Interactions of ^{2}P Atoms with Closed-Shell Diatomic Molecules: Alternative Diabatic Representations for the Electronic Anisotropy†

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The matrices of electrostatic and spin−orbit Hamiltonians for the system of a ^{2}P atom interacting with a closed shell diatomic molecule in uncoupled, coupled, and complex-valued representations for electronic diabatic basis functions are rederived, and the unitary transformations connecting them are given explicitly. The links to previous derivations are established and existing inconsistencies are identified and eliminated. It is proven that the block-diagonalization of a 6 × 6 matrix of the electronic Hamiltonian is a result of using the basis functions with well-defined properties with respect to time reversal. Consideration of time-reversal symmetry also enforces phase consistency relevant for applications to multisurface reactive scattering and photodetachment spectroscopy calculations, as well as for perspective studies of inelastic effects in cold and ultracold environments. These and further developments are briefly sketched.

I. Introduction

Many dynamical processes under focus of modern chemical physics are governed by interactions of open-shell species. Typical examples include chemical reactions of excited halogen and oxygen atoms with H_2 molecule,[1] photodetachment spectroscopy of weakly bound anions[2] and electronic to rotational energy transfer at ultracold temperatures.[3] Because these processes usually involve several coupled potential energy surfaces, it is convenient to formulate the dynamical problem in diabatic representation allowing the electronic Hamiltonian to have off-diagonal matrix elements. Therefore, the choice of the appropriate basis set of diabatic electronic functions and definite phase conventions is of prime importance. For dynamical applications, it is also desirable to get maximum advantage of using various symmetries of the Hamiltonian, in particular, the fundamental time-reversal symmetry,[4] to reduce the complexity of the problem and the number of dynamical equations to be solved.

As an illustrative example, we consider the X(^{2}P)−Y_2 interaction, where X is an atom (e.g., a ground-state halogen or an excited alkali) and the Y_2 molecule is assumed to be in the $^1\Sigma_g^+$ ground electronic state (a prototype being H_2). The theory of this simple system has attracted many researchers including some of us (see for example refs 5 and 6 and references therein) and is attracting further attention in view of interest in cold and ultracold collisions.[7] Most work only considered the adiabatic dynamics on the ground potential energy surface, but it is of great interest to assess the role of open shell effects: the relevant references are refs 8−15.

However, to the best of our knowledge, the only previous study that deals with time-reversal symmetry aspects on this system is that by Alexander et al.[14] These authors reported without derivation the expressions for the electronic Hamiltonian in the time-reversal-adapted Hund's case (a) basis.

Similarly, the diabatic coupling matrix elements used in that and subsequent references[16−21] are derived by exploiting the Hund's case (a) representation for electronic basis functions, which is obviously the best choice for systems in which the spin−orbit interaction is weak compared to potential anisotropy.[11,12] In the opposite limit of heavy X atoms, the Hund's case (c) coupling scheme offers more advantages,[11,12] and it is therefore desirable to obtain an analogue of the diabatic coupling matrix[14,15] in the Hund's case (c) representation.

The goal of this paper is therefore 3-fold. First, we provide a phase-consistent expression for the electronic Hamiltonian in the basis that explicitly takes into account the time-reversal symmetry. We rigorously prove that this representation leads to a 2-fold reduction of the dimensionality of the 6 × 6 real coupling matrix of refs 14 and 15. Second, we derive useful expressions for the coupling matrices in Hund's case (c) basis with and without consideration of time-reversal symmetry. Finally, unitary transformations connecting all the representations introduced here are derived. Along these lines, we establish the links to some previous derivations, using alternative notations for electronic and spin−orbit matrix elements, and correct some existing inconsistencies.

The paper is organized as follows. In section II, we show how to construct time-reversal symmetry adapted electronic basis sets in the uncoupled and coupled representations of angular momenta. Relationships among them are also given explicitly. A brief discussion on the possible implications of the results is given in section III.

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II. Theory

In this section, we derive the expressions for electrostatic and spin−orbit Hamiltonians for the system of a ^{2}P atom interacting with a closed shell diatomic molecule in uncoupled, coupled, and complex-valued representations for electronic diabatic basis functions. We also provide the unitary transformations connecting various representations and compare them with the previously published results.

