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Dispersion forces and long-range electronic transition dipole moments of alkali-metal dimer excited states

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A formalism of degenerate perturbation theory is presented, in which the initial basis set of functions is fully adapted to the perturbation. This full adaptation is obtained by imposing a simple condition which leads to an iteration procedure free of singularities. The formalism includes as a special case nondegenerate perturbation theory. By using it we calculate the dispersion coefficients of alkali-metal dimers for molecular states which dissociate into one atom in the ground state and the other in one of the first two *S*, *P*, or *D* excited states. The dispersion forces are extracted from the first- and second-order energy corrections. Model potentials are used in order to describe the motion of the valence electron in the field of the alkali-metal positive-ion core. Using the first-order wave-function correction, we investigate the leading terms of the long-range expansion of the electronic transition dipole moments. An extension of the Dalgarno-Lewis method is developed in order to handle the radial matrix elements which involves a reduced Green's function for real and complex energies. The results are compared with previous computations.

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I. INTRODUCTION

A knowledge of the potential-energy curves and electronic transition dipole moments of diatomic systems near the dissociation limit plays an important role in the study of cold collision processes and laser cooling and trapping of atoms. In this paper we study the dispersion coefficient between two alkali-metal atoms, one of which is excited in an *S*, *P*, or *D* state. We investigate also the long-range limits of the electronic transition dipole moments from the ground state to these excited states.

At large nuclear separations R where the overlap of the atomic charge distributions can be neglected but where the contribution of retardation effects is still unimportant, it is convenient to represent the internuclear interaction potential by an asymptotic expansion in inverse powers of R. The coefficients of this expansion are the dispersion coefficients. They can be computed using perturbation theory in which the perturbation is the Coulomb interaction between the atomic charge distributions. For alkali-metal atoms the approximation can be made from taking explicitly into account only the valence-electron contribution. That can be done by introducing a model potential describing the motion of the valence electron in the presence of a frozen core. In our paper we used the l-dependent model potentials derived in Ref. [1].

In Sec. II we present the formalism of "degenerate perturbation theory in a fully adapted basis." It is a natural development of perturbation theory which incorporates both the degenerate and nondegenerate cases. The essential feature consists of imposing certain conditions on the initial basis set of functions in order to avoid any singularities during the iteration procedure. Thus secular equations appear at the outset, constructed from conditions imposed on the initial basis set of functions. We use the theory in Sec. III to calculate the dispersion coefficients for the molecular states that dissociate into one atom in the ground state and the other in any of the first two *S*, *P*, or *D* excited states of alkali-metal atoms. For the *nS*-*mS* dissociation limit we compute the C_6, C_8, and C_{10} dispersion coefficients. For the *nS*-*mP* dissociation limit we compute the C_3, C_6, and C_8 coefficients and for the *nS*-*mD* dissociation limit we compute the C_5 and C_6 dispersion coefficients. The radial sums are computed using a complex integral representation similar to that described by Chan and Dalgarno [2] for the ground-state interaction. In Sec. IV we compute the long-range coefficients for the electronic transition dipole moments from the ground molecular state to those molecular states which dissociate into one atom in the ground state and the other into one of the first two *P* or *D* excited states. The theory is carried out for arbitrary light polarizations. The final results are particularized to linear and circular polarization. In Sec. V, we describe the numerical method used in the computation of the dispersion coefficients and the long-range coefficients of the electronic transition dipole moments. We develop an extension of the Dalgarno-Lewis method [3] in order to determine exactly the matrix elements which involve reduced radial Green's functions for real or complex energies. The numerical results are presented in Sec. VI. A critical comparison with previous computations is made. The conclusions are presented in Sec. VII. This paper has four appendixes which describe the analytical details.

II. DEGENERATE PERTURBATION THEORY IN A FULLY ADAPTED BASIS

Let H be a Hamiltonian which can be written as a sum of an unperturbed Hamiltonian H_0 and a perturbation term λV,

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$$H=H_0+\lambda V , \tag{1}$$

where λ is a real parameter. We assume that the eigenvalue problem for H_0 has been solved. Let $E_m^{(0)}$ be a degenerate eigenvalue of the unperturbed Hamiltonian and let $\mathcal{E}_m^{(0)}$ be its invariant subspace. There is more then one eigenvalue of H tending to $E_m^{(0)}$ when λ goes to zero. We denote these eigenvalues by E_{mp} and their invariant subspaces by $\mathcal{E}_{mp};p$ is a degeneracy index. In the limit as λ goes to zero, $E_{mp}\rightarrow E_m^{(0)}$ and $\mathcal{E}_{mp}$ becomes a subspace of $\mathcal{E}_m^{(0)}$. Because $\mathcal{E}_{mp}$ are disjoint subspaces for any λ, corresponding to different eigenvalues, in the limit $\lambda\rightarrow 0$ they become a disjoint partition of $\mathcal{E}_m^{(0)}$. An orthogonal complete set of eigenvectors of H_0 which respects this disjoint partition of the $\mathcal{E}_m^{(0)}$ subspace is a fully adapted basis for the perturbation problem.

In the conventional formulation of degenerate perturbation theory [4] the iteration procedure starts with an arbitrary orthogonal complete set of eigenvectors of H_0,

$$H_0\varphi_{nl}^{(0)}=E_n^{(0)}\varphi_{nl}^{(0)} , \tag{2}$$

where the second index of φ is the degeneracy index. The condition

$$\langle \varphi_{nl}^{(0)}|\varphi_{nl}^{(k)}\rangle=\delta_{0k}, \tag{3}$$

where $\varphi_{nl}^{(k)}$ are the kth-order corrections to the wave functions, is assumed. The adapted basis is built order by order, in the solution of the secular equations. For a given order of perturbation the construction of the secular equation involves an examination of the next higher order of perturbation in order to remove the singularities caused by the choice of the initial basis. This complicated procedure can be avoided if the initial basis is a fully adapted basis at the outset.

Suppose that we are interested in the E_{mp} states of H which tend to $E_m^{(0)}$ in the limit that λ goes to zero. The initial basis should be a fully adapted basis for the perturbation problem corresponding to the $\mathcal{E}_m^{(0)}$ subspace. We denote the components of this basis outside of the $\mathcal{E}_m^{(0)}$ subspace by $\varphi_{nl}^{(0)}$. They are arbitrary orthonormal eigenvectors of H_0 and they satisfy Eq. (2). The components of the basis which lie in the $\mathcal{E}_m^{(0)}$ subspace are denoted by $\Psi_{mp}^{(0)}$. They are also orthonormal eigenvectors of H_0 and obviously they satisfy the eigenvalue equation

$$H_0\Psi_{mp}^{(0)}=E_m^{(0)}\Psi_{mp}^{(0)} . \tag{4}$$

This basis is a fully adapted basis of the $\mathcal{E}_m^{(0)}$ subspace if

$$\langle \Psi_{mq}^{(0)}|\Psi_{mp}^{(k)}\rangle=\delta_{0k}\delta_{pq} . \tag{5}$$

Thus all the wave-function corrections $\Psi_{mp}^{(k)}$ for $k\geq 1$ are orthogonal on the $\mathcal{E}_m^{(0)}$ subspace. The condition given by Eq. (5) is not immediately useful but can be rewritten explicitly in each order of perturbation.

The equation for the first order of perturbation is

$$(H_0-E_m^{(0)})\Psi_{mp}^{(1)}=-V\Psi_{mp}^{(0)}+E_{mp}^{(1)}\Psi_{mp}^{(0)} . \tag{6}$$

Multiplying both sides of Eq. (6) by $\Psi_{mq}^{(0)}$ and integrating over configuration space we get

$$E_{mp}^{(1)}=\langle \Psi_{mp}^{(0)}|V|\Psi_{mp}^{(0)}\rangle , \tag{7}$$

and the condition

$$\langle \Psi_{mq}^{(0)}|V|\Psi_{mp}^{(0)}\rangle=\delta_{pq}E_{mp}^{(1)} , \tag{8}$$

which must be satisfied by $\Psi_{mp}^{(0)}$. Multiplying Eq. (6) with $\varphi_{nl}^{(0)}$ and integrating over configuration space we get for the coefficients of $\Psi_{mp}^{(1)}$ in our basis

$$a_{mpnl}^{(1)}=-\frac{\langle \varphi_{nl}^{(0)}|V|\Psi_{mp}^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}} \quad \text{for } n\neq m . \tag{9}$$

From Eq. (5) for $k=1$ we have $a_{mpmq}^{(1)}=0$ and so

$$\Psi_{mp}^{(1)}=-\sum_{nl}\varphi_{nl}^{(0)}\frac{\langle \varphi_{nl}^{(0)}|V|\Psi_{mp}^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}} , \tag{10}$$

where the sum is over all possible pairs of indices nl of the $\varphi_{nl}^{(0)}$ functions. Thus $\Psi_{mp}^{(1)}$ is orthogonal on the $\mathcal{E}_m^{(0)}$ subspace.

In the second order of perturbation we have the equation

$$(H_0-E_m^{(0)})\Psi_{mp}^{(2)}=-V\Psi_{mp}^{(1)}+E_{mp}^{(0)}\Psi_{mp}^{(0)}+E_{mp}^{(1)}\Psi_{mp}^{(1)} . \tag{11}$$

Again multiplying by $\Psi_{mq}^{(0)}$ and integrating over configuration space we get

$$E_{mp}^{(2)}=\langle \Psi_{mp}^{(0)}|V|\Psi_{mp}^{(1)}\rangle , \tag{12}$$

or using Eq. (10)

$$E_{mp}^{(2)}=-\sum_{nl}\frac{\langle \Psi_{mp}^{(0)}|V|\varphi_{nl}^{(0)}\rangle\langle \varphi_{nl}^{(0)}|V|\Psi_{mp}^{(0)}\rangle}{E_n^{(0)}-E_m^{(0)}} . \tag{13}$$

We get also the condition for the $\Psi_{mq}^{(0)}$ functions,

$$\langle \Psi_{mq}^{(0)}|V|\Psi_{mp}^{(1)}\rangle=\delta_{pq}E_{mp}^{(2)} , \tag{14}$$

where we used Eq. (5) for $k=1$. The coefficients of $\Psi_{mp}^{(2)}$ in our basis are found by multiplying in Eq. (11) by $\varphi_{nl}^{(0)}$ and integrating over configuration space,

$$a_{mpnl}^{(2)}=-\langle \varphi_{nl}^{(0)}|V-E_{mp}^{(1)}|\Psi_{mp}^{(1)}\rangle \quad \text{for } n\neq m . \tag{15}$$

From Eq. (5) with $k=2$ we have $a_{mpmq}^{(2)}=0$ and so

$$\Psi_{mp}^{(2)}=\sum_{nln'l'}\varphi_{nl}^{(0)}\frac{\langle \varphi_{nl}^{(0)}|V-E_{mp}^{(1)}|\varphi_{n'l'}\rangle\langle \varphi_{n'l'}|V|\Psi_{mp}^{(0)}\rangle}{(E_n^{(0)}-E_m^{(0)})(E_{n'}^{(0)}-E_m^{(0)})} . \tag{16}$$

Again the sum from Eq. (16) is over the indices of the $\varphi_{nl}^{(0)}$ functions and so $\Psi_{mp}^{(2)}$ is orthogonal on the $\mathcal{E}_m^{(0)}$ subspace.

In a similar fashion starting with the equation for the third order of perturbation,

$$(H_0-E_m^{(0)})\Psi_{mp}^{(3)} =-V\Psi_{mp}^{(2)}+E_{mp}^{(3)}\Psi_{mp}^{(0)}+E_{mp}^{(2)}\Psi_{mp}^{(1)}+E_{mp}^{(1)}\Psi_{mp}^{(2)} , \tag{17}$$

we get

$$E_{mp}^{(3)}=\langle \Psi_{mp}^{(0)}|V|\Psi_{mp}^{(2)}\rangle , \tag{18}$$

and the condition for the $\Psi_{mp}^{(0)}$ functions

$$\langle \Psi_{mq}^{(0)}|V|\Psi_{mp}^{(2)}\rangle=\delta_{pq}E_{mp}^{(3)} , \tag{19}$$

where we used Eq. (5) for $k=1$ and 2. The wave-function correction in the third order of perturbation theory is

$$\Psi_{mp}^{(3)} = -\sum_{nl} \varphi_{nl}^{(0)} \frac{\langle \varphi_{nl}^{(0)} | V - E_m^{(1)} | \Psi_{mp}^{(2)} \rangle}{E_n^{(0)} - E_m^{(0)}} + E_{mp}^{(2)} \sum_{nl} \varphi_{nl}^{(0)} \frac{\langle \varphi_{nl}^{(0)} | V | \Psi_{mp}^{(2)} \rangle}{(E_n^{(0)} - E_m^{(0)})^2} , \tag{20}$$

and so $\Psi_{mp}^{(3)}$ is orthogonal on the $\mathcal{E}_m^{(0)}$ subspace. Similar equations can be established in each order of perturbation.

