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Molecular theory of collision-induced fine-structure transitions in atomic oxygen

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A molecular theory of collision-induced fine-structure-level transitions in complex atoms is presented. The theory is applied to calculate the excitation cross sections for the fine-structure levels in the ^3P ground state of atomic oxygen. We discuss and compare the theory presented here with previous molecular theories.

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I. INTRODUCTION

Atomic oxygen plays an important role in the chemical reactions and the energy-transfer processes taking place in the terrestrial atmosphere [1–6] as well as the atmospheres of Venus and Mars [7,8]. Grossmann and Offermann [9] observed the 63- and 146-μm line emissions from the fine-structure levels of the ground state of atomic oxygen, and Sharma and co-workers [10–12] proposed a passive remote-sensing method, which depends on inverting these lines, to obtain the temperature and density of atomic oxygen in the thermosphere. The method assumes that the fine-structure populations are in thermodynamic equilibrium with the local translational temperature (LTE). In order to make definite predictions of the altitude regime in which the assumption of LTE is valid, the transition cross sections amongst the fine-structure levels of oxygen due to collisions with other oxygen atoms must be known.

Estimates for the fine-structure level-changing cross sections in oxygen-atom collisions were given by Allison and Burke [13]. They assumed that long-range forces, obtained by first-order perturbation theory of the atom-atom interaction, dominate the collision dynamics, and in order to simplify the system of coupled equations they did not take into account the fine-structure splitting of the ^3P ground state of oxygen. In this paper we develop a fully quantum-mechanical molecular theory of collision-induced fine-structure excitation in oxygen atoms. Both the molecular nature of the atom-atom interaction and the fine-structure splitting in the atoms are incorporated.

Molecular theories of fine-structure excitation in atomic collisions were introduced by Reid and Dalgarno [14], Reid [15], Mies [16], and Launay and Roueff [17], and Harel *et al.* [18] discussed the range of validity of these and other models. A general molecular theory developed by Singer, Freed, and Band [19] was used to study fine-structure excitation in the low-energy scattering of hydrogen with $C^+(^2P)$ [20]. Molecular theories have also been applied to calculate charge transfer into fine-structure levels during slow ion-atom collisions [21,22]. In this paper we present an alternative molecular theory based on a gauge-theory formulation of the method of perturbed stationary states (PSS) [23,24].

In Sec. II we outline the molecular scattering theory, and illustrate the relationship between the molecular states of the ground O_2 molecule and the atomic states which evolve from them in the separated atom limit. In order to establish a one-to-one correspondence between the molecular and atomic states we investigate the long-range atom-atom interaction. In Sec. III we construct the total system wave function and express it as an expansion over the adiabatic electronic eigenstates of O_2. We arrive at a set of coupled Schrödinger-like equations for the scattering amplitudes (PSS equations), but find that the nonadiabatic couplings in these equations persist in the separated atom limit. We induce a unitary matrix transformation, or gauge transformation [23,24], on the PSS scattering amplitudes and show that the nonadiabatic couplings of the transformed amplitudes are well behaved in the separated atom limit. In the new gauge the nuclear amplitudes are uncoupled in the asymptotic region, and we impose conventional scattering boundary conditions on them. The scattering equations are reduced to a set of coupled radial equations, and in Sec. IV we relate solutions to the coupled radial equations, with appropriate scattering boundary conditions, to the amplitude for two oxygen atoms in fine-structure states j_a and j_b, respectively, to make a transition into the states $j_{a'}$, $j_{b'}$. The formulation includes effects due to the symmetry of nuclear interchange in the O_2 system. We discuss and compare the theory presented here with previous molecular theories. Atomic units are used, unless otherwise stated, throughout the discussion.

II. MOLECULAR THEORY

In a space fixed coordinate system the nonrelativistic Hamiltonian for the O_2 system is

$$H(\mathbf{R}_1,\mathbf{R}_2,\mathbf{r}')=-\frac{1}{2M}\nabla^2_{R_1}-\frac{1}{2M}\nabla^2_{R_2}-\frac{1}{2}\sum_i^N\nabla^2_{r_i'}+\sum_i^N V_1(|\mathbf{R}_1-\mathbf{r}_i'|)+V_2(|\mathbf{R}_2-\mathbf{r}_i'|)+V_N(|\mathbf{R}_1-\mathbf{R}_2|)+V_{e\text{-}e}\;, \tag{1}$$

where $\mathbf{R}_1,\mathbf{R}_2$ are the position vectors for the two nuclei, $\mathbf{r}_i'$ are the position vectors for the electrons, and $\mathbf{r}'$ is shorthand for the set of N electronic variables $\mathbf{r}_1',\ldots,\mathbf{r}_N'$. V_1 and V_2 are the electron-nuclear interaction terms for the two identical nuclei, V_N is the internuclear repulsion potential, $V_{e\text{-}e}$ is the electron-electron interaction, and M is the mass of the oxygen nucleus. It is convenient to introduce a new set of variables

$$\mathbf{R}_{\text{c.m.}}=\frac{M(\mathbf{R}_1+\mathbf{R}_2)+\sum_i\mathbf{r}_i'}{2M+N}\;,$$

$$\mathbf{R}=\mathbf{R}_1-\mathbf{R}_2\;,$$

$$\mathbf{r}_i=\mathbf{r}_i'-\tfrac{1}{2}(\mathbf{R}_1+\mathbf{R}_2)\;, \tag{2}$$

where $\mathbf{R}_{\text{c.m.}}$ is the center of mass for the system, $\mathbf{r}_i\equiv\mathbf{r}$ are the position vectors for the electrons with respect to the center of mass of the nuclei, and $\mathbf{R}$ is the vector describing the internuclear distance and orientation. The coordinates for all dynamical variables are defined with respect to a space-fixed frame. Inserting Eq. (2) into Eq. (1) we get

$$H(\mathbf{R}_{\text{c.m.}},\mathbf{R},\mathbf{r})=H_{\text{c.m.}}+H_{\text{KE}}+V+V_{e\text{-}e}\;, \tag{3}$$

where $H_{\text{c.m.}}$ is the kinetic-energy operator for the center-of-mass motion and

$$H_{\text{KE}}=-\frac{1}{M}\nabla^2_R-\frac{1}{4M}\left[\sum_i^N\nabla_{r_i}\right]^2-\frac{1}{2}\sum_i^N\nabla^2_{r_i}\;, \tag{4}$$

$$V=\sum_i^N\left[V_1\left(\left|\frac{\mathbf{R}}{2}-\mathbf{r}_i\right|\right)+V_2\left(\left|\frac{\mathbf{R}}{2}+\mathbf{r}_i\right|\right)\right]+V_N(|\mathbf{R}|) \tag{5}$$

are the kinetic energy and electrostatic interaction Hamiltonians, respectively. We define an adiabatic Hamiltonian

$$H_{\text{AD}}(\mathbf{R},\mathbf{r})\equiv-\frac{1}{2}\sum_i\nabla^2_{r_i}-\frac{1}{4M}\left[\sum_i\nabla_{\mathbf{r}_i}\right]^2+V(\mathbf{R},\mathbf{r})+V_{e\text{-}e}\;. \tag{6}$$

Factoring out the center-of-mass motion, we represent the eigenstates Ψ of Hamiltonian (3) by the expansion

$$\Psi(\mathbf{R},\mathbf{r})=\sum_\gamma F_\gamma(\mathbf{R})\psi_\gamma(\mathbf{R},\mathbf{r})\;, \tag{7}$$

where the ψ_γ are orthogonal eigenstates of the adiabatic Hamiltonian

$$H_{\text{AD}}\psi_\gamma=\epsilon_\gamma(R)\psi_\gamma\;, \tag{8}$$

and γ is an index specifying the molecular quantum numbers of the adiabatic state. We define Born-Oppenheimer (BO) states as those adiabatic states in which the internuclear vector $\mathbf{R}$ is aligned along the $\hat{\mathbf{z}}$ axis of the space-fixed coordinate frame [25]. The quantum numbers associated with the BO states are

$$\gamma=\{\Lambda S\Sigma\Gamma\}\;, \tag{9}$$

where Λ is the component of the electronic orbital angular momentum along the $\hat{\mathbf{z}}$ axis, S,Σ are the total spin and spin projection along the $\hat{\mathbf{z}}$ axis, and Γ is any additional quantum number needed to fully specify the system. The quantum numbers associated with the discrete symmetries of nuclear inversion and reflection (for Σ states) through a plane including the internuclear axis, are related to the quantum numbers which specify the asymptotic atomic states (see Appendix A).

At large internuclear distances R, the BO molecular eigenstates $\psi_\gamma(R,\mathbf{r})$ are linear combinations of atomic states. We define the atomic states

$$|l_am_a\rangle\otimes|l_bm_b\rangle\otimes|S\Sigma\rangle\;, \tag{10}$$

where l_a,l_b are the eigenvalues of the electronic orbital angular momentum operators $\boldsymbol{l}_a,\boldsymbol{l}_b$ defined with respect to centers a,b located, respectively, at $\pm\hat{\mathbf{z}}R/2$, m_a,m_b are the projections of orbital angular momentum of each atom along the $\hat{\mathbf{z}}$ axis, and S and Σ are defined above. We introduce the product kets

$$|L\Lambda S\Sigma\rangle=(-1)^{l_b-l_a-\Lambda}\sum_{m_am_b}\sqrt{2L+1}\begin{pmatrix}l_a & l_b & L\\ m_a & m_b & -\Lambda\end{pmatrix}\times|l_am_a\rangle\otimes|l_bm_b\rangle\otimes|S\Sigma\rangle \tag{11}$$

which are eigenfunctions of the total, two-center, orbital angular momentum

$$\mathbf{L}=\boldsymbol{l}_a+\boldsymbol{l}_b\;,$$

$$\boldsymbol{l}_a=\sum_i\left[\mathbf{r}_i-\frac{R}{2}\hat{\mathbf{z}}\right]\times\mathbf{p}_i\;, \tag{12}$$

$$\boldsymbol{l}_b=\sum_j\left[\mathbf{r}_j+\frac{R}{2}\hat{\mathbf{z}}\right]\times\mathbf{p}_j\;,$$

and where index i identifies electrons on center a, $\mathbf{p}_i=-i\nabla_i$ is the momentum operator for electron i, and index j identifies the electrons associated with center b (see Appendix A for a more detailed description).

However, they are not eigenstates of the total electronic orbital angular momentum defined with respect to the molecular center

$$\mathcal{L}\equiv\sum_i^N[\mathbf{r}_i\times\mathbf{p}_i]\;, \tag{13}$$

where the sum is taken over all electrons. $\mathbf{L}$ and $\mathcal{L}$ are related, though, and using definition (12) and (13) we get

$$\mathbf{L}=\boldsymbol{\mathcal{L}}-R\hat{\mathbf{z}}\times\mathbf{P}\ ,$$

$$\mathbf{P}=\tfrac{1}{2}\left[\sum_i \mathbf{p}_i-\sum_j \mathbf{p}_j\right]\ . \tag{14}$$

A useful identity, which relates $\mathbf{L},\boldsymbol{\mathcal{L}}$ through a unitary transformation, is

$$\mathbf{L}=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)\boldsymbol{\mathcal{L}}\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)\ , \tag{15}$$

where the exponential is an electron translation operator.

The states defined in Eq. (11) diagonalize the molecular electronic inversion (parity) operator $\hat{\pi}$ (see Appendix A),

$$\hat{\pi}|L\Lambda S\Sigma\rangle=(-1)^{L+S}|L\Lambda S\Sigma\rangle\ , \tag{16}$$

and most molecular states can be immediately correlated with the atomic states $|L\Lambda S\Sigma\rangle$. We find that for singlet molecular states $S=0$, the gerade (g) Born-Oppenheimer states separate to $L=0$ or 2 atomic states, and the ungerade (u) states separate to $L=1$ atomic states. For triplet molecular states $S=1$, the g states separate to $L=1$ and the u states to $L=0$ and 2 states. For the quintet molecular state $S=2$, the gerade BO states separate to $L=0$ or 2 atomic states, and the ungerade BO states separate to $L=1$ states. There are 81 molecular states formed in the approach of two ^3P oxygen atoms and, according to the Wigner-Witmer rules [26], there exists a one-to-one correspondence between the atomic and molecular states except for the $b\,^1\Sigma_g^+$ and $2\,^1\Sigma_g^+$ states, the $A\,^3\Sigma_u^+$ and $2\,^3\Sigma_\mu^+$ states, and the $1\,^5\Sigma_g^+$ and $2\,^5\Sigma_g^+$ [27] states, which are different linear combinations of $|L=0\Lambda=0S\Sigma\rangle$ and $|L=2\Lambda=0S\Sigma\rangle$ states with $S=0$, 1, and 2, respectively. To determine the correct linear combinations, we must consider the nature of the interaction at large internuclear distances.

The long-range interaction energy between a pair of P-state atoms was discussed by Knipp [28], Chang [29], and Umanskij and Nikitin [30]. The leading term in the interaction energy at large R is obtained by solving the secular determinant

$$\det|\underline{I}E-\underline{H}|=0\ , \tag{17}$$

where matrix $\underline{H}$ contains elements

$$[\underline{H}]_{\gamma,\gamma'}=\langle\Sigma S\Lambda L|V_N|L'\Lambda'S'\Sigma'\rangle\ , \tag{18}$$

and we assume that electrostatic forces dominate the atom-atom interaction. We express the two-center interaction potential by a multipole series [29,31]

$$V_N=\sum_{Q=3}^{\infty}\frac{V_Q}{R^Q}\ , \tag{19}$$

where

$$V_Q=\sum_i\sum_j\sum_{L=1}^{Q-2}\sum_M g(L,M)Y_L^M(\hat{\mathbf{r}}_i)Y_{Q-L-1}^{-M}(\hat{\mathbf{r}}_j)r_i^Lr_j^{Q-L-1}\ , \tag{20}$$

the index i refers to the $2p$ electrons on atom a, j to the $2p$ electrons on atom b, and $g(L,M)$ is a coefficient given by Chang [29]. For interactions of neutral ^3P atoms, the leading term is the quadrupole-quadrupole interaction $Q=5$.

After some angular momentum algebra (see Appendix B), we obtain for the asymptotic element of the interaction potential

$$\langle\Sigma'S'\Lambda'L'|V_5|L\Lambda S\Sigma\rangle=\frac{6}{5}\frac{\langle r^2\rangle^2}{R^5}X(L'\Lambda',L\Lambda)\delta_{S,S'}\delta_{\Sigma,\Sigma'}\ , \tag{21}$$

where $\langle r^2\rangle$ is the radial expectation value of the $2p$ electrons in the oxygen atom. Numerical evaluation of the coefficient $X(L'\Lambda',L\Lambda)$ yields

$$X(2222)=\tfrac{1}{5},\quad X(2121)=-\tfrac{4}{5},\quad X(2020)=\tfrac{6}{5}\ . \tag{22}$$

All other matrix elements vanish and there is no mixing between the $|L=2\Lambda=0\rangle$ and $|L=0\Lambda=0\rangle$ states. We find that the asymptotic interaction energies of the molecular states have the form

$$\frac{C_5}{25}\frac{\langle r^2\rangle^2}{R^5} \tag{23}$$

with the values of C_5 listed in Table I. These values are in harmony with the results obtained by Knipp [28] and Chang [29]. In Table I we find that the $2\,^1\Sigma_g^+$ state is associated with $|L=2\Lambda=0S=0\Sigma=0\rangle$, and the $b\,^1\Sigma_g^+$ state is associated with $|L=0\Lambda=0S=0\Sigma=0\rangle$. Similar connections can be made for the triplet and quintet Σ states.

