$$

where

$$a_{3+} = -5.220\,,$$

$$a_{3-} = -14.897\,.$$

(In this Appendix I ignore fine-structure splittings between the 3s, 3p, and 3d levels of hydrogen, and I also ignore channels with a_i positive.) For dynamical reasons discussed in Ref. 7, the coupling between 3+ and 3− channels can be approximately neglected, and also photoabsorption by the 3+ channel is 10 to 100 times more likely than by the 3− channel. These features were verified experimentally,[18] as only a single series of resonances was observed.

Accordingly, to a first approximation the 3− channel can be ignored entirely. Then the total photodetachment cross section near H($n=3$) is a sum of two terms,

$$\sigma = \sigma_{\text{NR}} + \sigma_{\text{R}}\,. \tag{A2}$$

The term σ_{NR} is a constant nonresonant background contribution, while σ_{R} is the resonant term in the cross section which contains the infinite series of 3+ resonances below the $n=3$ threshold.

TABLE I. Ratios of H^- resonance parameters.

	Experiment (Ref. 18)	Eq. (A4)	Callaway (Ref. 19)	Morgan *et al.* (Ref. 20)	Oberoi (Ref. 21)	Chung (Ref. 22)	Lipsky *et al.* (Ref. 23)
$\epsilon_{2+}/\epsilon_{1+}$	0.057 ± 0.020	0.0597	0.0564	0.0394	0.0515	0.0444	0.0525
Γ_{2+}/Γ_{1+}	0.058 ± 0.011	0.0597	0.0572	0.0675			
q_{2+}/q_{1+}	0.830 ± 0.170	1.0					
$\epsilon_{2-}/\epsilon_{1-}$		0.1936	0.202	0.134	0.1926	0.1914	0.1935
Γ_{2-}/Γ_{1-}		0.1936	0.243	2.5			

In Ref. 7 the term σ_R was parametrized as in Secs. II and III, allowing for the interference of the 2+ and 3+ channels. When the interaction between two channels is sufficiently weak, the cross section below threshold reduces to a series of the more familiar isolated Fano profiles at energies ϵ_m relative to $\text{H}(n=3)$, for $m=1,2,\ldots$:

$$\sigma_R = \sigma_R (q_m + \xi_m)^2/(1+\xi_m^2)\,, \tag{A3}$$

where

$$\xi_m = (\epsilon - \epsilon_m)/(\tfrac{1}{2}\Gamma_m)\,.$$

When the long-range field is of the dipole type, the profile parameters describing separate resonances are simply related in terms of a parameter $\alpha = (-a - \frac{1}{4})^{1/2}$, with a given in Eq. (A1):

$$\begin{aligned} \sigma_R &= \text{const}\,, \\ q_{m+1} &= q_m\,, \\ \Gamma_{m+1} &= \Gamma_m \exp(-2\pi/\alpha)\,, \\ \epsilon_{m+1} &= \epsilon_m \exp(-2\pi/\alpha)\,. \end{aligned} \tag{A4}$$

For the 3+ channel, $\exp(-2\pi/\alpha) = 0.0597$, while for the 3− channel it equals 0.1936. The simple scaling laws of Eq. (A4) are compared in Table I with ratios of energy levels, widths, and shape parameters derived from an experiment and from complicated *ab initio* calculations. Only the + states were observed experimentally and the ratios agree with the simple predicted values to within experimental error. The recent calculation of Callaway[19] also agrees with the scaling law, although the earlier calculation of Morgan *et al.*[20] is in serious disagreement. (Results of other calculations are shown in Table I for comparison.) Thus Eq. (A4) can be used to predict the parameters of higher resonances once a low-lying resonance is know; alternatively, Eq. (A4) provides a check on the internal consistency of *ab initio* calculations.

As a final note, the fitted MQDT parameters of Ref. 7 can be used to predict the partial cross section for detachment from hydrogen in its $n=3$ states. Inspection of Fig. 2 of Ref. 7 shows that the total cross section is approximately constant up to a fraction of a volt above threshold, with values[7]

$$\sigma_R = 0.121\,a_0^2\,, \quad \sigma_{NR} = 0.166\,a_0^2\,. \tag{A5}$$

The nonresonant cross section pertains only to the $\text{H}(n=1)$ and $\text{H}(n=2)$ channels. However, Eqs. (2.20), (2.24), and (2.25) of the present article, when combined with the fitted parameters of Ref. 7, imply that the relative contributions to σ_R from $n=3$ and 2 are 17% and 83%, respectively. Thus the ratio of the intensity of the low-energy electrons to the total intensity is predicted to be less than 10%,

$$\sigma(n=3)/(\sigma_R + \sigma_{NR}) = 0.072\,. \tag{A6}$$

Similarly, the + channel amplitudes for exciting the separate hydrogenic levels are known by a simple calculation (see Gailitis and Damburg,[24] or Seaton[25]):

i	$T_i^{(+)}$
$3s\epsilon p$	−0.307
$3p\epsilon s$	0.488
$3p\epsilon d$	0.530
$3d\epsilon p$	−0.543
$3d\epsilon f$	−0.303 .

(A7)

Thus the separate contributions to $\sigma(n=3)$ should be in the energy-independent ratios

$$\sigma(3s) : \sigma(3p) : \sigma(3d) = 0.094 : 0.519 : 0.385\,. \tag{A8}$$

Finally, if the angular distribution of the lowest-energy photoelectrons is measured without resolving the nearly degenerate levels of $\text{H}(n=3)$, the amplitudes of Eq. (A7) imply a constant asymmetry parameter (up to ~0.1 eV) above threshold

$$\beta_+(n=3) = -0.614\,. \tag{A9}$$

The predictions (A6), (A8), and (A9) show the power of the semiempirical analysis, since the photoelectron angular distribution and some of the partial cross sections could be derived after fitting to the total cross section.

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