It is clear that Eq. (5) is equivalent to the following set of equations:

$$\begin{aligned} &\langle \Psi_{mp}^{(0)} | \Psi_{mp}^{(k)} \rangle = \delta_{0k} , \\ &\langle \Psi_{mq}^{(0)} | V | \Psi_{mp}^{(k)} \rangle = \delta_{pq} \langle \Psi_{mp}^{(0)} | V | \Psi_{mp}^{(k)} \rangle , \end{aligned} \tag{21}$$

and that Eqs. (21) imply Eq. (5). The first equation in (21) is the normalization equation of the perturbation theory, Eq. (3), which ensures that in the limit λ goes to zero, where the perturbation vanishes, the wave function is normalized to unity. The second equations are the secular equations which should be obeyed by the $\Psi_{mq}^{(0)}$ functions. Thus perturbation theory with the condition Eq. (5) leads to the same conclusion as conventional degenerate perturbation theory, except that the secular equations appear from the beginning as a condition for an adapted basis. The energy and wave-function corrections are established in each order without examining the next higher order of perturbation.

From Eqs. (8), (14), and (19) we conclude that in order to have a fully adapted basis for the $\mathcal{E}_m^{(0)}$ subspace it is sufficient that the function $\Psi_{mp}^{(0)}$ satisfy the condition

$$\sum_{\{nl\}} \left\langle \Psi_{mq}^{(0)} \left| V \frac{|\varphi_{n_1 l_1}\rangle\langle\varphi_{n_1 l_1}|}{(E_{n_1}^{(0)} - E_m^{(0)})^{\alpha_1}} V \cdots \times V \frac{|\varphi_{n_K l_K}\rangle\langle\varphi_{n_K l_K}|}{(E_{n_K}^{(0)} - E_m^{(0)})^{\alpha_K}} V \right| \Psi_{mp}^{(0)} \right\rangle = W_\alpha^K \delta_{pq} \tag{22}$$

for all $K \geq 0$, where $\sum_{\{nl\}}$ is the sum over all possible pairs of indices $(n_j l_j)$ for $j=1,\ldots,K$ of $\varphi_{nl}^{(0)}$ functions, $\alpha \equiv (\alpha_1,\ldots,\alpha_K)$ is a set of positive integer numbers, and W_α^K is an algebraic quantity. For $K=0$ the condition Eq. (22) reduces to Eq. (8). The condition to have a fully adapted basis for the $\mathcal{E}_m^{(0)}$ subspace Eq. (5) determines the choice of basis vectors in the $\mathcal{E}_m^{(0)}$ subspace.

In many cases it is easy to define an adapted basis before the iteration procedure and it is then more convenient to use this simple procedure. An example is the calculation of the dispersion coefficients for the excited states and the long-range limit for the electronic transition dipole moments which will be discussed in the next sections. In finding an adapted basis, the basis functions in the $\mathcal{E}_m^{(0)}$ subspace should respect the symmetry of both the H and H_0 Hamiltonians.

For the nondegenerate case the initial basis is automatically a fully adapted basis since $\mathcal{E}_m^{(0)}$ is a one-dimensional subspace and there is no ambiguity in the choice of the $\Psi_m^{(0)}$ vector. Indeed, in this case Eq. (5) reduces to the usual normalization condition of the nondegenerate perturbation theory. Discarding the degeneracy indices, the entire formalism is reduced to the conventional nondegenerate perturbation theory formalism and we may regard degenerate perturbation theory in a fully adapted base to be the natural formation of perturbation theory.

III. DISPERSION COEFFICIENTS

In this section we present the calculation of the dispersion coefficients which arise from the first- and second-order corrections for the energy in the perturbation theory. In the limit of infinite R the interaction between the two atoms is zero and the total Hamiltonian is the sum of the atomic Hamiltonian, which for our problem is the unperturbed Hamiltonian. We describe the alkali-metal atoms by an l-dependent model potential [1] and so only the contribution of the valence electron is taken explicitly into account. For large R the Coulomb interaction between the atoms may be expanded in a series of inverse powers of R [5]. For our problem the Coulomb interaction is the perturbation and it has the expression

$$V(\vec{r}_1,\vec{r}_2) = \sum_{l=1}^{\infty} \sum_{L=1}^{\infty} \frac{V_{lL}(\vec{r}_1,\vec{r}_2)}{R^{l+L+1}} , \tag{23}$$

where $\vec{r}_1$ and $\vec{r}_2$ are the positive vectors of the valence electrons of the two atoms. The coefficients $V_{lL}(\vec{r}_1,\vec{r}_2)$ are given by

$$V_{lL}(\vec{r}_1,\vec{r}_2) = (-1)^L 4\pi (\hat{l}\hat{L})^{-1/2} \times \sum_m K_{lL}^m r_1^l r_2^L Y_{lm}(\hat{r}_1) Y_{L-m}(\hat{r}_2) , \tag{24}$$

with $\hat{l} \equiv 2l+1, \hat{L} \equiv 2L+1$, and

$$K_{lL}^m = [\mathcal{C}_{l+L}^{l+m} \mathcal{C}_{l+L}^{L+m}]^{1/2} , \tag{25}$$

where $\mathcal{C}_n^k$ is the binomial coefficient $n!/k!(n-k)!$.

An orthogonal complete set of eigenvectors of the unperturbed Hamiltonian may be written

$$\varphi_{v_1 v_2} = \Phi_{v_1}(\vec{r}_1)\Phi_{v_2}(\vec{r}_2) , \tag{26}$$

where v is the set of quantum numbers $\{nlm\}$ and Φ_v is the atomic wave function. The corresponding eigenvalue is $E_{n_1 l_1} + E_{n_2 l_2}$, the sum of the individual atomic energies corresponding to Φ_{v1} and Φ_{v2}.

In this paper we study the molecular states which dissociate into one atom in the ground state and the other in an excited S, P, or D state. The zero-order correction for the energy is $E_{vg} + E_{ve}$ where $v_g \equiv \{n_g 00\}$ and $v_e \equiv \{n_e l_e m_e\}$. The basis functions in this subspace are chosen to be

$$\Psi_{m_e \beta}^{(0)} = \frac{1}{\sqrt{2}} [\varphi_{v_g v_e} + \beta \varphi_{v_e v_g}] . \tag{27}$$

The coefficient is given by $\beta = (-1)^{l_e} p\sigma$ where $p = \pm 1$ for even (g) and odd (u) molecular states and $\sigma = \pm 1$ for singlet and triplet molecular states, respectively. We will show that this basis is a fully adapted basis for the perturbation problem for the $E_{\nu_g}+E_{\nu_e}$ state subspace.

According to Eq. (22) we have to show that

$$F^{K\{\alpha\}}_{m_e'\beta'm_e\beta}=\sum_{\{\nu\nu'\}}\left\langle\Psi^{(0)}_{m_e'\beta'}\middle|V\frac{|\varphi_{\nu_1\nu_1'}\rangle\langle\varphi_{\nu_1\nu_1'}|}{\Delta_1^{\alpha_1}}V\cdots\right.$$

$$\left.\times V\frac{|\varphi_{\nu_K\nu_K'}\rangle\langle\varphi_{\nu_K\nu_K'}|}{\Delta_K^{\alpha_K}}V\middle|\Psi^{(0)}_{m_e\beta}\right\rangle , \tag{28}$$

where $\{\alpha\}\equiv\alpha_1,\ldots,\alpha_K$, $\{\nu\nu'\}\equiv\nu_1\nu_1',..,\nu_K\nu_K'$, and $\Delta_j\equiv E_{\nu_j}+E_{\nu_j'}-E_{\nu_e}-E_{\nu_g}$, satisfies the equation

$$F^{K\{\alpha\}}_{m_e'\beta'm_e\beta}=\delta_{m_em_e'}\delta_{\beta\beta'}F^{K\{\alpha\}}_{m_e\beta m_e\beta} , \tag{29}$$

for any $K\geq 0$. Using the notation from Appendix C, Eq. (C1), we have

$$2F^{K\{\alpha\}}_{m_e'\beta'm_e\beta}=W^{\nu_g\nu_e';K\{\alpha\}}_{\nu_g\nu_e}+\beta'W^{\nu_e'\nu_g;K\{\alpha\}}_{\nu_g\nu_e}$$

$$+\beta\beta'W^{\nu_e'\nu_g;K\{\alpha\}}_{\nu_e\nu_g}+\beta W^{\nu_g\nu_e';K\{\alpha\}}_{\nu_e\nu_g} , \tag{30}$$

where $\nu_e'\equiv\{n_el_em_e'\}$. From Eq. (C7) we find that $m_e'=m_e$ and so $\nu_e'=\nu_e$. Using Eqs. (C1) and (C8) we get

$$W^{\nu_e\nu_g;K\{\alpha\}}_{\nu_e\nu_g}=\sum_{\{lL\}}R^{-\sum_{j=1}^{K+1}(l_j+L_j+1)}(-1)^{\sum_{j=1}^{K+1}(l_j+L_j)}$$

$$\times W^{\nu_g\nu_e;K\{\alpha\}}_{\nu_g\nu_e;\{lL\}} . \tag{31}$$

From Eqs. (C5) and (C6) with $l_e'=l_e$ and $l_g'=l_g$, $\sum_{j=1}^{K+1}(l_j+L_j)$ must be even and

$$W^{\nu_e\nu_g;K\{\alpha\}}_{\nu_e\nu_g}=W^{\nu_g\nu_e;K\{\alpha\}}_{\nu_g\nu_e} . \tag{32}$$

We can show similarly that

$$W^{\nu_e\nu_g;K\{\alpha\}}_{\nu_g\nu_e}=W^{\nu_g\nu_e;K\{\alpha\}}_{\nu_e\nu_g} . \tag{33}$$

Thus

$$F^{K\{\alpha\}}_{m_e'\beta'm_e\beta}=\delta_{m_em_e'}\frac{1+\beta\beta'}{2}F^{K\{\alpha\}}_{m_e\beta} , \tag{34}$$

where

$$F^{K\{\alpha\}}_{m_e\beta}=W^{\nu_g\nu_e;K\{\alpha\}}_{\nu_g\nu_e}+\beta W^{\nu_e\nu_g;K\{\alpha\}}_{\nu_g\nu_e} . \tag{35}$$

Because β and β' can be only ± 1, the right side of Eq. (34) is zero if $\beta'\neq\beta$ and Eq. (29) is proved. Thus our basis is a fully adapted basis for our perturbation problem.

A. First-order perturbation

The energy correction in the first order of perturbation is given by Eq. (7) as

$$E^{(1)}_{m_e\beta}=\langle\Psi^{(0)}_{m_e\beta}|V|\Psi^{(0)}_{m_e\beta}\rangle , \tag{36}$$

where $\Psi^{(0)}_{m_e\beta}$ is defined by Eq. (27) and V by Eq. (23). The matrix element on the right side of Eq. (36) is a particular case of Eq. (28) for $K=0$ and so it obeys Eq. (35). Thus

$$E^{(1)}_{m_e\beta}=U^{\nu_g\nu_e}_{\nu_g\nu_e}+\beta U^{\nu_e\nu_g}_{\nu_g\nu_e} , \tag{37}$$

where we used the identity from Eq. (C4). Using the expansion in $1/R$ for U from Eq. (B2) and Eq. (B13), we have

$$E^{(1)}_{m_e\beta}=\beta\sum_{l=1}^{\infty}\sum_{L=1}^{\infty}\frac{1}{R^{l+L+1}}U^{\nu_e\nu_g}_{\nu_g\nu_e;lL} . \tag{38}$$

Introducing Eq. (B14) into Eq. (38) we get

$$E^{(1)}_{m_e\beta}=-\frac{C^{m_e\beta}_{2l_e+1}}{R^{2l_e+1}}\quad\text{for } l_e\geq 1 , \tag{39}$$

where $C^{m_e\beta}_{2l_e+1}$ are the coefficients

$$C^{m_e\beta}_{2l_e+1}=\frac{(-1)^{l_e+m_e+1}\beta}{2l_e+1}\mathcal{C}^{l_e+m}_{2l_e}(n_el_e|r^{l_e}|n_g0)^2 . \tag{40}$$

For the case where in the dissociation limit the second atom is in an S excited state, which we refer to as the *S*-*S* asymptote, the first-order correction for the energy is zero and so is the coefficient. For the case of the *S*-*P* asymptote, where in the dissociation limit the second atom is in a P state, the energy correction in the first order of perturbation is proportional to $1/R^3$, and for the *S*-*D* asymptote, where the second atom is in a D state, it is proportional to $1/R^5$. For these cases the coefficients are given by Eq. (40) with $l_e=1$ and $l_e=2$, respectively.

B. Second-order perturbation

The energy correction in the second order of perturbation is given by Eq. (13) and so

$$E^{(2)}_{m_e\beta}=-F^{11}_{m_e\beta} , \tag{41}$$

where $F^{11}_{m_e\beta}$ is defined by Eq. (28). Using Eq. (35) and the $1/R$ expansion for the W symbols Eq. (C1) we get

$$E^{(2)}_{m_e\beta}=-\sum_{\substack{ll'\\LL'}}\frac{1}{R^{l+L+l'+L'}}(W^{\nu_g\nu_e}_{\nu_g\nu_e;lLl'L'}+\beta W^{\nu_e\nu_g}_{\nu_g\nu_e;lLl'L'}) . \tag{42}$$

1. The S-S asymptote; $\nu_e\equiv\{n_e00\}$

For this case we have computed the contribution up to $1/R^{10}$ in the interaction energy. After analyzing the possible combinations of $\{lLl'L'\}$ quadruples from Eq. (C11) we conclude that

$$E^{(2)}_{m_e\beta}=-\frac{C_6^\beta}{R^6}-\frac{C_8^\beta}{R^8}-\frac{C_{10}^\beta}{R^{10}}-\cdots , \tag{43}$$

where C_6^β, C_8^β, and C_{10}^β are the dispersion coefficients.