Each BO state correlates to an atomic state $|L\Lambda S\Sigma\rangle$, and we identify the BO states with quantum numbers (9) where now the quantum number Γ is set to have the

TABLE I. Values of the parameter C_5, in units of $\langle r^2\rangle^2/25$, where $\langle r^2\rangle$ is the radial expectation value of the ^3P electrons in atomic oxygen.

Molecular state	Atomic state L	M	C_5
Singlets			
$a\,^1\Delta_g$	2	±2	6
$1\,^1\Pi_g$	2	±1	−24
$1\,^1\Pi_u$	1	±1	0
$c\,^1\Sigma_u^-$	1	0	0
$b\,^1\Sigma_g^+$	0	0	0
$2\,^1\Sigma_g^+$	2	0	36
Triplets			
$C\,^3\Delta_u$	2	±2	6
$1\,^3\Pi_u$	2	±1	−24
$1\,^3\Pi_g$	1	±1	0
$X\,^3\Sigma_g^-$	1	0	0
$A\,^3\Sigma_u^+$	0	0	0
$2\,^3\Sigma_u^+$	2	0	36
Quintets			
$^5\Delta_g$	2	±2	6
$^5\Pi_g$	2	±1	−24
$1\,^5\Pi_u$	1	±1	0
$^5\Sigma_u^-$	1	0	0
$1\,^5\Sigma_g^+$	0	0	0
$2\,^5\Sigma_g^+$	2	0	36

TABLE II. Connections between atomic and molecular states for two oxygen ^3P atoms.

Degeneracy	Λ	S	Inversion	Molecular state	Atomic state
2	± 2	0	g	$a\,{}^1\Delta_g$	$\lvert L=2\Lambda=\pm 2S=0\Sigma\rangle$
2	± 1	0	g	$1\,{}^1\Pi_g$	$\lvert L=2\Lambda=\pm 1S=0\Sigma\rangle$
2	± 1	0	u	$1\,{}^1\Pi_u$	$\lvert L=1\Lambda=\pm 1S=0\Sigma\rangle$
1	0	0	u	$c\,{}^1\Sigma_u^-$	$\lvert L=1\Lambda=0S=0\Sigma\rangle$
1	0	0	g	$b\,{}^1\Sigma_g^+$	$\lvert L=0\Lambda=0S=0\Sigma\rangle$
1	0	0	g	$2\,{}^1\Sigma_g^+$	$\lvert L=2\Lambda=0S=0\Sigma\rangle$
6	± 2	1	u	$C\,{}^3\Delta_u$	$\lvert L=2\Lambda=\pm 2S=1\Sigma\rangle$
6	± 1	1	u	$1\,{}^3\Pi_u$	$\lvert L=2\Lambda=\pm 1S=1\Sigma\rangle$
6	± 1	1	g	$1\,{}^3\Pi_g$	$\lvert L=1\Lambda=\pm 1S=1\Sigma\rangle$
3	0	1	g	$X\,{}^3\Sigma_g^-$	$\lvert L=1\Lambda=0S=1\Sigma\rangle$
3	0	1	u	$A\,{}^3\Sigma_u^+$	$\lvert L=0\Lambda=0S=1\Sigma\rangle$
3	0	1	u	$2\,{}^3\Sigma_u^+$	$\lvert L=2\Lambda=0S=1\Sigma\rangle$
10	± 2	2	g	${}^5\Delta_g$	$\lvert L=2\Lambda=\pm 2S=2\Sigma\rangle$
10	± 1	2	g	${}^5\Pi_g$	$\lvert L=2\Lambda=\pm 1S=2\Sigma\rangle$
10	± 1	2	u	$1\,{}^5\Pi_u$	$\lvert L=1\Lambda=\pm 1S=2\Sigma\rangle$
5	0	2	u	${}^5\Sigma_u^-$	$\lvert L=1\Lambda=0S=2\Sigma\rangle$
5	0	2	g	$1\,{}^5\Sigma_g^+$	$\lvert L=0\Lambda=0S=2\Sigma\rangle$
5	0	2	g	$2\,{}^5\Sigma_g^+$	$\lvert L=2\Lambda=0S=2\Sigma\rangle$

value L. Because we use the same set of quantum numbers to identify atomic and molecular states, we avoid confusion by expression a molecular BO state in the form

$$|\Lambda S\Sigma L\rangle \tag{24}$$

in order to stress that L is not a good quantum number in the molecular region. The eigenvalues associated with the discrete molecular symmetries are related to the quantum numbers L and S (see Appendix A). The detailed connections between all molecular and atomic states for the ground state of O_2 are given in Table II.

III. MOLECULAR-STATE EXPANSION

The Born-Oppenheimer states $|\Lambda S\Sigma L\rangle$ are eigenstates of $H_{\text{ad}}(\hat{\mathbf{z}}R)\equiv H_{\text{BO}}(R)$ and we express the adiabatic states (8) by

$$\psi_\gamma(\mathbf{R},\mathbf{r})=U(\hat{\mathbf{R}})|\Lambda S\Sigma L\rangle\ , \tag{25}$$

where $U(\hat{\mathbf{R}})$ is a rotation operator

$$U(\hat{\mathbf{R}})=\exp(-i\phi K_z)\exp(-i\theta K_y)\exp(i\phi K_z)\ , \tag{26}$$

θ,ϕ are, respectively, the polar and azimuthal angles specifying the orientation of $\mathbf{R}$, and $\mathbf{K}=\mathcal{L}+\mathbf{S}$, is the total angular momentum operator for the electrons. $U(\hat{\mathbf{R}})$ rotates the electronic coordinates into $\rho\equiv U(\hat{\mathbf{R}})\mathbf{r}U^{-1}(\hat{\mathbf{R}})$ so that

$$U(\hat{\mathbf{R}})(\mathbf{r}\cdot\hat{\mathbf{z}})U^{-1}(\hat{\mathbf{R}})=\rho\cdot\hat{\mathbf{z}}=\mathbf{r}\cdot\hat{\mathbf{R}}\ , \tag{27}$$

where unit vector $\hat{\mathbf{R}}$ is aligned with $\mathbf{R}=(R,\theta,\phi)$. Therefore

$$H_{\text{AD}}(\mathbf{R})=U(\hat{\mathbf{R}})H_{\text{BO}}(R)U^{-1}(\hat{\mathbf{R}})\ , \tag{28}$$

and $\psi_\gamma(\mathbf{R},\mathbf{r})$ are eigenstates of H_{ad} with eigenvalues $\epsilon_\gamma(R)$. We can use expansion (7) to derive the scattering equations for the amplitudes $F_\gamma(\mathbf{R})$. However, it is more convenient to introduce the expansion

$$\Psi(\mathbf{R},\mathbf{r})=\sum_\gamma F_\gamma(\mathbf{R})u_\gamma(\mathbf{R},\mathbf{r})\ , \tag{29}$$

where

$$u_\gamma(\mathbf{R},\mathbf{r})=U(\hat{\mathbf{R}})|j(R)\Omega j_a j_b\rangle\ , \tag{30}$$

and

$$|j(R)\Omega j_a j_b\rangle=\sum_{LS}\sum_{\Lambda\Sigma}[j,j_a,j_b,L,S]^{1/2}\times(-1)^{j+\Omega}\begin{pmatrix}L & j & S\\ \Lambda & -\Omega & \Sigma\end{pmatrix}\times\begin{Bmatrix}l_a & s_a & j_a\\ l_b & s_b & j_b\\ L & S & j\end{Bmatrix}|\Lambda S\Sigma L\rangle\ . \tag{31}$$

The quantum numbers for channel index $\gamma=\{j\Omega j_a j_b\}$ are related to the molecular quantum numbers (9) by 9-j and 3-j symbol selection rules. We used the shorthand notation $[a,b,\ldots,c]\equiv(2a+1)(2b+1)\cdots(2c+1)$, and the notation $|j(R)\Omega j_a j_b\rangle$, or $|\gamma(R)\rangle$, to stress that j is not a good quantum number in the molecular region. In the asymptotic $R\to\infty$ limit, the states $|j(R)\Omega j_a j_b\rangle$ converge to the atomic states $|j\Omega j_a j_b\rangle$, which are eigenstates of the total two-center angular momentum operators

$$\begin{aligned}
&\mathbf{j}^2|j\Omega j_a j_b\rangle=j(j+1)|j\Omega j_a j_b\rangle\ ,\\
&\mathbf{j}_z|j\Omega j_a j_b\rangle=\Omega|j\Omega j_a j_b\rangle\ ,\\
&\mathbf{j}_a^2|j\Omega j_a j_b\rangle=j_a(j_a+1)|j\Omega j_a j_b\rangle\ ,\\
&\mathbf{j}_b^2|j\Omega j_a j_b\rangle=j_b(j_b+1)|j\Omega j_a j_b\rangle\ ,
\end{aligned} \tag{32}$$

and where $\mathbf{j}=\mathbf{L}+\mathbf{S}$, $\mathbf{j}_a=\mathit{l}_a+\mathbf{S}_a$, $\mathbf{j}_b=\mathit{l}_b+\mathbf{S}_b$, and $\mathbf{S}_a,\mathbf{S}_b$ are the spin operators for the electrons centered at atoms

a and b, respectively. In deriving (32) we used definitions (11),(31) and standard recoupling techniques. The vector $\mathbf{j}$ does not commute with $\mathbf{K}=\boldsymbol{\mathcal{L}}+\mathbf{S}$. However, $\mathbf{j}$ and $\mathbf{K}$ are related by a unitary transformation. Using Eq. (15) we get

$$\mathbf{j}=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)\mathbf{K}\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R) \; . \tag{33}$$

The advantage of using expansion (29) is that, in the asymptotic limit, channel states (30) diagonalize the spin-orbit interaction at each atom. The states $|j(R)\Omega j_a j_b\rangle$ form a representation of the electronic parity operator $\hat{\pi}$. Using Eq. (16) in Eq. (31) we get

$$\hat{\pi}|j(R)\Omega j_a j_b\rangle=(-1)^{j+j_a+j_b}|j(R)\Omega j_b j_a\rangle \; , \tag{34}$$

where we make use of the symmetry properties of the 9-j symbols, and the fact $l_a=l_b=s_a=s_b=1$.

Treating the expansion coefficients F_γ, F_γ^* as variational parameters we require

$$\delta[\langle\Psi|H|\Psi\rangle-E\langle\Psi|\Psi\rangle]=0 \; , \tag{35}$$

where δ is an arbitrary variation of the set $\{F_\gamma(\mathbf{R})\},\{F_\gamma^*(\mathbf{R})\}$, and

$$H=\frac{-1}{2\mu}\nabla_R^2+H_{\mathrm{AD}} \; . \tag{36}$$

Inserting (29) into (35) we get

$$\delta\left\{\int d^3R\{\underline{F}^\dagger[\nabla_R-i\underline{\mathbf{A}}(\mathbf{R})]^2\underline{F} -2\mu\underline{F}^\dagger[\underline{V}(\mathbf{R})-E]\underline{F}\}\right\}=0 \; , \tag{37}$$

where $\underline{F}(\mathbf{R})$ is a column matrix whose elements $F_\gamma(\mathbf{R})$ are the wave functions corresponding to channel $\gamma=\{j\Omega j_a j_b\}$, and $\underline{V}$ and $\underline{\mathbf{A}}$ are, respectively, scalar and vector potentials described below. Carrying out the variations we arrive at the set of coupled equations

$$\frac{-1}{2\mu}(\underline{I}\nabla-i\underline{\mathbf{A}})^2\underline{F}(\mathbf{R})+\underline{V}(\mathbf{R})\underline{F}(\mathbf{R})=E\underline{F}(\mathbf{R}) \; , \tag{38}$$

where

$$\begin{aligned}
&[\mathbf{A}(\mathbf{R})]_{\gamma,\gamma'}=i\int d^3\mathbf{r}\,u_\gamma^*(\mathbf{R},\mathbf{r})\nabla_{\mathbf{R}}u_{\gamma'}(\mathbf{R},\mathbf{r}) \; ,\\
&[\underline{V}(\mathbf{R})]_{\gamma,\gamma'}=[\underline{W}(R)]_{\gamma,\gamma'}+\frac{[\underline{B}(R)]_{\gamma,\gamma'}}{2\mu} \; ,\\
&[\underline{B}(R)]_{\gamma,\gamma'}\equiv\sum_{k\neq\gamma,\gamma'}\mathbf{A}_{\gamma k}\cdot\mathbf{A}_{k\gamma'} \; ,\\
&[\underline{W}(R)]_{\gamma,\gamma'}=\sum_{\Lambda\Sigma}\sum_{LS}[j,j',j_a,j_a',j_b,j_b']^{1/2}[L,S]\\
&\qquad\times\begin{bmatrix} L & S & j\\ \Lambda & \Sigma & -\Omega\end{bmatrix}\begin{bmatrix} L & S & j'\\ \Lambda & \Sigma & -\Omega'\end{bmatrix}\\
&\qquad\times\begin{Bmatrix} l_a & s_a & j_a\\ l_b & s_b & j_b\\ L & S & j\end{Bmatrix}\begin{Bmatrix} l_a' & s_a' & j_a'\\ l_b' & s_b' & j_b'\\ L & S & j'\end{Bmatrix}\epsilon_{\Lambda SL}(R) \; ,
\end{aligned} \tag{39}$$

and $l_a=l_a'=l_b=l_b'=1$, $s_a=s_a'=s_b=s_b'=1$. In deriving (39) we used

$$\langle L'\Sigma'S'\Lambda'|H_{\mathrm{BO}}|\Lambda S\Sigma L\rangle=\delta_{\Lambda,\Lambda'}\delta_{L,L'}\delta_{S,S'}\delta_{\Sigma,\Sigma'}\epsilon_{\Lambda SL}(R) \; . \tag{40}$$

In order to calculate the S matrix for atomic transitions we need to investigate the behavior of the solutions to (38) in the separated atom limit. First we study the behavior of the vector potential $\underline{\mathbf{A}}$ in this limit. It is useful to express it in the form

$$\underline{\mathbf{A}}(\mathbf{R})=\underline{A}_R(R)\hat{\mathbf{R}}+\frac{\underline{A}_\theta(\theta\phi)}{R}\hat{\theta}+\frac{\underline{A}_\phi(\theta\phi)}{R\sin\theta}\hat{\phi} \; , \tag{41}$$

where $\hat{\mathbf{R}},\hat{\theta},\hat{\phi}$ are the spherical basis vectors in the space-fixed frame. Using Eqs. (26), (30), and (39) we get

$$\begin{aligned}
[\underline{\mathbf{A}}_R]_{\gamma,\gamma'}&=i\left\langle\gamma(R)\left|\frac{\partial}{\partial R}\right|\gamma'(R)\right\rangle \; ,\\
[\underline{\mathbf{A}}_\theta]_{\gamma,\gamma'}&=i\left\langle\gamma(R)\left|U^{-1}\frac{\partial U}{\partial\theta}\right|\gamma'(R)\right\rangle\\
&=\langle\gamma(R)|K_y\cos\phi-K_x\sin\phi|\gamma'(R)\rangle \; ,\\
[\underline{\mathbf{A}}_\phi]_{\gamma,\gamma'}&=i\left\langle\gamma(R)\left|U^{-1}\frac{\partial U}{\partial\phi}\right|\gamma'(R)\right\rangle\\
&=\langle\gamma(R)|K_z(\cos\theta-1)\\
&\qquad-\sin\theta[K_x\cos\phi+K_y\sin\phi]|\gamma'(R)\rangle \; .
\end{aligned} \tag{42}$$