A. Uncoupled Representation. We begin with a fully uncoupled representation $|L\Lambda S\Sigma\rangle$,[14,15] where $\hat{L}$ and $\hat{S}$ are electronic orbital and spin angular momenta of the atom X with the projections along the body-fixed Jacobi R axis Λ and Σ, respectively. Although the theory would apply for any L and S quantum numbers, for the X(^{2}P) example considered here $L = 1$ and $S = {}^1/_2$ and the simplified notation $|\Lambda\Sigma\rangle$ will be used in the following. Using the spherical harmonic expansions of the intermolecular potential,[11,12,15] the matrix of the electrostatic Hamiltonian can be expressed through the coefficients $V_{l\mu}$, which describe the electrostatic part of the intermolecular interaction including long-range contributions (such as dispersion and induction). The reader is referred to refs 15, 22, and 23 for explicit expressions in case of atom−diatom systems such as F(^{2}P) + H$_2$ and Cl(^{2}P) + H$_2$ and molecular dimers such as O$_2$($^3\Sigma^-$)−O$_2$($^3\Sigma^-$).

The phenomenological spin−orbit Hamiltonian can be written in the form

$$\hat{H}_{\rm SO} = \alpha\,\hat{L}_z\,\hat{S}_z + \beta\,\frac{\hat{L}_+\,\hat{S}_- + \hat{L}_-\,\hat{S}_+}{2} \tag{1}$$

where the matrix elements α and β couple the $|\Lambda\Sigma\rangle$ states with $\Lambda' = \Lambda$ and $\Lambda' = \Lambda \pm 1$, respectively.[14,24−26] In the asymptotic $R \rightarrow \infty$ limit, $\alpha = \beta$ and eq 1 reduces to[27]

$$\hat{H}_{\rm SO} = \alpha\,\hat{L}\cdot\hat{S} \tag{2}$$

with $\alpha \rightarrow \pm 2\delta/3$, where $\delta > 0$ is the fine structure splitting of the ^{2}P atomic term. The matrix element α can take positive or negative values, being for example positive for excited alkali atoms and negative for ground-state halogen atoms. Note that in ref 14 the spin−orbit Hamiltonian of the form (1) is defined with the constants $A = -\alpha/2$ and $B = -\beta/2$, which have the opposite signs. In contrast, the authors of ref 15 used a simplified spin−orbit Hamiltonian (2).

The full electronic Hamiltonian, as the sum of electrostatic and spin−orbit parts, is given by[15]

$$\mathbf{W}_{\Lambda\Sigma} = \begin{pmatrix} \mathbf{P} & -\mathbf{Q} \\ \mathbf{Q} & \mathbf{P} \end{pmatrix} \tag{3}$$

where the 3×3 submatrices $\mathbf{P}$ and $\mathbf{Q}$ have the form

$$\mathbf{P} = \left(\begin{array}{lll|l} \left|0\,\frac{1}{2}\right\rangle & \left|-1\,-\frac{1}{2}\right\rangle & \left|1\,-\frac{1}{2}\right\rangle & \\ \hline V_{00} + \frac{2}{5}V_{20} & 0 & \beta/\sqrt{2} & \left|0\,\frac{1}{2}\right\rangle \\ 0 & V_{00} - \frac{1}{5}V_{20} + \alpha/2 & -\frac{\sqrt{6}}{5}V_{22} & \left|-1\,-\frac{1}{2}\right\rangle \\ \beta/\sqrt{2} & -\frac{\sqrt{6}}{5}V_{22} & V_{00} - \frac{1}{5}V_{20} - \alpha/2 & \left|1\,-\frac{1}{2}\right\rangle \end{array}\right) \tag{4}$$

$$\mathbf{Q} = -\frac{1}{5}\left(\begin{array}{lll|l} \left|0\,-\frac{1}{2}\right\rangle & \left|1\,\frac{1}{2}\right\rangle & \left|-1\,\frac{1}{2}\right\rangle & \\ \hline 0 & \sqrt{3}V_{21} & -\sqrt{3}V_{21} & \left|0\,\frac{1}{2}\right\rangle \\ -\sqrt{3}V_{21} & 0 & 0 & \left|-1\,-\frac{1}{2}\right\rangle \\ \sqrt{3}V_{21} & 0 & 0 & \left|1\,-\frac{1}{2}\right\rangle \end{array}\right) \tag{5}$$

