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Electronic Interaction Anisotropy between Atoms in Arbitrary Angular Momentum States[†]

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A general tensorial expansion for the interaction potential between two atoms in arbitrary angular momentum states is derived and the relations between the expansion coefficients and the Born−Oppenheimer potentials of the diatomic molecule are obtained. It is demonstrated that a complete expansion of the interaction potential must employ tensors that are invariant under the inversion of the coordinate system, and the expansion in terms of conventional spherical harmonics is not adequate for the case of two atoms in states with nonzero electronic orbital angular momenta. The concept of the interaction anisotropy between two open-shell atoms is introduced. The correctness of the formalism is demonstrated by the example of two atoms in *P* states.

I. Introduction

Quantum chemistry calculations give an electronic interaction potential between two atoms in the molecule-fixed coordinate system. Collisions of atoms are described in the laboratory-fixed coordinate system and atomic collision theories are based on transformation relations between the molecule-fixed and space-fixed wave functions. The complexity of the wave function transformations often conceals the role of the electronic interaction potential in determining the dynamics of inelastic atomic collisions. It is desirable, therefore, to have a space-fixed representation of the electronic interaction potential which would allow for an analysis of collision mechanisms. Such potential forms would reflect the anisotropy of atom−atom interaction and provide simple techniques for the evaluation of the interaction potential matrix in a space-fixed basis of wave functions.

Callaway and Bauer[1] suggested that the interaction between an atom in a *P* state and a closed-shell atom can be represented by an effective potential of the form

$$V(\boldsymbol{R}, \hat{r}) = \sum_{k=0,2} V_k(R) P_k(\hat{r}\cdot\hat{R}) \tag{1}$$

where $\boldsymbol{R}$ is the vector joining the centers of mass of the atoms, $\boldsymbol{r}$ denotes collectively the position vectors of the electrons in the *P*-state atom and P_k is the Legendre polynomial of *k*th order.[2] Reid and Dalgarno[3,4] used expansion 1 to formulate a theory for fine-structure transitions in collisions of *P*-state atoms with helium. It follows from their expressions that collisional transfer of angular momentum is driven by the term $V_{k=2}(R)$ and the collision problem is equivalent to that of a diatomic molecule interacting with an inert gas atom. The part of the interaction with $k = 2$ represents the anisotropy of the electronic interaction between an atom in a *P* state and a closed-shell atom. Aquilanti and Grossi[5] derived the relations between the Legendre expansion terms V_k and the Born−Oppenheimer potentials of the diatomic molecule and generalized expression 1 to describe interactions between closed-shell atoms and atoms with higher electronic orbital angular momentum. The Legendre polynomials can be expanded in spherical harmonics

$$P_k(\hat{r}\cdot\hat{R}) = \frac{4\pi}{2k+1}\sum_q (-1)^q Y_{k-q}(\hat{R}) Y_{kq}(\hat{r}) \tag{2}$$

where $\hat{R}$ and $\hat{r}$ are the unit vectors with the direction of $\boldsymbol{R}$ and $\boldsymbol{r}$ defined in the laboratory coordinate system.[6,7] The results of Aquilanti and Grossi thus provided a direct representation of the interaction potential operator in the space-fixed coordinate frame. This proved to be useful for the analysis of atomic collisions in external fields and collisional reorientation of angular momentum at low energies.[8−10]

Dubernet and Hutson[11] presented a discussion of atom−molecule van der Waals complexes containing open-shell atoms and Σ-state molecules. The discussion was based on the assumption that the atom−molecule interaction potential can be represented by expansions commonly used in closed-shell diatom−diatom systems. Both space-fixed

$$V(\boldsymbol{R}, \hat{r}_{\mathrm{m}}, \hat{r}) = \sum_{k_1,k_2,k} \upsilon_{k_1,k_2,k}(R) \sum_{q_1,q_2,q} Y^*_{kq}(\hat{R}) \langle k_1 q_1 k_2 q_2 | kq\rangle Y_{k_1 q_1}(\hat{r}_{\mathrm{m}}) Y_{k_2 q_2}(\hat{r}) \tag{3}$$

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TABLE 1: Definition of Atomic and Molecular Quantum Numbers Used in This Article

L_A	electronic orbital angular momentum of atom A
S_A	electronic spin angular momentum of atom A
j_A	total electronic angular momentum of atom A: $\mathbf{j}_A = \mathbf{L}_A + \mathbf{S}_A$
L_B	electronic orbital angular momentum of atom B
S_B	electronic spin angular momentum of atom B
j_B	total electronic angular momentum of atom B: $\mathbf{j}_B = \mathbf{L}_B + \mathbf{S}_B$
L	total electronic orbital angular momentum of the diatomic system: $\mathbf{L} = \mathbf{L}_A + \mathbf{L}_B$
S	total spin angular momentum of the diatomic system: $\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B$
j	total electronic angular momentum of the diatomic system: $\mathbf{j} = \mathbf{j}_A + \mathbf{j}_B$
l	rotational angular momentum of the nuclei
J	total angular momentum of the system: $\mathbf{J} = \mathbf{j} + \mathbf{l}$
Λ_A	projection of $\mathbf{L}_A$ on the interatomic axis (body-fixed projection)
M_{L_A}	projection of $\mathbf{L}_A$ on the space-fixed quantization axis
m_{j_A}	projection of $\mathbf{j}_A$ on the space-fixed quantization axis
Λ_B	projection of $\mathbf{L}_B$ on the interatomic axis (body-fixed projection)
M_{L_B}	projection of $\mathbf{L}_B$ on the space-fixed quantization axis
m_{j_B}	projection of $\mathbf{j}_B$ on the space-fixed quantization axis
M_S	projection of $\mathbf{S}$ on the space-fixed quantization axis
m_j	projection of $\mathbf{j}$ on the space-fixed quantization axis
m_l	projection of $\mathbf{l}$ on the space-fixed quantization axis
Λ	projection of $\mathbf{L}$ on the interatomic axis (body-fixed projection)
Σ	projection of $\mathbf{S}$ on the interatomic axis (body-fixed projection)
Ω	projection of $\mathbf{J}$ and $\mathbf{j}$ on the interatomic axis: $\Omega = \Lambda + \Sigma$
M	projection of $\mathbf{J}$ on the space-fixed quantization axis

and body-fixed expansions were introduced and expressions for matrix elements in different coupling cases were derived.[12] The vector $\mathbf{r}_m$ describes the rotation of the diatomic molecule, and $\langle k_1q_1k_2q_2|kq\rangle$ is a Clebsch-Gordan coefficient. Zeimen et al.[13] obtained the same equation for the F(^{2}P) + H$_2$ interaction potential using a spherical tensor expansion invariant under inversion and rotation of the coordinate system.