We evaluate the separate atom limit of $\underline{\mathbf{A}}$ by replacing the molecular states $|\gamma(R)\rangle$ in Eq. (42) with the atomic states $|j\Omega j_a j_b\rangle$, and evaluate the asymptotic limit of the angular couplings $\underline{A}_\theta,\underline{A}_\phi$. The total electronic angular momentum $\mathbf{K}$ can be expressed in terms of the two-center angular momentum $\mathbf{j}$,

$$\mathbf{K}=\boldsymbol{\mathcal{L}}+\mathbf{S}=\mathbf{j}+R\hat{\mathbf{z}}\times\mathbf{P} \; , \tag{43}$$

where we used (14), $\mathbf{j}=\mathbf{L}+\mathbf{S}$, and $\mathbf{P}$ is an electronic-dipole operator whose matrix elements are, in general, nonzero. For this system, a homonuclear molecule, the dipole operator is odd under interchange of electrons associated with the two centers and its matrix elements with respect to antisymmetrized electronic wave functions vanish. Therefore, when evaluating the matrix elements of the total angular momentum operator $\mathbf{K}$ with the states $|\gamma(R)\rangle$, we are allowed to equate

$$\mathbf{K}=\mathbf{j} \; . \tag{44}$$

Because atomic states $|j\Omega j_a j_b\rangle$ diagonalize operators (32), we get

$$\lim_{R\to\infty}\underline{\mathbf{A}}\cdot\hat{\theta}\to\frac{\underline{\mathcal{A}}_\theta(\theta\phi)}{R};\quad \underline{\mathbf{A}}\cdot\hat{\phi}\to\frac{\underline{\mathcal{A}}_\phi(\theta\phi)}{R} \; , \tag{45}$$

where $\underline{\mathcal{A}}_\theta(\theta\phi),\underline{\mathcal{A}}_\phi(\theta\phi)$ are matrices defined on the two-sphere centered at the origin of the space-fixed coordinate system.

In this picture, which we call the molecular gauge, the coupled equations (38) suffer long-range nonadiabatic couplings which fall off no faster than the inverse power of R. The long-range behavior is a consequence of using the adiabatic electronic basis (25) or (30). We define a new basis related to the adiabatic basis by a unitary transformation. More precisely, we induce a gauge transformation on the set of coupled PSS equations. Gauge transformations are a class of unitary transformations where the set of transformed wave functions is related to the original set by a unitary matrix whose elements are functions of the coordinates of $\mathbf{R}$. In this sense gauge transformations are a multichannel generalization of a phase transformation. Although the scattering equations are not invariant [32] under gauge transformations, measurable quantities, such as cross sections, are. We use this freedom in choice of basis, or gauge, to transform the PSS equations into a more suitable form. We show that in the new gauge, which we call the atomic gauge, the vector potential $\underline{\mathbf{A}}$ is well behaved in the separated atom limit.

We introduce a new set of amplitudes $\underline{G}(\mathbf{R})$ related to the amplitudes $\underline{F}(\mathbf{R})$ by a unitary matrix $\underline{T}(\theta,\phi)$, so that

$$\underline{G}(\mathbf{R})=\underline{T}(\theta\phi)\underline{F}(\mathbf{R}) \ , \tag{46}$$

and where $\underline{G}(\mathbf{R})$ is a solution to (38) with the potentials $\underline{\mathbf{A}}(\mathbf{R}),\underline{V}(\mathbf{R})$ replaced by

$$\begin{aligned}\underline{\mathbf{A}}'(\mathbf{R})&=\underline{T}\,\underline{\mathbf{A}}(\mathbf{R})\underline{T}^{-1}+i\underline{T}\nabla_{\mathbf{R}}\underline{T}^{-1} \ ,\\ \underline{V}'(R)&=\underline{T}\,\underline{W}(R)\underline{T}^{-1}+\frac{\underline{T}\,\underline{B}(R)\underline{T}^{-1}}{2\mu} \ .\end{aligned} \tag{47}$$

Gauge transformation (46) can be interpreted as a redefinition of the molecular expansion basis. For example, the system wave function (29) is expressed by the equivalent expansions

$$\begin{aligned}\Psi(\mathbf{R},\mathbf{r})&=\sum_{\gamma}F_{\gamma}(\mathbf{R})u_{\gamma}(\mathbf{R},\mathbf{r})\\ &=\underline{u}(\mathbf{R},\mathbf{r})\underline{F}(\mathbf{R})\\ &=\underline{u}(\mathbf{R},\mathbf{r})\underline{T}^{-1}(\theta\phi)\underline{T}(\theta\phi)\underline{F}(\mathbf{R})\\ &=\sum_{\gamma}G_{\gamma}(\mathbf{R})\phi_{\gamma}(\mathbf{R},\mathbf{r}) \ ,\end{aligned} \tag{48}$$

where $\underline{F}(\mathbf{R}),\underline{u}(\mathbf{R},\mathbf{r})$ are column and row matrices respectively, and the new basis functions $\phi_{\gamma}(\mathbf{R},\mathbf{r})$ are related to the adiabatic basis (30)

$$\phi_{j\Omega j_a j_b}(\mathbf{R},\mathbf{r})=\sum_{j'\Omega' j_a' j_b'}U(\hat{\mathbf{R}})|j'(R)\Omega' j_a' j_b'\rangle \times[\underline{T}^{-1}(\theta\phi)]_{j\Omega j_a j_b}^{j'\Omega' j_a' j_b'} \ . \tag{49}$$

We construct the transformation matrix

$$\begin{aligned}[\underline{T}(\theta\phi)]_{\gamma,\gamma'}&=[\underline{T}(\theta\phi)]_{\gamma'}^{\gamma}\\ &=\langle j\Omega j_a j_b|T|j_a' j_b'\Omega' j'\rangle\\ &\equiv\langle j\Omega j_a j_b|\exp(-i\phi j_z)\exp(-i\theta j_y)\\ &\quad\times\exp(i\phi j_z)|j_a' j_b'\Omega' j'\rangle \ ,\end{aligned} \tag{50}$$

where $|j_a j_b \Omega j\rangle\equiv|\gamma\rangle$ is the atomic limit of the molecular state $|\gamma(R)\rangle$ and, for the sake of convenience, we introduced the alternative notation $T_{\gamma'}^{\gamma}$ to identify the γ,γ' components of matrix $\underline{T}$. T is a rotation operator which generates rotations of the electrons about their atomic centers. It is parametrized by the angles θ,ϕ, as well as the internuclear distance R, whereas the matrix elements (50) are parametrized by the angles θ,ϕ only. $U(\hat{\mathbf{R}})$ generates electron rotations about the molecular center. The rotation operators are related, and

$$T=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)U(\hat{\mathbf{R}})\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R) \ . \tag{51}$$

This identity is derived by expanding the exponentials in the definition for $U(\hat{\mathbf{R}})$, sandwiching the components of $\mathbf{K}$ between the translation operators, and applying identity (33) to each term in the expansion.

Using (42), (47), and (50) we get

$$\begin{aligned}[\underline{A}_{\theta}']_{\gamma,\gamma'}&=i\left[\sum_{\gamma'',\beta''}\langle\gamma|T|\gamma''\rangle\left\langle\gamma''(R)\left|U^{-1}\frac{\partial U}{\partial\theta}\right|\beta''(R)\right\rangle\langle\beta''|T^{-1}|\gamma'\rangle\right]+i\sum_{\gamma''}\langle\gamma|T|\gamma''\rangle\frac{\partial}{\partial\theta}\langle\gamma''|T^{-1}|\gamma'\rangle \ ,\\ [\underline{A}_{\phi}']_{\gamma,\gamma'}&=i\left[\sum_{\gamma'',\beta''}\langle\gamma|T|\gamma''\rangle\left\langle\gamma''(R)\left|U^{-1}\frac{\partial U}{\partial\phi}\right|\beta''(R)\right\rangle\langle\beta''|T^{-1}|\gamma'\rangle\right]+i\sum_{\gamma''}\langle\gamma|T|\gamma''\rangle\frac{\partial}{\partial\phi}\langle\gamma''|T^{-1}|\gamma'\rangle \ .\end{aligned} \tag{52}$$

The sum over the matrix index γ'' runs over all values $j\Omega j_a j_b$ included in expansion (29). Operator T generates rotations in the product space spanned by $|j\Omega j_a j_b\rangle$ and the elements of the transformation matrix are

$$\begin{aligned}[\underline{T}(\theta\phi)]_{\gamma,\gamma'}&=\langle j\Omega j_a j_b|\exp(-i\phi j_z)\exp(-i\theta j_y)\exp(i\phi j_z)|j_a' j_b'\Omega' j'\rangle\\ &=\exp(-i\phi(\Omega-\Omega'))d_{\Omega,\Omega'}^{j}(\theta)\delta_{j,j'}\delta_{j_a,j_a'}\delta_{j_b,j_b'}\\ &\equiv D_{\Omega,\Omega'}^{j}(\phi,\theta,-\phi)\delta_{j,j'}\delta_{j_a,j_a'}\delta_{j_b,j_b'} \ ,\end{aligned} \tag{53}$$

where $d_{\Omega,\Omega'}^{j}(\theta)$ is the reduced Wigner function (26). The sum over the channel index γ in the close-coupling expansion (29) includes all $(2j+1)$ members of a manifold with quantum number j, and when T acts upon any member $|j\Omega j_a j_b\rangle$ of the manifold the transformed vector remains orthogonal to any vector not in the channel set. Therefore $\langle\gamma|T|\gamma''\rangle$ is zero for all γ'' not included in the channel set and we can replace the matrix index sum in

(52) with a sum over a complete set. In the limit $R \rightarrow \infty$, $|\gamma(R)\rangle \rightarrow |\gamma\rangle$ and

$$\lim_{R\rightarrow\infty} \sum_{\gamma} |\gamma\rangle\langle\gamma(R)| \rightarrow \sum_{\gamma} |\gamma\rangle\langle\gamma| = \mathbf{I} \,, \tag{54}$$

where $\mathbf{I}$ is the identity operator for the electronic coordinates and we invoked the closure property of the electronic states. Using Eq. (54), Eq. (52) reduces to the simpler form

$$\begin{aligned} \lim_{R\rightarrow\infty} [\underline{A}'_{\theta}]_{\gamma,\gamma'} &\rightarrow i\langle\gamma|TU^{-1}\frac{\partial U}{\partial\theta}T^{-1}|\gamma'\rangle \\ &\quad + i\left\langle\gamma\left|T\frac{\partial T^{-1}}{\partial\theta}\right|\gamma'\right\rangle \,, \\ \lim_{R\rightarrow\infty} [\underline{A}'_{\theta}]_{\gamma,\gamma'} &\rightarrow i\left\langle\gamma\left|TU^{-1}\frac{\partial U}{\partial\theta}T^{-1}\right|\gamma'\right\rangle \\ &\quad + i\left\langle\gamma\left|T\frac{\partial T^{-1}}{\partial\phi}\right|\gamma'\right\rangle \,. \end{aligned} \tag{55}$$

$T^{-1}U \neq 1$, but expression (55) contains partial derivatives of the rotation operator U which, as shown explicitly in Eq. (42), has the effect of introducing terms linear in the operator $\mathbf{K}$. Because we are forming matrix elements with respect to the atomic states, we may use identity (44) and replace the molecular rotation operator in Eq. (55) with the two-center rotation operator T. That is, we equate

$$\begin{aligned} U^{-1}\frac{\partial U}{\partial\theta} &= T^{-1}\frac{\partial T}{\partial\theta} \,, \\ U^{-1}\frac{\partial U}{\partial\phi} &= T^{-1}\frac{\partial T}{\partial\phi} \,, \end{aligned} \tag{56}$$

where it is understood that the identities are valid only when taking matrix elements of the operators with the atomic states $|j\Omega j_a j_b\rangle$. Thus,

$$\lim_{R\rightarrow\infty} \underline{A}'_{\theta} \rightarrow 0; \quad \underline{A}'_{\phi} \rightarrow 0 \,, \tag{57}$$

where we differentiated (55) by parts and used the identity $TT^{-1}=1$. A detailed analysis of the asymptotic behavior of $\underline{\mathbf{A}}$ is given in Appendix C.

In the atomic gauge, the scalar potential matrix is

$$\begin{aligned} [\underline{W}'(R\theta\phi)]_{\gamma,\gamma'} = \sum_{\Lambda\Sigma}\sum_{LS} &[j,j',j_a,j'_a,j_b,j'_b]^{1/2}[L,S] \\ &\times \sum_{\Omega_1} D^{j}_{\Omega,\Omega_1}(\phi,\theta,-\phi) D^{j'}_{\Omega_1,\Omega'}(\phi,-\theta,-\phi) \begin{bmatrix} L & S & j \\ \Lambda & \Sigma & -\Omega_1 \end{bmatrix} \begin{bmatrix} L & S & j' \\ \Lambda & \Sigma & -\Omega_1 \end{bmatrix} \\ &\times \begin{Bmatrix} l_a & s_a & j_a \\ l_b & s_b & j_b \\ L & S & j \end{Bmatrix} \begin{Bmatrix} l'_a & s'_a & j'_a \\ l'_b & s'_b & j'_b \\ L & S & j' \end{Bmatrix} \epsilon_{\Lambda SL}(R) \,, \end{aligned} \tag{58}$$

where we used Eqs. (47), (53), and ignored the nonadiabatic scalar potential $\underline{B}(R)$ (see Appendix B). We assume that $\underline{B}/2\mu$ is a small correction to the scalar potential $\underline{W}$.

At this stage, we have not yet considered the spin-orbit interaction of the electrons with the nuclei. We approximate the spin-orbit interaction by including an additional term in Hamiltonian (3),

$$H_{\text{SO}}(\mathbf{R}) \equiv \sum_{i} l_{ia}\cdot\mathbf{S}_i\xi(|\mathbf{r}_{ia}|) + \sum_{j} l_{jb}\cdot\mathbf{S}_j\xi(|\mathbf{r}_{jb}|) \,, \tag{59}$$

where index i represents an electron centered on atom a located at $\mathbf{R}/2$, index j represents electrons centered on atom b located at $-\mathbf{R}/2$, and l_{ia}, $\mathbf{r}_{ia}$ are, respectively, the angular momentum and electronic coordinate of electron i with respect to center a. l_{jb},$\mathbf{r}_{jb}$ are the corresponding quantities with respect to center b, and the functions ξ are chosen so that (59) reproduces the correct atomic fine-structure splittings in the separated atom limit. In approximation (59) we have neglected two-center terms since we are only interested in the effect of the spin-orbit interaction in the separated atom limit.

