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Spin-electronic-rotational frame transformation for photoionization and Rydberg spectra of diatomic molecules

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The spin-rotational-electronic fine structure of molecular Rydberg and continuum states is considered. The frame transformation from the laboratory frame [Hund's case (e)] to the molecular frame [Hund's case (a)] is derived. Symmetry requirements are fully incorporated into the transformation, thus facilitating its practical use. Expressions for the dipole transition amplitudes in Hund's case (a), again fully symmetrized, are given, as well as their transformation to Hund's case (e) appropriate for excitation to discrete Rydberg states and the ionization continuum. Various examples of the transformation within the framework of collision theory and of multichannel quantum defect theory are described, and it is shown how the general frame transformation reduces to the transformations for molecules without electron spin. The present formulation can also be applied to the photoionization of aligned and oriented molecules, as well as to ''complete'' experiments. [S1050-2947(98)02803-0]

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I. INTRODUCTION

The famous coupling cases of Hund classify various ways in which the spin-electronic and rotational angular momenta of a molecule can be coupled together [1]. The simplest way to distinguish them is to consider the appropriate expression for the rotational energy-level pattern for each case. Thus, for Hund's cases (a), (b), (d), and (e) coupling the rotational levels are arranged, respectively, according to $BJ(J+1)$, $BN(N+1)$, $BN_c(N_c+1)$, and $BJ_c(J_c+1)$, where B is the rotational constant and J, N, N_c, and J_c are the total angular momentum of the molecule (exclusive of nuclear spins), the total angular momentum without electron spin, the total angular momentum of the cation without electron spin, and the total angular momentum of the cation including electron spin. Case (c) behaves like case (a), but, owing to strong spin-orbit coupling, the spin quantum number S is no longer sharply defined.

In 1990 three papers appeared, which dealt with the role of electron spin and molecular rotation in the photoionization and Rydberg excitation of diatomic molecules. First, Xie and Zare (XZ) [2] presented a compilation of spin-electronic-rotational dipole selection rules connecting initial molecular and final ion states of diatomic or linear molecules, whereby these states were assumed to belong to any of Hund's coupling cases (a), (b), or (c). Almost simultaneously, Raseev and Cherepkov [3] (RC) gave a general expression for the total and differential photoionization cross sections including molecular rotation and electron-spin polarization in molecules. Third, Lefebvre-Brion (LB) [4] gave a transformation between Hund's coupling cases (c) and (e), appropriate for the description of Rydberg series converging toward a spin-orbit-split ion ground state. More recently Nikitin and Zare [5] presented correlation diagrams connecting various Hund's cases in the limit where the total angular momentum is much larger than the electronic orbital angular momentum and electron spin.

Until about 1990, and with the exception of H_2, rotational resolution was only rarely attained in photoionization experiments. The recent dramatic increase in resolution brought about by novel threshold ionization techniques [6,7] changes this situation radically, and has spurred new interest in the subject. One aim of the present paper is to clarify the link between the expressions for differential cross sections including rotation and spin such as given by RC, and the various angular coupling cases considered by Hund as they are customarily used in the spectroscopy of discrete states. The transformation between various coupling cases is a standard practice in Rydberg spectroscopy. By contrast, in the theory of photoionization, the cross section is expressed in a coupling scheme appropriate for the separated fragments (ion plus electron) which corresponds to case (e), while the relevant transition amplitudes are built up inside or near the ion core where Hund's cases (a) or (c) provide a better description. The frame transformation between the various coupling schemes is thus implicit in the cross-section expressions, but it has only rarely been spelled out in detail.

Another link between spectroscopy and scattering theory arises through the occurrence of discrete autoionizing states which are embedded in the electronic continua, and autoionize through discrete-continuum channel interactions. In the theory the discrete wave-function components correspond to closed-channel asymptotic boundary conditions. The ensemble of asymptotic conditions for closed and open channels (continuum states) can be enforced simultaneously through a method such as multichannel quantum defect theory (MQDT) [8,9], where the electron-core interactions may include N_o open as well as N_c closed channels. The calculational procedure of MQDT involves the ''elimination'' of the N_c closed channels, yielding a scattering matrix whose dimension corresponds to the correct number N_o of open channels. Doing this yields resonant anomalies in the open channels at energies corresponding to the discrete autoionizing states. The open ionization channels are always best described in Hund’s case (e). However, the closed channels may often correspond to an intermediate coupling case, and the MQDT is ideally suited for handling such situations.

In the present paper we derive the transformation between Hund’s coupling cases (a) and (e). We show how the resulting spin-electronic-rotational frame transformation relates to the general framework of spin-resolved molecular photoionization and of molecular multichannel quantum defect (MQDT) and frame transformation theory. Unlike LB we choose case (a) rather than case (c) as the starting point in the molecule-fixed coordinate frame, because this case is usually considered to be the basic coupling case for diatomic molecules [10], and it appears to be the one which is best defined with respect to the various phase conventions involved [11]. Particular attention is given to parity (not explicitly taken into account by LB) and to electric dipole transitions (not considered by XZ and LB). The resulting expressions are more compact than those of RC, and they contain the spinless transformations such as given by Chang and Fano [12] as special cases. While several of the expressions and procedures discussed in the present paper are basically known, and can be found scattered throughout the literature, we draw them together here in an attempt to provide a unified view of scattering, spectroscopy, and photoionization of molecules carrying an electron spin.

The paper is organized as follows: Section II reviews the connection between momentum eigenstates and uncoupled and coupled angular momentum eigenstates in spin-resolved photoionization without specific reference to molecules. The coupled angular momentum representation is then used in the rest of the paper. Section III gives the transformation between Hund’s cases (e) and (a) for diatomic molecules. In Sec. IV a relationship is established between scattering theory in general and quantum defect theory in particular, and the frame transformation. Section V deals with electric dipole transitions, while Sec. VI is the conclusion. The main expressions of this paper are the following.

(a) Equations (1)–(6) connect the standard scattering formulation with the coupled angular momentum approach corresponding to Hund’s case (e).

(b) Equation (12) gives the transformation between Hund’s cases (e) and (a).

(c) The dipole transition moment expressions, Eqs. (20) and (21b), provide the amplitude to be introduced in cross-section expressions. The transition moments are related to Eqs. (29a) and (29b), which explicitly contain the radial integrals to be evaluated numerically.

II. COUPLED AND UNCOUPLED ANGULAR MOMENTUM REPRESENTATIONS IN THE LABORATORY FRAME

Several treatments of of photoionization have been presented, including those of RC [3], Dill and Dehmer [13], and Starace [14]. Here we follow that of Fano and Rau [15] (including much of their notation), and thus consider a ‘‘complete’’ photoionization experiment in which a photoelectron with momentum $\mathbf{k}_i$ emerging from a core in state i is observed, and its spin state as well as the internal state i of the core is determined. The k-normalized wave function at the particle analyzer corresponding to this situation is

$$\Psi_{\mathbf{k}_i}(\text{analyzer})=\psi_{J_{ci}M_{ci}p_{ci}}\chi_{m_{si}}(2\pi)^{-3/2}e^{i\mathbf{k}_i\mathbf{r}}, \tag{1}$$

where $\chi_{m_{si}}$ represents the normalized spin state of the photoelectron, J_{ci} and M_{ci} are the total angular momentum quantum numbers of the core in state i, and $(-1)^{p_{ci}}$ is the core parity. The plane wave in Eq. (1) may be expanded into spherical partial waves in the usual way as

$$\begin{aligned}\Psi_{\mathbf{k}_i}(\text{analyzer})=\psi_{J_{ci}M_{ci}p_{ci}}\chi_{m_{si}}&\\ &\times\sum_{l_i}\sum_{m_{li}=-l_i}^{+l_i}[i^{l_i}Y^*_{l_im_{li}}(\theta_k,\phi_k)]\\ &\times Y_{l_im_{li}}(\theta,\phi)\left(\frac{2}{\pi}\right)^{1/2}\frac{1}{2ik_ir}\\ &\times(i)^{-l_i}[e^{ik_ir}-(-1)^{l_i}e^{-ik_ir}].\end{aligned} \tag{2}$$

The asymptotic form of an energy normalized incoming-wave scattering wave function can be expressed in terms of the scattering matrix **S** as

$$\begin{aligned}\Psi^{(-)}_{\bar{I}}(\text{uncoupled})=\sum_{\bar{I}'}\psi_{J_{ci'}M_{ci'}p_{ci'}}\chi_{m_{si'}}&\\ &\times Y_{l_{i'}m_{li'}}(\theta,\phi)\left(\frac{1}{\pi k_{i'}}\right)^{1/2}\frac{1}{2ir}\\ &\times[e^{ik_{i'}r}\delta_{\bar{I}'\bar{I}}-e^{-ik_{i'}r}S^*_{\bar{I}'\bar{I}}],\end{aligned} \tag{3}$$

where we assume the energy to be in Rydberg units, i.e., $\epsilon_i=k_i^2$, and the factor $1/r$ corresponds to normalization of the radial function according to $\int\underline{\phi^*}\phi\, r^2\underline{dr}$. The channel indices indicated by capital letters, I' and$\underline{\ I}$ denote the core state as well as the partial wave, e.g., $\{I'\}=\{i',l_{i'},m_{li'}\}$. The bars on the indices denote the uncoupled representation, and the added exponent $(-)$ indicates the incoming wave normalization [14],

Equations (2) and (3) are connected by the requirement that the coefficients of the outgoing-wave components e^{ik_ir} must match. This is achieved by a superposition of the functions $\Psi^{(-)}_{\bar{I}}$(uncoupled) of Eq. (3), corresponding to the given i of Eq. (1):

$$\sum_{l_im_{li}}Y^*_{l_im_{li}}(\theta_k,\phi_k)\Psi^{(-)}_{i,\bar{l}_i,m_{li}}(\text{uncoupled}). \tag{4}$$

Equation (4) corresponds to the inclusion of an extra factor $\sqrt{k_i/2}$, and results in energy-normalized forms of the plane wave of Eqs. (1) and (2), plus scattered incoming-wave components. The incoming-wave components formally represent the state of the electron-ion system before the scattering event (cf., e.g., the discussion given by Starace [14]). In the photoionization processes of interest here they replace, as it were, the photon and the molecule in its initial state—the required information concerning the latter is included in the dipole transition amplitudes, as discussed in Sec. V.