The work of Aquilanti and Grossi, Dubernet and Hutson, and Zeimen et al. suggested that an open-shell atom behaves effectively as a homonuclear diatomic molecule upon interaction with a closed-shell atom or molecule. In the present work, we extend the tensor formalism used by Zeimen et al. to derive an effective operator form for interaction between two atoms in arbitrary angular momentum states. We show that an adequate expansion of the interaction potential between two open-shell atoms must employ spherical tensors invariant under inversion of the coordinate system and eq 3 is incomplete for the case of two atoms with nonzero electronic orbital angular momenta. We derive relations between the angular expansion terms and the Born−Oppenheimer potentials of the diatomic molecule and introduce the concept of interaction anisotropy in two open-shell atoms. On the basis of the expansions obtained, we formulate a theory of atom−atom collisions in external fields. Santra and Greene[14] have recently presented a tensorial analysis of long-range interaction potentials between two atoms in P states. The equations obtained in this work can be mapped on their expansions, thus providing the relationship between the Born−Oppenheimer states and the long-range terms of the interaction potential. The formalism presented here can be used for the analysis of Zeeman relaxation transitions whose occurrence may limit experiments on evaporative cooling and the magnetic trapping of atoms. Trapped atoms are usually in the Zeeman state with the highest energy and the Zeeman relaxation leads to trap loss.

Table 1 defines the notation for the atomic and molecular quantum numbers used in this article.

II. Effective Potential for Two Open-Shell Atoms

Consider two interacting atoms A and B in the states with electronic orbital ($\mathbf{L}_A$ and $\mathbf{L}_B$) and spin ($\mathbf{S}_A$ and $\mathbf{S}_B$) angular momenta. The molecular states $|L\Lambda\rangle|S\Sigma\rangle$ are defined in the limit of large interatomic distance R by the Clebsch-Gordan theorem

$$|L\Lambda(L_AL_B)\rangle = \sum_{\Lambda_A}\sum_{\Lambda_B}|L_A\Lambda_A\rangle|L_B\Lambda_B\rangle\langle L_A\Lambda_A L_B\Lambda_B|L\Lambda\rangle \tag{4}$$

and the analogous equation for $|S\Sigma\rangle$. The products $|L\Lambda\rangle|S\Sigma\rangle$ are related to molecular Born−Oppenheimer functions $|c\Lambda S\Sigma\rangle$ as follows:

$$|c\Lambda S\Sigma\rangle = \sum_{L}|L\Lambda(L_AL_B)\rangle|S\Sigma(S_AS_B)\rangle U^{\Lambda}_{L,c} \tag{5}$$

The quantum number c is used to distinguish between molecular states corresponding to the same values of Λ and S. Transformation 5 is valid at large interatomic separation where the atomic wave functions do not overlap and the exchange interaction is absent. The transformation coefficients $U^{\Lambda}_{L,c}$ are, therefore, independent of spin S. We propose to use transformation 5 at arbitrary values of R which leads to an effective representation of the electronic potential appropriate for the description of slow atom−atom collisions and the dissociation of diatomic molecules. This approach is consistent with previous studies of atomic collisions and molecular dissociation[15−18] which used a close coupling expansion in terms of atomic wave functions corresponding to states with given angular momenta L_A and L_B. It neglects the nonadiabatic couplings to other electronic states, which may be significant if states exist with adiabatic potentials that are close in energy.

The matrix elements of the electronic Hamiltonian

$$\langle c\Lambda S\Sigma|\hat{V}|c\Lambda S\Sigma\rangle = V_{c\Lambda S}(R) \tag{6}$$

are the nonrelativistic Born−Oppenheimer potentials of the molecule AB. The operator $\hat{V}$ in eq 6 can be expanded as

$$\hat{V} = \sum_{c\Lambda S\Sigma}|c\Lambda S\Sigma\rangle V_{c\Lambda S}(R)\langle c\Lambda S\Sigma| \tag{7}$$

which can be rewritten in the effective potential form

$$\hat{V} = \sum_{S}\sum_{\Sigma}|S\Sigma\rangle\langle S\Sigma|\hat{V}^S \tag{8}$$

where

$$\hat{V}^S = \sum_{L}\sum_{L'}\sum_{\Lambda}|L\Lambda(L_AL_B)\rangle\langle L'\Lambda(L_AL_B)|V^S_{L\Lambda;L'\Lambda}(R) \tag{9}$$

and

$$V^S_{L\Lambda;L'\Lambda}(R) = \sum_{c}U^{\Lambda,*}_{L,c}V_{c\Lambda S}(R)U^{\Lambda}_{L',c} \tag{10}$$

The transformation $U^{\Lambda}_{L,c}$ is an identity matrix when one of the interacting atoms is in an S state or when the quantum number L can be assigned to each state $V_{c\Lambda S}$ (see sections IV and V). Otherwise, it can be determined by numerical diagonalization of the leading term in the interaction potential multipole expansion at long range as was done, for example, for the O$^-$(^{2}P)−O(^{3}P) system in ref 19.

The summation over L and L' in eq 9 runs from $|L_A - L_B|$ to $L_A + L_B$ and S takes the values from $|S_A - S_B|$ to $S_A + S_B$. S_A, S_B, L_A, and L_B are kept fixed. This corresponds to the model of

Callaway and Bauer[1] and Dubernet and Hutson,[11] who integrated over the electronic distance coordinates and defined the effective potential for atom−atom and atom−molecule interactions as a function of electronic angular coordinates. Using the definition of the spherical tensor operators[20]

$$\hat{T}^k_Q(L, L') = \sum_{\Lambda}\sum_{\Lambda'} |L\Lambda(L_AL_B)\rangle\langle L'\Lambda'(L_AL_B)|(-1)^{L-\Lambda}\begin{pmatrix} L & k & L' \\ -\Lambda & Q & \Lambda' \end{pmatrix}(k)^{1/2} \tag{11}$$

and the orthogonality of 3j symbols, we rewrite eq 9 as a series over $\hat{T}^k_Q(L, L')$

$$\hat{V}^S = \sum_L\sum_{L'}\sum_k\sum_Q (k)^{1/2}\hat{T}^k_Q(L, L')\sum_{\Lambda}(-1)^{L-\Lambda}\begin{pmatrix} L & k & L' \\ -\Lambda & Q & \Lambda \end{pmatrix}V^S_{L\Lambda;L'\Lambda} \tag{12}$$

The symbols in parentheses are 3j symbols and $(k)^{1/2}$ is a shorthand notation for $(2k + 1)^{1/2}$.

Because the functions $|L\Lambda(L_AL_B)\rangle$ are referred to the molecular axis, eq 11 defines the tensor $\hat{T}^k_Q(L, L')$ in the body-fixed frame. It can be expressed in terms of the tensor $\hat{T}^k_q(L, L')$ defined in the space-fixed frame as follows:

$$\hat{T}^k_Q(L, L') = \sum_q \hat{T}^k_q(L, L')D^k_{qQ}(\hat{R}) \tag{13}$$

The $\hat{V}$ operator does not couple states with different values of Λ so that $Q = 0$ and the Wigner rotation matrix elements $D^k_{q,Q=0}$ are proportional to spherical harmonics $Y^*_{kq}(\hat{R})$ that depend on the polar angles of the vector $\hat{R}$.