If $\alpha = \beta = -2\delta/3$, the matrix $\mathbf{P}$ is reduced to the form given in ref 15. However, eq 8 in that paper contains misprints—wrong signs in front of the spin−orbit matrix elements between the $|0\ {}^1/_2\rangle$, $|1\ -{}^1/_2\rangle$ and $|1\ -{}^1/_2\rangle$, $|1\ -{}^1/_2\rangle$ basis functions.

As a consequence of the time-reversal symmetry,[4,28] the adiabatic potentials, which are the eigenvalues of the electronic Hamiltonian in eq 3, come in degenerate pairs (Kramer's doublets). Exploiting this symmetry, it is possible to bring the 6×6 real matrix (3) into a block-diagonal form by a complex-valued unitary transformation, whose explicit form is as follows

$$\mathbf{U} = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathbf{I} & {\rm i}\mathbf{I} \\ \mathbf{I} & -{\rm i}\mathbf{I} \end{pmatrix} \tag{6}$$

where $\mathbf{I}$ is a 3×3 unit matrix.

It is generated by the following transformation of the $|\Lambda\Sigma\rangle$ basis:

$$\begin{array}{ll} \frac{1}{\sqrt{2}}\left(\left|0\,\frac{1}{2}\right\rangle - {\rm i}\left|0\,-\frac{1}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|0\,\frac{1}{2}\right\rangle + {\rm i}\left|0\,-\frac{1}{2}\right\rangle\right) \\ \frac{1}{\sqrt{2}}\left(\left|-1\,-\frac{1}{2}\right\rangle - {\rm i}\left|1\,\frac{1}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|-1\,-\frac{1}{2}\right\rangle + {\rm i}\left|1\,\frac{1}{2}\right\rangle\right) \\ \frac{1}{\sqrt{2}}\left(\left|1\,-\frac{1}{2}\right\rangle - {\rm i}\left|-1\,\frac{1}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|1\,-\frac{1}{2}\right\rangle + {\rm i}\left|-1\,\frac{1}{2}\right\rangle\right) \end{array}$$

Note that the relationship between the left-hand side set and the right-hand one is not just a simple complex conjugation. Indeed, these linear combinations are time-reversal adapted basis functions, each function being the combination of a primitive function with its time-reversal partner. This can be verified by making use of the following relationship[4]

$$\hat{P}_t|\Lambda\Sigma\rangle = (-)^{\Lambda+\Sigma}|-\Lambda-\Sigma\rangle \tag{7}$$

where $\hat{P}_t$ is the time-reversal operator. The transformation involves interpreting both Λ and Σ (as well as their sum Ω, see below) as signless quantities (helicities[4,29]). Performing the similarity transformation using eq 6, we arrive at the 6×6 block-diagonal matrix

$$\bar{\mathbf{W}}_{\Lambda\Sigma} = \mathbf{U}\mathbf{W}_{\Lambda\Sigma}\mathbf{U}^\dagger = \begin{pmatrix} \mathbf{P} + {\rm i}\mathbf{Q} & 0 \\ 0 & \mathbf{P} - {\rm i}\mathbf{Q} \end{pmatrix} = \begin{pmatrix} \mathbf{V}_{\Lambda\Sigma} & 0 \\ 0 & \mathbf{V}_{\Lambda\Sigma}{}^* \end{pmatrix} \tag{8}$$

consisting of two complex conjugated 3×3 blocks $\mathbf{V}_{\Lambda\Sigma}$.[15]