An alternative way of constructing a wave function equivalent to Eq. (3) is to consider scattering states that have well-defined values of the total angular momentum J and parity p. An incoming-wave energy-normalized scattering wave function of this type has the asymptotic form

$$\Psi_I^{(-)}(\text{coupled}) = \sum_{I'} \Phi_{I'}^{(JMp)} \left(\frac{1}{\pi k_{i'}}\right)^{1/2} \frac{1}{2ir} \times [e^{ik_{i'}r}\delta_{I'I} - e^{-ik_{i'}r} S_{I'I}^{(JMp)*}]. \tag{5}$$

We refer to Eq. (5) as a ‘‘coupled’’ wave function because the angular $\mathbf{l}_i$ and spin $\mathbf{s}_i$ parts of the photoelectron are now coupled to the ionic core and included in the functions $\Phi_{I'}^{(JMp)}$ which represent eigenstates of the total angular momentum of the core plus photoelectron $\mathbf{J} = \mathbf{J}_{ci'} + \mathbf{j}_{i'}$ and of the total angular momentum of the photoelectron $\mathbf{j}_{i'} = \mathbf{l}_{i'} + \mathbf{s}_{i'}$. The $\Phi_{I'}^{(JMp)}$ have definite total parity $(-1)^p$. The radial part of the wave function of the continuum electron is separated and written explicitly in Eq. (5). M is the projection of the total molecular $\mathbf{J}$ in the laboratory frame. $S^{(JMp)}(E)$ is thus the scattering matrix defined for a given JMp. The channel indices indicated by capital letters, I' and I, now denote the partial wave and spin of the photoelectron, as well as the core state, e.g., $\{I\} = \{i, l_i, j_i\}$.

Equations (2) and (5) are again connected by the requirement that the coefficients of the outgoing-wave components e^{ik_ir} must match. The appropriate superposition analogous to Eq. (4) of the functions $\Psi_I^{(-)}$(coupled) of Eq. (5) corresponding to the given i of Eq. (1) is

$$\sum_{l_i m_{li} j_i m_{ji} JM} Y^*_{l_i m_{li}}(\theta_k, \phi_k)(2j_i+1)^{1/2}(2J+1)^{1/2} \times (-1)^{-(1/2)+l_i-m_{ji}-j_i+J_{ci}-M} \begin{pmatrix} 1/2 & l_i & j_i \\ m_{si} & m_{li} & -m_{ji} \end{pmatrix} \times \begin{pmatrix} j_i & J_{ci} & J \\ m_{ji} & M_{ci} & -M \end{pmatrix} \Psi^{(-)}_{i,l_i,j_i}(\text{coupled}). \tag{6}$$

The superposition Eq. (6) of the wave functions Eq. (5) again yields the energy-normalized form of the plane wave of Eq. (1) plus scattered incoming-wave components.

The uncoupled and coupled forms of the scattering matrix S and $S^{(JMp)}$, are linked through the alternative expansions of Eqs. (4) and (6), while the latter is linked to the reactance matrix $\mathbf{K}$ of MQDT, as we see in Sec. IV below. In the specific case of molecular photoionization the wave function $\Psi_I^{(-)}$(coupled) of Eq. (5) corresponds to Hund’s case (e) coupling. In Sec. III we consider the transformation to Hund’s case (a), which provides a more appropriate description of the short-range electron-ion collision process.

III. TRANSFORMATION BETWEEN HUND’S CASES (a) AND (e)

Usually when one refers to Hund’s coupling case (a), it is implied [10] that the following quantum numbers are good ones: the total angular momentum J of the molecule and its components M and Ω with respect to the laboratory and molecular axes, respectively. Further, the electronic orbital angular momentum component Λ on the molecular axis and the total electron spin S as well as its molecular component $\Sigma = \Omega - \Lambda$ are good quantum numbers. Taking account of the inversion symmetry we must add the total parity index p (cf. Sec. II). We must also take account of the electronic symmetry q of the molecule (reflection at a plane containing the nuclei, defined when $\Lambda = 0$); we shall see below that it is sufficient to introduce an electronic parity index for the isolated core q_c (called s^+ by XZ and defined below). Thus so far we have to consider seven independent spin-rotational-electronic quantum numbers describing a case (a) state. Nuclear spins are disregarded here, and symmetric molecules are not treated separately since they differ only in a trivial way.

Considering molecular Rydberg states, we may assume that the electronic orbital momentum component Λ is actually the sum of two contributions, one from the molecular ion core Λ_c, and one from the Rydberg electron λ, so that we have $\Lambda = \Lambda_c + \lambda$. Similarly the total spin $\mathbf{S}$ arises from the coupling of the core spin $\mathbf{S}_c$ and the Rydberg electron spin $\mathbf{s}$. Finally, in a channel formulation the Rydberg electronic wave function is conveniently expanded in spherical partial waves l, even though the Rydberg orbital angular momentum quantum number l may not be well defined in any actually observable state. In all, then, we have 11 quantum numbers characterizing a case (a) coupled Rydberg or ionization channel corresponding to the excitation of a single electron outside a molecular core.

Mulliken [1] was apparently the first to make reference to Hund’s case (e) (which Hund himself had not considered). For Rydberg states this coupling case is characterized by the fact the Rydberg electron including its spin is decoupled from the molecular ion core. Thus $\boldsymbol{l}$ and $\mathbf{s}$ couple to yield a resultant j, whereas the core rotates independently and is characterized by rotational quantum numbers J_c and Ω_c, as well as by the electronic quantum numbers Λ_c, q_c, and S_c. By contrast the molecule-fixed components Ω and Λ involving the outer electron are no longer defined, nor is the total spin S. In all we again have 11 quantum numbers to consider, with the difference that Λ, S, and Ω must be replaced by Ω_c, J_c and j. This state of affairs is summarized in Table I where minimal sets of Rydberg quantum numbers for Hund’s coupling cases (a) and (e) are collected and classified according to their ‘‘goodness.’’ In addition, ‘‘redundant’’ quantum numbers are also indicated, namely, those which can be expressed in terms of the minimal sets for cases (a) and (e), respectively. We see in particular that out of the 11 quantum numbers forming each minimal set, eight are common to both coupling cases, while only three are different. Therefore the transformation between the two coupling cases is conveniently denoted by

$$U^{(JMp,\Lambda_c S_c q_c, ls)}_{\Omega_c J_c j, S\Lambda\Omega} \equiv \langle \Omega_c J_c j | S\Lambda\Omega \rangle^{(JMp,\Lambda_c S_c q_c, ls)}. \tag{7}$$

In a well-specified context it will often be possible to omit some or all of the eight superscripts of the transformation elements of Eq. (7).

In view of the foregoing remarks we can now specify symmetrized case (e) and case (a) Rydberg wave functions as follows. Omitting the core index i occurring in Eqs. (1)–(6), for case (e) we write a vector-coupled product of electron states $|jm\rangle$ and symmetrized core states $|J_c\Omega_c M_c\rangle$,

TABLE I. Quantum numbers in Hund’s cases (a) and (e).

Case (a)	Case (e)	Remark
J,M,p,s	J,M,p,s	‘‘strictly’’ good quantum numbers in field-free space. $s=\frac{1}{2}$ for the electron; set $s=0$ if spins are disregarded.
Λ_c,S_c,q_c,l	Λ_c,S_c,q_c,l	electronic channel quantum numbers. ‘‘Badness’’ is accounted for by electronic channel interactions.
S,Λ,Ω	Ω_c,J_c,j	spin-roronic basis channel quantum numbers defining short-range (a) and asymptotic (e) channels. ‘‘Badness’’ is tantamount to a departure toward the opposite limit.
	‘‘redundant’’ quantum numbers:	
$\lambda=\Lambda-\Lambda_c$ $\Sigma=\Omega-\Lambda$	$\Sigma_c=\Omega_c-\Lambda_c$	
$\left.\begin{matrix}e\\ f\end{matrix}\right\}$ if $p-J\left(+\frac{1}{2}\right)\begin{cases}\text{even}\\ \text{odd}\end{cases}$		total parity quantum number; include term $(+\frac{1}{2})$ when J is a half-integer.
$\left.\begin{matrix}e_c\\ f_c\end{matrix}\right\}$ if $p+l-J_c\left(+\frac{1}{2}\right)\begin{cases}\text{even}\\ \text{odd}\end{cases}$		core parity quantum number; include term $(+\frac{1}{2})$ when J_c is a half-integer.
$\begin{pmatrix}+\\ -\end{pmatrix}_c$ if $p+l\equiv p_c\begin{cases}\text{even}\\ \text{odd}\end{cases}$		core parity quantum number.

$$|\Omega_c J_c j\rangle^{(JMp,\Lambda_c S_c q_c,ls)} = \sum_{m,M_c}(2J+1)^{1/2}(-1)^{-j+J_c-M}\begin{pmatrix} j & J_c & J\\ m & M_c & -M\end{pmatrix}|jm\rangle \times\frac{1}{\sqrt{2}}\frac{1}{(1+\Delta_1)^{1/2}}[|\Lambda_c\rangle|S_c\Sigma_c\rangle|J_c\Omega_c M_c\rangle + (-1)^{p-q_c-S_c+J_c+l}|-\Lambda_c\rangle|S_c-\Sigma_c\rangle|J_c-\Omega_c M_c\rangle], \tag{8a}$$

with

$$\Delta_1(\Lambda_c,\Omega_c)=\delta_{\Lambda_c 0}\delta_{\Omega_c 0}. \tag{8b}$$