The tensor $\hat{T}^k_q(L, L')$ is related to the tensorial product of tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ describing the rotation of electrons in atoms A and B, respectively[20]

$$\hat{T}^k_q(L, L') = \sum_{k_1}\sum_{k_2}\begin{Bmatrix} L_A & L_A & k_1 \\ L_B & L_B & k_2 \\ L & L' & k \end{Bmatrix}[(k_1)(k_2)(L)(L')]^{1/2}[\hat{T}^{k_1}(L_A)\otimes\hat{T}^{k_2}(L_B)]^{(k)}_q \tag{14}$$

where the symbol in curly brackets is a 9j symbol and

$$[\hat{T}^{k_1}(L_A)\otimes\hat{T}^{k_2}(L_B)]^{(k)}_q = \sum_{q_1}\sum_{q_2}\langle k_1q_1k_2q_2|kq\rangle\hat{T}^{k_1}_{q_1}(L_A)\hat{T}^{k_2}_{q_2}(L_B) \tag{15}$$

The tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ are defined as

$$\hat{T}^{k_1}_{q_1}(L_A) = \sum_{M_A}\sum_{M'_A}|L_AM_A\rangle\langle L_AM'_A|(-1)^{L_A-M_A}\begin{pmatrix} L_A & k_1 & L_A \\ -M_A & q_1 & M'_A \end{pmatrix}(k_1)^{1/2} \tag{16}$$

and

$$\hat{T}^{k_2}_{q_2}(L_B) = \sum_{M_B}\sum_{M'_B}|L_BM_B\rangle\langle L_BM'_B|(-1)^{L_B-M_B}\begin{pmatrix} L_B & k_2 & L_B \\ -M_B & q_2 & M'_B \end{pmatrix}(k_2)^{1/2} \tag{17}$$

where M_A and $M_A{}'$ and M_B and $M_B{}'$ are the projections of $\boldsymbol{L}_A$ and $\boldsymbol{L}_B$ on the space-fixed quantization axis.

Using eqs 12−14, we can write the effective potential $\hat{V}^S$ as a tensorial expansion in the space-fixed coordinate frame

$$\hat{V}^S = (4\pi)^{1/2}\sum_{k_1}\sum_{k_2}\sum_k V^S_{k_1,k_2,k}(R)\sum_{q_1}\sum_{q_2}\sum_q(-1)^{k_1-k_2}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix}\hat{T}^{k_1}_{q_1}(L_A)\hat{T}^{k_2}_{q_2}(L_B)Y_{kq}(\hat{R}) \tag{18}$$

with the expansion coefficients

$$V^S_{k_1,k_2,k}(R) = \sum_L\sum_{L'}\sum_{\Lambda}V^S_{L\Lambda;L'\Lambda}(R)(-1)^{L-\Lambda}\begin{pmatrix} L & k & L' \\ -\Lambda & 0 & \Lambda \end{pmatrix}[(k_1)(k_2)(k)(L)(L')]^{1/2}\begin{Bmatrix} L_A & L_A & k_1 \\ L_B & L_B & k_2 \\ L & L' & k \end{Bmatrix} \tag{19}$$

Equation 18 is the space-fixed representation of the effective electronic potential for interaction between two atoms in arbitrary states, and eq 19 provides the relation between the expansion coefficients $V^S_{k_1,k_2,k}$ and the matrix elements $V^S_{L\Lambda,L'\Lambda}$ which can be obtained from quantum chemistry calculations using eq 10.

Since the operator of the total interaction potential is diagonal also in the $|SM_S\rangle$ representation, eq 8 can be rewritten as

$$\hat{V} = \sum_S\sum_{M_S}|SM_S\rangle\langle SM_S|\hat{V}^S \tag{20}$$

thus providing the space-fixed effective representation of the total interaction potential.

Expansion 26 is different from eq 3 appropriate for two closed-shell diatomic molecules. A general relationship between the spherical harmonics and the spherical tensors $\hat{T}^k_q(l, l')$ is given in Appendix A. In the case considered here, the angular momenta L_A and L_B are good quantum numbers and the relationships between the tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ and the corresponding spherical harmonics are reduced to

$$Y_{k_1q_1}(\hat{r}_A) = \hat{T}^{k_1}_{q_1}(L_A)c_{k_1}(L_A) \tag{21}$$

and

$$Y_{k_2q_2}(\hat{r}_B) = \hat{T}^{k_2}_{q_2}(L_B)c_{k_2}(L_B) \tag{22}$$

with the coefficients $c_{k_1}(L_A)$ and $c_{k_2}(L_B)$ defined by

$$c_{k_1}(L_A) = (-1)^{L_A}\frac{(L_A)}{\sqrt{4\pi}}\begin{pmatrix} L_A & k_1 & L_A \\ 0 & 0 & 0 \end{pmatrix} \tag{23}$$

and the analogous expression for $c_{k_2}(L_B)$. The vectors $\hat{r}_A$ and $\hat{r}_B$ specify the orientation of the electronic orbitals of atoms A and B. It follows from eqs 21 and 22 that the coefficients of our tensorial expansion 18 are related to the coefficients of the spherical harmonics expansion 3 by

$$v_{k_1,k_2,k} = V_{k_1,k_2,k}/c_{k_1}(L_A)c_{k_2}(L_B) \tag{24}$$

Because the products of the 3j symbols

$$\begin{pmatrix} L_A & k_1 & L_A \\ 0 & 0 & 0 \end{pmatrix} \text{ and } \begin{pmatrix} L_B & k_2 & L_B \\ 0 & 0 & 0 \end{pmatrix}$$

vanish when k_1 or k_2 is odd, relation 24 does not exist for odd values of k_1 or k_2. Expansion 18 may thus include terms that cannot occur in the spherical harmonics expansion 3. The nonequivalence of expansions 18 and 3 arises from the different behavior of the tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ and the spherical harmonics under inversion of the coordinate system. As follows from definitions 16 and 17, the tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ are invariant under the inversion, whereas the spherical harmonics $Y_{k_1q_1}$ and $Y_{k_2q_2}$ acquire the factors $(-1)^{k_1}$ and $(-1)^{k_2}$. It will be shown in the following sections that the invariance of the tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ under inversion is critical for the complete representation of the potential (18).

III. Interaction Anisotropy in Two Open-Shell Atoms

The states of the separated atoms A and B are characterized by the total electronic angular momenta $\boldsymbol{j}_A$ and $\boldsymbol{j}_B$ and their projections m_{j_A} and m_{j_B} on the space-fixed quantization axis. Collisions between A and B may induce transitions between the angular momentum states. The angular momentum transfer or reorientation occurs due to the anisotropy of the atom−atom interaction. We distinguish between the internal anisotropy and the external anisotropy. The internal anisotropy drives transitions $|j_Am_{j_A}\rangle \rightarrow |j'_A, m_{j_A} + \Delta m_{j_A}\rangle$ that are accompanied by the transitions $|j_Bm_{j_B}\rangle \rightarrow |j'_B, m_{j_B} - \Delta m_{j_A}\rangle$ and in which there is no change in the total electronic angular momentum $\boldsymbol{j}$ and projection m_j. The internal anisotropy does not couple the electronic motion with the orbital motion of the nuclei, so it cannot induce angular momentum transfer in atoms with maximal or minimal projections of the electronic angular momentum (maximally or minimally stretched atoms). The external anisotropy drives transitions $|j_Am_{j_A}\rangle \rightarrow |j'_Am'_{j_A}\rangle$ that occur through the coupling of the total electronic angular momentum $\boldsymbol{j}$ with the rotational momentum of the nuclei $\boldsymbol{l}$. The external anisotropy is critical for Zeeman relaxation in maximally stretched (trapped) atoms. We show later in this section that the internal and external interaction anisotropies may be defined in terms of the expansion coefficients $V^S_{k_1,k_2,k}$ of eq 18.