Contribution $1/R^6$; $\{lLl'L'\}\equiv\{1111\}$. From Eqs. (43) and (42) we have

$$C_6^\beta=W^{\nu_e\nu_g}_{\nu_g\nu_e;1111}+\beta W^{\nu_e\nu_g}_{\nu_g\nu_e;1111} . \tag{44}$$

Using Eq. (C11) we get

$$C_6^\beta = \tfrac{2}{3}(S_1^0 + \beta S_2^0)\ , \tag{45}$$

where S_1^0 and S_2^0 are the following sums of radial matrix elements:

$$S_1^0 = \sum_{nm} \frac{(n1|r|n_g0)^2(m1|r|n_e0)^2}{E_{n1}+E_{m1}-E_{n_e0}-E_{n_g0}}\ , \tag{46}$$

$$S_2^0 = \sum_{nm} \frac{(n_g0|r|n1)(n1|r|n_e0)(n_g0|r|m1)(m1|r|n_e0)}{E_{n1}+E_{m1}-E_{n_e0}-E_{n_g0}} \tag{47}$$

The computation of these and other sums will be described later.

Contribution 1/R^8; $\{lLl'L'\} \equiv \{$1212$\}, \{$2121$\}$. From Eqs. (43) and (42) we have

$$C_8^\beta = W^{\nu_g\nu_e}_{\nu_g\nu_e;1212} + W^{\nu_g\nu_e}_{\nu_g\nu_e;2121} + \beta(W^{\nu_e\nu_g}_{\nu_g\nu_e;1212} + W^{\nu_e\nu_g}_{\nu_g\nu_e;2121})\ . \tag{48}$$

Using Eq. (C11) we get

$$C_8^\beta = S_3^0 + S_4^0 + 2\beta S_5^0\ , \tag{49}$$

where

$$S_3^0 = \sum_{nm} \frac{(n1|r|n_g0)^2(m2|r^2|n_e0)^2}{E_{n1}+E_{m2}-E_{n_e0}-E_{n_g}0}\ , \tag{50}$$

$$S_4^0 = \sum_{nm} \frac{(n2|r^2|n_g0)^2(m1|r|n_e0)^2}{E_{n2}+E_{m1}-E_{n_e0}-E_{n_g0}}\ , \tag{51}$$

$$S_5^0 = \sum_{nm} \frac{(n_e0|r|n1)(n1|r|n_g0)(n_e0|r^2|m2)(m2|r^2|n_g0)}{E_{n1}+E_{m2}-E_{n_e0}-E_{n_g0}}\ . \tag{52}$$

Contribution 1/R^{10}; $\{lLl'L'\} \equiv \{$2222$\}, \{$1313$\}, \{$3131$\}$. From Eqs. (43) and (42) we have

$$C_{10}^\beta = W^{\nu_g\nu_e}_{\nu_g\nu_e;2222} + W^{\nu_g\nu_e}_{\nu_g\nu_e;1313} + W^{\nu_g\nu_e}_{\nu_g\nu_e;3131} + \beta(W^{\nu_e\nu_g}_{\nu_g\nu_e;2222} + W^{\nu_e\nu_g}_{\nu_g\nu_e;1313} + W^{\nu_e\nu_g}_{\nu_g\nu_e;3131})\ . \tag{53}$$

Using Eq. (C11) we get

$$C_{10}^\beta = \tfrac{14}{5}S_6^0 + \tfrac{4}{3}(S_7^0 + S_8^0) + \beta(\tfrac{14}{5}S_9^0 + \tfrac{8}{3}S_{10}^0)\ , \tag{54}$$

where

$$S_6^0 = \sum_{nm} \frac{(n2|r^2|n_g0)^2(m2|r^2|n_e0)^2}{E_{n2}+E_{m2}-E_{n_e0}-E_{n_g0}}\ , \tag{55}$$

$$S_7^0 = \sum_{nm} \frac{(n1|r|n_g0)^2(m3|r^3|n_e0)^2}{E_{n1}+E_{m3}-E_{n_30}-E_{n_g0}}\ , \tag{56}$$

$$S_8^0 = \sum_{nm} \frac{(n3|r^3|n_g0)^2(m1|r|n_e0)^2}{E_{n3}+E_{m1}-E_{n_e0}-E_{n_g0}}\ , \tag{57}$$

$$S_9^0 = \sum_{nm} \frac{(n_e0|r^2|n2)(n2|r^2|n_g0)(n_e0|r^2|m2)(m2|r^2|n_g0)}{E_{n2}+E_{m2}-E_{n_e0}E_{n_g0}}\ , \tag{58}$$

$$S_{10}^0 = \sum_{nm} \frac{(n_e0|r|n1)(n1|r|n_g0)(n_e0|r^3|m3)(m3|r^3|n_g0)}{E_{n1}+E_{m3}-E_{n_e0}-E_{n_g0}}\ . \tag{59}$$

2. The S-P asymptote; $\nu_e \equiv \{n_e 1 m_e\}$.

Since in this case there is already a nonvanishing contribution from the first order of perturbation, proportional to $1/R^3$, we will study only the first two nonzero contributions which arise from the second order. After analysis of Eqs. (C13) and (C14) we conclude that these contributions are proportional to $1/R^6$ and $1/R^8$. Thus

$$E^{(2)}_{m_e\beta} = -\frac{C_6^{m_e\beta}}{R^6} - \frac{C_8^{m_e\beta}}{R^8} - \cdots\ , \tag{60}$$

where $C_6^{m_e\beta}$ and $C_8^{m_e\beta}$ are the dispersion coefficients.

Contribution 1/R^6; $\{lLl'L'\} = \{$1111$\}$. From Eqs. (60) and (42) we have

$$C_6^{m_e\beta} = W^{\nu_g\nu_e}_{\nu_g\nu_e;1111}\ . \tag{61}$$

The term proportional to β is zero because $W^{\nu_e\nu_g}_{\nu_g\nu_e;1111}=0$ because of Eqs. (C5) and (C6). Thus $C_6^{m_e\beta}$ does not depend on the value of β. Using Eq. (C13) we get

$$C_6^{m_e\beta}=A_1^{m_e}S_1^1+A_2^{m_e}S_2^1\ , \tag{62}$$

where

$$S_1^1={\sum_{nm}}'\frac{(n1|r|n_g0)^2(m0|r|n_e1)^2}{E_{n1}+E_{m0}-E_{n_e1}-E_{n_g0}}\ , \tag{63}$$

$$S_2^1=\sum_{nm}\frac{(n1|r|n_g0)^2(m2|r|n_e1)^2}{E_{n1}+E_{m2}-E_{n_e1}-E_{n_g0}}\ , \tag{64}$$

and where $A_1^{m_e}$ and $A_2^{m_e}$ are algebraic coefficients listed in the first two columns of Table I. The prime on the sum of Eq. (63) indicates that the case $(n=n_e, m=n_g)$ is excluded.

TABLE I. The algebraic coefficient A_k^m occurring in Eqs. (62) and (66).

	A_1^m	A_2^m	A_3^m	A_4^m	A_5^m	A_6^m	A_7^m	A_8^m	A_9^m	A_{10}^m
$m=0$	$\frac{4}{9}$	$\frac{22}{45}$	$\frac{18}{25}$	$\frac{129}{175}$	$\frac{3}{5}$	$\frac{18}{25}$	$\frac{48}{35}$	$-\frac{18}{25}$	$-\frac{18}{25}$	$-\frac{48}{25}$
$m=\pm 1$	$\frac{1}{9}$	$\frac{19}{45}$	$\frac{6}{25}$	$\frac{93}{175}$	$\frac{1}{5}$	$\frac{16}{25}$	$-\frac{24}{35}$	$-\frac{6}{25}$	$-\frac{6}{15}$	$\frac{24}{25}$

Contribution 1/R^8; $\{lLl'L'\}\equiv\{1212\},\{2121\},\{1122\},\{2211\},\{1221\},\{2112\},\{1311\},\{1113\}$. From Eqs. (60) and (42) using Eqs. (C5) and (C6) and the symmetry relations Eqs. (C8) and (C10) we find that the contributions of the $\{1122\}$ terms are equal to the contributions of the $\{2211\}$ terms and $\{1311\}$ to $\{1113\}$. Thus

$$C_8^{m_e\beta}=W^{\nu_g\nu_e}_{\nu_g\nu_e;1212}+W^{\nu_g\nu_e}_{\nu_g\nu_e;2121}+2W^{\nu_g\nu_e}_{\nu_g\nu_e;1311}+\beta(W^{\nu_e\nu_g}_{\nu_g\nu_e;1221}+W^{\nu_e\nu_g}_{\nu_g\nu_e;2112}+2W^{\nu_e\nu_g}_{\nu_g\nu_e;1122})\ . \tag{65}$$

Using Eqs. (C13) and (C14) we get

$$C_8^{m_e\beta}=\sum_{k=3}^{7}A_k^{m_e}S_k^1+\beta\sum_{k=8}^{10}A_k^{m_e}S_k^1\ , \tag{66}$$

where

$$S_3^1=\sum_{nm}\frac{(n1|r|n_g0)^2(m1|r|n_e1)^2}{E_{n1}+E_{m1}-E_{n_e1}-E_{n_g0}}\ , \tag{67}$$

$$S_4^1=\sum_{nm}\frac{(n1|r|n_g0)^2(m3|r^2|n_e1)^2}{E_{n1}+E_{m3}-E_{n_e1}-E_{n_g0}}\ , \tag{68}$$

$$S_5^1=\sum_{nm}\frac{(n2|r^2|n_g0)^2(m0|r|n_e1)^2}{E_{n2}+E_{m0}-E_{n_e1}-E_{n_g0}}\ , \tag{69}$$

$$S_6^1=\sum_{nm}\frac{(n2|r^2|n_g0)^2(m2|r|n_e1)^2}{E_{n2}+E_{m2}-E_{n_e1}-E_{n_g0}}\ , \tag{70}$$

$$S_7^1=\sum_{nm}\frac{(n1|r|n_g0)^2(n_e1|r|m2)(m2|r^3|n_e1)}{E_{n1}+E_{m2}-E_{n_e1}-E_{n_g0}}\ , \tag{71}$$

$$S_8^1=\sum_{nm}\frac{(n_31|r|n2)(n2|r^2|n_g0)(n_e1|r|m2)(m2|r^2|n_g0)}{E_{n2}+E_{m2}-E_{n_e1}-E_{n_g0}}\ , \tag{72}$$

$$S_9^1=\sum_{nm}\frac{(n_e1|r^2|n1)(n1|r|n_g0)(n_e1|r^2|m1)(m1|r|n_g0)}{E_{n1}+E_{m1}-E_{n_e1}-E_{n_g0}}\ , \tag{73}$$

$$S_{10}^1=\sum_{nm}\frac{(n_e1|r|n2)(n2|r^2|n_g0)(n_e1|r^2|m1)(m1|r|n_g0)}{E_{n2}+E_{m1}-E_{n_e1}-E_{n_g0}}\ , \tag{74}$$

and where $A_j^{m_e}$ for $j=3,\ldots,9$ are algebraic coefficients listed in Table I.

3. *The S-D asymptote;* $\nu_e\equiv\{n_e2m_e\}$

For this case we will study only the contributions proportional to $1/R^6$. This restriction was made first because there is already a contribution proportional to $1/R^5$ from the first order of perturbation and second, as we will see later, the numerical values for the $C_6^{m_e\beta}$ coefficients are very large and so the utility of the $1/R$ expansion is questionable. Thus

$$E^{(2)}_{m_e\beta}=-\frac{C_6^{m_e\beta}}{R^6}-\cdots\ , \tag{75}$$

where $C_6^{m_e\beta}$ is the dispersion coefficient. According to Eq. (42) for $\{lLl'L'\}\equiv\{1111\}$ we have

$$C_6^{m_e\beta}=W^{\nu_g\nu_e}_{\nu_g\nu_e;1111}+\beta W^{\nu_e\nu_g}_{\nu_g\nu_e;1111}\ . \tag{76}$$

Using the definition of the W symbols Eq. (C2) for $K=1$ and $\alpha_1=1$ we get the expression

$$C_6^{m_e\beta}=A_1^{m_e}S_1^2+A_2^{m_e}S_2^2+\beta A_3^{m_e}S_3^2\ , \tag{77}$$

where

$$S_1^2=\sum_{nm}\frac{(n1|r|n_g0)^2(m1|r|n_e2)^2}{E_{n1}+E_{m1}-E_{n_e2}-E_{n_g0}}\ , \tag{78}$$

$$S_2^2=\sum_{nm}\frac{(n1|r|n_g0)^2(m3|r|n_e2)^2}{E_{n1}+E_{m3}-E_{n_e2}-E_{n_g0}}\ , \tag{79}$$

$$S_3^2=\sum_{nm}\frac{(n_e2|r|n1)(n1|r|n_g0)(n_e2|r|m1)(m1|r|n_g0)}{E_{n1}+E_{m1}-E_{n_e2}-E_{n_g0}}\ , \tag{80}$$

and $A_1^{m_e}$, $A_2^{m_e}$, and $A_3^{m_e}$ are algebraic coefficients listed in Table II.

C. The sum of radial matrix elements

A major step in the computation of the dispersion coefficients is the evaluation of the sums of radial matrix elements from Eqs. (46), (47), (50)–(52), (55)–(59), (63), (64), (67)–(74), and (78)–(80). All of them are similar to each other in being sums over the intermediate states of both atoms.