Matrix elements of the spin-orbit Hamiltonian (59) with respect to adiabatic states (30) are

$$\begin{aligned} [\underline{H}_{\text{SO}}]_{\gamma,\gamma'} &= \langle\gamma(R)|U^{-1}(\hat{\mathbf{R}})H_{\text{SO}}(\mathbf{R})U(\hat{\mathbf{R}})|\gamma'(R)\rangle \\ &= \langle\gamma(R)|H_{\text{SO}}(R)|\gamma'(R)\rangle \,, \end{aligned} \tag{60}$$

where $H_{\text{SO}}(R)$ is the spin-orbit operator for the geometry $\mathbf{R}=R\hat{\mathbf{z}}$. In the separated atom limit the molecular states correlate to the atomic states (31) which diagonalize $H_{\text{SO}}(R)$ and

$$\lim_{R\rightarrow\infty} [\underline{H}_{\text{SO}}]_{\gamma,\gamma'} \rightarrow \delta_{\gamma,\gamma'}[\Delta E_a(j_a) + \Delta E_b(j_b)] \,, \tag{61}$$

where $\Delta E_a(j_a)$ and $\Delta E_b(j_b)$ are the fine-structure energy shifts of atoms a and b, respectively. In the atomic gauge expression (61) becomes

$$\underline{H}_{\text{SO}} \rightarrow \underline{H}'_{\text{SO}} = \underline{T}\,\underline{H}_{\text{SO}}\underline{T}^{-1} \,, \tag{62}$$

but

$$\underline{T}\,\underline{H}_{\mathrm{SO}}\underline{T}^{-1}=\sum_{\Omega''}D^{j}_{\Omega,\Omega''}(-\phi,\theta,\phi)D^{j}_{\Omega'',\Omega'}(-\phi,-\theta,\phi)$$
$$\times[\Delta E_a(j_a)+\Delta E_b(j_b)]\delta^{j'j_a'j_b'}_{jj_aj_b}$$
$$=[\underline{H}_{\mathrm{SO}}]_{\gamma,\gamma'}\ , \qquad (63)$$

where we used the closure properties of the Wigner functions [26].

Summarizing these results, we arrive at the set of coupled equations for the scattering amplitude $\underline{G}(\mathbf{R})$ in the atomic gauge,

$$\frac{-1}{2\mu}[\mathrm{I}\nabla-i\underline{\mathbf{A}}'(\mathbf{R})]^2\underline{G}(\mathbf{R})+[\underline{W}'(\mathbf{R})-\underline{E}]\underline{G}(\mathbf{R})=0\ , \qquad (64)$$

where $\underline{\mathbf{A}}'$ and $\underline{W}'(\mathbf{R})$ are given by Eq. (47), $\underline{E}$ is a diagonal matrix with entries

$$[\underline{E}]_{\gamma,\gamma'}=\delta_{\gamma,\gamma'}[E-\Delta E_a(j_a)-\Delta E_b(j_b)]\ , \qquad (65)$$

and E is the collision energy. Equation (64) replaces Eq. (38) derived in the molecular gauge.

In order to obtain numerical solutions for Eq. (64), we make an additional approximation, and ignore the nonadiabatic vector potential $\underline{\mathbf{A}}'$. We assume that nonadiabatic effects induced by the off-diagonal elements of the vector potential are small. This approximation is not valid in the molecular gauge since, in that case, the nonadiabatic vector coupling persists in the separated atom limit.

We simplify Eq. (64) by expressing the nuclear amplitudes $\underline{G}(\mathbf{R})$ as a sum of partial waves. The potential $\underline{W}'(R\theta\phi)$ is not rotational invariant so we need to perform a recoupling,

$$G_\gamma(\mathbf{R})=G_{j\Omega j_aj_b}(\mathbf{R})$$
$$=\sum_{lm}\sum_{JM}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}Y_{lm}(\theta\phi)[J]^{1/2}\frac{G^{JM}_{jlj_aj_b}(R)}{R}\ , \qquad (66)$$

where $G^{JM}_{jlj_aj_b}(R)$ is the JMth radial partial scattering amplitude. Using Eq. (66) we find

$$\nabla^2G_{j\Omega j_aj_b}(\mathbf{R})=\sum_{l'm'}\sum_{J'M'}\begin{pmatrix} j & l' & J'\\ \Omega & m' & -M'\end{pmatrix}[J']^{1/2}\frac{Y_{l'm'}(\theta\phi)}{R}$$
$$\times\left\{\frac{d^2}{dR^2}-\frac{l'(l'+1)}{R^2}\right\}G^{J'M'}_{jl'j_aj_b}(R)\ . \qquad (67)$$

We project out the JMth partial wave by multiplying Eq. (67) with

$$\sum_m Y^*_{lm}(\theta\phi)[J]^{1/2}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}\ , \qquad (68)$$

integrate over solid angle $d\hat{\Omega}$, and sum over Ω, to get

$$\sum_m\sum_\Omega\int d\hat{\Omega}\frac{Y^*_{lm}(\theta\phi)}{R}[J]^{1/2}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}\nabla^2G_{j\Omega j_aj_b}(\mathbf{R})$$
$$=\frac{1}{R}\left\{\frac{d^2}{dR^2}-\frac{l(l+1)}{R^2}\right\}G^{JM}_{jl'j_aj_b}(R)\ , \qquad (69)$$

where we have used

$$\sum_{mm'}\begin{pmatrix} j & l & J\\ m & m' & -M\end{pmatrix}\begin{pmatrix} j & l & J'\\ m & m' & -M'\end{pmatrix}=\frac{\delta_{J,J'}\delta_{M,M'}}{[J]}\ . \qquad (70)$$

In the same manner we get

$$\sum_m\sum_\Omega\int d\hat{\Omega}\,Y^*_{lm}(\theta\phi)[J]^{1/2}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}\frac{G_{j\Omega j_aj_b}(\mathbf{R})}{R}$$
$$=\frac{G^{JM}_{jlj_aj_b}(R)}{R}\ . \qquad (71)$$

Also,

$$\sum_m\sum_\Omega\int d\hat{\Omega}\,Y^*_{lm}(\theta\phi)[J]^{1/2}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}\sum_{\gamma'}W'_{\gamma,\gamma'}(R\theta\phi)G_{\gamma'}(\mathbf{R})$$
$$=\sum_m\sum_\Omega\int d\hat{\Omega}\,Y^*_{lm}(\theta\phi)[J]^{1/2}\begin{pmatrix} j & l & J\\ \Omega & m & -M\end{pmatrix}$$
$$\times\sum_{j'\Omega'j_a'j_b'}W'^{j\Omega j_aj_b}_{j'\Omega'j_a'j_b'}(\mathbf{R})\sum_{l'm'}\sum_{J'M'}Y_{l'm'}(\theta\phi)[J']^{1/2}\begin{pmatrix} j' & l' & J'\\ \Omega' & m' & -M'\end{pmatrix}\frac{G^{J'M'}_{j'l'j_a'j_b'}(R)}{R}\ . \qquad (72)$$

Evaluating expression (72) we find the integral (see Appendix D)

$$\int d\hat{\Omega}\,Y^*_{lm}(\theta\phi)Y_{l'm'}(\theta\phi)D^{j}_{\Omega,\Omega_1}(\phi,\theta-\phi)D^{j'}_{\Omega_1\Omega'}(\phi,-\theta,-\phi)$$
$$=[l,l']^{1/2}\sum_{qQ}[Q]\begin{pmatrix} l & j & Q\\ m & \Omega & q\end{pmatrix}\begin{pmatrix} l & j & Q\\ 0 & \Omega_1 & -\Omega_1\end{pmatrix}\begin{pmatrix} l' & j' & Q\\ m' & \Omega' & q\end{pmatrix}\begin{pmatrix} l' & j' & Q\\ 0 & \Omega_1 & -\Omega_1\end{pmatrix}\ . \qquad (73)$$

Inserting (73) into (72) we obtain

$$\sum_{\Omega m}\sum_{j'\Omega'}\sum_{j'_aj'_b}\sum_{\Lambda\Sigma}\sum_{LS}\sum_{Qq}\sum_{\Omega_1}\sum_{l'm'}\sum_{J'M'}[j,j',j_a,j'_a,j_b,j'_b,l,l',J,J']^{1/2}[L,S,Q]$$
$$\times\begin{pmatrix} j & l & J \\ \Omega & m & -M\end{pmatrix}\begin{pmatrix} L & S & j \\ \Lambda & \Sigma & -\Omega_1\end{pmatrix}\begin{pmatrix} L & S & j' \\ \Lambda & \Sigma & -\Omega_1\end{pmatrix}\begin{pmatrix} j' & l' & J' \\ \Omega' & m' & -M'\end{pmatrix}$$
$$\times\begin{pmatrix} l & j & Q \\ m & \Omega & q\end{pmatrix}\begin{pmatrix} l & j & Q \\ 0 & \Omega_1 & -\Omega_1\end{pmatrix}\begin{pmatrix} l' & j' & Q \\ m' & \Omega' & q\end{pmatrix}\begin{pmatrix} l' & j' & Q \\ 0 & \Omega_1 & -\Omega_1\end{pmatrix}\begin{Bmatrix} l_a & s_a & j_a \\ l_b & s_b & j_b \\ L & S & j\end{Bmatrix}\begin{Bmatrix} l'_a & s'_a & j'_a \\ l'_b & s'_b & j'_b \\ L & S & j'\end{Bmatrix}\epsilon_{\Lambda SL}(R)\frac{G^{J'M'}_{j'l'j'_aj'_b}(R)}{R} . \tag{74}$$

Contracting two pair of 3-j symbols we discover that (74) vanishes unless $J=J'$, $M=M'$, and it simplifies to

$$\sum_{j'l'j'_aj'_b} V^{jlj_aj_b}_{j'l'j'_aj'_b}(JM;R)\frac{G^{JM}_{j'l'j'_aj'_b}(R)}{R} , \tag{75}$$

where

$$V^{jlj_aj_b}_{j'l'j'_aj'_b}(JM;R)=\sum_{\Lambda\Sigma}\sum_{LS}\sum_{\Omega_1}[j,j',j_a,j'_a,j_b,j'_b,l,l']^{1/2}[L,S]$$
$$\times\begin{pmatrix} j & l & J \\ \Omega_1 & 0 & -\Omega_1\end{pmatrix}\begin{pmatrix} L & S & j \\ \Lambda & \Sigma & -\Omega_1\end{pmatrix}\begin{pmatrix} L & S & j' \\ \Lambda & \Sigma & -\Omega_1\end{pmatrix}\begin{pmatrix} j' & l' & J \\ \Omega_1 & 0 & -\Omega_1\end{pmatrix}$$
$$\times\begin{Bmatrix} l_a & s_a & j_a \\ l_b & s_b & j_b \\ L & S & j\end{Bmatrix}\begin{Bmatrix} l'_a & s'_a & j'_a \\ l'_b & s'_b & j'_b \\ L & S & j'\end{Bmatrix}\epsilon_{\Lambda SL}(R) \tag{76}$$

is a radial multipole potential. Combining Eqs. (69)–(76), Eq. (64) reduces to the coupled radial equations

$$-\frac{1}{2\mu}\left[\frac{d^2}{dR^2}-\frac{l(l+1)}{R^2}\right]G^{JM}_{jlj_aj_b}(R)+\sum_{j'l'j'_aj'_b}V^{jlj_aj_b}_{j'l'j'_aj'_b}(JM;R)G^{JM}_{j'l'j'_aj'_b}(R)=[E-\Delta E_a(j_a)-\Delta E_b(j_b)]G^{JM}_{jlj_aj_b}(R) . \tag{77}$$

In order to relate the solutions of Eq. (64) to the appropriate scattering boundary conditions, we need to investigate the behavior of the electronic basis (49) in the asymptotic $R\rightarrow\infty$ again. The total system wave function is

$$\Psi(\mathbf{R},\mathbf{r})=\sum_{\gamma} G(\mathbf{R})\phi_\gamma(\mathbf{R},\mathbf{r}) , \tag{78}$$

where $G(\mathbf{R})$ is a solution to Eq. (64) and $\phi_\gamma(\mathbf{R},\mathbf{r})$ is defined by Eq. (49). In the limit $R\rightarrow\infty$ we replace the molecular states $|j(R)\Omega j_aj_b\rangle$ with their atomic limit $|j\Omega j_aj_b\rangle$, and

$$\lim_{R\rightarrow\infty}\phi_{j\Omega j_aj_b}(\mathbf{R},\mathbf{r})=U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})|j\Omega j_aj_b\rangle , \tag{79}$$

where we employed the same arguments which led to Eq. (54), and replaced the sum over channels with a sum over a complete set of atomic states. $T(\mathbf{R})$ is the two-center rotation operator defined in Eq. (50) and, in the notation used here, the parametric dependence of T on R,θ,ϕ is explicit. We show below that states (79) describe approximate atomic states [33] of two approaching oxygen atoms whose total atomic angular momentum j is quantized along a fixed $\hat{\mathbf{z}}$ axis.

States (79) are eigenstates of

$$\begin{aligned}&U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}_zT(\mathbf{R})U^{-1}(\hat{\mathbf{R}}) ,\\ &U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}^2T(\mathbf{R})U^{-1}(\hat{\mathbf{R}}) ,\\ &U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}_a^2T(\mathbf{R})U^{-1}(\hat{\mathbf{R}}) ,\\ &U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}_b^2T(\mathbf{R})U^{-1}(\hat{\mathbf{R}}) ,\end{aligned} \tag{80}$$

where we used Eqs. (32) and (79). From identity (51) we get

$$T(\mathbf{R})U^{-1}(\hat{\mathbf{R}})=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)U(\hat{\mathbf{R}})\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)U^{-1}(\hat{\mathbf{R}}) \tag{81}$$

but

$$U(\hat{\mathbf{R}})(\mathbf{P}\cdot\hat{\mathbf{z}})U^{-1}(\hat{\mathbf{R}})=\mathbf{P}\cdot\hat{\mathbf{R}} , \tag{82}$$

so

$$U(\hat{\mathbf{R}})\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)U^{-1}(\hat{\mathbf{R}})=\exp(i\mathbf{P}\cdot\mathbf{R}) . \tag{83}$$

Therefore,

$$T(\mathbf{R})U^{-1}(\hat{\mathbf{R}})=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)\exp(i\mathbf{P}\cdot\mathbf{R}) . \tag{84}$$

Summarizing, we have

$$
\begin{aligned}
&U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}T(\mathbf{R})U^{-1}(\hat{\mathbf{R}}) \\
&\quad =\exp(-i\mathbf{P}\cdot\mathbf{R})\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)\mathbf{j}\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R) \\
&\qquad \times\exp(i\mathbf{P}\cdot\mathbf{R}) \\
&\quad =\exp(-i\mathbf{P}\cdot\mathbf{R})\mathbf{K}\exp(i\mathbf{P}\cdot\mathbf{R}) , \qquad (85)
\end{aligned}
$$

where we made use of Eq. (33). Expanding the exponents in the translation operators, invoking angular momentum commutation relations, and combining Eqs. (80) through (85) we get

$$
\begin{aligned}
U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})\mathbf{j}T(\mathbf{R})U^{-1}(\hat{\mathbf{R}})&=\exp(-i\mathbf{P}\cdot\mathbf{R})\mathbf{K}\exp(i\mathbf{P}\cdot\mathbf{R}) \\
&=\mathbf{K}+(\mathbf{P}\times\mathbf{R})\equiv\mathbf{j}(\mathbf{R}) . \qquad (86)
\end{aligned}
$$

$\mathbf{j}(\mathbf{R})$ is a generalization of the two-center electronic angular momentum (32), where now the atomic centers are located at $\pm\mathbf{R}/2$. The components of $\mathbf{j}(\mathbf{R})$ have the usual angular momentum commutation relations at a given value of $\mathbf{R}$, i.e., $[\mathbf{j}_a(\mathbf{R}),\mathbf{j}_b(\mathbf{R})]=i\epsilon_{abc}\mathbf{j}_c(\mathbf{R})$. We conclude that states (79) are eigenstates of $\hat{\mathbf{z}}\cdot\mathbf{j}(\mathbf{R})$, as well as $\mathbf{j}^2(\mathbf{R})$, $\mathbf{j}_a^2(\mathbf{R}),\mathbf{j}_b^2(\mathbf{R})$. Because states $|j\Omega j_a j_b\rangle$ form a representation for operator $T^{-1}(\mathbf{R})$, its action on these states induces a rotation about each atomic center so that the quantization axis, for each atom, is rotated through angles θ,ϕ. The subsequent action of rotation operator $U(\hat{\mathbf{R}})$ rotates the atomic states centered at $\pm(R/2)\hat{\mathbf{z}}$, so that their new centers are at the respective locations $\pm\mathbf{R}/2$. The end result is that states (79) are quantized along the $\hat{\mathbf{z}}$ direction for arbitrary orientation of the atomic centers (collision impact parameter). Figure 1 illustrates these rotations in the x-z plane. Alternatively, because of identity (84), we may think of the product of these rotations in the following way. Translation operator $\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)$ translates atomic orbitals defined at $\pm\hat{\mathbf{z}}R/2$ to the origin where they are coupled to form states quantized along the $\hat{\mathbf{z}}$ axis. The subsequent action of $\exp(-i\mathbf{P}\cdot\hat{\mathbf{R}})$ on them displaces these states, keeping the quantization axis fixed, to the new locations $\pm\mathbf{R}/2$.