In Eq. (8) the quantum numbers of the outer electron are l, s and j, and $|jm\rangle$, quantized in the laboratory frame, is understood to be formed by vector addition of $\boldsymbol{l}$ and $\mathbf{s}$ as in Eq. (6). The kets $|\Lambda_c\rangle$, $|S_c\Sigma_c\rangle$, $|J_c\Omega_c M_c\rangle$ and $|jm\rangle$ are, respectively, the electronic, spin, and rotational functions of the ionic core and the angular part of the function of the outer electron, where $\Sigma_c=\Omega_c-\Lambda_c$. The electronic core parity index q_c equals 1, when the core is in a Σ^- state and it is zero otherwise [2,16]. The ket Eq. (8) corresponds to the function $\Phi_I^{(JMp)}$ [Eq. (5)] for a diatomic molecule where the index I was defined in Sec. II as $\{I\}=\{i,l_i,j_i\}$, and the radial part of the wave function of the electron is not included. Equation (8) refers to a given electronic core state i, and the core index i is replaced by the core quantum numbers Ω_c, J_c, M_c, S_c, and q_c characterizing this state. The molecule-fixed projections Λ_c, Σ_c, and Ω_c and the core electronic symmetry index q_c which appear here are unspecified in the more general Eq. (5). We shall also see below (Table I) that the exponent of (-1) in the core part of Eq. (8) is defined such that the core has parity $(-1)^{p+l}\equiv(-1)^{p_c}$, as assumed in Eq. (1). Note that apart from the symmetrization the angular momentum coupling in Eq. (8) is the inverse to that given in Eq. (6). For case (a) we write

$$|S\Lambda\Omega\rangle^{(JMp,\Lambda_c S_c q_c,ls)} = \frac{1}{\sqrt{2}}\frac{1}{(1+\Delta_2)^{1/2}}\frac{1}{(1+\Delta_3)^{1/2}}\{[|\Lambda_c\rangle|l\lambda\rangle|S\Sigma\rangle|J\Omega M\rangle + (-1)^{p-q_c-S+J}|-\Lambda_c\rangle|l-\lambda\rangle|S-\Sigma\rangle|J-\Omega M\rangle] + \Delta_3(-1)^{p-q-S+J}[|\Lambda_c\rangle|l\lambda\rangle|S-\Sigma\rangle|J-\Omega M\rangle + (-1)^{p-q_c-S+J}|-\Lambda_c\rangle|l-\lambda\rangle|S\Sigma\rangle|J\Omega M\rangle]\}, \tag{9a}$$

where

$$\Delta_2(\Lambda_c,\Lambda,\Omega)=\delta_{\Lambda_c 0}\delta_{\Lambda 0}\delta_{\Omega 0} \tag{9b}$$

and

$$\Delta_3(\Lambda_c,\Lambda,\Omega)=(1-\delta_{\Lambda_c 0})\delta_{\Lambda 0}(1-\delta_{\Omega 0}) \tag{9c}$$

equals 1 when $\Lambda_c\neq 0$, $\Lambda=0$, and $\Omega\neq 0$, and 0 otherwise. Note that $\Delta_2\Delta_3$ is always zero. In Eq. (9) $q=0$ must be taken for $\Sigma>0$ and $q=1$ for $\Sigma<0$. The angular part of the function of the outer electron, $|l\lambda\rangle$ (with $\lambda=\Lambda-\Lambda_c$), is now quantized in the molecular frame. The spin function $|S\Sigma\rangle$ (also quantized in the molecular frame with $\Sigma=\Omega-\Lambda_c-\lambda$) is understood to be the result of the vector addition of $\mathbf{S}_c$ and $\mathbf{s}$. $|J\Omega M\rangle$ describes the rotational motion of the molecule as a whole. Note that the third and fourth terms in the bracket $\{\cdot\cdot\cdot\}$ of Eq. (9) (as well as the corresponding third factor preceding it), which yield the somewhat complicated appearance of Eq. (9), are actually present only in the particular case where $\Lambda=0$, $\Lambda_c\neq 0$, and $\Omega\neq 0$. They ensure that for $\Lambda=0$ the electronic orbital wave function always has a definite symmetry Σ^+ or Σ^-. This, and the significance of the electronic symmetry index q, is explained in Appendix A.

It appears worthwhile to specify which values can be taken by the various angular momentum components appearing in Eqs. (8) and (9) and in the frame transformation of Eq. (12) below. Since the basis functions in Eqs. (8) and (9) are symmetrized with respect to the molecule-fixed angular momentum components, we must ensure that a given combination is obtained only once. To this end we restrict one of the components to be *positive* or *zero*. We thus define $\Lambda_c\geqslant 0$. For Λ_c different from zero, λ then takes all values $+l,\ldots,-l$, which means that Λ takes all values $\Lambda_c+l,\ldots,\Lambda_c-l$. Note that for $l\geqslant\Lambda_c$ this prescription yields positive as well as negative values of Λ which correspond to *different* electronic states. Similarly, $\Sigma=\Omega-\Lambda$ takes all values $+S,\ldots,-S$, and $\Sigma_c=\Omega_c-\Lambda_c$ takes all values $+S_c,\ldots,-S_c$ (with the additional convention that $q=0$ for spin projections $\Sigma>0$ and $q=1$ for $\Sigma<0$, cf. Appendix A). The maximum number of states thus obtained is $2\times(2s+1)(2S_c+1)(2l+1)$. When, on the other hand Λ_c is zero, Λ in case (a) and Ω_c in case (e) are restricted to positive or zero values, and in general only half as many states are obtained. Finally, if $\Lambda_c=\Lambda=0$ in case (a), Ω is also restricted to be positive or zero.

Using the known effects [10,16] of the space-fixed inversion operator $E^\star$ on the various factors of the basis functions, namely,

$$E^\star|J\Omega M\rangle=(-1)^{J-\Omega}|J-\Omega M\rangle, \tag{10a}$$

$$E^\star|l\lambda\rangle=(-1)^{-\lambda}|l-\lambda\rangle, \tag{10b}$$

$$E^\star|S\Sigma\rangle=(-1)^{S-\Sigma}|S-\Sigma\rangle, \tag{10c}$$

$$E^\star|\Lambda_c\rangle=(-1)^{q_c-\Lambda_c}|-\Lambda_c\rangle \tag{10d}$$

[where, in Eq. (10d) $q_c=0$ except for Σ_c^- cores for which $q_c=1$], and taking note of Appendix A, we establish easily that

$$E^\star|\Omega_cJ_cj\rangle^{(JMp,\Lambda_cS_cq_c,ls)}=(-1)^p|\Omega_cJ_cj\rangle^{(JMp,\Lambda_cS_cq_c,ls)}, \tag{11a}$$

$$E^\star|S\Lambda\Omega\rangle^{(JMp,\Lambda_cS_cq_c,ls)}=(-1)^p|S\Lambda\Omega\rangle^{(JMp,\Lambda_cS_cq_c,ls)}. \tag{11b}$$

This result confirms that $p=$even or odd relates directly to the total parity, + or −, respectively, and thus the frame transformation of Eq. (12) below is diagonal in p. From Eqs. (11) it is straightforward to obtain the relationship between p and the e/f total parity quantum numbers on the one hand, and the e_c/f_c core parity quantum numbers on the other hand, as given in Table I. Remember that in case (e) the parity is that of the core times $(-1)^l$.

Standard angular momentum coupling techniques yield the frame transformation, i.e., the projection of case (e) onto case (a) states. We obtain

$$\begin{aligned}\langle\Omega_cJ_cj|S\Lambda\Omega\rangle^{(JMp,\Lambda_cS_cq_c,ls)}=&\left[\frac{(2S+1)(2j+1)(2J_c+1)}{(1+\Delta_1)(1+\Delta_2)(1+\Delta_3)}\right]^{1/2}(-1)^{S_c-\Omega_c+l+\Lambda+J+\Omega}\\
&\times\left[\begin{pmatrix} s & S_c & S\\ \Omega-\Lambda+\Lambda_c-\Omega_c & \Omega_c-\Lambda_c & -\Omega+\Lambda\end{pmatrix}\begin{pmatrix} l & s & j\\ \Lambda-\Lambda_c & \Omega-\Lambda+\Lambda_c-\Omega_c & -\Omega+\Omega_c\end{pmatrix}\begin{pmatrix} J_c & j & J\\ \Omega_c & \Omega-\Omega_c & -\Omega\end{pmatrix}\right.\\
&+\delta_{\Lambda_c0}(-1)^{p-q_c-S_c-J_c+l}\\
&\times\begin{pmatrix} s & S_c & S\\ \Omega-\Lambda+\Lambda_c+\Omega_c & -\Omega_c-\Lambda_c & -\Omega+\Lambda\end{pmatrix}\begin{pmatrix} l & s & j\\ \Lambda-\Lambda_c & \Omega-\Lambda+\Lambda_c+\Omega_c & -\Omega-\Omega_c\end{pmatrix}\begin{pmatrix} J_c & j & J\\ -\Omega_c & \Omega+\Omega_c & -\Omega\end{pmatrix}\\
&+\Delta_3(-1)^{p-q-S-J}\\
&\times\left.\begin{pmatrix} s & S_c & S\\ -\Omega-\Lambda+\Lambda_c-\Omega_c & \Omega_c-\Lambda_c & \Omega+\Lambda\end{pmatrix}\begin{pmatrix} l & s & j\\ \Lambda-\Lambda_c & -\Omega-\Lambda+\Lambda_c-\Omega_c & \Omega+\Omega_c\end{pmatrix}\begin{pmatrix} J_c & j & J\\ \Omega_c & -\Omega-\Omega_c & \Omega\end{pmatrix}\right],\end{aligned} \tag{12}$$