The internal interaction anisotropy includes the anisotropy arising from rotation of the atomic orbitals of atom A with respect to the atomic orbitals of atom B and the spin anisotropy due to the different exchange interactions of electrons in the molecular states with different total spin S. We postpone the discussion of the spin anisotropy until section VI and assume for this section that the electronic spin in atom B is zero. Thus, the molecular states all have spin $S = S_A$.

Using the relation between the tensor $\hat{T}^{k_1}_{q_1}(j_A, j'_A)$ that operates in the space of the functions $|j_Am_{j_A}\rangle$ and the $\hat{T}^{k_1}_{q_1}(L_A)$ tensor[20]

$$\hat{T}^{k_1}_{q_1}(L_A) = \sum_{j_A}\sum_{j'_A}\hat{T}^{k_1}_{q_1}(j_A, j'_A)(-1)^{L_A+S_A+j'_A+k_1}[(j_A)(j'_A)]^{1/2}\begin{Bmatrix} L_A & j_A & S_A \\ j'_A & L_A & k_1 \end{Bmatrix} \tag{25}$$

where the symbol in braces is a 6j symbol, we may express the matrix elements of interaction potential 18 in the basis of direct products $|j_Am_{j_A}\rangle|j_Bm_{j_B}\rangle|lm_l\rangle$. They have the form

$$\begin{aligned}\langle j_Am_{j_A}|\langle j_Bm_{j_B}|\langle lm_l|\hat{V}|j'_Am'_{j_A}\rangle|j'_Bm'_{j_B}\rangle|l'm'_l\rangle = \\ \sum_{k_1}\sum_{k_2}\sum_{k}V_{k_1,k_2,k}(R)\,[(k_1)(k_2)(k)(l\,)(l')(j_A)(j'_A)]^{1/2} \\ (-1)^{L_A+S_A+j_A+j'_A+j_B+k_2-m_{j_A}-m_{j_B}-m_l}\sum_{q_1}\sum_{q_2}\sum_{q}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix} \\ \begin{pmatrix} j_A & k_1 & j'_A \\ -m_{j_A} & q_1 & m'_{j_A} \end{pmatrix}\begin{pmatrix} j_B & k_2 & j'_B \\ -m_{j_B} & q_2 & m'_{j_B} \end{pmatrix}\begin{pmatrix} l & k & l' \\ -m_l & q & m'_l \end{pmatrix}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{Bmatrix} L_A & j_A & S_A \\ j'_A & L_A & k_1 \end{Bmatrix}\end{aligned} \tag{26}$$

We note that $j_B = L_B$, $m_{j_B} = M_{L_B}$, and $m'_{j_B} = M'_{L_B}$.

Equation 26 establishes that the term $V_{k_1=0,k_2=0,k=0}$ contributes only to the diagonal elements of the matrix so that the V_{000} part of interaction 18 is purely isotropic. The terms with $k_1 = k_2 > 0$ and $k = 0$ may couple the states with different values of (j_A, m_{j_A}) and (j_B, m_{j_B}) but they do not couple the states with different values of l, j, m_l, or $m_j = m_{j_A} + m_{j_B}$. These terms represent the internal anisotropy. The terms with $k > 0$ couple different l and j states. They correspond to the external anisotropy.

IV. Matrix Elements in the Scattering Basis

The state of the diatomic molecule AB is described by the total angular momentum $\boldsymbol{J}$, the projection of $\boldsymbol{L}$ onto the AB axis Λ and the value of the total spin $\boldsymbol{S}$. Singer et al.[15] showed that the molecular states $|JMc\Lambda S\Sigma\rangle$ are related in the limit of large interatomic distances R to space-fixed atomic states in the fully coupled representation $|JMjlj_Aj_B\rangle$ as follows:

$$\begin{aligned}|JMjlj_Aj_B\rangle = \sum_{c}\sum_{\Lambda}\sum_{S}\sum_{\Sigma}|JMc\Lambda S\Sigma\rangle(-1)^{l-J-\Omega}\langle j - \Omega J\Omega|l0\rangle \\ [(S)(j_A)(j_B)]^{1/2}\sum_{L}(L)^{1/2}\sum_{\Lambda_A}\sum_{\Lambda_B}\langle L_A\Lambda_AL_B\Lambda_B|L\Lambda\rangle\langle L\Lambda S\Sigma|j\Omega\rangle \\ \begin{Bmatrix} L_A & S_A & j_A \\ L_B & S_B & j_B \\ L & S & j \end{Bmatrix}\langle\Lambda_A\Lambda_B|c\Lambda\rangle\end{aligned} \tag{27}$$

where $\langle\Lambda_A\Lambda_B|\Lambda\rangle$ is the transformation related to the matrix $U^{\Lambda}_{L,c}$ in eq 10 through the equation

$$U^{\Lambda}_{L,c} = \sum_{\Lambda_A}\sum_{\Lambda_B}\langle\Lambda_A\Lambda_B|c\Lambda\rangle\langle L_A\Lambda_AL_B\Lambda_B|L\Lambda\rangle \tag{28}$$

The functions $|JMjlj_Aj_B\rangle$ are defined as

$$\begin{aligned}|JMjlj_Aj_B\rangle = \sum_{M_{L_A}}\sum_{M_{S_A}}\sum_{M_{L_B}}\sum_{M_{S_B}}\sum_{m_{j_A}}\sum_{m_{j_B}}\sum_{m_j}\sum_{m_l}|L_AM_{L_A}\rangle|S_AM_{S_A}\rangle \\ |L_BM_{L_B}\rangle|S_BM_{S_B}\rangle|lm_l\rangle\,\langle L_AM_{L_A}S_AM_{S_A}|j_Am_{j_A}\rangle \\ \langle L_BM_{L_B}S_BM_{S_B}|j_Bm_{j_B}\rangle\langle j_Am_{j_A}j_Bm_{j_B}|jm_j\rangle\langle jm_jlm_l|JM\rangle\end{aligned} \tag{29}$$

Relationship 27 was used by several authors as a basis for atomic collision theories[16−18,22−25] and diatomic molecule dissociation studies.[26−41]

The basis $|JMjlj_Aj_B\rangle$ is the most convenient representation of the wave function for studies of collisions in the absence of external fields. The total angular momentum J is a good quantum number and the matrix elements of the Hamiltonian are independent of M. The matrix elements of the operator (20) in the basis $|JMjlj_Aj_B\rangle$ can be evaluated analytically. To do that, we express the wave functions $|JMjlj_Aj_B\rangle$ in terms of the uncoupled space-fixed basis functions as follows:

$$|JMjlj_\mathrm{A}j_\mathrm{B}\rangle = \sum_S\sum_{M_S}\sum_{m_j}\sum_{m_l}\sum_{M_{L_A}}\sum_{M_{L_B}}\sum_f\sum_{m_f}|L_\mathrm{A}M_{L_A}\rangle|L_\mathrm{B}M_{L_B}\rangle|SM_S\rangle |lm_l\rangle\,\langle jm_jlm_l|JM\rangle\langle L_\mathrm{A}M_{L_\mathrm{A}}L_\mathrm{B}M_{L_\mathrm{B}}|fm_f\rangle\langle fm_fSM_S|jm_j\rangle [(S)(f)(j_\mathrm{A})(j_\mathrm{B})]^{1/2}\begin{Bmatrix} L_\mathrm{A} & S_\mathrm{A} & j_\mathrm{A} \\ L_\mathrm{B} & S_\mathrm{B} & j_\mathrm{B} \\ f & S & j \end{Bmatrix} \quad (30)$$