We conclude that states (79) form an asymptotic basis, quantized along a fixed direction in the space-fixed frame, for which we may define an S matrix.

IV. TRANSITION CROSS SECTIONS

The coupled radial Eqs. (77), for the N-channel wave functions are solved numerically. Each partial wave has N independent solutions and we construct an $N\times N$ matrix whose columns are the N solution vectors to Eq. (77)

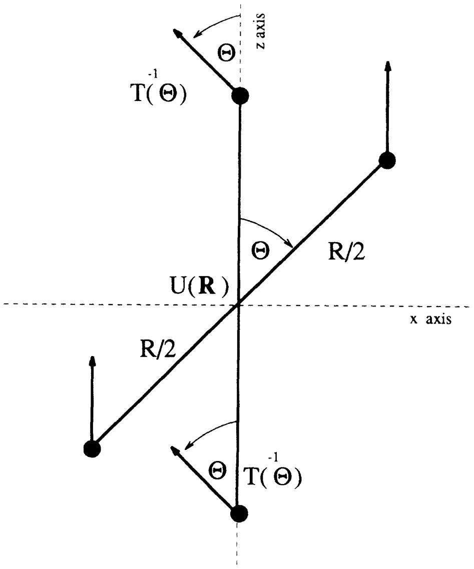

FIG. 1. Action of rotation operators $T^{-1}(\theta\phi),U(\hat{\mathbf{R}})$ on atomic orbitals located at $\pm R/2$ on the z axis. We consider the case where $\phi=0$; R is the internuclear distance.

$$\underline{G}(JM,R)\equiv G_{jlj_aj_b}^{j'l'j_a'j_b'}(JM,R) . \qquad (87)$$

The superscript, or column index, identifies a particular solution to (77) and the subscript, or row index, identifies the channel index. For each partial wave we impose the boundary condition

$$
\begin{aligned}
&\underline{G}(JM,R=0)=0 , \\
&\lim_{R\to\infty}\underline{G}(JM,R)=\underline{f}(R)\underline{C} ,
\end{aligned}
\qquad (88)
$$

where $\underline{C}$ is a constant matrix, the elements of $\underline{f}(R)$ are

$$
\begin{aligned}
&[\underline{f}(R)]_{\beta}^{\beta'}=\frac{1}{\sqrt{k_\beta}}[\delta_{\beta,\beta'}j_l(k_\beta R)+K_{\beta,\beta'}(JM)\eta_l(k_\beta R)] , \\
&\beta\equiv\{jlj_a,j_b\},\quad \beta'\equiv\{j'l'j_a'j_b'\} \qquad (89) \\
&k_\beta=\sqrt{2\mu[E-\Delta E_a(j_a)-\Delta E_b(j_b)]}\equiv k_{j_aj_b} ,
\end{aligned}
$$

and j_l,η_l are, respectively, the regular and irregular Bessel-Ricatti functions. $K_{\beta,\beta'}(JM)\equiv\underline{K}(JM)$ is a real symmetric matrix and we choose the constant $\underline{C}$ so that

$$\lim_{R\to\infty}G_{jlj_aj_b}^{j'l'j_a'j_b'}(JM,R)=\frac{1}{\sqrt{k_{j_aj_b}}}\left[\exp\left[-ik_{j_aj_b}R+i\frac{l\pi}{2}\right]\delta_{jlj_aj_b}^{j'l'j_a'j_b'}-S_{jlj_aj_b}^{j'l'j_a'j_b'}(JM)\exp\left[ik_{j_aj_b}R-i\frac{l\pi}{2}\right]\right] , \qquad (90)$$

where $S_{jlj_aj_b}^{j'l'j_a'j_b'}(JM)$ is an element of the S matrix for the JMth partial wave. Comparing Eq. (90) with Eq. (89) we find

$$\underline{S}(JM)=\frac{\underline{I}+i\underline{K}(JM)}{\underline{I}-i\underline{K}(JM)} . \qquad (91)$$

Because the radial equation (77) is independent of the magnetic quantum number M, we introduce the shorthand notation $\underline{S}(J)\equiv\underline{S}(JM)$. The wave amplitude for the system in an initial electronic state $j'\Omega' j'_a j'_b$ is expressed in terms of the functions $G^{JM}_{jlj_aj_b}(R)$ which, in turn, are linear combinations of the amplitudes $G^{j'l'j'_aj'_b}_{jlj_aj_b}(JM,R)$. We choose the linear combination

$$G^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\mathbf{R})=\sum_{lm}\sum_{l'm'}\sum_{JM}\begin{bmatrix} j & l & J \\ \Omega & m & -M\end{bmatrix}\begin{bmatrix} j' & l' & J \\ \Omega' & m' & -M\end{bmatrix} Y_{lm}(\theta\phi)Y^{*}_{l'm'}(\theta_i\phi_i)[J]\left[\frac{2\pi i^{l+1}}{k^{1/2}_{j'_aj'_b}}\right]\frac{G^{j'l'j'_aj'_b}_{jlj_aj_b}(JM,R)}{R} \tag{92}$$

so that in the limit $R\rightarrow\infty$, $G^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\mathbf{R})$ has the asymptotic form

$$G^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\mathbf{R})\rightarrow\delta^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}\exp(i\mathbf{K}_i\cdot\mathbf{R})+f^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\theta\phi;\theta_i\phi_i)\frac{\exp(ik_{j_aj_b}R)}{R}\ , \tag{93}$$

where $f^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\theta\phi;\theta_i\phi_i)$ is the amplitude for the system to undergo a transition from an electronic state $j'\Omega'j'_aj'_b$ to $j\Omega j_aj_b$ and for the nuclei to scatter into solid angle $d\theta(\sin\theta)d\phi$ following an initial approach along the incident wave vector $\mathbf{K}_i$ with polar angles $\theta_i\phi_i$. Comparing expression (93) with (92) we find that the scattering amplitudes are expressed in terms of the S matrix,

$$f^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\theta\phi;\theta_i\phi_i)=\sum_{lm}\sum_{l'm'}\sum_{JM}\begin{bmatrix} j & l & J \\ \Omega & m & -M\end{bmatrix}\begin{bmatrix} j' & l' & J \\ \Omega' & m' & -M\end{bmatrix} Y_{lm}(\theta\phi)Y^{*}_{l'm'}(\theta_i\phi_i)[J]\frac{2\pi i}{\sqrt{k_{j'_aj'_b}k_{j_aj_b}}}[\underline{I}-\underline{S}(J)]^{j'l'j'_aj'_b}_{jlj_aj_b}\ . \tag{94}$$

We define the total cross section for the two oxygen atoms to undergo a transition from state $j'_aj'_b$ to j_aj_b,

$$\sigma(j'_aj'_b\rightarrow j_aj_b)\equiv\frac{v_{j_aj_b}}{v_{j'_aj'_b}}\frac{1}{(2j'_a+1)(2j'_b+1)}\sum_{\Omega\Omega'}\sum_{j'j}\frac{1}{4\pi}\int d\hat{\Omega}\,d\hat{\Omega}_i|f^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}(\theta\phi;\theta_i\phi_i)|^2\ , \tag{95}$$

where $v_{j'_aj'_b}, v_{j_aj_b}$ are, respectively, the initial and final relative velocities of the projectiles. We integrate over the scattering solid angle $d\hat{\Omega}$ average over the solid angle, $d\hat{\Omega}_i$ of the incident wave, sum and average over the total angular momenta $j\Omega j'\Omega'$, to get

$$\sigma(j'_aj'_b\rightarrow j_aj_b)=\frac{\pi}{k^2_{j'_aj'_b}(2j'_a+1)(2j'_b+1)}\sum_{j'l'jl}\sum_{J}(2J+1)|\underline{T}(J)^{j'l'j'_aj'_b}_{jlj_aj_b}|^2\ , \tag{96}$$

where we used Eq. (94), invoked orthogonality of the spherical harmonics, contracted 3-j symbols, and defined

$$\underline{T}(J)^{j'l'j'_aj'_b}_{jlj_aj_b}=[\underline{I}-\underline{S}(J)]^{j'l'j'_aj'_b}_{jlj_aj_b}\ . \tag{97}$$

The above discussion does not take into account the fact that the oxygen nuclei are identical particles and that the total wave function for the system must be symmetric under the interchange of the nuclei. In our coordinate system the interchange of nuclei corresponds to the inversion, $\mathbf{R}\rightarrow-\mathbf{R}$. According to (49) the electronic expansion states in the atomic gauge are

$$\begin{aligned}\phi_{j\Omega j_aj_b}(\mathbf{R},\mathbf{r})&=\sum_{j'\Omega'j'_aj'_b}U(\mathbf{R})|j'(R)\Omega'j'_aj'_b\rangle[\underline{T}^{-1}(\theta\phi)]^{j'\Omega'j'_aj'_b}_{j\Omega j_aj_b}\\ &=\sum_{\Omega'}U(\mathbf{R})|j'(R)\Omega'j'_aj'_b\rangle\exp[-i\phi(\Omega'-\Omega)]d^{j}_{\Omega,\Omega'}(\theta)\ .\end{aligned} \tag{98}$$

We need to know how these states behave under nuclear inversion $\mathbf{R}\rightarrow-\mathbf{R}$. First we examine the behavior of the rotation operator $U(\theta,\phi)$ under the operation $\mathbf{R}\rightarrow-\mathbf{R}$, or $\theta\rightarrow\pi-\theta,\phi\rightarrow\pi+\phi$. We get

$$U(-\hat{\mathbf{R}})=U(\pi-\theta,\pi+\phi)=\exp(-iK_z\phi)\exp(-iK_z\pi)\exp(iK_y\theta)\exp(-iK_y\pi)\exp(iK_z\phi)\exp(iK_z\pi)\ , \tag{99}$$

where we used definition (26). We reexpress Eq. (99) as

$$U(-\hat{\mathbf{R}})=U(\hat{\mathbf{R}})\exp(-i\phi K_z)U(\pi,\pi)\exp(i\phi K_z)\ , \tag{100}$$

where the operator

$$U(\pi,\pi)=\exp(-iK_z\pi)\exp(-iK_y\pi)\exp(iK_z\pi) \tag{101}$$

transforms the electronic coordinates $\mathbf{r}_i$ into

$$
\begin{aligned}
&U^{\dagger}(\pi,\pi)x_i U(\pi,\pi)=-x_i \ , \\
&U^{\dagger}(\pi,\pi)y_i U(\pi,\pi)=y_i \ , \\
&U^{\dagger}(\pi,\pi)z_i U(\pi,\pi)=-z_i \ ,
\end{aligned}
\tag{102}
$$

for all i. Because of Eq. (102) we can equate

$$U(\pi,\pi)=\hat{\pi}\sigma(xz)\exp(-iS_z\pi)\exp(-iS_y\pi)\exp(iS_z\pi) \ , \tag{103}$$

where $\hat{\pi},\sigma(xz)$ are the molecular inversion and reflection through the x-z plane operators, respectively (see Appendix A), and we used the fact that $\mathbf{S}$ commutes with all spatial operators. Combining these results we get

$$\phi_{j\Omega j_a j_b}(-\mathbf{R},\mathbf{r})=\sum_{\Omega'} U(\hat{\mathbf{R}})\exp(-iK_z\phi)U(\pi,\pi)\exp(i\Omega'\phi)|j(R)\Omega' j_a j_b\rangle \exp[-i\phi(\Omega'-\Omega)](-1)^{(\Omega'-\Omega)}d^{j}_{\Omega,\Omega'}(\pi-\theta) \ . \tag{104}$$

Now [26]

$$d^{j}_{\Omega,\Omega'}(\pi-\theta)=(-1)^{j+\Omega}d^{j}_{\Omega',-\Omega}(\theta) \tag{105}$$

and inserting Eqs. (105) and (A30) into (104) we get

$$
\begin{aligned}
\phi_{j\Omega j_a j_b}(-\mathbf{R},\mathbf{r})&=(-1)^{j+j_a+j_b}\sum_{\Omega'} U(\hat{\mathbf{R}})|j(R)\Omega' j_b j_a\rangle \exp[-i\phi(\Omega'-\Omega)]d^{j}_{\Omega,\Omega'}(\theta) \\
&=(-1)^{j+j_a+j_b}\phi_{j\Omega j_b j_a}(\mathbf{R},\mathbf{r}) \ .
\end{aligned}
\tag{106}
$$

Because of relation (34), we conclude that transformation $\mathbf{R}\rightarrow -\mathbf{R}$, acting on states (98), is equivalent to the action of the electronic parity operator $\hat{\pi}$ on them. That is,

$$\phi_{j\Omega j_a j_b}(-\mathbf{R},\mathbf{r})=(-1)^{j+j_a+j_b}\phi_{j\Omega j_b j_a}(\mathbf{R},\mathbf{r})=\hat{\pi}\phi_{j\Omega j_a j_b}(\mathbf{R},\mathbf{r}) \ . \tag{107}$$

Electronic states (98) have the same transformation properties under nuclear inversion as states (31) have under electron inversion about the molecular center.