A different phase convention appears to have been applied by Alexander et al.[14] It is therefore interesting to rewrite the matrix $\mathbf{V}_{\Lambda\Sigma}$ in the notation of ref 14. Making use of the linking relationships

$$\begin{aligned} V_\Sigma &= V_{00} + \frac{2}{5}V_{20} & V_1 &= \frac{\sqrt{3}}{5}V_{21} \\ V_\Pi &= V_{00} - \frac{1}{5}V_{20} & V_2 &= -\frac{\sqrt{6}}{5}V_{22} \\ A &= -\frac{\alpha}{2} & B &= -\frac{\beta}{2} \end{aligned} \tag{9}$$

and permuting the second and third rows and the second and third columns, one arrives at

$$\begin{pmatrix} V_\Sigma & -\mathrm{i}V_1 - \sqrt{2}B & \mathrm{i}V_1 \\ \mathrm{i}V_1 - \sqrt{2}B & V_\Pi + A & V_2 \\ -\mathrm{i}V_1 & V_2 & V_\Pi - A \end{pmatrix} \tag{10}$$

Comparison with the matrices indicated by the letter **H** in eq 29 of ref 14 and its complex conjugate reveals that the latter are connected to (9) by a simple unitary basis set transformation using diagonal matrices of the type diag(1, ±i, ±i).

An advantage of using eq 8 is that at long range, where only the spin−orbit coupling survives, the imaginary off-diagonal factors disappear.[15]

B. Coupled Representation. Now we pass to the coupled representation for the electronic wave functions $|J\Omega\rangle$, where the total electronic angular momentum $\hat{J}$ is the vectorial sum of $\hat{L}$ and $\hat{S}$. Both representations are connected by the standard orthogonal transformation between Hund's cases (a) and (c) in terms of Clebsch−Gordan vector coupling coefficients:[30−32]

$$|J\Omega\rangle = \sum_{\Lambda,\Sigma} \langle L\Lambda S\Sigma|J\Omega\rangle|\Lambda\Sigma\rangle \tag{11}$$

where the values of Λ and Σ in the sum cannot be chosen independently, being $\Omega = \Lambda + \Sigma$. The matrix **W**, see eq 3, in the $|J\Omega\rangle$ basis set can thus be expressed as

$$\mathbf{W}_{J\Omega} = \mathbf{C}\mathbf{W}_{\Lambda\Sigma}\mathbf{C}^\dagger = \begin{pmatrix} \mathbf{C}_u & 0 \\ 0 & \mathbf{C}_l \end{pmatrix}\begin{pmatrix} \mathbf{P} & -\mathbf{Q} \\ \mathbf{Q} & \mathbf{P} \end{pmatrix}\begin{pmatrix} \mathbf{C}_u & 0 \\ 0 & \tilde{\mathbf{C}}_l \end{pmatrix} \tag{12}$$

where the upper and lower blocks of the **C** matrix are as follows

$$\mathbf{C}_u = \frac{1}{3}\begin{pmatrix} -\sqrt{3} & 0 & \sqrt{6} \\ 0 & 3 & 0 \\ \sqrt{6} & 0 & \sqrt{3} \end{pmatrix} \qquad \mathbf{C}_l = \frac{1}{3}\begin{pmatrix} \sqrt{3} & 0 & -\sqrt{6} \\ 0 & 3 & 0 \\ \sqrt{6} & 0 & \sqrt{3} \end{pmatrix} \tag{13}$$

and the tilde indicates transposition. Making the indicated 3 × 3 matrix multiplications, we get the matrix $\mathbf{W}_{J\Omega}$ in the coupled basis and the notations of ref 14:

$$\left(\begin{array}{llllll} \left|\frac{1}{2}\,\frac{1}{2}\right\rangle & \left|\frac{3}{2}-\frac{3}{2}\right\rangle & \left|\frac{3}{2}\,\frac{1}{2}\right\rangle & \left|\frac{1}{2}-\frac{1}{2}\right\rangle & \left|\frac{3}{2}\,\frac{3}{2}\right\rangle & \left|\frac{3}{2}-\frac{1}{2}\right\rangle \\ \hline \frac{1}{3}(V_\Sigma + 2V_\Pi + 2A + 4B) & \frac{\sqrt{6}}{3}V_2 & -\frac{\sqrt{2}}{3}(V_\Sigma - V_\Pi + B - A) & 0 & \frac{\sqrt{3}}{3}V_1 & -V_1 \\ \frac{\sqrt{6}}{3}V_2 & V_\Pi - A & \frac{\sqrt{3}}{3}V_2 & \frac{\sqrt{3}}{3}V_1 & 0 & \frac{\sqrt{6}}{3}V_1 \\ -\frac{\sqrt{2}}{3}(V_\Sigma - V_\Pi + B - A) & \frac{\sqrt{3}}{3}V_2 & \frac{1}{3}(2V_\Sigma + V_\Pi + A - 4B) & -V_1 & -\frac{\sqrt{6}}{3}V_1 & 0 \\ 0 & \frac{\sqrt{3}}{3}V_1 & -V_1 & \frac{1}{3}(V_\Sigma + 2V_\Pi + 2A + 4B) & -\frac{\sqrt{6}}{3}V_2 & \frac{\sqrt{2}}{3}(V_\Sigma - V_\Pi + B - A) \\ \frac{\sqrt{3}}{3}V_1 & 0 & -\frac{\sqrt{6}}{3}V_1 & -\frac{\sqrt{6}}{3}V_2 & V_\Pi - A & \frac{\sqrt{3}}{3}V_2 \\ -V_1 & \frac{\sqrt{6}}{3}V_1 & 0 & \frac{\sqrt{2}}{3}(V_\Sigma - V_\Pi + B - A) & \frac{\sqrt{3}}{3}V_2 & \frac{1}{2}(2V_\Sigma + V_\Pi + A - 4B) \end{array}\right) \tag{14}$$

It is interesting to note that the matrix representation (14) of the spin−orbit interaction is no longer diagonal when the two constants A and B are *different*. This is an expected result because the Clebsch−Gordan transformation diagonalizes the operator given by eq 2, which becomes equal to that of eq 1 only asymptotically (see section IIA). Because the off-diagonal spin−orbit couplings in eq

14 are proportional to the differences of the kind $A - B$, we expect their magnitude to be greatly reduced with respect to electrostatic and diagonal spin−orbit matrix elements.

Asymptotically, when $B = A = \delta/3$, we have

$$\mathbf{W}_{J\Omega} = \begin{pmatrix} V_{00} + \frac{2}{3}\delta & -\frac{2}{5}V_{22} & -\frac{\sqrt{2}}{5}V_{20} & 0 & \frac{1}{5}V_{21} & -\frac{\sqrt{3}}{5}V_{21} \\ -\frac{2}{5}V_{22} & V_{00} - \frac{1}{5}V_{20} - \frac{1}{3}\delta & -\frac{\sqrt{2}}{5}V_{22} & \frac{1}{5}V_{21} & 0 & \frac{\sqrt{2}}{5}V_{21} \\ -\frac{\sqrt{2}}{5}V_{20} & -\frac{\sqrt{2}}{5}V_{22} & V_{00} + \frac{1}{5}V_{20} - \frac{1}{3}\delta & -\frac{\sqrt{3}}{5}V_{21} & -\frac{\sqrt{2}}{5}V_{21} & 0 \\ 0 & \frac{1}{5}V_{21} & -\frac{\sqrt{3}}{5}V_{21} & V_{00} + \frac{2}{3}\delta & \frac{2}{5}V_{22} & \frac{\sqrt{2}}{5}V_{20} \\ \frac{1}{5}V_{21} & 0 & -\frac{\sqrt{2}}{5}V_{21} & \frac{2}{5}V_{22} & V_{00} - \frac{1}{5}V_{20} - \frac{1}{3}\delta & -\frac{\sqrt{2}}{5}V_{22} \\ -\frac{\sqrt{3}}{5}V_{21} & \frac{\sqrt{2}}{5}V_{21} & 0 & \frac{\sqrt{2}}{5}V_{20} & -\frac{\sqrt{2}}{5}V_{22} & V_{00} + \frac{1}{5}V_{20} - \frac{1}{3}\delta \end{pmatrix} \tag{15}$$

where the notations of ref 15 are used. Up to the shift of energy origin by $\delta/3$ and the definition $\lambda = -2\delta/3$, this matrix is identical to that derived by Schatz and co-workers.[13]

The representation (15) has the advantage over the uncoupled $|\Lambda\Sigma\rangle$ one (3) of diagonalizing the spin−orbit operator. As a Hund's (c) case, the new expressions for the $\mathbf{W}_{J\Omega}$ matrix should be useful for the description of collision systems exhibiting a pronounced spin−orbit coupling, compared with the electronic interaction anisotropy.