An efficient way to separate these sums into independent contributions of each atom was pointed out in Ref. [2] for the case of the ground-ground interaction. It consists in using the following integral representation [6] (for other equivalent representations see Ref. [7]):

$$\frac{1}{a+b}=\frac{2}{\pi}\int_0^\infty d\omega\,\mathrm{Re}\left[\frac{1}{a-i\omega}\right]\mathrm{Re}\left[\frac{1}{b-i\omega}\right]\ , \tag{81}$$

where by Re we denote the real part. Equation (81) is valid only for $a>0$ and $b>0$. In this way the sums are separated into a product of two sums, each of them over the intermediate states of only one atom. The final result is an integral over the product of multipole polarizabilities of complex frequencies, which in turn may be computed using the Dalgarno-Lewis method [3]. This procedure includes the sum over the continuum spectrum and is exact.

TABLE II. The algebraic coefficients A_k^m occurring in Eq. (77).

	A_1^m	A_2^m	A_3^m
$m=0$	$\frac{2}{5}$	$\frac{16}{35}$	$\frac{2}{5}$
$m=\pm1$	$\frac{1}{3}$	$\frac{3}{7}$	$-\frac{4}{15}$
$m=\pm2$	$\frac{2}{15}$	$\frac{12}{35}$	$\frac{2}{15}$

Equation (81) must be used with care, because a or b may be a negative quantity. For those cases where $a>0$ and $b<0, 1/(a+b)$ can be replaced by

$$\frac{1}{a+b}+\frac{1}{a-b}+\frac{2}{\pi}\int_0^\infty d\omega\,\mathrm{Re}\left[\frac{1}{a-i\omega}\right]\mathrm{Re}\left[\frac{1}{b-i\omega}\right]\ , \tag{82}$$

the last two terms canceling each other. This substitution permits a complete sum over atomic states in the integral.

The cases where such a problem occurs depend on the succession of the excited atomic levels. In Table III are listed the excited atomic levels lying below the first excited F state for each alkali-metal atom.

We carried out computations for the first two S, P, and D excited states of each alkali-metal atom. In total there are 230 sums to be computed. We discuss a few special examples, in order to point out the utility of Eqs. (81) and (82).

For the case of the Li(2S)-Li(3S) asymptote Eq. (46) becomes

$$S_1^0=\sum_{nm}\frac{(nP|r|2S)^2(mP|r|3S)^2}{(E_{nP}-E_{2S})+(E_{mP}-E_{3S})}\ . \tag{83}$$

Here we take $a=E_{nP}-E_{2S}$, which is positive for any n, and $b=E_{mP}-E_{3S}$, which is positive except for $m=2$, as Table III shows. For those cases where both a and b are positive we used Eq. (81) and for the cases where $m=2$ we used Eq. (82). After the summation over n and m we get

$$S_1^0=\frac{2}{\pi}\int_0^\infty d\omega\,\mathrm{Re}[(2S|rg_p(E_{2S}+i\omega)r|2S)]\mathrm{Re}[(3S|rg_p(E_{3S}+i\omega)r|3S)] \\ +(2P|r|3S)^2[(2S|rg_p(E_{2S}-E_{2P}+E_{3S})r|2S)+(3S|rg_p(E_{2S}+E_{2P}-E_{3S})r|3S)]\ , \tag{84}$$

where g_p is the radial Green's function for the angular momentum P.

Another interesting case is the Li(2S)-Li(2P) asymptote for which Eq. (63) becomes

$$S_1^1={\sum_{nm}}'\frac{(nP|r|2S)^2(mS|r|2P)^2}{(E_{nP}-E_{2S})+(E_{mS}-E_{2P})}\ , \tag{85}$$

where $\sum'$ indicates that the term for $(n=2, m=2)$ is excluded. For the cases where m is equal to 2 and $n>2$ we use Eq. (82) and for the rest Eq. (81). We get

$$S_1^1=\frac{2}{\pi}\int_0^\infty d\omega\,\mathrm{Re}[(2S|rg_p(E_{2S}+i\omega)r|2S)]\mathrm{Re}[(2P|rg_s(E_{2P}+i\omega)r|2P)] \\ +(2P|r|2S)^2[(2S|rg_p'(E_{2P})r|2S)+(2S|rg_p(2E_{2S}-E_{2P})r|2S)]\ , \tag{86}$$

TABLE III. The excited atomic levels lying energetically below the first excited F state of each alkali-metal atom.

Li	Na	K	Rb	Cs
$2S$	$3S$	$4S$	$5S$	$6S$
$2P$	$3P$	$4P$	$5P$	$6P$
$3S$	$4S$	$5S$	$4D$	$5D$
$3P$	$3D$	$3D$	$6S$	$7S$
$3D$	$4P$	$5P$	$6P$	$7P$
$4S$	$5S$	$4D$	$5D$	$6D$
$4P$	$4D$	$6S$	$7S$	$8S$
$4D$	$4F$	$4F$	$4F$	$4F$
$4F$				

where by $g_p'(E_{2P})$ we denote the reduced radial Green's function for angular momentum P omitting the $2P$ state.

Also for the Li($2S$)-Li($2P$) asymptote an interesting situation occurs for the S_3^1 sum from Eq. (67) which becomes

$$S_3^1=\sum_{nm}\frac{(nP|r|2S)^2(mP|r^2|2P)^2}{(E_{nP}-E_{2P})+(E_{mP}-E_{2S})} . \tag{87}$$

Here $b=E_{mP}-E_{2S}$ is positive for any m and $a=E_{nP}-E_{2P}$. For $n=2, a=0$ and neither Eq. (81) nor Eq. (82) applies, so that this term must be treated separately. For the rest of the terms with $n\geq 3$ we use Eq. (81) and otherwise Eq. (82). Finally we get

$$\begin{aligned}S_3^1=\frac{2}{\pi}\int_0^\infty d\omega\, &\mathrm{Re}[(2P|r^2g_p(E_{2S}+i\omega)r^2|2P)]\\ &\times\mathrm{Re}[(2S|rg_p'(E_{2P}+i\omega)r|2S)]\\ &+(2P|r|2S)^2(2P|r^2g_p(E_{2S})r^2|2P) ,\end{aligned} \tag{88}$$

where $g_p'(E_{2P}+i\omega)$ is the radial reduced Green's function for angular momentum P, omitting the $2P$ state, for complex energy. However, the denominator in Eq.(87) can be rewritten with $a=E_{nP}-E_{2S}$ and $b=E_{mP}-E_{2P}$. Now we have $b=0$ for $m=2$ and we get

$$\begin{aligned}S_3^1=\frac{2}{\pi}\int_0^\infty d\omega\, &\mathrm{Re}[(2P|r^2g_p'(E_{2P}+i\omega)r^2|2P)]\\ &\times\mathrm{Re}[(2S|rg_p(E_{2S}+i\omega)r|2S)]\\ &+(2P|r^2|2P)^2(2S|rg_p(E_{2S})r|2S) ,\end{aligned} \tag{89}$$

Equation (88) and Eq. (89) are equivalent to each other and provide a very good test for the accuracy of the numerical computations. More details about the numerical computations will be given later.

Every sum can be treated in this way in order to separate it into quantities which depend only on a single atom. Among the alkali-metal atoms certain symmetries occur because of the similar succession of the excited levels, as shown in Table III. For example, the structure of the sums for Cs($6S$)-Cs($5D$) is similar to those for Na($3S$)-Na($3D$) and those of Rb($5S$)-Rb($7S$) to K($4S$)-K($6S$), which brings some simplification at the level of numerical computation.

IV. LONG-RANGE COEFFICIENTS OF THE ELECTRONIC TRANSITION DIPOLE MOMENT

In this section we study the long-range limit of the electronic transition dipole moments from the ground molecular state to those molecular states which dissociate into one atom in the ground state and the other into a P or D excited state. As for the interaction energy, the transition dipole moment can be represented in the limit of large nuclear separations by a series in inverse powers of R. We present those contributions which arise from the zero and first order of perturbation.

The electronic transition dipole moment is defined as

$$D_{m_e\beta}(\hat{s})=\langle\Psi_{m_e\beta}|\hat{s}\cdot(\vec{r}_1+\vec{r}_2)|\Psi_g\rangle , \tag{90}$$

where Ψ_g is the ground-molecular-state wave function, $\Psi_{m_e\beta}$ is the excited-molecular-state wave function, and $\hat{s}$ is the polarization vector. Later we will particularize the results to linear and circular polarizations.

In the long-range limit the wave function from Eq. (90) may be approximated by the perturbation series and the electronic transition moment written as

$$D_{m_e\beta}=D_{m_e\beta}^{(0)}+D_{m_e\beta}^{(1)}+\cdots . \tag{91}$$

In Eq. (91),

$$D_{m_e\beta}^{(0)}=\langle\Psi_{m_e\beta}^{(0)}|\hat{s}\cdot(\vec{r}_1+\vec{r}_2)|\Psi_g^{(0)}\rangle \tag{92}$$

is the zero-order contribution, where $\Psi_g^{(0)}$ is the ground-state molecular wave function in the limit of infinite nuclear separation,

$$\Psi_g^{(0)}=\varphi_{v_gv_g} . \tag{93}$$

The first-order correction $D_{m_e\beta}^{(1)}$ can be written as

$$D_{m_e\beta}^{(1)}=D_{m_e\beta}^{10}+D_{m_e\beta}^{01} , \tag{94}$$

where

$$D_{m_e\beta}^{10}=\langle\Psi_{m_e\beta}^{(1)}|\hat{s}\cdot(\vec{r}_1+\vec{r}_2)|\Psi_g^{(0)}\rangle , \tag{95}$$

$$D_{m_e\beta}^{01}=\langle\Psi_{m_e\beta}^{(0)}|\hat{s}\cdot(\vec{r}_1+\vec{r}_2)|\Psi_g^{(1)}\rangle . \tag{96}$$

We will call $D_{m_e\beta}^{10}$ the left contribution and $D_{m_e\beta}^{01}$ the right contribution since the first-order correction to the wave function enters on the left or on the right side of the matrix element. The matrix element which has on both sides the first-order correction to the wave function occurs in the second order of perturbation, together with the matrix elements which have the second-order correction to the wave function on the left or the right side and the zero-order correction to the wave function on the other side.

A. Zero-order conribution $D_{m_e\beta}^{(0)}$

Introducing Eqs. (93) and (27) in Eq. (92) and using the notation from Eq. (D8) we get

$$D^{(0)}_{m_e\beta}\frac{1}{\sqrt{2}}\left(B^{\nu_g\nu_e}_{\nu_g\nu_g}+\beta B^{\nu_e\nu_g}_{\nu_g\nu_g}\right) . \tag{97}$$

Using Eqs. (D10) and (D9) we get

$$D^{(0)}_{m_e\beta}=\frac{1+\beta}{\sqrt{2}}\left(T^{\nu_e\nu_g}_{\nu_g\nu_g}+T^{\nu_g\nu_e}_{\nu_g\nu_g}\right) . \tag{98}$$

Since $\nu_e \neq \nu_g$ from Eq. (D3) we conclude that the second T symbol in Eq. (98) is zero and using Eq. (D4) we get finally

$$D^{(0)}_{m_e\beta}=\delta_{\beta_1}\delta_{l_e1}d^{(0)}\hat{s}\cdot\hat{e}^*_{m_e} , \tag{99}$$

where

$$d^{(0)}=\sqrt{\tfrac{2}{3}}(n_e1|r|n_g0) . \tag{100}$$

As expected, the zero-order contribution is not zero only for $l_e=1$ and $\beta=1$.

B. First-order contribution $D^{(1)}_{m_e\beta}$

The first-order correction $D^{(1)}_{m_e\beta}$, Eq. (94), is the sum of the left and right contributions Eqs. (95) and (96). In the left contribution Eq. (95) the first-order correction to the wave function $\Psi^{(1)}_{m_e\beta}$ is a result of degenerate perturbation theory and in the right contribution $\Psi^{(1)}_g$ is obtained from nondegenerate perturbation theory. Thus the computation of the left and right contributions requires different approaches.