The integrals

$$\langle L_\mathrm{A}M_{L_\mathrm{A}}|\langle L_\mathrm{B}M_{L_\mathrm{B}}|\langle SM_S|\langle lm_l|\hat{V}|L_\mathrm{A}M'_{L_\mathrm{A}}\rangle|L_\mathrm{B}M'_{L_\mathrm{B}}\rangle|S'M'_S\rangle|l'm'_l\rangle = \delta_{SS'}\delta_{M_SM_S'}\langle L_\mathrm{A}M_{L_\mathrm{A}}|\langle L_\mathrm{B}M_{L_\mathrm{B}}|\langle lm_l|\hat{V}^S|L_\mathrm{A}M'_{L_\mathrm{A}}\rangle|L_\mathrm{B}M'_{L_\mathrm{B}}\rangle|l'm_l'\rangle \quad (31)$$

can be evaluated using the Wigner-Eckart theorem. They are

$$\langle L_\mathrm{A}M_{L_\mathrm{A}}|\langle L_\mathrm{B}M_{L_\mathrm{B}}|\langle lm_l|\hat{V}^S|L_\mathrm{A}M'_{L_\mathrm{A}}\rangle|L_\mathrm{B}M'_{L_\mathrm{B}}\rangle|l'm_l'\rangle = \sum_{k_1}\sum_{k_2}\sum_k V^S_{k_1,k_2,k}(R)\sum_{q_1}\sum_{q_2}\sum_q(-1)^{k_1-k_2}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} [(l)(l')(k_1)(k_2)(k)]^{1/2}\,(-1)^{L_\mathrm{A}-M_{L_\mathrm{A}}+L_\mathrm{B}-M_{L_\mathrm{B}}-m_l}\begin{pmatrix} L_\mathrm{A} & k_1 & L_\mathrm{A} \\ -M_{L_\mathrm{A}} & q_1 & M'_{L_\mathrm{A}} \end{pmatrix} \begin{pmatrix} L_\mathrm{B} & k_2 & L_\mathrm{B} \\ -M_{L_\mathrm{B}} & q_2 & M'_{L_\mathrm{B}} \end{pmatrix}\begin{pmatrix} l & k & l' \\ -m_l & q & m'_l \end{pmatrix} \quad (32)$$

Combining eqs 30 and 32 and using repeatedly eq 26 of section 8.7.4 in the book of Varshalovich et al.,[6] we obtain, after some angular momentum algebra, the matrix elements of the interaction potential

$$\langle JMjlj_\mathrm{A}j_\mathrm{B}|\hat{V}|JMj'l'j_\mathrm{A}'j_\mathrm{B}'\rangle = \sum_S\sum_{k_1}\sum_{k_2}\sum_k V^S_{k_1,k_2,k}(R)\sum_f\sum_{f'} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}[(j_\mathrm{A})(j_\mathrm{A}')(j_\mathrm{B})(j_\mathrm{B}')(j)(j')(l)(l')(S)^2(k_1)(k_2)(k)(f)^2(f')^2]^{1/2} (-1)^{f+k+J-S}\begin{Bmatrix} L_\mathrm{A} & S_\mathrm{A} & j_\mathrm{A} \\ L_\mathrm{B} & S_\mathrm{B} & j_\mathrm{B} \\ f & S & j \end{Bmatrix}\begin{Bmatrix} L_\mathrm{A} & S_\mathrm{A} & j_\mathrm{A}' \\ L_\mathrm{B} & S_\mathrm{B} & j_\mathrm{B}' \\ f' & S & j' \end{Bmatrix}\begin{Bmatrix} L_\mathrm{A} & L_\mathrm{A} & k_1 \\ L_\mathrm{B} & L_\mathrm{B} & k_2 \\ f & f' & k \end{Bmatrix} \begin{Bmatrix} j & j' & k \\ l' & l & J \end{Bmatrix}\begin{Bmatrix} j & j' & k \\ f' & f & S \end{Bmatrix} \quad (33)$$

Equation 33 can also be derived with graphical methods of angular momentum algebra as shown in Appendix B.

The total parity of the system given by $(-1)^{L_\mathrm{A}+L_\mathrm{B}+l}$ is conserved and the interaction potential operator 18 cannot couple the states with $l - l'$ odd when both L_A and L_B are conserved. The index k, therefore, takes only even values. There is no restriction on the values of k_1 and k_2 which vary from 0 to $2L_\mathrm{A}$ and $2L_\mathrm{B}$, respectively.

Equation 33 emphasizes that a general space-fixed expansion of the atom−atom interaction potential must be of the form (18) rather than the spherical harmonics expansion 3. If we had used spherical harmonics instead of the tensors $\hat{T}^{k_1}_{q_1}(L_\mathrm{A})$ and $\hat{T}^{k_2}_{q_2}(L_\mathrm{B})$ in expansion 18, eq 33 would contain the products of three $3j$ symbols

$$\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L_\mathrm{A} & k_1 & L_\mathrm{A} \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L_\mathrm{B} & k_2 & L_\mathrm{B} \\ 0 & 0 & 0 \end{pmatrix} \quad (34)$$

and only the terms with even k_1 and k_2 would contribute to the matrix elements. Although this is sufficient for the case when one of the atoms is in the electronic S state, the terms with even values of k_1 and k_2 do not form a complete representation of the interaction potential between two atoms in arbitrary states. The lack of completeness of the spherical harmonics expansion will be illustrated in the example of two atoms in P states in the next section.

V. Interaction of Two *P*-State Atoms

It was noted by Zygelman and co-workers[16,17] that the long-range interaction between two atoms in P states does not couple different L states of the molecule (see also ref 42). The Born−Oppenheimer potentials of the molecule, therefore, may be labeled by the quantum number L that becomes the total electronic orbital angular momentum of AB in the limit $R = \infty$.[16] The transformation $U^\Lambda_{L,c}$ in eq 10 is an identity matrix. Zygelman and co-workers[16] presented a table identifying the Born−Oppenheimer potentials with the $V_\Lambda(L, S) = V^S_{L\Lambda;L\Lambda}$ terms for the case of two oxygen atoms in the ^3P state (see Table 1 of their paper). Similar correlations can be made for any homonuclear molecule composed of two atoms in P states.