An interesting question is whether a transformation can be constructed that brings the matrix $\mathbf{W}_{J\Omega}$ into the block-diagonal form with two complex conjugated blocks

$$\bar{\mathbf{W}}_{J\Omega} = \mathcal{U}\mathbf{W}_{J\Omega}\mathcal{U}^{\dagger} = \begin{pmatrix} \mathbf{V}_{J\Omega} & 0 \\ 0 & \mathbf{V}_{J\Omega}{}^{*} \end{pmatrix} \tag{16}$$

Exploiting the time-reversal symmetry, we succeeded in showing that the required matrix $\mathcal{U}$ executing such a transformation is

$$\mathcal{U} = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathbf{I} & \mathrm{i}\mathcal{S} \\ \mathbf{I} & -\mathrm{i}\mathcal{S} \end{pmatrix} \tag{17}$$

where $\mathcal{S}$ is a 3 × 3 diagonal matrix diag(1, −1, −1).

The corresponding basis set

$$\begin{array}{ll} \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\,\frac{1}{2}\right\rangle + \mathrm{i}\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}\,\frac{1}{2}\right\rangle - \mathrm{i}\left|\frac{1}{2}\,-\frac{1}{2}\right\rangle\right) \\ \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\,-\frac{3}{2}\right\rangle - \mathrm{i}\left|\frac{3}{2}\,\frac{3}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\,-\frac{3}{2}\right\rangle + \mathrm{i}\left|\frac{3}{2}\,\frac{3}{2}\right\rangle\right) \\ \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\,\frac{1}{2}\right\rangle - \mathrm{i}\left|\frac{3}{2}\,-\frac{1}{2}\right\rangle\right) & \frac{1}{\sqrt{2}}\left(\left|\frac{3}{2}\,\frac{1}{2}\right\rangle + \mathrm{i}\left|\frac{3}{2}\,-\frac{1}{2}\right\rangle\right) \end{array}$$

obeys time-reversal symmetry as above. One can check it explicitly by making use of the following relationship[33] for the action of the time-reversal operator $\hat{P}_t$ on the basis functions of the coupled representation:

$$\hat{P}_t|J\Omega\rangle = -\mathrm{i}(-)^{J-\Omega}|J - \Omega\rangle \tag{18}$$

Taking into account that this operator is antilinear and antisymmetric, it is easy to prove that the functions on the right-hand side are the time-reversal partners of those on the left-hand side.[24,25]

It can be verified by a straightforward calculation that the complex 3 × 3 blocks $\mathbf{V}_{J\Omega}$ (16) of the $\mathbf{W}_{J\Omega}$ matrix in eq 14 are given by

$$\mathbf{V}_{J\Omega} = \begin{pmatrix} \frac{1}{3}(V_{\Sigma} + 2V_{\Pi} + 2A + 4B) & \frac{\sqrt{6}}{3}V_2 & -\frac{\sqrt{2}}{3}(V_{\Sigma} - V_{\Pi} + B - A) \\ \frac{\sqrt{6}}{3}V_2 & V_{\Pi} - A & \frac{\sqrt{3}}{3}V_2 \\ -\frac{\sqrt{2}}{3}(V_{\Sigma} - V_{\Pi} + B - A) & \frac{\sqrt{3}}{3}V_2 & \frac{1}{3}(2V_{\Sigma} + V_{\Pi} + A - 4B) \end{pmatrix} + \mathrm{i}\begin{pmatrix} 0 & -\frac{\sqrt{3}}{3}V_1 & V_1 \\ \frac{\sqrt{3}}{3}V_1 & 0 & -\frac{\sqrt{6}}{3}V_1 \\ -V_1 & \frac{\sqrt{6}}{3}V_1 & 0 \end{pmatrix} \tag{19}$$