1. The left contribution $D^{10}_{m_e\beta}$

The first-order correction to the wave function $\Psi^{(1)}_{m_e\beta}$ is given by Eq. (10) which for our problem becomes

$$\Psi^{(1)}_{m_e\beta}=-\sum_{\nu_1\nu_2}{}' \varphi_{\nu_1\nu_2}\frac{U^{\nu_1\nu_2}_{\nu_g\nu_e}+\beta U^{\nu_1\nu_2}_{\nu_e\nu_g}}{E_{\nu_1}+E_{\nu_2}-E_{\nu_e}-E_{\nu_g}} , \tag{101}$$

where the sum is over all the possible pairs of indices except $\nu_e\nu_g$ and $\nu_g\nu_e$. Introducing Eqs. (101) and (93) in Eq. (95) and using the notation from Eq. (D8) and the $1/R$ expansion of the U symbols, Eq. (B2), we get

$$D^{10}_{m_e\beta}=\frac{1}{\sqrt{2}}\sum_{l=1}^{\infty}\sum_{L=1}^{\infty}\frac{1}{R^{l+L+1}}\left(D^{10}_{m_e\beta\beta;lL}+\beta\bar{D}^{10}_{m_e\beta;lL}\right) , \tag{102}$$

where

$$D^{10}_{m_e\beta;lL}=-\sum_{\nu_1\nu_2}{}'\frac{U^{\nu_g\nu_e}_{\nu_1\nu_2;lL}B^{\nu_1\nu_2}_{\nu_g\nu_g}}{E_{\nu_1}+E_{\nu_2}-E_{\nu_e}-E_{\nu_g}} , \tag{103}$$

$$\bar{D}^{10}_{m_e\beta;lL}=-\sum_{\nu_1\nu_2}{}'\frac{U^{\nu_e\nu_g}_{\nu_1\nu_2;lL}B^{\nu_1\nu_2}_{\nu_g\nu_g}}{E_{\nu_1}+E_{\nu_2}-E_{\nu_e}-E_{\nu_g}} . \tag{104}$$

Using Eqs. (B8) and (D10) we have

$$\bar{D}^{10}_{m_e\beta;lL}=(-1)^{l+L}D^{10}_{m_e\beta;lL} . \tag{105}$$

From Eqs. (D9) and (D4) it follows that l_1 and l_2 from the ν_1 and ν_2 indices could be 1 and 0 or 0 and 1, respectively. From Eq. (B6) we have $l+l_e+l_1=$(even) and $L+l_2=$(even) so that $(-1)^{l+L}=(-1)^{l_e+1}$ and Eq. (102) becomes

$$D^{10}_{m_e\beta}=\frac{1+(-1)^{l_e+1}\beta}{\sqrt{2}}\sum_{lL}\frac{1}{R^{l+L+1}}D^{10}_{m_e\beta;lL} . \tag{106}$$

The computation of $D^{10}_{m_e\beta;lL}$ starts from Eq. (103) where we substitute the B symbol with its expression from Eq. (D9). The term proportional to $T^{\nu_2\nu_1}_{\nu_g\nu_g}$ is zero since from Eq. (D3) $\nu_1=\nu_g$ and from Eq. (B13) we have $U^{\nu_g\nu_e}_{\nu_g\nu_2;lL}=0$, so that

$$D^{10}_{m_e\beta;lL}=-\sum_{\nu_1}{}'\frac{U^{\nu_1\nu_g}_{\nu_g\nu_e;lL}T^{\nu_1\nu_g}_{\nu_g\nu_g}}{E_{\nu_1}-E_{\nu_e}} , \tag{107}$$

where we used Eq. (B10) in order to invert the upper and lower indices for the U symbols. Finally, using Eqs. (B14) and (D4) we get the following expression for the left contribution:

$$\begin{aligned}D^{10}_{m_e\beta}=&\frac{(-1)^{l_e+1}+\beta}{3\sqrt{2}R^{l_e+2}}(-1)^{m_e}\hat{l}_e^{-1/2}K^{m_e}_{1l_e}\\&\times(n_el_e|r^{l_e}|n_g0)(n_g0|rg'_p(E_{n_el_e})r|n_g0)\\&\times\hat{s}\cdot\hat{e}^*_{m_e} ,\end{aligned} \tag{108}$$

where $g'_p(E_{n_el_e})$ is the radial reduced Green's function for angular momentum P omitting the $E_{n_el_e}$ state. Obviously if $l_e\neq 1$ it reduces to the usual radial Green's function for angular momentum P.

2. The right contribution $D^{01}_{m_e\beta}$

The first-order correction of the ground-state wave function $\Psi^{(1)}_g$ is a result of nondegenerate perturbation theory given by Eq. (10) where the second indices of the Ψ functions are discarded. In our notation it becomes

$$\Psi^{(1)}_g=-\sum_{\nu_1\nu_2}{}'\varphi_{\nu_1\nu_2}\frac{U^{\nu_1\nu_2}_{\nu_g\nu_g}}{E_{\nu_1}+E_{\nu_2}-2E_{\nu_g}} , \tag{109}$$

where the sum is over all possible pairs of indices except $\nu_g\nu_g$. Introducing Eq. (109) in Eq. (96) and following a similar procedure as for the left contribution, we get

$$\begin{aligned}D^{01}_{m_e\beta}=&\frac{(-1)^{l_e+1}+\beta}{3\sqrt{2}R^{l_e+2}}(-1)^{m_e}\hat{l}_e^{-1/2}K^{m_e}_{1l_e}(n_el_e|r^{l_e}|n_g0)\\&\times(n_g0|rg_p(2E_{n_g0}-E_{n_el_e})r|n_g0)\hat{s}\cdot\hat{e}^*_{m_e} ,\end{aligned} \tag{110}$$

where g_p is the radial Green's function for angular momentum P.

3. Both contributions

Collecting the results from the left and right contributions, Eqs. (108) and (110), we conclude that the first-order correction to the transition dipole moment is

$$D^{(1)}_{m_e\beta}=\frac{d^{(1)}_{m_e\beta}}{R^{l_e+2}}\hat{s}\cdot\hat{e}^{*}_{m_e} , \tag{111}$$

where

$$d^{(1)}_{m_e\beta}=\frac{(-1)^{l_e+1}+\beta}{3\sqrt{2}}(-1)^{m_e}\hat{l}_e^{-1/2}K^{m_e}_{1l_e}(n_el_e|r^{l_e}|n_g0)$$
$$\times[(n_g0|rg'_p(E_{n_el_e})r|n_g0)$$
$$+(n_g0|rg_p(2E_{n_g0}-E_{n_el_e})r|n_g0)] . \tag{112}$$

For linear polarization $\hat{s}=\hat{e}_0\equiv\hat{e}_z$ and for circular polarization $\hat{s}=\hat{e}_{\pm 1}\equiv\mp(1/\sqrt{2})(\hat{e}_x\pm i\hat{e}_y)$ for positive and negative helicity, respectively. The ratio between $d^{(1)}_{m_e\beta}$ for linear polarization and circular polarization is -2 for the final state *S-P* and $-\sqrt{3}$ for the final state *S-D*.

V. NUMERICAL COMPUTATION

The numerical problem consists in the computation of radial matrix elements involving a Green's function. We distinguish four types of such matrix elements; a radial Green's function for real energy, a radial Green's function for complex energy, a reduced radial Green's function for real energy, and a reduced radial Green's function for complex energy. Our procedure for solving these problems is based on the Dalgarno-Lewis method [3]. The first and the second types of matrix elements were studied in detail in Refs. [8] and [1], respectively. Here we will present the procedure which we adopted for the third and fourth types of matrix elements.

Let $\mathcal{M}$ be the generic matrix element

$$\mathcal{M}=\langle\varphi_f|g'_l(\Omega)|\varphi_i\rangle , \tag{113}$$

where $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are two-vectors, g'_l is the reduced radial Green's operator for angular momentum l omitting the E_{nl} state, and Ω is a complex number with $\mathrm{Re}\Omega<0$. Let $|\chi\rangle$ be the vector

$$|\chi\rangle=g'_l(\Omega)|\varphi_i\rangle . \tag{114}$$

Then Eq. (113) can be rewritten as

$$\mathcal{M}=\langle\varphi_f|\chi\rangle . \tag{115}$$

Let h_l be the radial Schrödinger operator for angular momentum l. Then $|\chi\rangle$ will obey the equation

$$(\Omega-h_l)|\chi\rangle=|\varphi_i\rangle , \tag{116}$$

with the condition

$$\langle E_{nl}|\chi\rangle=0 , \tag{117}$$

since in Eq. (114) we have a reduced radial Green's function that excludes the E_{nl} state. Thus $|\chi\rangle$ is orthogonal to the $|E_{nl}\rangle$ eigenvector. An efficient way to implement, at the numerical level, the condition Eq. (117) is to extract from the inhomogeneous term the component along the $|E_{nl}\rangle$ vector and replace Eqs. (116) and (117) by

$$(\Omega-h_l)|\chi\rangle=|\varphi_i\rangle-|E_{nl}\rangle\langle E_{nl}|\varphi_i\rangle . \tag{118}$$

Multiplying both sides of Eq. (118) by $\langle E_{nl}|$ we see that for $\Omega\neq E_{nl}$ the solution of Eq. (118) is orthogonal to $|E_{nl}\rangle$ and the value $\mathcal{M}$ is given directly by Eq. (115). However, if $\Omega=E_{nl}$ an ambiguity in the definition of $|\chi\rangle$ by Eq. (118) remains and the condition Eq. (117) must be explicitly enforced. Thus for this case Eq. (115) should be replaced by

$$\mathcal{M}=\langle\varphi_f|\chi\rangle-\langle\varphi_f|E_{nl}\rangle\langle E_{nl}|\chi\rangle . \tag{119}$$

Because the inhomogeneity from Eq. (118) is already orthogonal to $|E_{nl}\rangle$ the component of $|\chi\rangle$ along $|E_{nl}\rangle$ arises only from numerical errors and so the matrix element $\langle E_{nl}|\chi\rangle$ from Eq. (119) should be a small number. This is also a very good test of the accuracy of the eigenfunctions used in the computation.

The value of $\mathcal{M}$ for $\Omega\neq E_{nl}$ could also be computed using Eqs. (116) and (119). In this case $|\chi\rangle$ would have a large component of the $|E_{nl}\rangle$ vector, the orthogonal component of $|E_{nl}\rangle$ would be affected by numerical uncertainties, and the final result would be subjected to large errors. This problem becomes more severe when $|\varphi_i\rangle$ contains a large component of the $|E_{nl}\rangle$ vector and when Ω is close to E_{nl}. Thus the procedure defined by Eqs. (118) and (119) is preferable for the computation of the matrix element $\mathcal{M}$ from Eq. (113). Nevertheless, for $\Omega=E_{nl}$ the numerical solution of Eq. (116) explodes to infinity and it is impossible to recover any value for the matrix element. Hence we used Eqs. (118) and (119) to compute the matrix elements involving a reduced radial Green's function.

If the energy of the Green's function is complex, we follow a similar procedure to that in Ref. [1] in which Eq. (118) is written as a system of two coupled inhomogeneous differential equations for the real and imaginary components of $|\chi\rangle$.

Further tests were made in order to ensure the accuracy of the subroutines. If $|\varphi_i\rangle\neq|\varphi_f\rangle$ then $|\varphi_i|$ and $|\varphi_f\rangle$ may be interchanged and $|\varphi_f\rangle$ will occur in the right side of Eq. (118). For our program this test gave the same value for the matrix element up to the machine error. Further, if $\Omega\neq E_{nl}$, then

$$\mathcal{M}=\langle\varphi_f|g_l(\Omega)|\varphi_i\rangle-\frac{\langle\varphi_f|E_{nl}\rangle\langle E_{nl}|\varphi_i\rangle}{\Omega-E_{nl}} , \tag{120}$$

where on the right side we have a complete radial Green's function. For our program this test gives a confidence limit of more than eight digits.

For the discretization scheme for solving the second-order differential equation we chose the Numerov method with variable step described in Ref. [8], with the bound-wave-function-type boundary conditions. The integral over ω in equations such as Eq. (84) was done using a Lagrange-rational method with 64 points. We found that for our type of integrands this method is faster and very precise compared to adaptive methods with error control, which are also more expensive in terms of the number of evaluations of the integrand.

VI. DISCUSSION OF RESULTS

A. Dispersion coefficients

We carried out calculations of dispersion coefficients for molecular states which dissociate into one atom in the ground state and the other in either of the first two S, P, or D excited states, for Li, Na, K, Rb, and Cs. The representation of the potential curves by a series in inverse powers of R is valid only for $R > R_c$ where R_c is the Le Roy [9] radius

$$R_c = 2[(n_g 0|r^2|n_g 0)^{1/2} + (n_e l_e|r^2|n_e l_e)^{1/2}] . \qquad (121)$$

Our values for the dispersion coefficients are accompanied by estimates of the Le Roy radius, in order to indicate the range of validity of the $1/R$ expansion. The expansion may be used for values of R smaller than R_c provided the contributions of the exchange terms are added.

1. The S-S asymptote

For the S-S asymptote we report in Table IV the values of C_6, C_8, and C_{10} for the cases where the second atom is in the first excited S state. We include the values of C_6, C_8, and C_{10} computed by Vigne-Maeder [10] using a model potential in the frame of a "natural state of interacting systems" theory, and the values of C_6 and C_8 for Li and Na computed by Bussery and Aubert-Frecon [11] using perturbation theory and model potentials of Klapisch [12]. The results are mostly in satisfactory agreement except for small discrepancies in the values of C_8 and C_{01} for Cs which may be attributed to the different model potentials used in the calculations. The model potential for Cs of Ref. [10] has two parameters and no core-polarization term while our model potential has five parameters [1] and includes a core-polarization term. For heavy alkali-metal atoms the static dipole polarizability of the positive-ion core is large and the core-polarization term is very important in obtaining a good description of the wave functions.

TABLE IV. The dispersion coefficients C_6, C_8, and C_{10} for the interaction between the ground and first excited S state atoms for the symmetries $\beta = \pm 1$. Brackets represent powers of ten.