with the additional convention that $q=0$ for $\Sigma=\Omega-\Lambda>0$ and $q=1$ for $\Sigma=\Omega-\Lambda<0$ (cf. Appendix A). From Eqs. (8) and (9), we see that for $\Lambda_c=0$ we have the following additional requirements:

$$\Lambda_c=\Omega_c=0\rightarrow p-q_c-S_c+J_c+l=\text{even}, \tag{13a}$$

$$\Lambda_c=\Lambda=\Omega=0\rightarrow p-q_c-S+J=\text{even} \tag{13b}$$

which ensure that only the + combination occurs for states with zero angular momentum components. Both these requirements have been taken into account in deriving Eq. (12), and when not satisfied Eq. (12) gives a transformation element of zero. Thus, in practice, for given values of q_c, S_c, J_c, and l (or q_c, S, and J), these conditions tell us which value of the parity index p yields a nonzero transformation element. Note that the second and third terms in the bracket $[\cdots]$ containing $3j$ symbols in Eq. (12) take account of the special cases where $\Lambda_c=0$ or $\Lambda=0$, and one of them at most is nonzero in any given situation (cf. Appendix A). Note also that the second and third triple products of $3j$ symbols are obtained from the first by the simple substitution $\Omega_c\rightarrow-\Omega_c$ and $\Omega\rightarrow-\Omega$, respectively. Recall, finally, that the quantum number components in Eq. (12) take the values and signs specified in the paragraph preceding Eq. (10), thus determining the dimension of the matrix formed by the elements of Eq. (12). The frame transformation matrix is unitary, and it is diagonal in the electronic core state i.

The frame transformation for a spinless molecule is obtained by setting $s=S=S_c=0$ in Eq. (12). The resulting expressions for Hund's case (d) are given in Appendix B, where the special case $\Lambda_c=0$ ($^1\Sigma^+$ or $^1\Sigma^-$ core) is also considered.

IV. USE OF THE FRAME TRANSFORMATION IN SCATTERING AND QUANTUM DEFECT CALCULATIONS

In this section we present an outline of how the spin-electronic-rotational frame transformation derived in Sec. III may be used in the framework of scattering and quantum defect theories, and how it enters the calculation of photoexcitation and photoionization cross sections. The reader is referred to Refs. [8] and [9] for a detailed discussion of quantum defect theory in atoms and molecules, and to Ref. [14] for a review of the application of scattering theory to photoionization processes.

A. Structure of reactance matrices in MQDT

In the following we discuss the structure of $\Psi_I^{(-)}$(coupled) of Eq. (5), and relate it to the frame transformation derived in the Sec. IV. In the framework of MQDT the electron-core interactions are embodied in a real symmetric nondiagonal reactance matrix $\mathbf{K}^{(JMp)}$, which consists of open ($\mathbf{K}^{oo}$), closed ($\mathbf{K}^{cc}$), and interaction ($\mathbf{K}^{co}=\mathbf{K}^{oc}$), submatrices. The QDT calculational procedures involve the elimination of the N_c closed channels, yielding the physical reactance matrix $\mathbf{K}(E)^{(JMp)}$ whose dimension is restricted to the number N_o of open channels, i.e., to the degree of degeneracy of the continuum, and which is connected to the scattering matrix appearing in Eq. (5) by the well-known relation $\mathbf{K}(E)=-i[\mathbf{S}(E)-1][\mathbf{S}(E)+1]^{-1}$. $\mathbf{K}(E)$ and $\mathbf{K}$ distinguish the $N_o\times N_o$ and $N\times N$ reactance matrices. $\mathbf{K}(E)$ has poles near the energies E corresponding to bound states associated with closed channels, whereas the full $N\times N$ reactance matrix $\mathbf{K}(N=N_c+N_o)$ will generally be a smoother function of energy. Frame transformation theory uses the fact that the scattered electron experiences two different coupling situations depending on whether it is far from the ion core, close to it or inside it. These correspond, respectively, to the asymptotic or to the eigenchannel coupling scheme, whereby the electron is appropriately described in the laboratory or in the molecular coordinate frame. The actual scattering off the core takes place while the electron is coupled into the molecular or body frame. The reactance matrix can therefore be written in the form

$$K_{II'}=\sum_{\beta,\beta'=1}^{N}U_{I\beta}K_{\beta\beta'}(U^{\mathrm{tr}})_{\beta'I'}\,. \tag{14}$$

Here $U_{I\beta}$ are the frame transformation matrix elements of Eq. (12), $K_{\beta\beta'}=\tan\pi\mu_{\beta\beta'}$ are short-range or body-frame reactance matrix elements, μ are quantum defects, and $\pi\mu$ are related phase shifts. The channels β correspond to Hund's case (a) coupling as specified by Eq. (9). As in Eq. (5) the channel indices $\{I\}=\{i,l_i,j_i\}$ stand for the core state where i reflects the electronic core state as well as the associated core quantum numbers specified in the case (e) function of Eq. (8). The indices l_i and j_i are the electron partial-wave expansion index and spin. The same is true for the Greek indices β in Eq. (14), which represent the partial-wave index l_i and the core state i with associated core quantum numbers common to cases (e) and (a) [upper indices in Eq. (7)], as well as the case (a) quantum numbers S, Λ, and Ω. The greek indices here and later refer to the body-frame character of these quantities—we avoid the usual eigenchannel notation α here since $K_{\beta\beta'}$ in Eq. (14) is only block diagonal for each core state i, but may have nonzero elements connecting channels differing in i or l_i. We thus distinguish the channels β from the ''true'' eigenchannels α which correspond to full diagonalization of $\mathbf{K}$. This type of ''partial'' eigenchannel was employed previously by Ross and Jungen [17].

Equation (14) reduces the problem of constructing a spin-electronic-rotational reactance matrix $K_{II'}$ to that of evaluating a matrix $K_{\beta\beta'}$ in the molecular frame, which is the frame customarily used in *ab initio* calculations. The laboratory frame channels satisfy case (e) coupling as specified by Eq. (8) [case (d) in the absence or neglect of spins]. Channel-coupling matrix elements between channels I and I' can arise in two ways: from the nondiagonality of either ($\tan\pi\mu$) or of the frame transformation matrix $\mathbf{U}$. The basic assumption here is that the case (a) quantum numbers S, Λ, and Ω are preserved during the electron-ion-scattering process, and consequently the matrix has only elements $\tan\pi\mu_{\beta\beta'}$ diagonal in these quantum numbers. [If the spin-orbit coupling is very strong, S and Λ may lose their meanings, such that ultimately only Ω is conserved in the body-frame representation. This situation corresponds to Hund's case (c), which we do not consider in detail here.] By contrast, $\tan\pi\mu_{\beta\beta'}$ may have elements that are nondiagonal in l, Λ_c, or S_c. The couplings between different channels β may have different physical origins of the type discussed by Lefebvre-Brion and Field [18] in their book on spectral perturbations in diatomic molecules.

We illustrate this with a few examples of nondiagonal body-frame reactance matrices. First of all, coupling between channels differing in l only occurs because of the nonspherical nature of the molecular electronic Hamiltonian at short range. A well-known example is the NO molecule where the observed nominal ''s''σ and ''d''σ Rydberg series associated with the NO$^+X^1\Sigma^+$ core have strongly mixed l character [19]. In this example we have $S=\frac{1}{2}$, $\Lambda=0$, $\Omega=\frac{1}{2}$,

$$\beta=(X^1\Sigma^+)s\sigma,\quad \text{i.e.,}\ \Lambda_c=0,\quad S_c=0,\quad q_c=0,\quad l=0,$$

and

$$\beta=(X^1\Sigma^+)d\sigma,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=0,\quad q_c=0,\quad l=2,$$

where $(X^1\Sigma^+)$ represents the electronic wave function of the core, and $l\lambda$ represents the outer electron. Second, channels differing in the electronic core state Λ_c are coupled as a consequence of electron correlation effects which simultaneously change either the l and/or the λ value of the Rydberg electron. A well-known example is afforded by the Hopfield series of N_2 [20]. Here one has $S=\Lambda=\Omega=0$ ($^1\Sigma_u^+$ symmetry),

$$\beta=(B^2\Sigma_u^+)s\sigma_g,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=\tfrac{1}{2},\quad q_c=0,\quad l=0,$$

and

$$\beta=(B^2\Sigma_u^+)d\sigma_g,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=\tfrac{1}{2},\quad q_c=0,\quad l=2.$$

The Rydberg series corresponding to these channels are preionized by the additional open channels

$$\beta=(A^2\Pi_u)d\pi_g,\quad \text{i.e.,}\quad \Lambda_c=1,\quad S_c=\tfrac{1}{2},\quad q_c=0,\quad l=2$$

and

$$\beta=(X^2\Sigma_g^+)p\sigma_u,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=\tfrac{1}{2},\quad q_c=0,\quad l=1.$$

Electron correlation can also lead to strong channel interactions between channels that correspond to different multiplicity of the core (different S_c). An example of this type involving channels of $^3\Sigma^-$ overall symmetry is known for O_2 ($S=1$, $\Lambda=0$, $\Omega=0$, ±1) [21]. Here the Rydberg series corresponding to

$$\beta=(B^2\Sigma_g^-)p\sigma_u,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=\tfrac{1}{2},\quad q_c=1,\quad l=1$$

is preionized by the open channel

$$\beta=(b^4\Sigma_g^-)p\sigma_u,\quad \text{i.e.,}\quad \Lambda_c=0,\quad S_c=\tfrac{3}{2},\quad q_c=1,\quad l=1,$$

where the Rydberg $p\sigma_u$ electrons are different, since they are associated with different core states; in other words, the interacting channels differ in two spin orbitals as in the preceding example.