For the $\mathbf{W}_{J\Omega}$ matrix represented by eq 15, the 3 × 3 block acquires particularly simple form due to the asymptotic approximation to the spin−orbit coupling (2):

$$\mathbf{V}_{J\Omega} = V_{00}\mathbf{I} - \frac{1}{5}\begin{pmatrix} 0 & 2V_{22} & \sqrt{2}V_{20} \\ 2V_{22} & V_{20} & \sqrt{2}V_{22} \\ \sqrt{2}V_{20} & \sqrt{2}V_{22} & -V_{20} \end{pmatrix} + \frac{1}{3}\delta\begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} + \frac{\mathrm{i}}{5}\begin{pmatrix} 0 & V_{21} & -\sqrt{3}V_{21} \\ -V_{21} & 0 & \sqrt{2}V_{21} \\ \sqrt{3}V_{21} & -\sqrt{2}V_{21} & 0 \end{pmatrix} \quad (20)$$

The expression (20) coincides with that given in eq 13 of ref 15 (in the latter the numerical factor $2\sqrt{3}/5$ multiplying V_{22} should be $2 \times 3/5$). Equations 14−19 provide the new expressions for diabatic couplings between the states of definite total electronic angular momentum J and its projection Ω.

Comparing the matrices $\mathbf{U}$ and $\mathscr{U}$, we see that the transformation (17) between the real Hund's case (c) functions and their time-reversal counterparts is very different from that given by eq 6 for the Hund's case (a). This is related to the structure of the Clebsch−Gordan matrix in eq 13: the block $\mathbf{C}_u$ is a symmetric matrix whereas the $\mathbf{C}_l$ is not. There seems to be some confusion on this point,[15] which is eliminated in the present paper.

C. Relationships among the Diabatic Representations. Coupled and uncoupled representations are related by the matrix $\mathbf{C}$; see eq 12. When the time-reversal symmetry is implemented, the link between the two basis sets is given by an orthogonal matrix $\bar{\mathbf{C}}$, which connects $\bar{\mathbf{W}}_{\Lambda\Sigma}$ and $\bar{\mathbf{W}}_{J\Omega}$

$$\bar{\mathbf{C}}\,\bar{\mathbf{W}}_{\Lambda\Sigma}\,\bar{\mathbf{C}}^{\dagger} = \bar{\mathbf{W}}_{J\Omega} \quad (21)$$

Inserting eq 8 in the left-hand side and eqs 16 in the right-hand side of eq 21, we can prove that

$$\bar{\mathbf{C}}\mathbf{U} = \mathscr{U}\mathbf{C} \quad (22)$$

The matrix $\mathscr{U}$, see eq 17, is closely connected with the matrix $\mathbf{U}$, see eq 6:

$$\mathscr{U} = \mathbf{U}\begin{pmatrix} \mathbf{I} & 0 \\ 0 & \mathscr{T} \end{pmatrix} \quad (23)$$

From eq 22, exploiting this latter relation, we finally obtain

$$\bar{\mathbf{C}} = \begin{pmatrix} 0 & \mathbf{C}_u \\ \mathbf{C}_u & 0 \end{pmatrix} \quad (24)$$

where $\mathbf{C}_u$ is given in eq 13. The relationships among the diabatic representations introduced above are schematically illustrated in Figure 1.