For $L_\mathrm{A} = L_\mathrm{B} = 1$, eq 19 gives the following relations between the expansion coefficients $V^S_{k_1,k_2,k}$ and the Born−Oppenheimer potentials $V_\Lambda(L, S)$

$$V_{000} = \frac{1}{3}[V_\Sigma(L=0) + V_\Sigma(L=1) + V_\Sigma(L=2) + 2V_\Pi(L=1) + 2V_\Pi(L=2) + 2V_\Delta(L=2)]$$

$$V_{110} = \frac{1}{\sqrt{3}}V_\Sigma(L=0) + \frac{\sqrt{3}}{6}V_\Sigma(L=1) - \frac{1}{2\sqrt{3}}V_\Sigma(L=2) + \frac{\sqrt{3}}{3}V_\Pi(L=1) - \frac{1}{\sqrt{3}}V_\Pi(L=2) - \frac{1}{\sqrt{3}}V_\Delta(L=2)$$

$$V_{112} = -\frac{\sqrt{6}}{6}V_\Sigma(L=1) - \frac{1}{\sqrt{6}}V_\Sigma(L=2) + \frac{1}{\sqrt{6}}V_\Pi(L=1) - \frac{1}{\sqrt{6}}V_\Pi(L=2) + \frac{2}{\sqrt{6}}V_\Delta(L=2)$$

$$V_{202} = \frac{1}{3\sqrt{2}}V_\Sigma(L=1) - \frac{1}{3\sqrt{2}}V_\Sigma(L=2) - \frac{1}{3\sqrt{2}}V_\Pi(L=1) - \frac{1}{3\sqrt{2}}V_\Pi(L=2) + \frac{2}{3\sqrt{2}}V_\Delta(L=2)$$

$$V_{022} = V_{202}$$

$$V_{220} = \frac{5}{3\sqrt{5}}V_\Sigma(L=0) - \frac{\sqrt{5}}{6}V_\Sigma(L=1) + \frac{1}{6\sqrt{5}}V_\Sigma(L=2) - \frac{\sqrt{5}}{3}V_\Pi(L=1) + \frac{1}{3\sqrt{5}}V_\Pi(L=2) + \frac{1}{3\sqrt{5}}V_\Delta(L=2)$$

$$V_{222} = -\frac{7}{3\sqrt{14}}V_\Sigma(L=1) + \frac{1}{3\sqrt{14}}V_\Sigma(L=2) + \frac{14}{6\sqrt{14}}V_\Pi(L=1) + \frac{1}{3\sqrt{14}}V_\Pi(L=2) - \frac{2}{3\sqrt{14}}V_\Delta(L=2)$$

$$V_{224} = \sqrt{\frac{18}{35}}V_\Sigma(L=2) - 2\sqrt{\frac{8}{35}}V_\Pi(L=2) + \frac{2}{\sqrt{70}}V_\Delta(L=2) \quad (35)$$

The matrix of transformation 35 has rank 6 so that it can be inverted and the Born−Oppenheimer potentials can be written in terms of the $V_{k_1,k_2,k}$ coefficients.

There are eight coefficients $V_{k_1,k_2,k}$ in eq 35. The terms V_{022} and V_{202} are equal due to the symmetry of eq 19 with respect to the interchange of k_1 and k_2. The remaining six coefficients are linearly dependent because, following the model of Zygelman et al.,[16,17] we have omitted the coupling $\langle L = 0, \Lambda = 0|\hat{V}|L = 2, \Lambda = 0\rangle$ and labeled the Born−Oppenheimer potential with the L quantum number. The matrix elements $\langle L = 0, \Lambda = 0|\hat{V}|L = 2, \Lambda = 0\rangle$ may be introduced as shown by van Vroonhoven and Groenenboom in their study of oxygen photodissociation.[42] Relation 19 between the terms $\langle L = 0, \Lambda = 0|\hat{V}|L = 2, \Lambda = 0\rangle$ and $V_{k_1,k_2,k}$ removes the linear dependence of the six coefficients $V_{k_1,k_2,k}$.

Relation 35 can also be obtained by applying transformation 27 to matrix 33. Using the orthogonality property of the 9*j*-symbols,[6] we can write

$$V_\Lambda(L, S) = \sum_j \sum_{j'} \sum_l \sum_{l'} [(L)^2 (j)(j')(l)(l')]^{1/2} \langle j - \Omega J\Omega|l0\rangle \langle j' - \Omega J\Omega|l'0\rangle \langle L\Lambda S\Sigma|j\Omega\rangle \langle L\Lambda S\Sigma|j'\Omega\rangle \sum_{k_1,k_2,k} V^S_{k_1,k_2,k} [(k_1)(k_2)(k)]^{1/2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} (-1)^{L+J-S+l+l'+k} \begin{Bmatrix} L_A & L_A & k_1 \\ L_B & L_B & k_2 \\ L & L & k \end{Bmatrix} \begin{Bmatrix} j & j' & k \\ l' & l & J \end{Bmatrix} \begin{Bmatrix} j & j' & k \\ L & L & S \end{Bmatrix} \quad (36)$$

We have confirmed by numerical calculations that eq 36 gives the same relations between the Born−Oppenheimer potentials and the $V_{k_1,k_2,k}$ terms as eq 19 independently of the values of J, S, S_A, S_B, and Σ. Equation 36 again emphasizes that a complete representation of the interaction potential operator (18) must employ the tensors $\hat{T}^{k_1}_{q_1}(L_A)$ and $\hat{T}^{k_2}_{q_2}(L_B)$ rather than conventional spherical harmonics. The use of spherical harmonics would exclude the terms with $k_1 = k_2 = 1$ from relation 35, and the system of six equations with six independent variables would be reduced to a system of six equations with five independent variables.

We have verified that eqs 35 and 36 give the correct relations by computing the matrix elements (33) for the case of two oxygen atoms in the ^3P state. The results we obtained are identical to the matrix elements given by eq 76 of Zygelman et al.[16]

VI. Atom−Atom Collisions in External Fields

Expansion 18 is particularly convenient for the analysis of atomic collisions in external magnetic or electric fields.[9,21] The total Hamiltonian of the atoms A and B can be written in atomic units as

$$\hat{H} = -\frac{1}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\boldsymbol{l}^2}{2\mu R^2} + \hat{U} \quad (37)$$

where

$$\hat{U} = \hat{V}^{\rm SO}_{\rm A} + \hat{V}^{\rm SO}_{\rm B} + \hat{V}^{\rm f}_{\rm A} + \hat{V}^{\rm f}_{\rm B} + \hat{V}_{\rm dd} + \hat{V} \quad (38)$$

μ is the reduced mass of the colliding atoms, $\hat{V}^{\rm SO}$ is the spin−orbit interaction in atom A or B, $\hat{V}^{\rm f}$ describes the interaction of the atoms with external fields, $\hat{V}_{\rm dd}$ is the magnetic dipolar interaction, and $\hat{V}$ is the interatomic interaction potential (18). When the splitting of the degenerate atomic levels due to interaction with external fields is comparable to or larger than the strength of the spin−orbit interaction, the collision theory is best formulated in the uncoupled space-fixed representation of the wave function

$$\Psi = R^{-1}\sum_i F_i(R)\phi_i \quad (39)$$

where

$$\phi_i = |S_A M_{S_A}\rangle |L_A M_{L_A}\rangle |S_B M_{S_B}\rangle |L_B M_{L_B}\rangle |l m_l\rangle \quad (40)$$

and Ψ is the total wave function of the system.[10,21] The matrices of $\hat{V}^{\rm f}_{\rm A}$ and $\hat{V}^{\rm f}_{\rm B}$ are diagonal in the basis 40, and the matrices of the spin−orbit interactions can be obtained with the standard angular momentum algebra.[10,43] The matrix of the magnetic dipolar interaction $\hat{V}_{\rm dd}$ can be evaluated as described, for example, in ref 10. The role of this interaction is negligible compared to the spin−orbit interaction and the electronic interaction anisotropy, when one or both of the colliding atoms are in states with nonzero electronic orbital angular momentum. The numerical diagonalization of the matrix $\mathbf{H}_{\rm as} = \mathbf{V}^{\rm SO}_{\rm A} + \mathbf{V}^{\rm SO}_{\rm B} + \mathbf{V}^{\rm f}_{\rm A} + \mathbf{V}^{\rm f}_{\rm B}$ yields the energies of the scattering channels and the diagonalizing transformation matrix **C**.