We now turn to the discussion of channel interactions which are taken into account through the frame transformation matrices **U** in Eq. (14). We first consider the situation when the core obeys pure case (a) coupling [case (b) in the absence or neglect of electron spin]. Interactions between channels differing in Ω_c, J_c, and j arise through the frame transformation. When the energy is very low such that the Rydberg electron is confined to the zone near the core, these interactions lead to a transition toward case (a). Conversely, to the extent that the low-energy Rydberg electron has some amplitude outside the inner region, states characterized by different values of S, Λ, and Ω become coupled.

In addition to the rotational-electronic channel interactions (l uncoupling) the so-called spin-orbit autoionization belongs to this class of channel couplings. Several papers appeared recently dealing with the photoionization of the halogen halides HCl, HBr, and HI. The cations of all these molecules have strong spin-orbit coupling and large rotational constants. Omitting the rotational quantum numbers we can characterize the Rydberg series as:

$$I=(X^2\Pi_{1/2})j,\quad \text{i.e.,}\quad \Omega_c=\tfrac{1}{2},\quad \Lambda_c=1,\quad S_c=\tfrac{1}{2},$$

$$q_c=0,\quad l,\quad s=\tfrac{1}{2}.$$

They are preionized by the open channels

$$I=(X^2\Pi_{3/2})j,\quad \text{i.e.,}\quad \Omega_c=\tfrac{3}{2},\quad \Lambda_c=1,\quad S_c=\tfrac{1}{2},$$

$$q_c=0,\quad l,\quad s=\tfrac{1}{2}.$$

The coupling arises through the fact that the case (e) to case (a) transformation is nondiagonal, and the singlet and triplet body-frame quantum defects are not equal. Spin-orbit autoionization and was initially discussed in Ref. [22]. More recently, several MQDT studies have been made of the photoionization from the ground state of neutral HI, or of double-resonance ionization via the $D^1\Pi$ state in HCl/DCl or via the $F^1\Delta$ state in HBr [23–26]. The main purpose of these studies was the analysis of the evolution of the angular momentum coupling from Hund's case (a) toward case (e) as the principal quantum number n increases.

A further potential source of channel interaction would be the presence of nonadiabatic coupling within the core. For instance, in the O_2 example mentioned above, $^2\Sigma$ and $^4\Sigma$ follow case (b) rather than case (a) due to the uncoupling of the spin $\mathbf{S}_c$ from the core, and similarly in the N_2 example there is a transition from case (a) toward case (b) with increasing J_c in the $N_2{}^+$ $A^2\Pi$ core state. In such a case each core state no longer corresponds to a single ket $|J_c\Omega_cM_c\rangle$ as indicated in Eq. (8), but rather is a superposition of several such functions with different Ω_c. The frame transformation matrix $\mathbf{U}_{I\beta}$ to be used in Eq. (14) is therefore the matrix product

$$U_{I\beta}=\sum U_{I,ca}U_{ca,\beta}, \tag{15}$$

where the matrix with elements $U_{I,ca}$ gives the decomposition of the spin-rotational core levels i of the core into pure case (a) core states [but case (e) for the electron plus core system] as assumed in Eq. (8), and $U_{ca,\beta}$ corresponds to the case (e) $\rightarrow$case (a) transformation of Eq. (12). An analogous situation is encountered in the rotational frame transformation for asymmetric top molecules where the case (d) to case (b) transformation connects pure symmetric top functions, but each core level is represented by a superposition of several symmetric top functions [27].

B. Resonant behavior of the scattering matrix

The preceding discussion focussed on the structure of the full $N\times N$ MQDT reactance matrices disregarding whether a given channel was open or closed. In the following we connect these to the asymptotic behavior of the wave function, and in particular to the scattering matrices of Sec. II.

In the eigenchannel approach the matrix $\mathbf{S}(E)^{(JMp)}$ of Eq. (5) is expressed in terms of its eigenvectors $T_{I\rho}$ and the eigenvalues $2\pi\tau_\rho$ of the open-channel interaction as

$$S_{I'I}^{(JMp)*}=e^{-i\eta_{I'}}\left[\sum_{\rho=1}^{N_o}T_{I'\rho}e^{-2i\pi\tau_\rho}(T^{\mathrm{tr}})_{\rho I}\right]e^{-i\eta_I}, \tag{16}$$

where η_I and $\eta_{I'}$ are the phase shifts due to the asymptotic Coulomb field in channels I and I'. The indices ρ thus denote the eigenstates of the interaction between the open (continuum) channels for given JMp, and N_o is the number of open channels at the given energy as in the preceding section. The multichannel wave function Ψ_ρ corresponding to eigenstates ρ of the open-channel interaction is an expansion over closed as well as open channels,

$$\Psi_\rho = \sum_{I=1}^{N} \left\{ \sum_{I'=1}^{N} \Phi_{I'}^{(JMp)} [f_{I'}(r)\mathcal{C}_{I'I} - g_{I'}(r)\mathcal{S}_{I'I}] \right\} B_{I\rho}, \tag{17}$$

where $f_{I'}(r)$ and $g_{I'}(r)$ are regular and irregular radial Coulomb functions, and $\mathbf{K} = \mathcal{S}\mathcal{C}^{-1}$ is the $N \times N$ reactance matrix of Eq. (14) (here the sine-type matrix $\mathcal{S}$ is not to be confused with the scattering matrix). The channel amplitudes $B_{I\rho}$ are determined in a diagonalization procedure in which the closed channel components of Ψ_ρ are forced to vanish at large r, and the open-channel components all assume the same phase shift $\pi\tau_\rho$ due to the non-Coulombic (i.e., short range) forces. That is we require Ψ_ρ to take the asymptotic form

$$\Psi_\rho \rightarrow \sum_{I'=1}^{N_o} \Phi_{I'}^{(JMp)} T_{I'\rho} \left(\frac{1}{\pi k_{i'}} \right)^{1/2} \sin(k_{i'} r + \eta_{I'} + \pi\tau_\rho). \tag{18}$$

The resulting N channel amplitudes $B_{I\rho}$ vary rapidly with energy in the vicinity of a bound state associated with a closed channel N_c. The superposition of eigenchannel functions Ψ_ρ,

$$\Psi_I^{(-)}(\text{coupled}) = \sum_{\rho=1}^{N_o} [\Psi_\rho e^{-i\pi\tau_\rho} (T^{\text{tr}})_{\rho I}] e^{-i\eta_I}, \tag{19}$$

then yields asymptotically the incoming-wave normalized scattering wave function of Eq. (5) with $\mathbf{S}^{(JMp)*}$ as given by Eq. (16). Equation (19) links the eigenchannel form of Eqs. (17) and (14) to the asymptotic scattering expression of Eq. (5), and the influence of the closed channels is now implicitly included within the Ψ_ρ of Eq. (17).

V. DIPOLE TRANSITION AMPLITUDES

A. General framework

In the present section we turn to the discussion of dipole transition amplitudes involved in the photoionization process. The physical picture of a photoionization process is as follows. The optical transition occurs preferentially while the electron is in the inner zone, where its kinetic and potential energies are comparable to the photon energy (cf. Fano [28]). This means that the absorption process itself is adequately described by a dipole transition moment $D_{\beta''}^{\beta'}$ (β' and β'' are the upper and lower states, respectively) in the case (a) formulation appropriate at short range. Once excited, the electron may roam to larger distances from the core, where it undergoes a transformation to the laboratory frame [Eq. (5)] before actually departing toward the apparatus which is set to detect a specific asymptotic channel i (see Sec. II).

In Sec. II and IV we discussed several alternative forms of the wave function representing a highly excited molecule fragmenting into a single electron and a molecular core. These are

$$\Psi_{\mathbf{k}_i}(\text{analyzer}) \ [\text{Eq. (2), complex}],$$

$$\Psi_I^{(-)}(\text{uncoupled}) \ [\text{Eq. (3), complex}],$$

$$\Psi_I^{(-)}(\text{coupled}) \ [\text{Eq. (5), complex}],$$

$$\Psi_\rho \ [\text{Eq. (17), real}].$$

To each form of the wave function there corresponds a transition dipole amplitude, e.g.,

$$D_{\beta''}^{I(-)}(\text{coupled}) \ [\text{Eq. (20) below, corresponding to } \Psi_I^{(-)}(\text{coupled})],$$

$$D_{\beta''}^{\rho} \ [\text{Eq. (21) below, corresponding to } \Psi_\rho],$$

where, for example, $D_{\beta''}^{\rho} = \langle \rho | r | \beta'' \rangle$, and β'' represents the initial (lower) state of the transition which for simplicity we assume to follow case (a) coupling (as indicated by the greek index). The generalization of the present formulation to situations where both the upper and lower states are represented by a multichannel wave function is straightforward, and will not be presented here. In the following we will relate the transition amplitudes to the real quantities

$$D_{\beta''}^{\rho'} \ [\text{Eqs. (21b) and (23) below}],$$

which are expressed entirely in the molecular frame and are analogous to the dipole transition moments obtained in quantum-chemical calculations.