III. Discussion and Perspectives

In this paper, we have presented detailed and rigorous analysis of the diabatic coupling matrices describing the interaction between an open-shell atom and a closed-shell diatomic molecule. Using a well-studied example of a ^{2}P atom, we obtained explicit expressions for the diabatic matrices of the electronic Hamiltonian in coupled and uncoupled angular momentum representations. For both schemes, the time-reversal symmetrization has been implemented to construct the complex-valued representations of the reduced dimensionality. Unitary transformations with a consistent phase convention between all the representations have been presented. The links to and among the previously derived formulas were established and some inaccuracies were identified and corrected.

$$\begin{tikzcd} \mathbf{W}_{J\Omega} \arrow[r, leftrightarrow, "\mathscr{U}"] \arrow[d, leftrightarrow, "\mathbf{C}"'] & \bar{\mathbf{W}}_{J\Omega} \arrow[d, leftrightarrow, "\bar{\mathbf{C}}"] \\ \mathbf{W}_{\Lambda\Sigma} \arrow[r, leftrightarrow, "\mathbf{U}"'] & \bar{\mathbf{W}}_{\Lambda\Sigma} \end{tikzcd}$$

Figure 1. Schematic illustration of the relationships among the diabatic matrices for the electrostatic-plus-spin−orbit Hamiltonians in the uncoupled ($|\Lambda\Sigma\rangle$) and coupled ($|J\Omega\rangle$) representations without (left) and with (right) implementation of the time-reversal symmetry. The four unitary transformations $\mathbf{U}$, $\mathbf{C}$, $\mathscr{U}$ and $\bar{\mathbf{C}}$ act according to eqs 8, 12, 16 and 21, respectively.

Implementation of the time-reversal symmetry provides a general recipe for reducing the dimensionality of multisurface quantum problem. As far as numerical applications are concerned, a conservative estimate of the efficiency gained could be obtained as follows. If N is the number of channels to be included in the dynamical treatment, the multiplication or inversion of a real $N \times N$ matrix (3) will require N^3 operations. If the complex 3 × 3 representation (8) is used instead, we get $(N/2)^3 = N^3/8$ operations on complex numbers. Because multiplication of two complex numbers involves 4 times the number of operations associated with multiplication of two real numbers, the calculations in the complex 3 × 3 basis are 2 times more efficient. Moreover, it should be noted that 3 × 3 representations obtained here lead to real matrices in the $R \rightarrow \infty$ limit where the V_1 (or V_{21}) matrix element vanishes. In this case, a 8-fold reduction of the computational effort is predicted, which may be advantageous for carrying out long-range propagation. Complex-valued representations could be also convenient for adiabatic applications when the proper symmetry-adapted eigenvectors are required.

The case of a ^{2}P atom must be considered as the most known example. Extensions to open-shell atoms with arbitrary spin and electronic angular momentum require only minor modifications along a well-established line of approach,[22,23,30,31] which exploits a formal analogy between the interactions of an open-shell atom and that of a rigid rotor. In this sense, the avenues of developments of the present work bear analogies with recent progress on the electronic interaction anisotropy between two open-shell atoms.[34] The angular momentum algebra machinery would be very similar, provided the molecular anisotropy interaction is expanded in Legendre polynomials. The main difference lies of course in the dimensionality of the interaction potential terms, which in the atom−atom case only depend on R. In general, the five $V_{l\mu}$ terms can be made to depend on the three variables chosen to describe the atom−diatom as a three-body problem,[15] although a hierarchy of simplifications can be effective, for example, when the molecule is approximated as a rigid rotor (vibrations neglected), or when its rotational anisotropy is averaged out.

Moreover, this paper only dealt with matrix representations of the electronic interaction and can be considered as a starting point for the treatment of the full dynamics. Such a treatment requires the introduction into the Hamiltonian of additional operators: the orbital angular momentum of the relative atom−

diatom motion and the rotational angular momentum of the diatom itself. Interesting future work would be to explore alternative coupling schemes for all angular momenta that are appropriate for a given system. This may also serve as a guide for the development of decoupling approximations to describe the dynamics of inelastic events, keeping in the formulation the operators and couplings adapted to a given system for specific ranges of collision energies, total angular momenta and atom–diatom distances.

The cases to which this theory can be applied offer an ample phenomenology: the ultracold conditions appear particularly suited for drastic approximations for both vibrations and rotations. We hope that this study helps to indicate how to classify such a phenomenology as long as information on the $V_{l\mu}$ radial potential terms is accumulated from experimental, ab initio and semiempirical sources on systems of specific interest.

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