We may, therefore, express the system wave function in the symmetric form

$$\Psi(\mathbf{R},\mathbf{r})=\sum_{j\Omega j_a j_b} G^{j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(\mathbf{R})\phi_{j\Omega j_a j_b}(\mathbf{R},\mathbf{r}) \ , \tag{108}$$

where now the scattering amplitudes must obey the symmetry relation

$$G^{j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(-\mathbf{R})=(-1)^{j+j_a+j_b}G^{j'\Omega' j_a' j_b'}_{j\Omega j_b j_a}(\mathbf{R}) \ . \tag{109}$$

We replace expansion (92) with

$$
\begin{aligned}
G^{j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(\mathbf{R})=&\sum_{lm}\sum_{l'm'}\sum_{JM}\begin{bmatrix} j & l & J \\ \Omega & m & -M\end{bmatrix}\begin{bmatrix} j' & l' & J \\ \Omega' & m' & -M\end{bmatrix} Y_{lm}(\theta\phi)Y^{*}_{l'm'}(\theta_i\phi_i) \\
&\times[J]\frac{2\pi i^{l+1}}{Rk^{1/2}_{j_a' j_b'}}\{G^{j'l'j_a'j_b'}_{jlj_aj_b}(JM,R)+(-1)^{j+l+j_a+j_b}G^{j'l'j_a'j_b'}_{jlj_bj_a}(JM,R)\} \ .
\end{aligned}
\tag{110}
$$

The asymptotic limit for the symmetrized amplitude $\underline{G}(\mathbf{R})$ is

$$
\begin{aligned}
G^{\prime j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(\mathbf{R})\rightarrow&\,\delta^{j'\Omega'}_{j\Omega}[\delta^{j_a'j_b'}_{j_aj_b}\exp(i\mathbf{K}_i\cdot\mathbf{R})+(-1)^{j+j_a+j_b}\exp(-i\mathbf{K}_i\cdot\mathbf{R})\delta^{j_a'j_b'}_{j_bj_a}] \\
&+[f^{j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(\theta\phi;\theta_i\phi_i)+(-1)^{j+l+j_a+j_b}f^{j'\Omega' j_a' j_b'}_{j\Omega j_b j_a}(-\theta+\pi\ \phi+\pi;\theta_i\phi_i)]\frac{\exp(ik_{j_aj_b}R)}{R} \ ,
\end{aligned}
\tag{111}
$$

and the expression for the total inelastic collision cross sections becomes

$$
\begin{aligned}
\sigma(j_a'j_b'\rightarrow j_aj_b)=&\frac{v_{j_aj_b}}{v_{j_a'j_b'}}\frac{1}{(2j_a'+1)(2j_b'+1)}\frac{1}{2} \\
&\times\sum_{\Omega\Omega'}\sum_{j'j}\frac{1}{4\pi}\int d\hat{\Omega}\,d\hat{\Omega}_i|f^{j'\Omega' j_a' j_b'}_{j\Omega j_a j_b}(\theta\phi;\theta_i\phi_i)+(-1)^{j+l+j_a+j_b}f^{j'\Omega' j_a' j_b'}_{j\Omega j_b j_a}(-\theta+\pi\ \phi+\pi;\theta_i\phi_i)|^2 \ ,
\end{aligned}
\tag{112}
$$

where we have included an additional factor of $\frac{1}{2}$ in order to insure that the incoming flux is normalized to unity. Inserting expression (94) into Eq. (112), employing parity properties of the spherical harmonics and the orthogonality relations for the 3-j symbols, we get

$$\sigma(j_a'j_b'\rightarrow j_aj_b)=\frac{\pi}{2k^2_{j_a'j_b'}(2j_a'+1)(2j_b'+1)}\sum_{j'l'jl}\sum_{J}(2J+1)|\underline{T}^{j'l'j_a'j_b'}_{jlj_aj_b}(J)+(-1)^{j+l+j_a+j_b}\underline{T}^{j'l'j_a'j_b'}_{jlj_bj_a}(J)|^2 \; . \tag{113}$$

V. RESULTS AND DISCUSSION

Equation (113) was used to calculate the total cross sections $\sigma(j_a'j_b'\rightarrow j_aj_b)$ for the collision energies corresponding to the range of temperatures $T\approx 680-2000$ K. Results for the excitation cross sections, $\sigma(j_aj_b\rightarrow j_a'j_b')$, including a detailed description of the computational aspects, will be reported in a follow-up paper. In conclusion, we briefly summarize the theoretical method introduced above.

The O_2 system wave function was expressed by a close-coupled expansion, where the channel states are adiabatic eigenstates of the electronic Hamiltonian (6). We integrated out the electronic degrees of freedom and arrived at a set of coupled equations (38), for the scattering amplitudes. These are essentially the PSS equations. The nonadiabatic vector coupling matrix $\underline{\mathbf{A}}$ is treated as a gauge potential [23,24], and we found that this coupling persists in the separated atom region. The long-range coupling prevents us from imposing standard asymptotic boundary conditions on the scattering amplitudes. It has been recognized that in certain cases the PSS equations suffer what appear to be anomalous long-range nonadiabatic couplings and translation factors have been introduced to eliminate such couplings [34]. Here we used a different procedure, we introduced a gauge transformation and derived a new set of coupled equations (64). In the new gauge, which we call the atomic gauge, the nonadiabatic couplings are well behaved in the asymptotic region.

We could solve the scattering equations in the original (molecular) gauge, but in order to satisfy the gauge invariance of the scattering matrix we would need to impose unusual asymptotic boundary conditions.

The spirit of our program is similar to the molecular theories of Mies [16], Launay and Roueff [17], and Singer, Fried, and Band [19]. Our theoretical development differs in some important aspects, described below.

Mies applied a molecular theory to calculate the excitation of the ^2P_J levels in ground-state fluorine by impacts with protons. In his molecular treatment all coordinates are defined with respect to an origin located at the center of mass of the fluorine atom. As long as electron transfer to the proton is neglected it is acceptable to define all angular momenta with respect to one center, which Mies took to be the fluorine center of mass. Launay and Roueff [17] apply the method of Mies to calculate the excitation of ^2P_J levels of C^+ by impacts with hydrogen atoms. They define all angular momenta with respect to an origin located at the heavy atom. Because we are dealing with the collision of complex atoms, both of which have nonzero electronic angular momenta, the procedure of Mies is not applicable here. We distinguish between two total angular momentum operators, the total electronic angular momentum $\mathbf{K}$ with respect to the molecular center, and the total two-center angular momentum $\mathbf{j}$. The former operator generates rotations about the molecular center, and the latter one generates rotations in the product space of two-center states. The role of the two distinct rotations is crucial when we take the asymptotic limit of electronic molecular states to form atomic states. This is discussed at length in Sec. IV, and illustrated in Fig. 1. The theory of Singer, Fried, and Band also applies to interactions of two complex atoms, and they do distinguish angular momentum quantum numbers for different atomic fragments. They construct molecular states out of atomic states using standard recoupling techniques and define a total electronic angular momentum. However they do not appear to make a distinction between this, a total two-center angular momentum, and the total electronic angular momentum which generates rotations about the molecular center. The recent discussion by Kimura *et al.* [35] appears also not to distinguish between the total electron angular momentum and the sum of the atomic angular momentum.

In the cited molecular theories [16–20], the Born-Oppenheimer separation into electronic and nuclear wave functions is carried out in a noninertial, body-fixed coordinate frame in which the quantization axis is aligned along the internuclear vector $\mathbf{R}$. This is a standard procedure in molecular physics [36]. The wave function in the body frame is then transformed back into the space-fixed frame, since that is where the scattering boundary conditions are defined. For example, Mies in Eq. (4.9) of his paper constructs a space-fixed molecular state as a linear combination of BO electronic states

$$|Rjm_j\rangle=\sum_{\Omega}D^{j*}_{m_j,\Omega}(\phi,\theta,0)|Rj\Omega\rangle \; , \tag{114}$$

where we used the notation of Mies [16]. $D^{j*}_{m_j,\Omega}(\phi,\theta,0)$ is a Wigner rotation matrix, j is the total electronic angular momentum defined with respect to the origin of the fluorine atom, m_j is the magnetic quantum number, and Ω is the total electronic angular momentum along the z axis of the body frame. $|R_j\Omega\rangle$ is the body-frame molecular state and $|Rjm_j\rangle$ is the space-fixed molecular state. Such a procedure is also advocated in the work of Ref. [19] and an analogous expression is given by Eq. (II.11) in their paper.

In our treatment, Born-Oppenheimer and atomic states are defined with respect to the same quantization axis, the $\hat{\mathbf{z}}$ axis of the space-fixed frame. We define Born-

Oppenheimer states as those adiabatic states, defined in the space-fixed frame, where the nuclei are aligned along the $\hat{\mathbf{z}}$ axis. We construct adiabatic states for arbitrary nuclear orientation $\hat{\mathbf{R}}$ by an active rotation (26) on the BO states. Equation (26) is analogous in relation to Eq. (114) above. However, our basis set, comprised of Born-Oppenheimer states, does not form a finite matrix representation for the rotations defined around the molecular center. In the asymptotic limit the electronic wave functions evolve into atomic states $|j\Omega j_a j_b\rangle$, and these states define a representation of the product group of rotations around each atomic center. In the case of complex atoms these states do not, in general, comprise a representation of rotations around the molecular center. In other words, a finite set of BO states or the atomic states which evolve from them in the separated atom limit does not transform into each other under the action of operator $U(\hat{\mathbf{R}})$ on them, and we argue that relation (114) is necessarily incomplete. The comparison with the theory of Singer, Fried, and Band is further complicated by the fact that they use quantum number j to identify irreducible representations (Wigner matrix) of the rotation group, which is used to transform the molecular states from the body to space-fixed frame. However, in their discussion, j is associated with the two-center rotation operator, not the operator which generates rotations about the molecular center.

Our procedure depends on the fact that the expectation values of the dipole operator (14) vanish in the separated atom limit of the O_2 system. Otherwise the transformation from the molecular to atomic gauge does not eliminate all off-diagonal asymptotic couplings. In cases where the dipole coupling does not vanish, the present theory must be generalized.

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APPENDIX A: DISCRETE SYMMETRIES OF ATOMIC AND MOLECULAR STATES

We construct two-center atomic states out of sums and products of atomic orbitals. We treat the oxygen atoms in the frozen-core approximation and consider only the $2p$ electrons for each atom. In the space-fixed frame we define electronic coordinates associated with each atomic center a,b, respectively,

$$\begin{aligned}\mathbf{r}_{ia}&=\mathbf{r}_i-\frac{\mathbf{R}}{2}, \quad i=1,4 \;,\\ \mathbf{r}_{jb}&=\mathbf{r}_j+\frac{\mathbf{R}}{2}, \quad j=5,8 \;,\end{aligned} \tag{A1}$$

where the molecular coordinates $\mathbf{r}_i$ are defined in Eq. (2), the atomic centers are located on the $\hat{\mathbf{z}}$ axis, and $\mathbf{R}=\hat{\mathbf{z}}R$. We take for the orbital atomic wave functions, eigenstates of the angular momenta,

$$\begin{aligned}\boldsymbol{l}_a&=\sum_{i=1,4}\mathbf{r}_{ia}\times\mathbf{p}_i \;,\\ \boldsymbol{l}_b&=\sum_{j=5,8}\mathbf{r}_{jb}\times\mathbf{p}_j \;,\end{aligned} \tag{A2}$$

for centers a,b, respectively. We form the product

$$\begin{aligned}|L\Lambda\rangle\equiv&(-1)^{l_b-l_a-\Lambda}\\ &\times\sum_{m_a m_b}\sqrt{2L+1}\begin{bmatrix} l_a & l_b & L\\ m_a & m_b & -\Lambda\end{bmatrix}\\ &\times\phi_{l_a m_a}(r_{1a},\ldots,r_{4a})\phi_{l_b m_b}(r_{5b},\ldots,r_{8b}) \;,\end{aligned} \tag{A3}$$

where the functions $\phi_{l_a m_a},\phi_{l_b m_b}$ are eigenstates of $\hat{\mathbf{z}}\cdot\boldsymbol{l}_a,\hat{\mathbf{z}}\cdot\boldsymbol{l}_b,\boldsymbol{l}_a^2,\boldsymbol{l}_b^2$, respectively. The states $|L\Lambda\rangle$ are eigenstates of $\mathbf{L}^2$ and $\mathbf{L}_z$, where $\mathbf{L}=\boldsymbol{l}_a+\boldsymbol{l}_b$. It is also useful to express states (A3) in the form

$$|L\Lambda\rangle=\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)|L\Lambda\rangle_O \;, \tag{A4}$$

where $\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)$ is an electron translation operator, $\mathbf{P}$ is defined in (14), and $|L\Lambda\rangle_O$ is given by Eq. (A3) with the arguments of the orbital functions $\mathbf{r}_{ia},\mathbf{r}_{jb}$ replaced by the coordinates $\mathbf{r}_i,\mathbf{r}_j$, respectively. States $|L\Lambda\rangle_O$ are independent of the nuclear coordinates (R,θ,ϕ), and one can use Eq. (31) to define states $|j\Omega j_a j_a\rangle_O$ which are also independent of the nuclear parameters.

We introduce the molecular inversion operator $\hat{\pi}$ defined so that

$$\hat{\pi}^{\dagger}\mathbf{r}_i\hat{\pi}=-\mathbf{r}_i, \quad i=1,8 \;. \tag{A5}$$