Recalling Sec. IV B, it is an easy matter to establish the amplitude for a dipole transition from an initial lower state β'' to a final state $\Psi_I^{(-)}(\text{coupled})$. Based on Eq. (19), we write

$$D_{\beta''}^{I(-)}(\text{coupled}) = \sum_{\rho=1}^{N_o} [D_{\beta''}^{\rho} e^{-i\pi\tau_\rho} (T^{\text{tr}})_{\rho I}] e^{-i\eta_I}, \tag{20}$$

where, from Eq. (17),

$$D_{\beta''}^{\rho} = \sum_{I=1}^{N} D_{\beta''}^{I} B_{I\rho}. \tag{21a}$$

The real dipole amplitudes $D_{\beta''}^{I}$ correspond to the transitions from β'' to the function inside the bracket $\{\cdots\}$ in Eq. (17), and are not to be confused with the complex quantities $D_{\beta''}^{I(-)}(\text{coupled})$ of Eq. (20). Superposing the dipole amplitudes of Eq. (20) in the same way as the $\Psi_I^{(-)}(\text{coupled})$ functions are superposed in Eq. (6) yields the amplitude in the direction $\mathbf{k}$ corresponding to Eq. (1) with added incoming components. $D_{\beta''}^{\rho}$ in Eq. (20) replaces, as it were, half of the scattering process described by the scattering matrix Eq. (16), namely, the product $e^{-i\eta_{I'}} T_{I'\rho} e^{-i\pi\tau_\rho}$ describing the incoming wave components. The effective amplitude $D_{\beta''}^{\rho}$ is a coherent sum over all N channels, N_o open and N_c closed, with the channel-mixing amplitudes $B_{I\rho}$ and the $D^I_{\beta''}$.

The dipole amplitudes $D^I_{\beta''}$ in turn can be resolved into products of frame transformation matrix elements $U_{I\beta}$ and the real short-range dipole amplitudes $D^{\beta'}_{\beta''}$ as follows: We replace the channel amplitudes $B_{I\rho}$ by an alternative frame-transformed set $A_{\beta'\rho}$ according to

$$B_{I\rho}=\sum_{\beta'=1}^{N} U_{I\beta'}A_{\beta'\rho}. \tag{22}$$

We further use the well-known fact (see, e.g., Ref. [8]) that the energy dependence of the Coulomb functions related to the fine-structure quantum numbers (here Ω_c, J_c, and j) becomes negligible in the region near the core such that we can replace $f_{I'}(r)$ by $f_{i'l'}(r)$ and $g_{I'}(r)$ by $g_{i'l'}(r)$. Thus using the fact that $\mathbf{U}$ is diagonal in i' and l', we obtain for r values not too far from the core,

$$\Psi_\rho \approx \sum_{\beta'}\left\{\sum_{\beta}\left(\sum_{I'}\Phi^{(JMp)}_{I'}U_{I'\beta}\right)\times[f_{il}(r)\mathcal{C}_{\beta\beta'}-g_{il}(r)\mathcal{S}_{\beta\beta'}]\right\}A_{\beta'\rho}$$
$$\equiv\sum_{\beta'}\left\{\sum_{\beta}X^{(JMp)}_{\beta}[f_{il}(r)\mathcal{C}_{\beta\beta'}-g_{il}(r)\mathcal{S}_{\beta\beta'}]\right\}A_{\beta'\rho}, \tag{23}$$

where the functions $X^{(JMp)}_{\beta}$, obtained from the $\Phi^{(JMp)}_{I'}$ by transforming to the molecular frame, are equivalent to the case (a) functions of Eq. (9). Similarly, the cosine- and sine-type matrix elements $\mathcal{C}$ and $\mathcal{S}$ of Eq. (23) yield the *molecule-fixed* reactance matrix according to $\mathbf{K}=\mathcal{S}\mathcal{C}^{-1}$ [with elements $K_{\beta\beta'}$; cf. Eq. (14)]. The reader is reminded that the matrices with elements $\mathcal{C}_{\beta\beta'}$ and $\mathcal{S}_{\beta\beta'}$ are assumed to be diagonal in the case (a) quantum numbers S, Λ, and Ω. We thus obtain the alternative form of Eq. (21a),

$$D^{\rho}_{\beta''}=\sum_{\beta'=1}^{N} D^{\beta'}_{\beta''}A_{\beta'\rho}, \tag{21b}$$

where $D^{\beta'}_{\beta''}$ corresponds to the dipole amplitude for the transition from the lower state β'' to the function inside the bracket $\{\cdots\}$ in Eq. (23), and represents the desired case (a) to case (a) dipole amplitude. Further,

$$D^{I}_{\beta''}=\sum_{\beta'=1}^{N} U_{I\beta'}D^{\beta'}_{\beta''}. \tag{24}$$

We now briefly consider the particular case where resonance phenomena are absent or may be neglected; that is, all the channels are open, or the closed channels are physically irrelevant. This is the situation usually considered in scattering theory. In this case N_o equals N, and the eigenstates ρ of the scattering matrix coincide with the eigenchannels β' (see, e.g., Ref. [29]). These quantities then take the simple forms

$$T_{I\rho}=U_{I\beta'}, \tag{25a}$$

$$\tau_\rho=\mu_{\beta'}, \tag{25b}$$

$$B_{I\beta'}=U_{I\beta'}. \tag{25c}$$

The photoionization amplitude [Eq. (20)] for forming the system in the final channel I reduces to the simple expression

$$D^{I(-)}_{\beta''}(\text{coupled})=\sum_{\beta'=1}^{N}[D^{\beta'}_{\beta''}e^{-i\pi\mu_{\beta'}}(U^{\text{tr}})_{\beta' I}]e^{-i\eta_I}, \tag{26}$$

which describes the so-called ‘‘direct’’ photoionization process as a sequence of four successive stages: (i) photoabsorption at short range, $\beta''\rightarrow\beta'$; (ii) half-scattering off the core with phase shift, $\pi\mu_{\beta'}$; (iii) recoupling $\beta'\rightarrow I$ at larger distance; and (iv) half-scattering in the asymptotic Coulomb field with phase shift η_I and, finally, transformation to the uncoupled particle representation of Eq. (1) by means of Eq. (6).

The above type of expression is well known. We recall it here since it permits us to relate our expressions to those of other authors. For instance, the quantity $\langle J_c\Omega_c, lj|T(J)|\Omega''\rangle$ in Eq. (10b) of RC [to be entered into their Eq. (19) for the angular distribution of photoelectrons with defined spin polarization], corresponds to the amplitude $D^{I(-)}_{\beta''}$ of Eq. (20), while their Eq. (6) corresponds to the present coupled superposition Eq. (6). The product $D^{\beta'}_{\beta''}e^{-i\pi\mu_{\beta'}}$ represents the incoming-wave normalized molecule-fixed partial-wave dipole amplitude. The quantities $I^{L}_{\mathbf{k},n}$ and $I^{V}_{\mathbf{k},n}$ [Eqs. (4.1) and (4.2) of Ref. [30], or Eqs. (37) and (38) of Ref. [31]] derived by McKoy and co-workers correspond to expressions (20) and (26) of the present paper, with two differences. First, these authors used a uncoupled representation, and, second, these authors do not give the details of the expansion of the vector $\mathbf{k}$. However, the relation to the present Eqs. (20) and (26) is obvious.

Finally, $D^{\beta'}_{\beta''}$ is the standing-wave-normalized molecule-fixed partial-wave dipole amplitude which is used frequently in applications of molecular quantum defect theory. Here we limit ourselves to spelling out $D^{\beta'}_{\beta''}$ for transitions in diatomic molecules. Equations (20) and (21b), or Eq. (26), can then be used together with the frame transformation Eq. (12) to construct the desired full dipole amplitude. Here we do not give the formulas for the photoionization cross section in terms of dipole amplitudes. The corresponding expressions are known [e.g., Eqs. (7.69) and (2.9) of Ref. [15], or Eqs. (17)–(20) of RC].

B. Hund’s case (a) dipole transition amplitudes

In the present context of spin-electronic-rotational channel interactions, the asymptotic channels I are the case (e) states of Eq. (8), while the short-range eigenchannels β are the case (a) states of Eq. (9). The dipole amplitude $D^{\beta'}_{\beta''}$ of Eq. (21b) corresponds to this situation. Here we consider a photoexcitation process from the ground state or a transition between Rydberg states. For simplicity, we again assume that the lower state follows Hund’s case (a) strictly, and moreover that electronic channel interactions and l mixing occur only in the upper state. In practice, if the lower state is itself a Rydberg state, one will have to sum over the relevant lower state channel indices exactly as outlined here for the upper-state channels [Eqs. (20) and (21) above, and Eq. (28) below]. If, on the other hand, the lower state is a non-Rydberg state the labels $i''\Lambda''_c q''_c l''$ have no strict meaning and should be suppressed, and the explicit lower state radial function in Eq. (29) must be replaced accordingly. The electric dipole transition leaves the spin quantum numbers S_c and S (and of course s) unchanged. The labels S_c and s are therefore omitted from the following expressions. The molecule-fixed standing-wave dipole amplitude $D^{\beta'}_{\beta''}$ of Eq. (21b) takes the form

$$D^{S'\Lambda'\Omega',J'M'p',i'\Lambda'_c q'_c l'}_{S''\Lambda''\Omega'',J''M''p'',i''\Lambda''_c q''_c l''}(m_\gamma)=[(2J'+1)(2J''+1)]^{1/2}\left[\frac{1+(-1)^{p'+p''+1}}{2}\right]\left[(-1)^{M''+m_\gamma}\begin{pmatrix} J' & 1 & J'' \\ M' & -m_\gamma & -M''\end{pmatrix}\right]$$
$$\times(-1)^{-\Omega''}\sum_{\nu=-1}^{+1}\left\{\begin{pmatrix} J' & 1 & J'' \\ \Omega' & \nu & -\Omega''\end{pmatrix} g^{S'\Lambda'\Omega',i'\Lambda'_c q'_c l'}_{S''\Lambda''\Omega'',i''\Lambda''_c q''_c l''}(\nu)\right.$$
$$\left.+(-1)^{p'-S'+J'+q'_c}\begin{pmatrix} J' & 1 & J'' \\ -\Omega' & \nu & -\Omega''\end{pmatrix} g^{S'-\Lambda'-\Omega',i'-\Lambda'_c q'_c l'}_{S''\Lambda''\Omega'',i''\Lambda''_c q''_c l''}(\nu)\right\}, \tag{27}$$