The uncoupled space-fixed basis 40 is related to the total spin representation

$$|S_A M_{S_A}\rangle |L_A M_{L_A}\rangle |S_B M_{S_B}\rangle |L_B M_{L_B}\rangle = \sum_{S,M_S} |S M_S\rangle |L_A M_{L_A}\rangle |L_B M_{L_B}\rangle \langle S M_S|S_A M_{S_A} S_B M_{S_B}\rangle \quad (41)$$

Using eqs 41 and 32, it is straightforward to obtain the matrix elements of the interaction potential (20) in the uncoupled basis.

The solution of the close coupled equations at a fixed total energy E

$$\left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + 2\mu E\right] F_{\alpha l m_l}(R) = 2\mu \sum_{\alpha' l' m_l'} [\mathbf{C}^{\rm T}\mathbf{U}\mathbf{C}]_{\alpha l m_l;\alpha' l' m_l'} F_{\alpha' l' m_l'}(R) \quad (42)$$

subject to the boundary conditions

$$F^{\alpha l m_l}_{\alpha' l' m_l'}(R \to 0) \to 0$$

$$F^{\alpha l m_l}_{\alpha' l' m_l'}(R \to \infty) \sim \delta_{\alpha\alpha'}\delta_{ll'}\delta_{m_l m_l'}\exp[-{\rm i}(k_\alpha R - \pi l/2)] - \left(\frac{k_\alpha}{k_{\alpha'}}\right)^{1/2} S_{\alpha' l' m_l';\alpha l m_l} \exp[{\rm i}(k_{\alpha'} R - \pi l'/2)] \quad (43)$$

gives the S matrix or the probability amplitudes for transitions between the eigenstates of the $\mathbf{C}^{\rm T}\mathbf{H}_{\rm as}\mathbf{C}$ matrix labeled by the indexes α, l, and m_l. The notation k_α is used for the wavenumber corresponding to channel α.

The projections of the total angular momenta $\boldsymbol{j}_A$ and $\boldsymbol{j}_B$ remain good quantum numbers in external magnetic or electric fields. The transformation **C** does not mix states with different values of m_{j_A} or m_{j_B} and the index α corresponds to channels $|m_{j_A}\rangle|m_{j_B}\rangle$. The transitions between the $|m_{j_A}\rangle|m_{j_B}\rangle$ states may be induced by the anisotropy of interaction 18 and the spin anisotropy. The spin anisotropy arises from the difference of the exchange interaction in molecular states with different total spin S and manifests itself in the splitting of the states with the same Λ and L. The spin anisotropy induces the reorientation of spin M_{S_A} in atom A at the expense of the spin projection M_{S_B} of atom B, hence the name. The spin anisotropy conserves the sum $M_S = M_{S_A} + M_{S_B}$. The internal anisotropy of operator 18 is equivalent to the spin anisotropy in that it changes the projection M_{L_A} at the expense of M_{L_B} and conserves the sum $M_L = M_{L_A} + M_{L_B}$.

The recent success of experiments on magnetic trapping and evaporative cooling of atoms has stimulated the study of Zeeman relaxation in atomic collisions. The trapped atoms are in their maximally stretched state in which the electronic spin and orbital angular momenta have the maximal projections. The internal interaction anisotropy cannot induce the relaxation in collision of maximally stretched atoms and the Zeeman transitions are induced only by the terms $V_{k_1,k_2,k}$ with $k > 0$. Relation 19 provides a measure of the interaction anisotropy. If the Born−Oppenheimer potentials for interactions between two atoms are known, eq 18 may be used for a comparative analysis of the Zeeman relaxation and collisional transfer of angular momentum in different systems, and the magnitudes of the Zeeman relaxation rate constants may be estimated using the distorted-wave approximation.

VII. Summary

We have derived a general tensorial expansion for the interaction potential between two atoms in arbitrary angular momentum states and related the expansion coefficients to the Born−Oppenheimer potentials of the diatomic molecule. The representation of the interaction potential is given in the laboratory coordinate system. The relations obtained define the electronic interaction anisotropy. The collision problem of two atoms in arbitrary states can be reformulated with the use of our expansion. Our expansion is particularly convenient for the analysis of scattering in the presence of external magnetic or electric fields. We have demonstrated that a complete expansion of the interaction potential must employ tensors that are invariant under the inversion of the coordinate system, and the expansion in terms of conventional spherical harmonics is not adequate for the case of two atoms in states with nonzero electronic orbital angular momenta. The correctness of our procedure has been demonstrated by the example of two atoms in *P* states. The anisotropy of the electronic interaction drives the Zeeman predissociation,[44] collisionally induced Zeeman relaxation, spin−orbit transitions, and spin−orbit predissociation. Given the relations between the Born−Oppenheimer potentials and the tensorial expansion coefficients we obtained, it is possible to analyze qualitatively the efficiency of these processes in different systems simply by comparing the interaction anisotropies. This is useful for planning cold atom experiments which may be severely limited by the occurrence of collisional angular momentum transfer.

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Appendix A. Relation between Spherical Harmonics and Spherical Tensors

The tensor $\hat{T}^k_q(l, l')$ can be defined as a function of *l* and *l*′ as follows:[20]

$$\hat{T}^k_q(l, l') = \sum_{m_l}\sum_{m_l'} |lm_l\rangle\langle l'm_l'|(-1)^{l-m_l}\begin{pmatrix} l & k & l' \\ -m_l & q & m_l' \end{pmatrix}(k)^{1/2} \tag{44}$$

Since

$$\sum_l\sum_{m_l}|lm_l\rangle\langle lm_l| = 1 \tag{45}$$

we can write for the spherical harmonics Y_{kq}

$$Y_{kq} = \sum_l\sum_{m_l}|lm_l\rangle\langle lm_l|Y_{kq}\sum_{l'}\sum_{m_l'}|l'm_l'\rangle\langle l'm_l'| \tag{46}$$

The integral over three spherical harmonics is

$$\langle lm_l|Y_{kq}|l'm_l'\rangle = \left[\frac{(l)(l')(k)}{4\pi}\right]^{1/2}(-1)^{-m_l}\begin{pmatrix} l & k & l' \\ -m_l & q & m_l' \end{pmatrix}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \tag{47}$$

so that eq 46 can be rewritten as

$$Y_{kq} = \sum_l\sum_{l'}\hat{T}^k_q(l, l')c_k(l, l'), \tag{48}$$

where

$$c_k(l, l') = (-1)^l\left[\frac{(l)(l')}{4\pi}\right]^{1/2}\begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix}. \tag{49}$$

The matrix elements of the spherical harmonics are, therefore, proportional to the matrix elements of the tensor $\hat{T}^k_q(l, l')$

$$\langle lm_l|Y_{kq}|l'm_l'\rangle = c_k(l, l')\langle lm_l|\hat{T}^k_q|l'm_l'\rangle. \tag{50}$$

Equations 48 and 50 show that spherical harmonics can always be replaced with spherical tensors $\hat{T}^k_q(l, l')$, but not vice versa.