Using Eqs. (A1) and (A5) we find

$$\begin{aligned}\hat{\pi}^{\dagger}\mathbf{r}_{ia}\hat{\pi}&=-\mathbf{r}_i-\frac{\mathbf{R}}{2}=-\mathbf{r}_{ib}=\hat{\pi}_b^{\dagger}\mathbf{r}_{ib}\hat{\pi}_b \;,\\ \hat{\pi}^{\dagger}\mathbf{r}_{jb}\hat{\pi}&=-\mathbf{r}_j+\frac{\mathbf{R}}{2}=-\mathbf{r}_{ja}=\hat{\pi}_a^{\dagger}\mathbf{r}_{ja}\hat{\pi}_a \;,\end{aligned} \tag{A6}$$

where $\hat{\pi}_a,\hat{\pi}_b$ are the atomic parity operators associated with centers a and b, respectively. Now

$$\begin{aligned}\hat{\pi}\phi_{l_a m_a}(r_{1a},\ldots,r_{4a})\phi_{l_b m_b}(r_{5b},\ldots,r_{8b})&=\phi_{l_a m_a}(-r_{1b},\ldots,-r_{4b})\phi_{l_b m_b}(-r_{5a},\ldots,-r_{8a})\\ &=\phi_{l_a m_a}(r_{1b},\ldots,r_{4b})\phi_{l_b m_b}(r_{5a},\ldots,r_{8a}) \;,\end{aligned} \tag{A7}$$

where we have used the fact that the atomic orbitals are odd-parity states and there is an even number of electrons at each atomic center. Therefore,

$$\hat{\pi}|L\Lambda\rangle=(-1)^{l_b-l_a-\Lambda}\sum_{m_am_b}\sqrt{2L+1}\begin{bmatrix} l_a & l_b & L \\ m_a & m_b & -\Lambda \end{bmatrix}\phi_{l_am_a}(r_{1b},\ldots,r_{4b})\phi_{l_bm_b}(r_{5a},\ldots,r_{8a})$$

$$=(-1)^{l_b-l_a-\Lambda}\sum_{m_am_b}\sqrt{2L+1}(-1)^{l_a+l_b+L}\begin{bmatrix} l_a & l_b & L \\ m_a & m_b & -\Lambda \end{bmatrix}P\phi_{l_am_b}(r_{5b},\ldots,r_{8b})\phi_{l_bm_a}(r_{1a},\ldots,r_{4a})$$

$$=(-1)^{L}P|L\Lambda\rangle\ , \tag{A8}$$

where $P=P^{\dagger}$ is an electron permutation operator defined so that

$$P\mathbf{r}_1P=\mathbf{r}_5,\quad P\mathbf{r}_2P=\mathbf{r}_6,\quad P\mathbf{r}_3P=\mathbf{r}_7,\quad P\mathbf{r}_4P=\mathbf{r}_8\ , \tag{A9}$$

and we used the fact that $l_a=l_b=1$, and $P^2=1$. In the same manner we construct the spin function

$$|S\Sigma\rangle=(-1)^{s_b-s_a-\Sigma}\sum_{m_am_b}\sqrt{2S+1}\begin{bmatrix} s_a & s_b & S \\ m_a & m_b & -\Sigma \end{bmatrix}\xi_{s_am_a}(1,\ldots,4)\xi_{s_bm_b}(5,\ldots,8)\ , \tag{A10}$$

where ξ are spin functions and $s_a=s_b=1$. The inversion operator $\hat{\pi}$ does not affect the spin coordinates, therefore

$$\hat{\pi}|S\Sigma\rangle=|S\Sigma\rangle \tag{A11}$$

and

$$P|S\Sigma\rangle=(-1)^{s_b-s_a-\Sigma}\sum_{m_am_b}\sqrt{2S+1}\begin{bmatrix} s_a & s_b & S \\ m_a & m_b & -\Sigma \end{bmatrix}\xi_{s_am_a}(5,\ldots,8)\xi_{s_bm_b}(1,\ldots,4)$$

$$=(-1)^{S}|S\Sigma\rangle \tag{A12}$$

since $s_a=s_b=1$. Thus

$$\hat{\pi}(|L\Lambda\rangle\otimes|S\Sigma\rangle)=(-1)^{L}(P|L\Lambda\rangle)\otimes|S\Sigma\rangle$$

$$=(-1)^{L+S}P(|L\Lambda\rangle\otimes|S\Sigma\rangle)\ . \tag{A13}$$

Finally we construct, as required by the Pauli principle, a total antisymmetrized atomic state. Although the p electrons in the oxygen atoms are equivalent, we are concerned with the ground P state terms only, and, therefore, we simply express the symmetrized states by

$$|L\Lambda S\Sigma\rangle_A\equiv\frac{1}{\sqrt{8!}}\sum_{p_i}(-1)^{p_i}|L\Lambda\rangle\otimes|S\Sigma\rangle\ , \tag{A14}$$

where the sum over p_i represents all possible electron permutations. Using Eqs. (A13) and (A14) we get

$$\hat{\pi}|L\Lambda S\Sigma\rangle_A=(-1)^{L+S}|L\Lambda S\Sigma\rangle_A\ . \tag{A15}$$

Throughout the text proper symmetrization of the states $|L\Lambda S\Sigma\rangle$ is implicit and the subscript A is dropped.

We also consider the reflection symmetry of the atomic and molecular states with respect to reflection in the x-z plane of the laboratory coordinate system. We define the molecular reflection operator $\sigma(xz)$ so that

$$\sigma^{\dagger}(xz)x_i\sigma(xz)=x_i\ ,$$

$$\sigma^{\dagger}(xz)z_i\sigma(xz)=z_i\ , \tag{A16}$$

$$\sigma^{\dagger}(xz)y_i\sigma(xz)=-y_i\ ,$$

for all i. In our coordinate system $\mathbf{R}=\hat{\mathbf{z}}R$ and so the molecular reflection operator $\sigma(xz)$ is equivalent to products of atomic reflection operators $\sigma_a(xz),\sigma_b(xz)$, which are defined by the relations

$$\sigma_a^{\dagger}(xz)x_{ia}\sigma_a(xz)=x_{ia}\ ,$$

$$\sigma_a^{\dagger}(xz)z_{ia}\sigma_a(xz)=z_{ia}\ , \tag{A17}$$

$$\sigma_a^{\dagger}(xz)y_{ia}\sigma_a(xz)=-y_{ia}\ ,$$

for $i=1,\ldots,4$ and analogous relations for reflections of the coordinates $\mathbf{r}_{jb}$. Therefore,

$$\sigma(xz)=\sigma_a(xz)\sigma_b(xz)\ . \tag{A18}$$

We may relate products of the atomic parity and reflection operators with rotations about the atomic centers, i.e.,

$$\hat{\pi}_a\sigma_a(xz)=R_a(\pi,\pi)$$

$$\equiv\exp(-il_{a_z}\pi)\exp(-il_{a_y}\pi)\exp(il_{a_z}\pi)\ ,$$

$$\hat{\pi}_b\sigma_b(xz)=R_b(\pi,\pi) \tag{A19}$$

$$\equiv\exp(-il_{b_z}\pi)\exp(-il_{b_y}\pi)\exp(il_{b_z}\pi)\ ,$$

where we used

$$R_a^{\dagger}(\pi,\pi)x_{ia}R_a(\pi,\pi)=-x_{ia}\ ,$$

$$R_a^{\dagger}(\pi,\pi)y_{ia}R_a(\pi,\pi)=y_{ia}\ ,$$

$$R_a^{\dagger}(\pi,\pi)z_{ia}R_a(\pi,\pi)=-z_{ia}\ ,$$

for $i=1,\ldots,4$, and the analogous relations for the operator $R_b(\pi,\pi)$. Using (A18), (A19), and $\hat{\pi}_a^2=\hat{\pi}_b^2=1$, we get

$$\sigma(xz)=\hat{\pi}_a\hat{\pi}_bR_a(\pi,\pi)R_b(\pi,\pi)\ . \tag{A20}$$

Therefore,

$$\sigma(xz)|L\Lambda\rangle=(-1)^{l_b-l_a-\Lambda}\sum_{m_a m_b}\sqrt{2L+1}\begin{bmatrix} l_a & l_b & L \\ m_a & m_b & -\Lambda \end{bmatrix} R_a(\pi,\pi)R_b(\pi,\pi)\phi_{l_a m_a}(r_{1a},\ldots,r_{4a})\phi_{l_b m_b}(r_{5b},\ldots,r_{8b}) , \tag{A21}$$

where we have used the fact that $\phi_{l_a m_a},\phi_{l_b m_b}$ are both odd atomic parity eigenstates. Now,

$$\begin{aligned} R_a(\pi,\pi)\phi_{l_a m_a} &= \sum_{m'}\exp[i\pi(m_a-m')]\times|l_a m'\rangle\langle m' l_a|\exp(-i\pi l_{a_y})|l_a m_a\rangle \\ &= \sum_{m'}\exp[i\pi(m_a-m')]\times|l_a m'\rangle d^{l_a}_{m',m_a}(\pi)=(-1)^{l_a-m_a}\phi_{l_a-m_a} , \end{aligned} \tag{A22}$$

where we replaced the matrix element of a rotation operator with a reduced Wigner function [26].

Also,

$$R_b(\pi,\pi)\phi_{l_b m_b}=(-1)^{l_b-m_b}\phi_{l_b-m_b} . \tag{A23}$$

Combining Eqs. (A22) and (A21) we get

$$\begin{aligned} R_a R_b|L\Lambda\rangle &= (-1)^{l_b-l_a-\Lambda}\sum_{m_a m_b}\sqrt{2L+1}\begin{bmatrix} l_a & l_b & L \\ m_a & m_b & -\Lambda \end{bmatrix}(-1)^{l_a+l_b-m_a-m_b}\phi_{l_a-m_a}(r_{1a},\ldots,r_{4a})\phi_{l_b-m_b}(r_{5b},\ldots,r_{8b}) \\ &= (-1)^{l_b-l_a-\Lambda}\sum_{m_a m_b}\sqrt{2L+1}\begin{bmatrix} l_a & l_b & L \\ m_a & m_b & \Lambda \end{bmatrix}(-1)^{L+m_a+m_b}\phi_{l_a m_a}(r_{1a},\ldots,r_{4a})\phi_{l_b m_b}(r_{5b},\ldots,r_{8b}) \\ &= (-1)^{L-\Lambda}|L-\Lambda\rangle , \end{aligned} \tag{A24}$$

or

$$\sigma(xz)|L\Lambda S\Sigma\rangle=(-1)^{L-\Lambda}|L-\Lambda S\Sigma\rangle . \tag{A25}$$

Although the atomic states $|L\Lambda S\Sigma\rangle$ are not, in general, eigenstates of $\sigma(xz)$, they do form a representation of the molecular reflection operator $\sigma(xz)$.

In the main text and in Appendix B we show that the molecular eigenstates of $H_{\mathrm{BO}}(R,\mathbf{r})$ can be put in a one-to-one correspondence with the atomic states $|L\Lambda S\Sigma\rangle$, and since H_{BO} commutes with $\hat{\pi}$ and $\sigma(xz)$ the molecular states also form a representation for these operators. We choose the phase convention so that relations (A15) and (A25) also hold for the molecular Born-Oppenheimer functions which merge into $|L\Lambda S\Sigma\rangle$ in the separated atom limit, i.e.,

$$\begin{aligned} \hat{\pi}|\Lambda S\Sigma L\rangle &= (-1)^{L+S}|\Lambda S\Sigma L\rangle , \\ \sigma(xz)|\Lambda S\Sigma L\rangle &= (-1)^{L-\Lambda}|-\Lambda S\Sigma L\rangle . \end{aligned} \tag{A26}$$

Although the spin coordinates do not change under spatial transformations, the operator

$$U_S(\pi,\pi)=\exp(-iS_z\pi)\exp(-iS_y\pi)\exp(iS_z\pi) \tag{A27}$$

rotates spin states similar to the way the spatial operator $R(\pi,\pi)$ rotates spatial functions. Following similar procedures outlined above we find

$$U_S(\pi,\pi)|\Lambda S\Sigma L\rangle=(-1)^{S-\Sigma}|\Lambda S-\Sigma L\rangle . \tag{A28}$$

Using definition (103) and Eqs. (A26) and (A28) we get

$$U(\pi,\pi)|\Lambda S\Sigma L\rangle=(-1)^{-\Lambda-\Sigma}|-\Lambda S-\Sigma L\rangle . \tag{A29}$$

Also,

$$U(\pi,\pi)|j(R)\Omega j_a j_b\rangle=(-1)^{j_a+j_b+\Omega}|j(R)-\Omega j_b j_a\rangle , \tag{A30}$$

where we have used Eqs. (31) and (A29) and symmetry properties of the 9-j symbols.

APPENDIX B: ASYMPTOTIC ATOM-ATOM INTERACTION

We define atomic states $|l_a m_a\rangle,|l_b m_b\rangle$, which are eigenstates of $l_a^2,\hat{\mathbf{z}}\cdot l_a$ and $l_b^2,\hat{\mathbf{z}}\cdot l_b$, respectively. For P states $l_a=l_b=1$, and for the sake of brevity we label them by azimuthal quantum numbers only. Using the multipole expansion (20), and after some angular momentum algebra, we obtain for the asymptotic element of the interaction potential

$$\langle m_{a'} m_{b'}|V_5|m_a m_b\rangle=\frac{54}{\pi}\frac{\langle r^2\rangle^2}{R^5}R(m_a,m_{a'};m_b,m_{b'}) , \tag{B1}$$

where r^2 is the expectation value for a single p electron of oxygen, and R is a sum of products of 3-j symbols

$$R(m_a,m_{a'};m_b,m_b)=(-1)^{m_a+m_{a'}+m_b+m_{b'}}$$
$$\times\sum_{\mu,\mu'} g(L=2,\mu)\sum_{\mu_1,\mu_1'}\sum_{\mu_2,\mu_2'}\sum_{\mu_3,\mu_3'}(-1)^{\mu_{1'}+\mu_{3'}}\begin{bmatrix}1 & 1 & 1\\ \mu_2 & \mu_1 & -m_a\end{bmatrix}\begin{bmatrix}1 & 1 & 1\\ \mu_2 & \mu_1' & -m_{a'}\end{bmatrix}\begin{bmatrix}1 & 2 & 1\\ -\mu_1' & \mu & \mu_1\end{bmatrix}$$
$$\times\begin{bmatrix}1 & 1 & 1\\ \mu_3 & \mu' & -m_b\end{bmatrix}\begin{bmatrix}1 & 1 & 1\\ \mu_3' & \mu' & -m_{b'}\end{bmatrix}\begin{bmatrix}1 & 2 & 1\\ -\mu_3' & -\mu & \mu_3\end{bmatrix}. \qquad \text{(B2)}$$

The matrix element of V_5 can be expressed more simply by introducing a 6-*j* coefficient in the form

$$\langle m_{a'}m_{b'}|V_5|m_am_b\rangle=\frac{54}{\pi}\frac{\langle r^2\rangle^2}{R^5}\begin{Bmatrix}1 & 1 & 2\\ 1 & 1 & 1\end{Bmatrix}^2\sum_{\mu} g(L=2,\mu)(-1)^{m_{a'}+m_{b'}}\begin{bmatrix}1 & 1 & 2\\ -m_a & m_{a'} & -\mu\end{bmatrix}\begin{bmatrix}1 & 1 & 2\\ -m_b & m_{b'} & \mu\end{bmatrix}. \qquad \text{(B3)}$$

Now define the states

$$|L\Lambda\rangle=(-1)^{\Lambda}\sqrt{2L+1}\sum_{m_am_b}\begin{bmatrix}1 & 1 & L\\ m_b & m_a & -\Lambda\end{bmatrix}|m_a\rangle\otimes|m_b\rangle\ . \qquad \text{(B4)}$$

Then

$$\langle L'\Lambda'|V_5|L\Lambda\rangle=\frac{54}{\pi}\frac{\langle r^2\rangle^2}{R^5}\begin{Bmatrix}1 & 1 & 2\\ 1 & 1 & 1\end{Bmatrix}^2$$
$$\times\sum_{\mu} g(2,\mu)\sqrt{(2L+1)(2L'+1)}$$
$$\times\sum_{\mu_a,\mu_{a'}}\sum_{\mu_b,\mu_{b'}}(-1)^{\mu_a+\mu_b}\begin{bmatrix}1 & 1 & L\\ \mu_b & \mu_a & -\Lambda\end{bmatrix}\begin{bmatrix}1 & 1 & L'\\ \mu_{b'} & \mu_{a'} & -\Lambda'\end{bmatrix}\begin{bmatrix}1 & 1 & 2\\ -\mu_a & \mu_{a'} & -\mu\end{bmatrix}\begin{bmatrix}1 & 1 & 2\\ -\mu_b & \mu_{b'} & \mu\end{bmatrix}. \qquad \text{(B5)}$$

Now

$$g(2,\mu)=\frac{4\pi}{5}\frac{4!}{(2-\mu)!(2+\mu)!} \qquad \text{(B6)}$$

and

$$\begin{Bmatrix}1 & 1 & 2\\ 1 & 1 & 1\end{Bmatrix}=\frac{1}{6}\ . \qquad \text{(B7)}$$