where the quantities g are symmetrized electronic dipole transition moments:

$$g^{S'\Lambda'\Omega',i'\Lambda'_c q'_c l'}_{S''\Lambda''\Omega'',i''\Lambda''_c q''_c l''}(\nu)=\sum_{i(\Lambda_c,q_c),l}\left\{\left[\frac{1}{(1+\Delta_2)(1+\Delta''_2)}\right]^{1/2}\left[\frac{1+\Delta_3\Delta''_3(-1)^{q+q''}}{\sqrt{1+\Delta_3}\sqrt{1+\Delta''_3}}\right]d^{\Lambda',i\Lambda_c q_c l;\Lambda',i'\Lambda'_c q'_c l'}_{\Lambda'',i''\Lambda''_c q''_c l''}(\nu)\right.$$
$$\left.+(-1)^{q_c+q}\left[\frac{1}{(1+\Delta_2)(1+\Delta''_2)}\right]^{1/2}\left[\frac{\Delta_3+\Delta''_3(-1)^{q+q''}}{\sqrt{1+\Delta_3}\sqrt{1+\Delta''_3}}\right]d^{-\Lambda',i-\Lambda_c q_c l';\Lambda',i'\Lambda'_c q'_c l'}_{\Lambda'',i''\Lambda''_c q''_c l''}(\nu)\right\}. \tag{28}$$

These are in turn expressed in terms of unsymmetrized dipole transition amplitudes d specified in Eqs. (29) below. In Eqs. (27) and (28), we explicitly indicate the quantum numbers associated with channels β, β', and β''.

The quantum number m_γ in Eq. (27) is the photon polarization in the laboratory frame, i.e., $m_\gamma=0$ or ±1 depending on whether the space-fixed component Z or $(X\pm iY)/\sqrt{2}$ is considered [cf., e.g., expressions (17)–(20) of RC]. ν is the polarization in the molecular frame. The rotational factors multiplying the first electronic transition moment in Eq. (27) correspond precisely to the direction cosine matrix elements $\alpha_{Z,q},(2)^{-1/2}(\alpha_{X,q}\pm i\alpha_{Y,q})$ $(q=x,y,z)$ with phases as given by Hougen [10] in his Tables 6 and 7. For unpolarized light the third bracket $[\cdots]$ on the right-hand side of Eq. (27) containing the dependence on M'' and M' is to be replaced [10] by $\sqrt{\pm1/3}$ where the minus sign is taken for molecules possessing an odd number of electrons. [The complex factor i resulting in the latter case is compensated for by a corresponding complex factor arising from the half-integral exponent of $(-1)^{-\Omega''}$ in Eq. (27).]

Turning to Eq. (28) we note that the Σ_β in the second line of Eq. (23) reappears as the sum over core states i and associated partial wave components l in Eq. (28). Correspondingly the unsymmetrized dipole amplitudes d exhibit a double dependence on excited state channel indices whose origin are the double indices of the elements $\mathcal{C}_{\beta\beta'}$ and $\mathcal{S}_{\beta\beta'}$ in Eq. (23). Notice further how all the factors arising from symmetrization and expressed in terms of $\Delta_2(\Lambda_c,\Lambda,\Omega)$, $\Delta_3(\Lambda_c,\Lambda,\Omega)$, and q [defined in Eqs. (9b) and (9c) and Appendix A] are condensed in the brackets $[\cdots]$ multiplying the unsymmetrized electronic transition moments d in Eq. (28). We see in particular that if $\Delta_3=\Delta''_3=1$, $q+q''$ must be even, i.e., the well-known selection rule $\Sigma^+\leftrightarrow\Sigma^+$, $\Sigma^-\leftrightarrow\Sigma^-$, $\Sigma^+\not\leftrightarrow\Sigma^-$ is recovered.

The unsymmetrized electronic transition moments $d^{\beta,\beta'}_{\beta''}$ for excitation of the outer electron have the form

$$d^{\Lambda',i\Lambda_c q_c l;\Lambda',i'\Lambda'_c q'_c l'}_{\Lambda'',i''\Lambda''_c q''_c l''}(\nu)=[(2l+1)(2l''+1)]^{1/2}(-1)^{\Lambda''-\Lambda''_c}\begin{pmatrix} l & 1 & l'' \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & 1 & l'' \\ \Lambda'-\Lambda_c & \nu & -\Lambda''+\Lambda''_c\end{pmatrix}$$
$$\times\delta_{ii''}\delta_{\Lambda_c\Lambda''_c}\delta_{q_c q''_c}\langle f_{k_i l}(r)\mathcal{C}_{\beta\beta'}-g_{k_i l}(r)\mathcal{S}_{\beta\beta'}|r|f_{k_{i''}l''}(r)\mathcal{C}_{\beta''\beta''}-g_{k_{i''}l''}(r)\mathcal{S}_{\beta''\beta''}\rangle. \tag{29a}$$

On the left-hand side of Eq. (29a), and below in Eq. (29b), we used the expanded form of the labeling of β and β' with all quantum numbers given explicitly, while on the right-hand side we use the shorthand notation. The last factor in Eq. (29a) is the energy-dependent purely radial transition integral. Each bra and ket involved in the integral is understood to stand for the radial part of Eq. (23) for given β,β', as well as its continuation inside the core. k_i is the electron wave number in channel

i as in Eqs. (2) and (3), with $k_i = i/\nu_i$ for bound states and ν_i the effective principal quantum number. There is the alternative possibility that the *core* rather than the outer electron is excited. In this event the electronic transition moment will be given by

$$d^{\Lambda',i\Lambda_c q_c l;\Lambda',i'\Lambda'_c q'_c l'}_{\Lambda'',i''\Lambda''_c q''_c l''}(\nu) = \langle i\Lambda_c q_c|\mathbf{r}_\nu|i''\Lambda''_c q''_c\rangle \delta_{ll''}\delta_{\Lambda'-\Lambda_c,\Lambda''-\Lambda''_c}\langle f_{k_i l}(r)\mathcal{C}_{\beta\beta'} - g_{k_i l}(r)\mathcal{S}_{\beta\beta'}|f_{k_{i''}l''}(r)\mathcal{C}_{\beta''\beta''} - g_{k_{i''}l''}(r)\mathcal{S}_{\beta''\beta''}\rangle, \tag{29b}$$

where the shorthand notation β is as used before. In Eq. (29b) $\mathbf{r}_\nu$ stands for the molecule-fixed components z or $(x \pm iy)/\sqrt{2}$ of the dipole moment operator, respectively. The dipole amplitude $d^{\beta,\beta'}_{\beta''}(\nu)$ relates to the asymptotic standing wave functions associated with the **K** matrix, and therefore is always real. The transition moments Eqs. (29a) and (29b) have the dimension of a *length* if discrete-discrete transitions are considered, and normalization to unity is used. Their dimension is length$\times$[energy]$^{-1/2}$ if a photoionization process is considered with the initial state normalized to unity and the continuum normalized to the energy. Finally, in the framework of MQDT, both the initial and final states may be normalized to the energy irrespective of their discrete or continuous character, so that the dimension of the transition moments will be (length)$\times$[energy]$^{-1}$.

In summary then, Eqs. (27)–(29) relate the body-frame case (a) to case (a) rotational-electronic dipole transition moments to the purely radial electronic amplitudes $\langle f_{k_i l}(r)\mathcal{C}_{\beta\beta'} - g_{k_i l}(r)\mathcal{S}_{\beta\beta'}|r|f_{k_{i''}l''}(r)\mathcal{C}_{\beta''\beta''} - g_{k_{i''}l''}(r)\mathcal{S}_{\beta''\beta''}\rangle$ for excitation of the outer electron, or alternatively to the dipole amplitudes for core excitation, $\langle i\Lambda_{ci}|\mathbf{r}_\nu|i''\Lambda''_c\rangle$, and the radial Rydberg overlap integral $\langle f_{k_i l}(r)\mathcal{C}_{\beta\beta'} - g_{k_i l}(r)\mathcal{S}_{\beta\beta'}|f_{k_{i''}l''}(r)\mathcal{C}_{\beta''\beta''} - g_{k_{i''}l''}(r)\mathcal{S}_{\beta''\beta''}\rangle$. The somewhat unwieldy form of Eq. (28) is more apparent than real, since Δ_2 and Δ_3 are zero in most cases and they never differ from zero simultaneously. In addition, if there are no electronic channel interactions as well as l mixing (as, e.g., in high orbital angular momentum states) there will be no off-diagonal matrix elements $\mathcal{C}_{\beta\beta'}$ and $\mathcal{S}_{\beta\beta'}$ in Eq. (29), and hence with $\beta = \beta'$ the awkward (but necessary) double dependence of the d's on excited state channel indices β and β' disappears as does the sum in Eq. (28).

VI. CONCLUSION

In this paper we have discussed molecular electronic photoexcitation processes, putting discrete and continuum transitions on an equal footing. We combined the scattering theoretical formulation for the final-state wave function with Hund's angular momentum coupling schemes which are usually restricted to the spectroscopy of discrete-discrete transitions. We have taken account of the electron spins, and our derivation takes full account of the symmetry requirements in the initial and final states, which in previous work were either only partially included, or only in the context of simpler coupling situations. One consequence of this is that parity selection rules such as derived by XZ are replaced by the simple requirement that $p'' + p_c + l$ must be odd in a one-photon transition. The proper symmetry of Σ^+ and Σ^- electronic states has been fully taken into account here—for the first time as far as we are aware.