		R_c	β	C_6	C_8	C_{10}	Ref.
Li	$2S$-$3S$	30.0	+1	3.110[4]	4.514[6]	1.250[9]	
				3.188[4]	4.455[6]	1.232[9]	[10]
				3.121[4]	4.472[6]		[11]
				3.090 [4]			[13]
			−1	1.381[4]	3.539[6]	1.064[9]	
				1.365[4]	3.431[6]	1.014[9]	[10]
				1.365[4]	3.392[6]		[11]
Na	$3S$-$4S$	31.31	+1	2.519[4]	5.418[6]	1.650[9]	
				2.511[4]	5.376[6]	1.606[9]	[10]
				2.517[4]	5.580[6]		[11]
			−1	1.430[4]	4.146[6]	1.374[9]	
				1.427[4]	3.738[6]	1.226[9]	[10]
				1.560[4]	4.460[6]		[11]
K	$4S$-$5S$	35.9	+1	6.368[4]	16.32[6]	5.945[9]	
				6.276[4]	15.92[6]	5.993[9]	[10]
			−1	3.289[4]	11.99[6]	4.855[9]	
				3.228[4]	11.57[6]	4.774[9]	[10]
Rb	$5S$-$6S$	37.2	+1	7.324[4]	20.81[6]	8.038[9]	
				7.362[4]	10.06[6]	7.906[9]	[10]
			−1	3.805[4]	15.03[6]	6.505[9]	
				3.784[4]	14.48[6]	6.358[9]	[10]
Cs	$6S$-$7S$	39.6	+1	10.65[4]	33.70[6]	14.11[9]	
				10.16[4]	30.81[6]	13.04[9]	[10]
			−1	5.290[4]	23.57[6]	11.27[9]	
				5.046[4]	20.89[6]	9.763[9]	[10]

In Table V, we report the calculated values of C_6, C_8, and C_{10} dispersion coefficients for the case where the second atom is in the second S excited state. The value of C_6 for Li $2S$-$3S$ agrees well with that of Caves [13]. We know of no other published values.

2. The S-P asymptote

For the S-P asymptote we computed the C_3, C_6, and C_8 coefficients. In Table VI we present the results for the case where the second atom is in the first excited P state. We list also the computed values from Refs. [10] and [14]. The computation of Bussery and Aubert-Frecon [14] neglects the contribution of continuum states while our computation, based on the Dalgarno-Lewis method, includes it. Further, our model potential should be superior to the Klapisch model potential in giving accurate results for high excited states.

The values of C_3 may be compared with empirical values determinable from measurements of the radiative lifetime of the $n\,^2P$ excited states. The empirical values are compared to the results of our calculation in Table VII. They appear to agree within the possible experimental uncertainties.

TABLE V. The dispersion coefficients C_6, C_8, and C_{10} for the interaction between the ground and second excited S state atoms for the symmetries $\beta = \pm 1$. Brackets represent powers of ten.

		R_c	β	C_6	C_8	C_{10}
Li	$2S$-$4S$	49.6	+1	6.712[4]	5.691[7]	5.228[10]
			−1	6.575[4]	5.700[7]	5.231[10]
Na	$3S$-$5S$	51.3	+1	7.622[4]	6.282[7]	6.158[10]
			−1	6.939[4]	6.290[7]	6.162[10]
K	$4S$-$6S$	56.9	+1	14.63[4]	22.82[7]	18.12[10]
			−1	15.21[4]	23.47[7]	18.14[10]
Rb	$5S$-$7S$	58.6	+1	16.33[4]	31.62[7]	23.05[10]
			−1	17.42[4]	31.57[4]	23.07[10]
Cs	$6S$-$8S$	61.5	+1	22.91[4]	31.28[7]	37.56[10]
			−1	23.80[4]	29.47[7]	37.60[10]

There are occasional significant differences between our values of C_6 and C_8 and those of Refs. [10] and [14]. The discrepancies for the C_8 coefficients and especially for π symmetry between these three calculations are particularly large. For the S-P asymptote the contribution of excited states with angular momentum up to F is im-

TABLE VI. The dispersion coefficients C_3, C_6, and C_8 for the interaction between the ground S and first excited $P\sigma$ and $P\pi$ state atoms for the symmetries $\beta = \pm 1$. For the coefficients, brackets enclose powers of ten.

		R_c	β	C_3	C_6	C_8	Ref.
Li	$2S$-$2P\sigma$	18.8	+1	11.01	2.066[3]	2.705[5]	
				10.99	2.025[3]	2.657[5]	[10]
				11.02	1.927[3]	2.296[5]	[14]
			−1	−11.01	2.066[3]	9.880[5]	
				−10.99	2.025[3]	9.644[5]	[10]
				−11.02	1.937[3]	11.24[5]	[14]
	$2S$-$2P\pi$		+1	−5.503	1.401[3]	10.21[4]	
				−5.494	1.374[3]	9.987[4]	[10]
				−5.510	1.301[3]	9.920[4]	[14]
			−1	5.503	1.401[3]	4.756[4]	
				5.494	1.374[3]	4.726[4]	[10]
				5.510	1.301[3]	3.162[4]	[14]
Na	$3S$-$3P\sigma$	21.5	+1	12.26	4.094[3]	7.025[5]	
				12.51	4.164[3]	6.775[5]	[10]
				12.95	4.144[3]	7.180[5]	[14]
			−1	−12.26	4.094[3]	21.20[5]	
				−12.51	4.164[3]	20.78[5]	[10]
				−12.95	4.144[3]	24.21[5]	[14]
	$3S$-$3P\pi$		+1	−6.128	2.636[3]	2.171[5]	
				−6.225	2.686[3]	2.100[5]	[10]
				−6.480	2.669[3]	2.301[5]	[14]
			−1	6.128	2.636[3]	8.559[4]	
				6.225	2.686[3]	8.229[4]	[10]
				6.480	2.669[3]	5.556[4]	[14]
K	$4S$-$4P\sigma$	25.1	+1	17.33	9.393[3]	1.975[6]	
				17.54	9.651[3]	1.892[6]	[10]
				18.68	10.13[3]	2.454[6]	[14]
			−1	−17.33	9.393[3]	6.712[6]	
				−17.54	9.651[3]	6.439[6]	[10]
				−18.68	10.13[3]	8.376[4]	[14]
	$4S$-$4P\pi$		+1	−8.665	6.291[3]	7.623[5]	
				−8.768	6.465[3]	7.132[5]	[10]
				−9.340	6.868[3]	5.814[5]	[14]
			−1	8.665	6.291[3]	2.893[5]	
				8.768	6.465[3]	2.624[5]	[10]
				9.340	6.868[3]	−3.734[4]	[14]
Rb	$5S$-$5P\sigma$	26.5	+1	18.40	12.05[3]	2.805[6]	
				18.80	12.56[3]	2.662[6]	[10]
				20.13	16.12[3]	4.056[6]	[14]
			−1	−18.40	12.05[3]	9.462[6]	
				−18.80	12.56[3]	8.964[6]	[10]
				−20.13	16.12[3]	13.74[6]	[14]
	$5S$-$5P\pi$		+1	−9.202	8.047[3]	11.32[5]	
				−9.400	8.407[3]	10.11[5]	[10]
				−10.06	11.35[3]	6.744[5]	[14]
			−1	9.202	8.047[3]	4.203[5]	
				9.400	8.407[3]	3.512[5]	[10]
				10.06	11.35[3]	−4.733[5]	[14]
Cs	$6S$-$6P\sigma$	28.4	+1	20.95	17.39[3]	5.040[6]	
				21.53	19.51[3]	5.061[6]	[10]
				24.27	26.09[3]	6.417[6]	[14]
			−1	−20.95	17.39[3]	16.56[6]	
				−21.53	19.51[3]	16.25[6]	[10]
				−24.27	26.09[3]	24.51[6]	[14]
	$6S$-$6P\pi$		+1	−10.47	11.83[3]	2.256[6]	
				−10.76	13.21[3]	2.078[6]	[10]
				−12.13	18.61[3]	1.729[6]	[14]
			−1	10.47	11.83[3]	9.131[5]	
				10.76	13.21[3]	7.790[5]	[10]
				12.13	18.61[3]	−4.643[5]	[14]

portant and some of the discrepancy may be due to different model potentials. It appears also that in the calculations of C_8 in Ref. [14] the contribution of terms $\{lLl'L'\} \equiv \{1212\}$, $\{2121\}$, $\{1221\}$, and $\{2112\}$ may have been overlooked, causing the values for the K, Rb, and Cs π states with symmetry $\beta = -1$ to have the wrong sign.

In Table VIII, we report the computed values of C_3, C_6, and C_8 for the case where the second atom is in the second P excited state and we compare them to the values of C_3 and C_6 for Li and Na from [11]. The agreement for C_6 is very good especially for Li where the Klapisch model potential and the representation of the high excited states by hydrogenlike functions used in [11] are realistic. A factor of about 3 between our values for C_3 and those from [11] suggests that there is an algebraic error in [11].

3. The S-D asymptote

We report in Tables IX and X the results for C_5 and C_6 for the case where the second atom is in the first or second excited D state, respectively, and the values for C_5 and C_6 for the Na $3S$-$3D$ asymptote from [11]. The results are in good agreement. The slight differences may be explained by the model potentials and by the truncation approximation which is adopted in [11]. For the rest of the coefficients it appears that there are no other calculations in the literature.

The value of C_6 is large in comparison with the value of C_5. The large value of C_6 occurs because energetically

TABLE VII. Theoretical and experimental values of $|C_3|$ for nS-$nP\sigma$ interaction.

	n	Calculated	Experimental	Ref.
Li	2	11.01	11.05±0.05	[15]
			10.95±0.09	[16]
			10.92±0.02	[17]
Na	3	12.26	12.31±0.02	[17]
			12.54±0.23	[18]
			12.34±0.07	[19]
K	4	17.33	16.64±0.30	[19]
			17.36±0.33	[18]
			17.80±0.34	[20,21]
Rb	5	18.40	18.03±0.35	[20]
			18.18±0.57	[22]
Cs	6	20.95	21.0±0.5	[18]
			19.6±0.9	[23]
			21.6±0.2	[24]

TABLE VIII. The dispersion coefficients C_3, C_6, and C_8 for the interactions between the ground and second excited $P\sigma$ and $P\pi$ states for the symmetries $\beta=\pm 1$. For the coefficients, brackets enclose powers of ten.

		R_c	β	C_3	C_6	C_8	Ref.
Li	$2S$-$3P\sigma$	34.3	+1	3.364[−2]	3.814[4]	2.702[7]	
				8.600[−2]	3.843[4]		[11]
			−1	−3.364[−2]	3.814[4]	2.533[7]	
				−8.600[−2]	3.843[4]		[11]
	$2S$-$3P\pi$		+1	−1.682[−2]	2.002[4]	1.535[6]	
				−4.300[−2]	2.033[4]		[11]
			−1	1.682[−2]	2.022[4]	3.714[5]	
				4.300[−2]	2.033[4]		[11]
Na	$3S$-$4P\sigma$	38.4	+1	8.432[−2]	4.806[4]	8.368[7]	
				24.00[−2]	5.100[4]		[11]
			−1	−8.432[−2]	4.806[4]	8.558[7]	
				−24.00[−2]	5.100[4]		[11]
	$3S$-$4P\pi$		+1	−4.216[−2]	2.602[4]	1.548[7]	
				−12.00[−2]	2.779[4]		[11]
			−1	4.216[−2]	2.602[4]	1.558[7]	
				12.00[−2]	2.779[4]		[11]
K	$4S$-$5P\sigma$	42.9	+1	9.225[−2]	10.67[4]	19.38[7]	
			−1	−9.225[−2]	10.67[4]	20.43[7]	
	$4S$-$5p\pi$		+1	−4.612[−2]	5.738[4]	3.300[7]	
			−1	4.612[−2]	5.738[4]	3.468[7]	
Rb	$5S$-$6P\sigma$	44.7	+1	14.28[−2]	12.56[4]	25.12[7]	
			−1	−14.28[−2]	12.56[4]	26.19[7]	
	$5S$-$6P\pi$		+1	−7.141[−2]	6.779[4]	4.372[7]	
			−1	7.141[−2]	6.779[4]	4.504[7]	
Cs	$6S$-$7P\sigma$	47.1	+1	14.82[−2]	17.30[4]	36.51[7]	
			−1	−14.82[−2]	17.30[4]	38.76[7]	
	$6S$-$7P\pi$		+1	−7.411[−2]	9.329[4]	6.280[7]	
			−1	7.411[−2]	9.329[4]	6.639[7]	

the $2P$ level of Li lies midway between the $2S$ and $3D$ levels and for Na, K, Rb, and Cs the first P state lies midway between the ground state and the second excited D state, producing a large contribution to the $S_1^2$and S_3^2 sums of Eqs. (78) and (80), respectively, from the term where $n=m$ is the first excited P state. The large denominator leads to large values of C_6 for Li($2S$)-Li($3D$) in Table IX and Na($3S$)-Na($4D$), K($4S$)-K($4D$), Rb($5S$)-Rb($5D$), and Cs($6S$)-Cs($6D$) in Table X. For Li the $4D$ and $4F$ states are energetically close to each other as are the $3D$ and $4P$ states of Na, leading to a large value of S_2^2 from Eq. (79) for Li and large values for all three sums Eqs. (77)–(79) for Na. Hence the large values of C_6 for Li($2S$)-Li($4D$) and Na($3S$)-Na($3D$). For K($4S$)-K($3D$), Rb($5S$)-Rb($4D$), and Cs($6S$)-Cs($5D$) these aspects are less critical and the ratio between the C_6 and C_5 coefficients is smaller than in the previous cases though still large in comparison with the Le Roy radius R_c, given in Table IX.

These and similar features will propagate into higher-order coefficients and higher-order perturbation theory, leading to still more rapidly increasing values. The expansion in powers of $1/R$, which is an asymptotically divergent expansion, may not be useful for the interaction of highly excited states. Even for the case of the interaction of S and D states, its range of applicability is restricted to very large values of R.