Hence

$$\langle L'\Lambda'|V_5|L\Lambda\rangle=\frac{54}{\pi}\frac{\langle r^2\rangle^2}{R^5}\frac{4\pi}{5}\frac{1}{36}X(L'\Lambda',L\Lambda)\ , \qquad \text{(B8)}$$

where

$$X(L'\Lambda',L\Lambda)=\sum_{\mu}\frac{4!}{(2-\mu)!(2+\mu)!}\sum_{\mu_a,\mu_{a'}}\sqrt{(2L+1)(2L'+1)}\begin{bmatrix}1 & 1 & L\\ \Lambda-\mu_a & \mu_a & -\Lambda\end{bmatrix}\begin{bmatrix}1 & 1 & L'\\ -\mu_{a'}+\Lambda' & \mu_{a'} & -\Lambda'\end{bmatrix}$$
$$\times(-1)^{\Lambda}\begin{bmatrix}1 & 1 & 2\\ -\mu_a & \mu_{a'} & -\mu\end{bmatrix}\begin{bmatrix}1 & 1 & 2\\ -\Lambda+\mu_a & -\mu_{a'}+\Lambda' & \mu\end{bmatrix}. \qquad \text{(B9)}$$

Numerical evaluation yields, for the nonvanishing contributions,

$$X(2222)=\tfrac{1}{5},\quad X(2121)=-\tfrac{4}{5},\quad X(2020)=\tfrac{6}{5}\ . \qquad \text{(B10)}$$

APPENDIX C: ASYMPTOTIC BEHAVIOR OF THE NONADIABATIC COUPLING

We express the components of the vector potential (42) in the form

$$\underline{\mathbf{A}}_{\theta}\equiv\underline{\mathbf{K}}_y\cos\phi-\underline{\mathbf{K}}_x\sin\phi\ ,$$
$$\underline{\mathbf{A}}_{\phi}=\underline{\mathbf{K}}_z(\cos\theta-1)-\sin\theta(\underline{\mathbf{K}}_x\cos\phi+\underline{\mathbf{K}}_y\sin\phi)\ , \qquad \text{(C1)}$$

where $\underline{\mathbf{K}}_i \equiv \langle \gamma(R)|\mathbf{K}_i|\gamma'(R)\rangle$ is the matrix, with respect to the BO states, of the ith component of the total electronic angular momentum $\mathbf{K}$. In Eq. (50) we introduced a transformation matrix $\underline{T}$ whose elements are

$$[\underline{T}(\theta\phi)]_{\gamma,\gamma'} = \langle j\Omega j_a j_b|T|j'_a j'_b \Omega' j\rangle$$
$$\equiv \langle j\Omega j_a j_b|\exp(-i\phi j_z)\exp(-i\theta j_y)\exp(i\phi j_z)|j'_a j'_b \Omega' j\rangle \ . \tag{C2}$$

Because atomic states $|j\Omega j_a j_b\rangle$ form a representation for $\mathbf{j}$, we may express $\underline{T}$ in the form

$$\underline{T} = \exp(-i\phi\underline{\mathbf{j}}_z)\exp(-i\theta\underline{\mathbf{j}}_y)\exp(i\phi\underline{\mathbf{j}}_z) \ , \tag{C3}$$

where $\underline{\mathbf{j}}$ is the matrix representation of $\mathbf{j}$ with respect to the atomic states. $\underline{T}$ transforms the components of $\underline{\mathbf{A}}$ into

$$\underline{\mathbf{A}}' = \underline{T}\,\underline{\mathbf{A}}\,\underline{T}^{-1} + i\underline{T}\nabla_{\mathbf{R}}\underline{T}^{-1} \ . \tag{C4}$$

We use (C3) to evaluate the angular components of the derivative term in Eq. (C4) and get

$$i\underline{T}\frac{\partial}{\partial\theta}\underline{T}^{-1} = \underline{T}[-\underline{\mathbf{j}}_y\cos\phi + \underline{\mathbf{j}}_x\sin\phi]\underline{T}^{-1} \ ,$$
$$i\underline{T}\frac{\partial}{\partial\phi}\underline{T}^{-1} = \underline{T}\underline{\mathbf{j}}_z\underline{T}^{-1} - \underline{\mathbf{j}}_z$$
$$= \underline{T}[\underline{\mathbf{j}}_z(1-\cos\theta) + \sin\theta(\underline{\mathbf{j}}_x\cos\phi + \underline{\mathbf{j}}_y\sin\phi)]\underline{T}^{-1} \ , \tag{C5}$$

where we made use of elementary properties of the rotation matrices. Combining the first term in (C4) and (C5), we get

$$\begin{aligned}\underline{\mathbf{A}}'_\theta &= \underline{T}(\underline{\mathbf{K}}_y - \underline{\mathbf{j}}_y)\underline{T}^{-1}\cos\phi - \underline{T}(\underline{\mathbf{K}}_x - \underline{\mathbf{j}}_x)\underline{T}^{-1}\sin\phi \ ,\\ \underline{\mathbf{A}}'_\phi &= \underline{T}(\underline{\mathbf{K}}_z - \underline{\mathbf{j}}_z)\underline{T}^{-1}(\cos\theta - 1) - \sin\theta\,\underline{T}[(\underline{\mathbf{K}}_x - \underline{\mathbf{j}}_x)\cos\phi + (\underline{\mathbf{K}}_y - \underline{\mathbf{j}}_y)\sin\phi]\underline{T}^{-1} \ .\end{aligned} \tag{C6}$$

Following the discussion in Sec. III we replace the matrix elements of the total molecular angular momentum $\mathbf{K}$ with the matrix elements of the two-center total angular momentum $\mathbf{j}$, or

$$\langle \gamma(R)|\mathbf{K}|\gamma'(R)\rangle = \langle \gamma(R)|\mathbf{j}|\gamma'(R)\rangle = [\underline{\mathbf{j}}]_{\gamma,\gamma'} + [\underline{\Delta\mathbf{j}}(R)]_{\gamma,\gamma'} \tag{C7}$$

where we have expressed it in terms of its asymptotic atomic limit $[\underline{\mathbf{j}}]_{\gamma,\gamma'} \equiv \langle \gamma|\mathbf{j}|\gamma'\rangle$, and a remainder term $\underline{\Delta\mathbf{j}}(R)$. The latter term gives the purely molecular contribution to the matrix element. Inserting (C7) into (C6) we obtain

$$\begin{aligned}\underline{\mathbf{A}}'_\theta &= \underline{T}\underline{\Delta\mathbf{j}}_y(R)\underline{T}^{-1}\cos\phi - \underline{T}\underline{\Delta\mathbf{j}}_x(R)\underline{T}^{-1}\sin\phi \ ,\\ \underline{\mathbf{A}}'_\phi &= -\sin\theta\,\underline{T}[\underline{\Delta\mathbf{j}}_x(R)\cos\phi + \underline{\Delta\mathbf{j}}_y(R)\sin\phi]\underline{T}^{-1} \ .\end{aligned} \tag{C8}$$

The quantities $\underline{\Delta\mathbf{j}}(R)$ may be evaluated, for large values of R, using perturbation theory. According to the multipole expansion (19), the leading-order correction to the atomic-state electronic wave functions, due to the atom-atom interaction, falls off no slower than R^{-3} in the asymptotic region. Therefore, the elements of $\underline{\Delta\mathbf{j}}(R)$, and, $\underline{\mathbf{A}}'_\theta, \underline{\mathbf{A}}'_\phi$, fall off no slower than R^{-3} at large R.

To evaluate the asymptotic limit of the radial component of the vector potential, we could transform the radial components, in the molecular gauge, into the atomic gauge by a similar procedure used above for the angular components. Instead, we evaluate it directly in the atomic gauge from the definition

$$\hat{\mathbf{R}}\cdot\mathbf{A}'_{\gamma,\gamma'}(\mathbf{R}) = i\langle \phi_\gamma|(\hat{\mathbf{R}}\cdot\nabla_{\mathbf{R}})|\phi_{\gamma'}\rangle \ , \tag{C9}$$

where now ϕ_γ are atomic states (49), and the bracket notation implies integration over all electronic coordinates. Taking the asymptotic limit we replace states ϕ_γ by their asymptotic form (79) to get

$$\lim_{R\to\infty}\hat{\mathbf{R}}\cdot\mathbf{A}'_{\gamma,\gamma'}(\mathbf{R}) = i\langle j_{b'}j_{a'}\Omega' j'|T(\mathbf{R})U^{-1}(\hat{\mathbf{R}})(\hat{\mathbf{R}}\cdot\nabla_{\mathbf{R}})U(\hat{\mathbf{R}})T^{-1}(\mathbf{R})|j\Omega j_a j_b\rangle$$
$$= i\langle j_{b'}j_{a'}\Omega' j'|\exp(-i\mathbf{P}\cdot\hat{\mathbf{z}}R)\exp(i\mathbf{P}\cdot\mathbf{R})(\hat{\mathbf{R}}\cdot\nabla_{\mathbf{R}})\exp(-i\mathbf{P}\cdot\mathbf{R})\exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)|j\Omega j_a j_b\rangle \ , \tag{C10}$$

where we used Eq. (84). These matrix elements are expectation values of the derivative operators with respect to the translated states

$$|j\Omega j_a j_b\rangle_O \equiv \exp(i\mathbf{P}\cdot\hat{\mathbf{z}}R)|j\Omega j_a j_b\rangle \ , \tag{C11}$$

which are independent of R,θ,ϕ [see Eq. (A4), and the discussion below it]. Therefore, we rewrite Eq. (C10),

$$\lim_{R\to\infty} -i\hat{\mathbf{R}}\cdot\mathbf{A}'_{\gamma,\gamma'}(\mathbf{R}) = {}_O\langle j_{b'}j_{a'}\Omega' j'|\exp(i\mathbf{P}\cdot\mathbf{R})\hat{\mathbf{R}}\cdot\nabla_{\mathbf{R}}\exp(-i\mathbf{P}\cdot\mathbf{R})|j\Omega j_a j_b\rangle_O$$
$$= {}_O\langle j_{b'}j_{a'}\Omega' j'|\hat{\mathbf{R}}\cdot(\nabla_{\mathbf{R}} - i\mathbf{P})|j\Omega j_a j_b\rangle_O = 0 \ , \tag{C12}$$

where we used the fact that the matrix elements for the dipole operator **P** vanish, and that states $|j\Omega j_a j_b\rangle_O$ are independent of **R**.

Finally, we evaluate the asymptotic limit of the nonadiabatic scalar potential matrix. In the atomic gauge its matrix elements are given by

$$B'_{\gamma,\gamma'}(\mathbf{R})=\sum_{k\neq\gamma\gamma'}\mathbf{A}'_{\gamma,k}(\mathbf{R})\cdot\mathbf{A}'_{k,\gamma'}(\mathbf{R}) , \tag{C13}$$

where the matrix elements

$$\mathbf{A}'_{\gamma,k}(\mathbf{R})$$

are defined above, and index k denotes atomic states not included in the channel set. We rewrite expression (C13) as [24]

$$\begin{gathered}-\underline{B}'(\mathbf{R})=i\nabla_{\mathbf{R}}\cdot\underline{\mathbf{A}}'+\underline{\mathbf{A}}'\cdot\underline{\mathbf{A}}'+\underline{C}'(\mathbf{R}) ,\\ \underline{C}'_{\gamma,\gamma'}(\mathbf{R})\equiv\langle\phi_\gamma|\nabla^2_{\mathbf{R}}|\phi_{\gamma'}\rangle .\end{gathered} \tag{C14}$$

The first two terms are evaluated using the asymptotic expression for $\underline{\mathbf{A}}'$ discussed above. To evaluate the last term we repeat steps (C10) through (C12), to get

$$\lim_{R\to\infty}\underline{C}'_{\gamma,\gamma'}(\mathbf{R})={}_O\langle j_{b'}j_{a'}\Omega'j'|(\nabla_{\mathbf{R}}-i\mathbf{P})^2|j\Omega j_a j_b\rangle_O . \tag{C15}$$

Because this expression contains a term quadratic in the dipole operator **P**, it does not vanish in the asymptotic limit. However, the nonvanishing terms contribute only to the diagonal components of $\underline{B}'$ and so they give rise to additional, but small, corrections to the asymptotic energy shifts.

APPENDIX D: INTEGRAL OF PRODUCTS OF WIGNER COEFFICIENTS

We need to evaluate

$$\int d\hat{\Omega}\, Y^*_{lm}(\theta\phi)Y_{l'm'}(\theta\phi)D^{j}_{\Omega,\Omega_1}(\phi,\theta,-\phi)D^{j'}_{\Omega_1\Omega'}(\phi,-\theta,-\phi) . \tag{D1}$$

We use the identity [26]

$$Y_{lm}(\theta\phi)=\left[\frac{2l+1}{4\pi}\right]^{1/2}\exp(i\phi m)d^{l}_{m0}(\theta) \tag{D2}$$

and definition (53) to rewrite Eq. (D1),

$$\frac{[l,l']^{1/2}}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\, d\theta\exp[i\phi(m'+\Omega'-m-\Omega)]d^{l}_{m0}(\theta)d^{l'}_{m'0}(\theta)d^{j}_{\Omega\Omega_1}(\theta)d^{j'}_{\Omega_1\Omega'}(-\theta) . \tag{D3}$$

We use the Clebsh-Gordon series [26] to express the product $d^{l}_{m0}(\theta)d^{j}_{\Omega\Omega_1}(\theta)$ in the form

$$d^{l}_{m0}(\theta)d^{j}_{\Omega\Omega_1}(\theta)=\sum_{Qq}[Q]\begin{bmatrix}l & j & Q\\ m & \Omega & q\end{bmatrix}\begin{bmatrix}l & j & Q\\ 0 & \Omega_1 & -\Omega_1\end{bmatrix}d^{Q}_{q-\Omega_1}(\theta) . \tag{D4}$$

Similarly, we get

$$d^{l'}_{m'0}(\theta)d^{j'}_{\Omega_1\Omega'}(-\theta)=\sum_{Qq}[Q]\begin{bmatrix}l' & j' & Q\\ m' & \Omega' & q\end{bmatrix}\begin{bmatrix}l' & j' & Q\\ 0 & \Omega_1 & -\Omega_1\end{bmatrix}d^{Q}_{q-\Omega_1}(\theta) . \tag{D5}$$

Using the selection rule $m+\Omega-m'-\Omega'=0$, and the identity

$$\int_0^{\pi}d\theta(\sin\theta)d^{Q}_{q,q'}(\theta)d^{Q'}_{q,q'}(\theta)=\frac{2\delta_{Q,Q'}}{2Q+1} , \tag{D6}$$

we get

$$\begin{aligned}&\int d\hat{\Omega}\, Y^*_{lm}(\theta\phi)Y_{l'm'}(\theta\phi)D^{j}_{\Omega,\Omega_1}(\phi,\theta,-\phi)D^{j'}_{\Omega_1\Omega'}(\phi,-\theta,-\phi)\\ &\qquad=[l,l']^{1/2}\sum_{qQ}[Q]\begin{bmatrix}l & j & Q\\ m & \Omega & q\end{bmatrix}\begin{bmatrix}l & j & Q\\ 0 & \Omega_1 & -\Omega_1\end{bmatrix}\begin{bmatrix}l' & j' & Q\\ m' & \Omega' & q\end{bmatrix}\begin{bmatrix}l' & j' & Q\\ 0 & \Omega_1 & -\Omega_1\end{bmatrix} .\end{aligned} \tag{D7}$$

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