Our hope is that the present work clarifies and unifies the various formulations of the angular momentum coupling and transition moment amplitudes found in the literature. Far from the core, Hund's case (e) coupling is common to both the spin-resolved photoionization and discrete-discrete Rydberg spectroscopy. The dipole transition amplitude builds up in the inner region close to the core where case (a) or case (c) coupling prevails. Correspondingly, the transition moment is transformed to Hund's case (e), appropriate in the asymptotic situation of two distinct fragments. When an excited state is embedded in the electronic continuum the effective coupling situation may strongly vary with energy, a complication that is naturally accounted for through the use of MQDT. The frame transformation and dipole transition moment expressions given here have been used routinely and extensively by the authors for several years, albeit mostly in situations where the electron spins can be neglected. These applications include electronic single-channel situations [case (d)–case (d) high-l transitions [32]], electronic multichannel situations involving l mixing [33] or interactions between channels corresponding to different core states [34] as well as the calculation of rotationally resolved cross sections including spin polarization [35].

In this paper we have expressed the final-state wave function in a total angular momentum-coupling scheme. An alternative approach based on the ''transferred'' angular momentum j_t was introduced in Refs. [36] and [37], and was also used as one of two alternative coupling schemes by RC. This alternative approach explicitly introduces the photon angular momentum into the coupling scheme, and has provided particular insight into the photoionization process itself. However, this approach has found only limited use in molecules, possibly because the connection to the spectroscopy is not as easily established as in the total angular momentum coupling scheme.

We stress finally that the transition moments $D^{I(-)}_{\beta''}$(coupled) of Eq. (20) can be used in a variety of problems which have not been considered in detail here. In each such case it is sufficient to establish the relevant cross-section expressions in terms of the $D^{I(-)}_{\beta''}$(coupled). We mention photoionization of aligned and oriented molecules [38] prepared in the initial state through n-photon excitation and ionized by an additional photon [39] or in the final state by measuring the polarization of the fluorescence of the ion [40]. ''Complete'' experiments have also been carried out with molecules [41]. Reference [41] deals with the inversion of experimental data with the aim of extracting the module of the complex quantities $D^{I(-)}_{\beta''}$(coupled) as well as their relative phases. This is achieved by measuring the difference between the rotationally resolved cross sections obtained with left and right circularly polarized light. Therefore it appears that the transformations derived in the present paper are useful in the spectroscopy of excited states and other contexts.

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APPENDIX A: SYMMETRY PROPERTIES OF THE CASE (a) BASIS EQ. (9) FOR $\Lambda=0$

The case (a) spin-roronic basis of Eq. (9) is defined such that for $\Lambda=0$ the electronic orbital part can be factored out and has definite Σ^+ or Σ^- symmetry. We verify this by checking all possible cases in turn.

(a) $\Lambda=0$, $\Lambda_c=0$, any Ω: $\Delta_3=0$ in Eq. (9c), and only the first bracket $[\cdot\cdot\cdot]$ is present in Eq. (9); $\lambda=0$ and the electronic orbital part $|\Lambda_c=0\rangle|l,\lambda=0\rangle$ can be factored out. Equations (10b) and (10d) give

$$E^*|\Lambda_c=0\rangle|l,\lambda=0\rangle=(-1)^{q_c}|\Lambda_c=0\rangle|l,\lambda=0\rangle, \quad \text{(A1)}$$

i.e., $q_c=0$ (1) yields ${}^S\Sigma^+_\Omega$ (${}^S\Sigma^-_\Omega$) electronic symmetry, respectively.

(b) $\Lambda=0$, $\Lambda_c\neq0$, $\Omega=0$: $\Delta_3=0$ in Eq. (9c), and again only the first bracket $[\cdot\cdot\cdot]$ is present in Eq. (9), and $\lambda=-\Lambda_c$ and $\Sigma=\Omega-\Lambda=0$. Equation (9) takes the form

$$\begin{aligned}|S,\Lambda=0,\Omega=0\rangle=\frac{1}{\sqrt{2}}&[|\Lambda_c\rangle|l,-\Lambda_c\rangle+(-1)^{p-q_c-S+J}\\ &\times|-\Lambda_c\rangle|l,+\Lambda_c\rangle]|S,\Sigma=0\rangle|J,\Omega=0,M\rangle.\end{aligned} \quad \text{(A2)}$$

Application of the space-fixed inversion operation to the electronic orbital factor yields $E^*[\cdot\cdot\cdot]=(-1)^{p-S+J}[\cdots]$, i.e., levels with $p-S+J$ even (odd) belong to a ${}^S\Sigma^+_0$ (${}^S\Sigma^-_0$) electronic state, respectively.

(c) $\Lambda=0$, $\Lambda_c\neq0$, $\Omega\neq0$: $\Delta_3=1$ in Eq. (9c), and both brackets $[\cdots]$ in Eq. (9) are present with $\lambda=-\Lambda_c$ and $\Sigma=\Omega-\Lambda\neq0$. The terms of Eq. (9) can be rearranged as

$$\begin{aligned}|S,\Lambda=0,\Omega\neq0\rangle=\tfrac{1}{2}&[|\Lambda_c\rangle|l,-\Lambda_c\rangle+(-1)^{q-q_c}\\ &\times|-\Lambda_c\rangle|l,+\Lambda_c\rangle]\\ &\times[|S\Sigma\rangle|J\Omega M\rangle+(-1)^{p-q-S+J}|\\ &\times|S-\Sigma\rangle|J-\Omega M\rangle],\end{aligned} \quad \text{(A3)}$$

where the electronic-orbital and the electron-spin-rotational factors of the case (a) wave function are now symmetrized separately. With Eqs. (10) we verify easily that E^* applied to the electronic orbital factor yields $E^*[\cdot\cdot\cdot]=(-1)^q[\cdot\cdot\cdot]$ and E^* applied to the spin-rotational factor yields $E^*[\cdot\cdot\cdot]=(-1)^{p-q}[\cdot\cdot\cdot]$, with the result that the total wave function has total parity $(-1)^p$, while the electronic orbital factor has Σ^+ or Σ^- character depending on whether $q=0$ or 1. In order to avoid double occurrences of the same spin-rotational wave function $\Sigma=\Omega-\Lambda$ in Eq. (A3) should in principle be restricted to positive values as this was done already for Λ_c in Sec. III. At the same time the electronic symmetry index takes the values $q=0$ and 1. The same states are obtained if instead we let the spin component $\Sigma=\Omega-\Lambda$ take positive as well as negative values, in line with the practice adopted in Sec. III, with the additional proviso that $q=0$ for $\Sigma>0$ and $q=1$ for $\Sigma<0$. We adopt this latter convention here.

APPENDIX B: FRAME TRANSFORMATION FOR SPINLESS MOLECULES

When $s=S=S_c=0$, Hund's case (a) is replaced by case (b), and case (e) is replaced by case (d). We then have

$$J\rightarrow N,\quad J_c\rightarrow N_c,\quad \Omega\rightarrow\Lambda,\quad \Omega_c\rightarrow\Lambda_c,\quad j\rightarrow l.$$

The first and third symbols in each ket of Eqs. (8) and (9) are now redundant, and can be omitted. In all there are now seven instead of 11 quantum numbers in the minimal set, of which six are common to both coupling cases. The frame transformation elements thus take the form

$$\begin{aligned}\langle N_c|\Lambda\rangle^{(NM_p,\Lambda_c q_c l)}=&\frac{1}{(1+\delta_{\Lambda 0}\delta_{\Lambda_c 0})^{1/2}}\frac{1}{(1+\delta_{\Lambda_c 0})^{1/2}}\\ &\times(2N_c+1)^{1/2}(-1)^{N-\Lambda}\\ &\times[1+\delta_{\Lambda_c 0}(-1)^{p-q_c-N_c+l}]\\ &\times\begin{pmatrix}N_c & l & N\\ \Lambda_c & \Lambda-\Lambda_c & -\Lambda\end{pmatrix}.\end{aligned} \quad \text{(B1)}$$

Note that, according to the remarks made after Eq. (13) above, Λ takes values $\Lambda_c-l,\ldots,\Lambda_c+l$ when $\Lambda_c\geqslant0$. [For example, in a molecule with a II ionic core and an excited d electron there will be two types of molecular II states, arising from $\Lambda=-1$ ($d\delta$ electron, $\lambda=-2$) and $\Lambda=+1$ ($d\sigma$ electron, $\lambda=0$), respectively.] As pointed out previously [27], Eq. (B1) differs from that given by Chang and Fano [12], which takes incorrect account of factors $\sqrt{2}$ arising from symmetrization. We finally consider the special case where $\Lambda_c=0$. The symbol Λ_c can now also be omitted, and Eq. (B1) reduces further to

$$\begin{aligned}\langle N_c|\Lambda\rangle^{(NMp,q_c l)}=&\left[\frac{2}{(1+\delta_{\Lambda 0})}\right]^{1/2}(2N_c+1)^{1/2}\\ &\times(-1)^{N-\Lambda}\left[\frac{1+(-1)^{p-q_c-N_c+l}}{2}\right]\\ &\times\begin{pmatrix}N_c & l & N\\ 0 & \Lambda & -\Lambda\end{pmatrix}.\end{aligned} \quad \text{(B2)}$$

Note that here Λ is again restricted to values $0,\ldots,+l$. The above expression is very well known, and has been widely used in applications of molecular multichannel quantum defect theory. Notice, however, how in the form given here full account has been taken of the parity requirements: In the case, e.g., of a ${}^1\Sigma^+$ core ($q_c=0$) with given l and total parity p, Eq. (B2) tells us right away that $p-N_c+l$ must be *even*, which means that only core levels with either *even* or *odd* N_c are coupled together.

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