Appendix B. Matrix Elements in the Scattering Basis: Graphical Derivation

The matrix elements of the interaction potential operator (20) written in the form

$$\hat{V} = (4\pi)^{1/2}\sum_{k_1,k_2,k,S} V^S_{k_1,k_2,k}(R)(-1)^{k_1-k_2}\sum_{M_S}|SM_S\rangle\langle SM_S| \sum_{l,l'}c_k(l, l')\sum_{q_1,q_2,q}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix}\hat{T}^{k_1}_{q_1}(L_A, L_A{}')\hat{T}^{k_2}_{q_2}(L_B, L_B{}')\hat{T}^k_q(l, l') \tag{51}$$

can be readily evaluated in the coupled space fixed basis (29) as

$$\langle JMjlj_Aj_B|\hat{V}|J'M'j'l'j_A'j_B'\rangle = (4\pi)^{1/2}\sum_{k_1,k_2,k,S}V^S_{k_1,k_2,k}(R)(-1)^{k_1-k_2}\sum_{l,l'}c_k(l, l')X^S_{k_1,k_2,k,l,l'} \tag{52}$$

where

$$X^S_{k_1,k_2,k,l,l'} = \sum_{q_1,q_2,q,M_{L_A},M_{S_A},M_{L_B},M_{S_B},m_{j_A},m_{j_B},m_j,m_l,M_{L_A}',M_{S_A}',M_{L_B}',M_{S_B}',m_{j_A}',m_{j_B}',m_j',m_l',M_S} (-1)^{L_A-M_{L_A}+L_B-M_{L_B}+l-m}[(k_1)(k_2)(k)]^{1/2}\langle L_AM_{L_A}S_AM_{S_A}|j_Am_{j_A}\rangle \langle L_BM_{L_B}S_BM_{S_B}|j_Bm_{j_B}\rangle\langle j_Am_{j_A}j_Bm_{j_B}|jm_j\rangle\langle jm_jlm_l|JM\rangle \langle L_A'M_{L_A}'S_A'M_{S_A'}'|j_A'm_{j_A}'\rangle\langle L_B'M_{L_B}'S_B'M_{S_B}'|j_B'm_{j_B}'\rangle\langle j_A'm_{j_A}'j_B'm_{j_B}'|j'm_j'\rangle \langle j'm_j'l'm_l'|J'M'\rangle\begin{pmatrix} L_A & k_1 & L_A' \\ -M_{L_A} & q_1 & M_{L_A}' \end{pmatrix}\begin{pmatrix} L_B & k_2 & L_B' \\ -M_{L_B} & q_2 & M_{L_B}' \end{pmatrix} \begin{pmatrix} l & k & l' \\ -m_l & q & m_l' \end{pmatrix}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix}\langle S_AM_{S_A}S_BM_{S_B}|SM_S\rangle \langle S_A'M_{S_A}'S_B'M_{S_B}'|SM_S\rangle \tag{53}$$

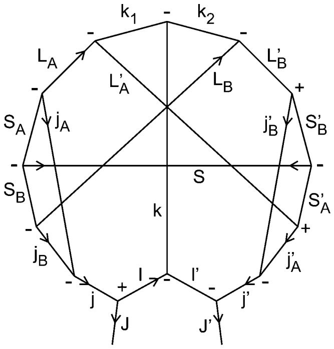

Figure 1. Graphical representation of X (eq 54).

We prime all of the quantum numbers in the ket in order to label the lines in the following diagram unambiguously. The factor $X^S_{k_1,k_2,k,l,l'}$ can be written as

$$X^S_{k_1,k_2,k,l,l'} = [(j_\mathrm{A})(j'_\mathrm{A})(j_\mathrm{B})(j'_\mathrm{B})(j)(j')(J)(J')(k_1)(k_2)(k)]^{1/2}(S)X \tag{54}$$

where X is represented by the diagram in Figure 1. The summation in eq 53 can be evaluated using graphical methods.[7] First, we "cut" the diagram across the J and J' lines. This yields $\delta_{M,M'}\delta_{J,J'}(J)^{-1}$ and a closed diagram. Cutting the resulting diagram across the j, k, and j' lines leads to a product of a 6-j symbol and an 18-j symbol

$$X^S_{k_1,k_2,k,l,l'} = \delta_{M,M'}\delta_{J,J'}(-1)^{L_\mathrm{A}+L'_\mathrm{A}-S_\mathrm{A}-S'_\mathrm{A}+j_\mathrm{A}+j'_\mathrm{A}-j'-l-k-J} [(j_\mathrm{A})(j'_\mathrm{A})(j_\mathrm{B})(j'_\mathrm{B})(j)(j')(k_1)(k_2)(k)]^{\frac{1}{2}}(S)$$

$$\begin{Bmatrix} j & j' & k \\ l' & l & J \end{Bmatrix} \left\{ \begin{array}{cccccc} k_1 & L_A & S_A & S'_B & L'_B & k_2 \\ & & \multicolumn{2}{c}{S} & & \\ L'_A & j_A & & & j'_B & L_B \\ & & \multicolumn{2}{c}{k} & & \\ S'_A & j'_A & j' & j & j_B & S_B \end{array} \right\} \tag{55}$$

The 18-j symbol corresponds to case (P) in Appendix 4 of ref 45. It is given by

$$\sum_{f,f'}(f)(f')(-1)^{k_1+k_2+L'_\mathrm{A}+L_\mathrm{B}+S_\mathrm{B}+S'_\mathrm{A}-j_\mathrm{B}-j'_\mathrm{A}+j+j'} \begin{Bmatrix} j & j' & k \\ f' & f & S \end{Bmatrix}$$

$$\begin{Bmatrix} L_\mathrm{A} & L'_\mathrm{A} & k_1 \\ L_\mathrm{B} & L'_\mathrm{B} & k_2 \\ f & f' & k \end{Bmatrix} \begin{Bmatrix} S_\mathrm{A} & L_\mathrm{A} & j_\mathrm{A} \\ S_\mathrm{B} & L_\mathrm{B} & j_\mathrm{B} \\ S & f & j \end{Bmatrix} \begin{Bmatrix} S'_\mathrm{B} & L'_\mathrm{B} & j'_\mathrm{B} \\ S'_\mathrm{A} & L'_\mathrm{A} & j'_\mathrm{A} \\ S & f' & j' \end{Bmatrix} \tag{56}$$

After substitution of eqs 55 and 56 into eq 52, reordering the 9-j symbol and combining all the phase factors, we obtain eq 33.

References and Notes

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(2) Here and throughout this article, we denote vectors, vector operators, and matrixes by bold symbols; unit vectors, tensors and other operators by a hat over symbols, and the dot product of two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ by $(\mathbf{r}_1 \cdot \mathbf{r}_2)$.

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