B. Long-range coefficients for electronic transition dipole moment

In Table XI we report the calculated values of the first two leading terms Eqs. (100) and (112) of the $1/R$ expansion of the transition dipole moment from the ground state to those molecular states which dissociate to one atom in the ground state and another in one of the first two excited P states. There appears to be no other direct calculation of these coefficients but some indirect comparisons can be made. The absolute value of $d^{(0)}$ is the positive square root of $|C_3|$ so that its reliability is established by the comparison of C_3 in Table VII. For the transition to the $2S$-$2P$ asymptote of Li, we can extract values of $d^{(0)}$ and $d^{(1)}$ from the *ab initio* calculation of the transition dipole moment as a function of R, Ref. [25]. From the fitting procedure, we derive -299.17 for $d_{01}^{(1)}$ compared to our prediction of -283.07 and 138.23 for $d_{\pm 11}^{(1)}$ compared to our prediction of 141.53.

In Table XII, we give the values of the leading term of the $1/R$ expansion of the electron transition dipole moment from the ground state to those molecular states which dissociate to one atom in the ground state and the other in one of the first two excited D states. The coefficient $d^{(0)}=0$ and the first nonvanishing term varies as $1/R^5$. The first-order coefficients are $d_{0\text{-}1}^{(1)}$ for linear

TABLE IX. The dispersion coefficients C_5, and C_6 for the interaction between the ground and first excited D σ, π, and δ states for symmetries $\beta=\pm1$. Brackets represent powers of ten.

		R_c	β	C_5	C_6	Ref.
Li	$2S$-$3D\sigma$	30.8	+1	−4.498[2]	−1.663[4]	
			−1	4.498[2]	2.039[4]	
	$2S$-$3D\pi$		+1	2.999[2]	14.96[3]	
			−1	−2.999[2]	−9.718[3]	
	$2S$-$3D\delta$		+1	−7.497[1]	−1.323[3]	
			−1	7.497[1]	11.02[3]	
Na	$3S$-$3D\sigma$	31.0	+1	−5.783[2]	4.059[4]	
				−5.210[2]	4.123[4]	[11]
			−1	5.783[2]	1.867[4]	
				5.210[2]	1.974[4]	[11]
	$3S$-$3D\pi$		+1	3.855[2]	1.842[4]	
				3.480[2]	1.931[4]	[11]
			−1	−3.855[2]	3.303[4]	
				−3.480[2]	3.363[4]	[11]
	$3S$-$3D\delta$		+1	−9.639[1]	1.766[4]	
				−8.700[1]	1.800[4]	[11]
			−1	9.639[1]	1.035[4]	
				8.700[1]	1.083[4]	[11]
K	$4S$-$3D\sigma$	29.4	+1	−1.320[3]	6.423[4]	
			−1	1.320[3]	1.743[4]	
	$4S$-$3D\pi$		+1	8.800[2]	1.956[4]	
			−1	−8.800[2]	5.076[4]	
	$4S$-$3D\delta$		+1	−2.200[2]	2.598[4]	
			−1	2.200[2]	1.038[4]	
Rb	$5S$-$4D\sigma$	28.2	+1	−1.465[3]	5.049[4]	
			−1	1.465[3]	1.289[4]	
	$5S$-$4D\pi$		+1	9.766[2]	1.481[4]	
			−1	−9.766[2]	3.988[4]	
	$5S$-$4D\delta$		+1	−2.441[2]	20.58[3]	
			−1	2.441[2]	8.045[3]	
Cs	$6S$-$5D\sigma$	25.6	+1	−1.443[3]	30.61[3]	
			−1	1.443[3]	6.253[3]	
	$6S$-$5D\pi$		+1	9.622[2]	7.806[3]	
			−1	−9.622[2]	24.04[3]	
	$6S$-$5D\delta$		+1	−2.405[2]	12.47[3]	
			−1	2.405[2]	4.348[3]	

polarization corresponding to a Σ-Σ transition and $d^{(1)}_{\pm1\text{-}1}$ for circular polarization corresponding to a Σ-Π transition.

VII. CONCLUSIONS

A formalism of degenerate perturbation theory was presented. We required that the initial basis set of functions be fully adapted to the perturbation. This is represented by Eq. (5). The iteration procedure proceeds smoothly, order by order, without any other requirements for modifying the initial basis set. The formalism includes the nondegenerate case. Indeed, if we restrict the range of possible degeneracy indices to one we get the well-known formalism of nondegenerate perturbation theory. For this reason we regard the "degenerate perturbation theory in a fully adapted basis" as a useful unification of the formalisms of nondegenerate and degenerate perturbation theories.

This paper is a nontrivial application of perturbation

TABLE X. The dispersion coefficients C_5 and C_6 for the interactions between the ground and second excited D σ, π, and δ states for the symmetries $\beta=\pm1$. Brackets represent powers of ten.

		R_c	β	C_5	C_6
Li	$2S$-$4D\sigma$	53.2	+1	−79.19	7.626[4]
			−1	79.19	7.733[4]
	$2S$-$4D\pi$		+1	52.79	6.712[4]
			−1	−52.79	6.641[4]
	$2S$-$4D\delta$		+1	−13.20	3.650[4]
			−1	13.20	3.668[4]
Na	$3S$-$4D\sigma$	53.4	+1	−88.47	7.942[4]
			−1	88.47	9.334[4]
	$3S$-$4D\pi$		+1	58.98	8.120[4]
			−1	−58.98	7.193[4]
	$3S$-$4D\delta$		+1	−14.74	4.479[4]
			−1	14.74	4.943[4]
K	$4S$-$4D\sigma$	49.7	+1	−23.98	14.15[4]
			−1	23.98	14.14[4]
	$4S$-$4D\pi$		+1	15.98	12.49[4]
			−1	−15.98	12.50[4]
	$4S$-$4D\delta$		+1	−3.996	7.547[4]
			−1	3.996	7.541[4]
Rb	$5S$-$5D\sigma$	48.1	+1	−0.5079	11.32[4]
			−1	0.5079	13.68[4]
	$5S$-$5D\pi$		+1	0.3386	11.88[4]
			−1	−0.3386	10.31[4]
	$5S$-$5D\delta$		+1	−0.0847	6.494[4]
			−1	0.0847	7.281[4]
Cs	$6S$-$6D\sigma$	45.5	+1	−248.3	39.34[4]
			−1	248.3	13.31[4]
	$6S$-$6D\pi$		+1	165.5	13.93[4]
			−1	−165.5	31.32[4]
	$6S$-$6D\delta$		+1	−41.38	15.80[4]
			−1	41.38	7.110[4]

TABLE XI. The leading two coefficients in the expansion of the electronic transition dipole moments between the ground and first excited S and P states of the interacting atom pairs.

		$d^{(0)}$	$d^{(1)}_{01}$	$d^{(1)}_{\pm11}$	Ref.
Li	$2S$-$2P$	−3.3175	−283.07	141.53	
		−3.3400	−299.17	138.23	[25]
		−3.3167			[26]
	$2S$-$3P$	0.1834	−16.904	8.4521	
		0.1767			[27]
Na	$3S$-$3P$	−3.5007	284.26	142.13	
		−3.5425			[28]
	$3S$-$4P$	−0.2904	41.917	−20.959	
		−0.3197			[5]
K	$4S$-$4P$	−4.1630	−615.54	307.77	
		−4.1475			[29]
	$4S$-$5P$	−0.3037	68.049	−34.024	
		−0.2827			[5]
Rb	$5S$-$5P$	−4.2899	−696.78	348.43	
		−4.2804			[5]
	$5S$-$6P$	−0.3779	95.662	−47.831	
		−0.3609			[5]
Cs	$6S$-$6P$	−4.5768	−931.98	465.99	
		−4.6529			[5]
	$6S$-$7P$	−0.3850	116.80	−58.401	
		−0.3894			[5]

TABLE XII. The leading coefficients in the expansion of the electronic transition dipole moments between the ground and second excited S and P states of the interacting atom pairs. Brackets represent powers of ten.

		$d^{(1)}_{0-1}$	$d^{(1)}_{\pm 1-1}$
Li	2S-3D	−2.0197[3]	1.1661[3]
	2S-4D	−7.3411[2]	4.2384[2]
Na	3S-3D	3.0323[3]	−1.7507[3]
	3S-4D	8.2805[2]	−4.7808[2]
K	4S-3D	−1.0698[4]	6.1765[3]
	4S-4D	−8.3192[2]	4.8031[2]
Rb	5S-4D	−1.6548[4]	9.5544[3]
	5S-5D	−2.5026[1]	1.4449[1]
Cs	6S-5D	−4.6892[4]	2.7073[4]
	6S-6D	4.2292[3]	−2.4417[3]

theory. The dispersion coefficients are extracted directly from the energy corrections. The long-range coefficients of the electronic transition dipole moment are computed using the wave-function corrections. Beyond the formalism itself the results have their own value. They give a quantitative description of the long-range interaction between atomic systems. Some of our results appear to be new, especially those which involve D states or the second S and P excited states as well as the long-range coefficients of the electronic transition dipole moment, and others improve on exciting computations. Our calculations have two advantages. They use an accurate model potential and an exact evaluation of the second-order sums. We developed an extension of the Dalgarno-Lewis method in order to handle the radial matrix elements which involve reduced radial Green's functions.

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APPENDIX A: THE 3*jm* SYMBOLS

In this Appendix we give some relations involving the integral of a product of three Y_{lm} functions. We define the following 3jm symbols:

$$\langle j_1m_1|j_2m_2|j_3m_3\rangle = (4\pi)^{1/2}\int Y_{j_1m_1}(\hat{r})Y_{j_2m_2}(\hat{r})Y_{j_3m_3}(\hat{r})d\Omega_{\hat{r}} \ . \tag{A1}$$

Using the Clebsch-Gordan algebra we get the following expression for the 3jm symbols in terms of 3j coefficients:

$$\langle j_1m_1|j_2m_2|j_3m_3\rangle = (-1)^{m_1}(\hat{j}_1\hat{j}_2\hat{j}_3)^{1/2}\begin{bmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{bmatrix} \times \begin{bmatrix} j_1 & j_2 & j_3 \\ -m_1 & m_2 & m_3 \end{bmatrix} . \tag{A2}$$

The 3jm symbol is zero if $j_1+j_2+j_3=$(odd) or if $m_1 \neq m_2+m_3$. Based on properties of the 3j coefficients the following symmetry relations hold:

$$\langle j_1m_1|j_2m_2|j_3m_3\rangle$$

$$= \langle j_1-m_1|j_2-m_2|j_3-m_3\rangle \ , \tag{A3}$$

$$= (-1)^{m_1+m_2}\langle j_2-m_2|j_1-m_1|j_3m_3\rangle \ , \tag{A4}$$

$$= \langle j_1m_1|j_3m_3|j_2m_2\rangle \ , \tag{A5}$$

$$= (-1)^{m_1+m_3}\langle j_3-m_3|j_2m_2|j_1-m_1\rangle \ . \tag{A6}$$

We restrict the list to those relations which occur in the calculation presented in this paper. We make use of

$$\langle j_1m_1|j_2m_2|00\rangle = \delta_{j_1j_2}\delta_{m_1m_2} \ , \tag{A7}$$

$$\langle 00|j_2m_2|j_3m_3\rangle = (-1)^{m_2}\delta_{j_2j_3}\delta_{m_2-m_3} \ . \tag{A8}$$

APPENDIX B: THE *U* SYMBOLS

Let $U^{\nu_1'\nu_2'}_{\nu_1\nu_2}$ be the matrix element

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2} = \langle \varphi_{\nu_1'\nu_2'}|V|\varphi_{\nu_1\nu_2}\rangle \ , \tag{B1}$$

where the index ν stands for the triplet $\{nlm\}$,$\varphi_{\nu\nu'}$ is defined by Eq. (26), and V by Eq. (23). Using the expansion of V in inverse powers of R we get

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2} = \sum_{l=1}^{\infty}\sum_{L=1}^{\infty}\frac{1}{R^{l+L+1}}U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL} \ , \tag{B2}$$

where

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL} = \langle \varphi_{\nu_1'\nu_2'}|V_{lL}|\varphi_{\nu_1\nu_2}\rangle \ . \tag{B3}$$

Introducing the expression for φ from Eq. (26) and V_{lL} from Eq. (24) into the right-hand side of Eq. (B3) we get

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL} = (-1)^L(\hat{l}\hat{L})^{-1/2} \times \sum_m K^m_{lL}\langle l_1'm_1'|lm|l_1m_1\rangle\langle l_2'm_2'|L-m|l_2m_2\rangle \times (n_1'l_1'|r^l|n_1l_1)(n_2'l_2'|r^L|n_2l_2) \ , \tag{B4}$$

where $\langle \ | \ | \ \rangle$ are the 3jm symbols defined in Appendix A and $(\ | \ | \ )$ are the radial matrix elements. The K^m_{lL} coefficients are defined by Eq. (25) and they obey the relations

$$K^m_{lL} = K^m_{Ll} = K^{-m}_{lL} \ . \tag{B5}$$

From the properties of the 3jm symbols we obtain

$$u^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL} = 0 \quad \text{if } l_1'+l_1+l=\text{(odd)or } 1_2'+l_2+l=\text{(odd)} \ , \tag{B6}$$

and

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL} = 0 \quad \text{if } m_1'+m_2' \neq m_1+m_2 \ . \tag{B7}$$

From Eqs. (B4) and (B5) we have

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL}=(-1)^{l+L}U^{\nu_2'\nu_2'}_{\nu_2\nu_1;Ll} \ . \tag{B8}$$

Using Eqs. (B4), (B5), and (A3) we get

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL}=U^{\bar{\nu}_1'\bar{\nu}_2'}_{\bar{\nu}_1\bar{\nu}_2;lL} \ , \tag{B9}$$

where if $\nu\equiv\{nlm\}$ then $\bar{\nu}\equiv\{nl-m\}$. Using Eqs. (B4), (A6), and (B8) we get the third symmetry relation

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL}=U^{\nu_1\nu_2}_{\nu_1'\nu_2';lL} \ . \tag{B10}$$

From the last two relations we get two more symmetry relations for $U^{\nu_1'\nu_2'}_{\nu_1\nu_2}$,

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2}=U^{\bar{\nu}_1'\bar{\nu}_2'}_{\bar{\nu}_1\bar{\nu}_2} \ , \tag{B11}$$

$$U^{\nu_1'\nu_2'}_{\nu_1\nu_2}=U^{\nu_1\nu_2}_{\nu_1'\nu_2'} \ . \tag{B12}$$

We list below several useful expressions of $U^{\nu_1'\nu_2'}_{\nu_1\nu_2;lL}$ for some particular values of the indices.

$$U^{n00n_2l_2m_2}_{n00n_1l_1m_1;lL}=0 \ , \tag{B13}$$

$$U^{n_1l_1m_1n00}_{n00n_2l_2m_2;lL}=\delta_{ll_1}\delta_{Ll_2}\delta_{m_1m_2}(-1)^{l_2+m_2}(\hat{l}_1\hat{l}_2)^{-1/2} \times K^{m_1}_{l_1l_2}(n_1l_1|r^{l_1}|n0(n0)|r^{l_2}|n_2l_2) \ , \tag{B14}$$

$$U^{n_1l_1m_1n_2l_2m_2}_{n00n00;lL}=\delta_{ll_1}\delta_{Ll_2}\delta_{m_1-m_2}(-1)^{l_2}(\hat{l}_1\hat{l}_2)^{-1/2} \times K^{m_1}_{l_1l_2}(n_1l_1|r^{l_1}|n0)(n_2l_2|r^{l_2}|n0) \ , \tag{B15}$$

$$U^{n_1l_1m_1n_2l_2m_2}_{n_g00n_e1m_e;lL}=\delta_{ll_1}\delta_{m_2m_e-m_1}(-1)^{L}(\hat{l}\hat{L})^{-1/2} \times \sum_{\sigma=\pm 1}\delta_{l_2L+\sigma}K^{m_1}_{lL}\langle l_2m_2|L-m_1|1m_e\rangle \times(n_1l_1|r^{l}|n_g0)(n_2l_2|r^{L}|n_e1) \ . \tag{B16}$$

APPENDIX C: THE *W* symbols

The *W* symbols are a straightforward generalization of the *U* symbols presented in Appendix B. They appear in higher orders of perturbation and are defined as

$$W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g'}=\sum_{\{lL\}}R^{-\sum_{j=1}^{k+1}(l_j+L_j+1)}W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g';\{lL\}} \ , \tag{C1}$$

where

$$W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g';\{lL\}} =\sum_{\{\nu\nu'\}}\frac{U^{\nu_e\nu_e'}_{\nu_1\nu_1';l_1L_1}U^{\nu_1\nu_1'}_{\nu_2\nu_2';l_2L_2}\cdots U^{\nu_K\nu_K'}_{\nu_g\nu_g';l_{K+1}L_{K+1}}}{\Delta^{\alpha_1}_{1g}\Delta^{\alpha_2}_{2g}\cdots\Delta^{\alpha_K}_{Kg}} \ . \tag{C2}$$

We used the following notations:

$$\begin{aligned} &\{\alpha\}\equiv\alpha_1,\alpha_2,\ldots,\alpha_K \ , \\ &\{lL\}\equiv l_1L_1,l_2L_2,\ldots,l_{K+1}L_{K+1} \ , \\ &\{\nu\nu'\}\equiv\nu_1\nu_1',\nu_2\nu_2',\ldots,\nu_K\nu_K' \ , \\ &\Delta_{jg}=E_{n_jl_j}+E_{n_j'l_j'}-E_{n_gl_g}-E_{n_g'l_g'} \ . \end{aligned} \tag{C3}$$

The α_j are integer numbers. For $K=0$ the *W* symbols reduce to the *U* symbols

$$W^{\nu_e\nu_e';0}_{\nu_g\nu_g'}\equiv U^{\nu_e\nu_e'}_{\nu_g\nu_g'} \ . \tag{C4}$$

From Eqs. (B6) and (B7) it follows that the *W* symbols are nonzero only if

$$l_e+l_g+\sum_{j=1}^{K+1}l_j=(\text{even}) \ , \tag{C5}$$

$$l_e'+l_g'+\sum_{j=1}^{K+1}l_j'=(\text{even}) \ , \tag{C6}$$

and

$$m_g+m_g'=m_e+m_e' \ . \tag{C7}$$

Based on the *U*-symbol symmetry relations Eqs. (B8), (B9), and (B10) we get the following symmetry relations for *W* symbols:

$$W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g';\{lL\}}=(-1)^{\sum_{j=1}^{K+1}(l_j+L_j)}W^{\nu_e'\nu_e;K\{\alpha\}}_{\nu_g'\nu_g;\{Ll\}} \ , \tag{C8}$$

$$W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g';\{lL\}}=W^{\bar{\nu}_e\bar{\nu}_e';K\{\alpha\}}_{\bar{\nu}_g\bar{\nu}_g';\{lL\}} \ , \tag{C9}$$

where as usual if $\nu\equiv\{nlm\}$ then $\bar{\nu}\equiv\{nl-m\}$. For the case where $E_{\nu_e}+E_{\nu_e'}=E_{\nu_g}+E_{\nu_g'}$ we have

$$W^{\nu_e\nu_e';K\{\alpha\}}_{\nu_g\nu_g';\{lL\}}=W^{\nu_g\nu_g';K\{\alpha\}}_{\nu_e\nu_e';\overline{\{lL\}}} \ , \tag{C10}$$

where $\overline{\{lL\}}\equiv l_{K+1}L_{K+1},l_KL_K,\ldots,l_1L_1$.

The most common *W* symbols through our paper are for $K=1$ and $\alpha_1=1$ denoted simply by $W^{\nu_e\nu_e'}_{\nu_g\nu_g';lLl'L'}$. Below we give the expression of this symbol for some particular values of indexes which occur through this paper:

$$W^{n_1'00n_2'00}_{n_100n_200;lLl'L'}=\delta_{ll'}\delta_{LL'}(\hat{l}\hat{L})^{-1}\mathcal{C}^{2l}_{2(l+l)}\sum_{nm}\frac{(n_10|r^l|nl)(nl|r^l|n_1'0)(n_20|r^L|mL)(mL|r^L|n_2'0)}{E_{nl}+E_{mL}-E_{n_10}-E_{n_20}} \ , \tag{C11}$$

where we used the binomial identity

$$\sum_m \mathcal{C}^{l+m}_{l+L}\mathcal{C}^{L+m}_{l+L}=\mathcal{C}^{2l}_{2(l+L)} \ . \tag{C12}$$

Using Eqs. (B16) and (B10) we get

$$W^{n_g00n_e1m_e}_{n_g00n_e1m_e;lLl'L'}=\delta_{ll'}\sum_{\sigma,\sigma'=\pm1}\delta_{L+\sigma L'+\sigma'}(-1)^{L+L'}(\hat{l}\hat{L}\hat{l}'\hat{L}')^{-1/2}$$
$$\times\sum_{\mu}K^{\mu}_{lL}K^{\mu}_{l'L'}\langle L+\sigma m_e-\mu|L-\mu|1m_e\rangle\langle L+\sigma m_e-\mu|L'-\mu|1m_e\rangle \ .$$
$$\times\sum_{n_1n_2}\frac{(n_1l|r^l|n_g0)^2(n_2L+\sigma|r^L|n_e1)(n_2L+\sigma|r^{L'}|n_e1)}{E_{n_1l}+E_{n_2L+\sigma}-E_{n_e1}-E_{n_g0}} \ , \tag{C13}$$

and

$$W^{n_e1m_en_g00}_{n_g00n_e1m_e;lLl'L'}=\sum_{\sigma,\sigma'=\pm1}\delta_{l'l+\sigma}\delta_{LL'+\sigma'}(-1)^{L+L'}(\hat{l}\hat{L}\hat{l}'\hat{L}')^{-1/2}$$
$$\times\sum_{\mu}K^{m_e-\mu}_{lL}K^{\mu}_{l'L'}\langle l'\mu|l\mu-m_e|1m_e\rangle\langle Lm_e-\mu|L'-\mu|1m_e\rangle$$
$$\times\sum_{n_1n_2}\frac{(n_1l'|r^l|n_e1)(n_1l'|r^{l'}|n_g0)(n_2L|r^L|n_g0)(n_2L|r^{L'}|n_e1)}{E_{n_1l'}+E_{n_2L}-E_{n_e1}-E_{n_g0}} \ . \tag{C14}$$

APPENDIX D: THE *T* AND *B* SYMBOLS

In this Appendix we introduce two new symbols related to the dipole matrix elements which are needed in the study of electronic transition dipole moments. We start from the identity

$$\hat{s}\cdot\hat{r}Y_{lm}(\hat{r})=(-1)^{l+m}\sum_{\sigma=\pm1}(-1)^{(1+\sigma)/2}\left[l+\frac{1+\sigma}{2}\right]^{1/2}\sum_{\mu q}\begin{bmatrix}l+\sigma & 1 & l\\ \mu & q & -m\end{bmatrix}Y_{l+\sigma\mu}(\hat{r})\hat{s}\cdot\hat{e}_q \ , \tag{D1}$$

where $\hat{s}$ is an arbitrary complex unit vector and $\hat{e}_q$ are the spherical unit vectors; $\hat{e}_0=\hat{e}_z$, $\hat{e}_{\pm1}=\mp(1/\sqrt{2})(\hat{e}_x\pm i\hat{e}_y)$. We define the following *T* symbol:

$$T^{\nu_1'\nu_2'}_{\nu_1\nu_2}=\langle\varphi_{\nu_1'\nu_2'}|\hat{s}\cdot\vec{r}_1|\varphi_{\nu_1\nu_2}\rangle \ , \tag{D2}$$

where $\varphi_{\nu\nu'}(\vec{r}_1,\vec{r}_2)$ are defined by Eq. (26). Using Eq. (D1) we get

$$T^{\nu_1'\nu_2'}_{\nu_1\nu_2}=\delta_{\nu_2\nu_2'}(-1)^{l_1+m_1}\sum_{\sigma=\pm1}\delta_{l_1'l_1+\sigma}(-1)^{(1+\sigma)/2}\left[l_1+\frac{1+\sigma}{2}\right]^{1/2}\begin{bmatrix}l_1' & 1 & l_1\\ m_1' & m_1-m_1' & -m_1\end{bmatrix}(n_1'l_1'|r|n_1l_1)\hat{s}\cdot\hat{e}_{m_1-m_1'} \ . \tag{D3}$$

A simple expression holds for the case $\nu_1\equiv\{n_g00\}$:

$$T^{nlmn_xl_xm_x}_{n_g00n_xl_xm_x}=\delta_{l_1}\frac{1}{\sqrt{3}}(n1|r|n_g0)\hat{s}\cdot\hat{e}_m^* \ . \tag{D4}$$

From the relation $\hat{e}_q^*=(-1)^q\hat{e}_{-q}$, we obtain the following symmetry relations:

$$T^{\nu_1'\nu_2'}_{\nu_1\nu_2}(\hat{s}^*)=(-1)^{m_1+m_1'}[T^{\bar{\nu}_1'\bar{\nu}_2'}_{\bar{\nu}_1\bar{\nu}_2}(\hat{s})]^* \ , \tag{D5}$$

$$T^{\nu_1'\nu_2'}_{\nu_1\nu_2}(\hat{S}^*)=[T^{\nu_1\nu_2}_{\nu_1'\nu_2'}(\hat{s})]^* \ , \tag{D6}$$

where the asterisk indicates the complex conjugate operator. Combining Eqs. (D5) and (D6) we get the third symmetry relation for the *T* symbols,

$$T^{\nu_1'\nu_2'}_{\nu_1\nu_2}(\hat{s})=(-1)^{m_1+m_1'}T^{\bar{\nu}_1\bar{\nu}_2}_{\bar{\nu}_1'\bar{\nu}_2'}(\hat{s}) \ . \tag{D7}$$

The *B* symbols are defined to be

$$B^{\nu_1'\nu_2'}_{\nu_1\nu_2}=\langle\varphi_{\nu_1'\nu_2'}|\hat{s}\cdot(\vec{r}_1+\vec{r}_2)|\varphi_{\nu_1\nu_2}\rangle \ . \tag{D8}$$

Using Eq. (D2) we get

$$B^{\nu_1'\nu_2'}_{\nu_1\nu_2}=T^{\nu_1'\nu_2'}_{\nu_1\nu_2}+T^{\nu_2'\nu_1'}_{\nu_2\nu_1} \ . \tag{D9}$$

It is clear from Eq. (D9) that the *B* symbols satisfy the following symmetry relation:

$$B^{\nu_1'\nu_2'}_{\nu_1\nu_2}=B^{\nu_2'\nu_1'}_{\nu_2\nu_1} \ . \tag{D10}$$

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