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Analytic non-adiabatic derivative coupling terms for spin-orbit MRCI wavefunctions. II. Derivative coupling terms and coupling angle for $\mathrm{KHe}\left(\mathrm{A}^2\mathbf{\Pi}_{1/2}\right) \Leftrightarrow \mathrm{KHe}\left(\mathrm{B}^2\mathbf{\Sigma}_{1/2}\right)$

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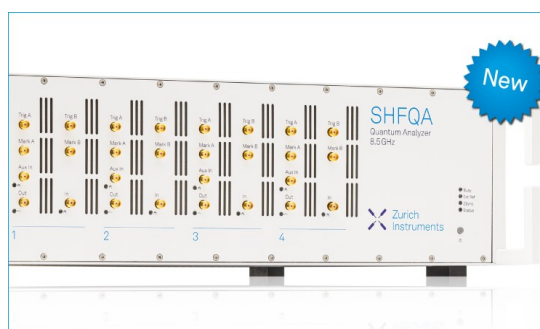# Analytic non-adiabatic derivative coupling terms for spin-orbit MRCI wavefunctions. II. Derivative coupling terms and coupling angle for KHe(A$^2\Pi_{1/2}$) ⇔ KHe(B$^2\Sigma_{1/2}$)

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ABSTRACT

A method for calculating the analytic nonadiabatic derivative coupling terms (DCTs) for spin-orbit multi-reference configuration interaction wavefunctions is reviewed. The results of a sample calculation using a Stuttgart basis for KHe are presented. Additionally, the DCTs are compared with a simple calculation based on the Nikitin's 3 × 3 description of the coupling between the Σ and Π surfaces, as well as a method based on Werner's analysis of configuration interaction coefficients. The nonadiabatic coupling angle calculated by integrating the radial analytic DCTs using these different techniques matches extremely well. The resultant nonadiabatic energy surfaces for KHe are presented.

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I. INTRODUCTION

Collisionally induced changes to states split by the spin-orbit interaction are of importance in calculating the dynamics of many systems, including Diode-Pumped Alkali Lasers (DPALs) in which alkali metals interact with noble gasses to produce laser radiation.[1–5] In such cases, the application of the Born-Oppenheimer approximation to separate the nuclear and electronic Hamiltonian is insufficient to appropriately model system dynamics. The coupling between electronic and nuclear states is quantified by nonadiabatic derivative coupling terms (DCTs) and the resultant off-diagonal energy coupling surface.[6,7] We are thus motivated to calculate DCTs for M + Ng systems, where M = K, Rb, or Cs and Ng = He, Ne, or Ar,[8,9] in which this coupling occurs strongly between states separated only by the spin-orbit energy.

In a DPAL, alkali atoms in vapor are pumped to the $^2P_{3/2}$ state, which then are de-excited to the $^2P_{1/2}$ by collision with a buffer gas, typically a noble gas or hydrocarbon. Lasing then takes place as the alkali atoms radiatively decay to the $^2S_{1/2}$ state. In order to properly model the collisional de-excitation and understand the methods available to enhance the population inversion, the calculation of the nonadiabatic potential energy surfaces is required.[10]

In this paper, we explore the DCTs, resultant coupling angle, and nonadiabatic potential energy surfaces of one of these systems, KHe. We are primarily focused on the radial derivative couplings, i.e., those that arise from change in the distance between the K and He nuclei. Lewis has explored the angular derivative couplings and their connection to the Coriolis coupling elsewhere.[11] KHe was chosen because of its relative simplicity for speedy calculations and the availability of a spin-orbit potential. Additionally, experiments have shown KHe to be a promising DPAL candidate.[12]
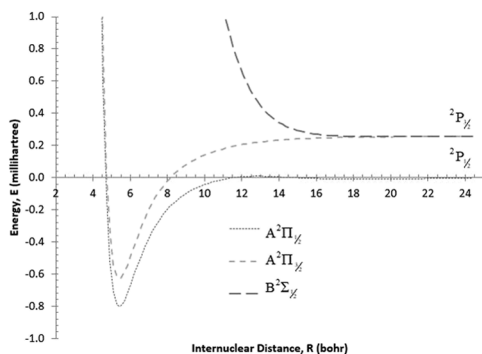
FIG. 1. K He MRCI energy surfaces.

Energy surfaces for the first three excited states of KHe are shown in Fig. 1.

In order to calculate these DCTs, we apply the formalism outlined in Paper I,[13] as implemented in COLUMBUS[14–16] and NWCHEM,[17] to KHe. Additionally, a method based on Nikitin's 3×3 method[18] developed by Lewis[11] is reviewed and compared. Finally, a parsimonious method devised by Werner[19] and employed by Alexander[20,21] is applied and compared.

II. CALCULATIONS OF DERIVATIVE COUPLING TERMS AND ADIABATIC MIXING ANGLE

A. Method 1: Direct analytic calculation of DCTs

In this method, DCTs for KHe are calculated analytically in the modified COLUMBUS and NWCHEM programs using a Stuttgart basis set.[22,23] In addition to the DCTs we explore here, Belcher has shown that the modified density matrices correctly predict the multi-reference configuration interaction (MRCI) energies, and the modified energy gradients agree well with finite-difference methods.[12]

As a transition term, DCTs suffer an additional complexity that nontransition quantities do not. Each MRCI wavefunction may have an arbitrary phase factor, which does not affect the energy expectation value or its gradient. Let

$$\left|\psi_I'\right\rangle = e^{-i\theta}\left|\psi_I\right\rangle. \tag{1}$$

Then, for an operator $\hat{A}$,

$$\begin{aligned}
\left\langle\psi_I'\middle|\hat{A}\middle|\psi_I'\right\rangle &= e^{i\theta}\left\langle\psi_I\middle|\hat{A}e^{-i\theta}\middle|\psi_I\right\rangle \\
&= e^{i\theta}e^{-i\theta}\left\langle\psi_I\middle|\hat{A}e^{-i\theta}\middle|\psi_I\right\rangle \\
&= \left\langle\psi_I\middle|\hat{A}\middle|\psi_I\right\rangle,
\end{aligned} \tag{2}$$

and so the phase factor is superfluous in this case. If we instead consider a transition property between different wavefunctions, we find that the phase does indeed matter

$$\begin{aligned}
\left\langle\psi_I'\middle|\hat{A}\middle|\psi_J'\right\rangle &= e^{i\theta_I}\left\langle\psi_I\middle|\hat{A}e^{-i\theta_J}\middle|\psi_J\right\rangle \\
&= e^{i\theta_I}e^{-i\theta_J}\left\langle\psi_I\middle|\hat{A}\,e^{-i\theta_J}\middle|\psi_J\right\rangle \\
&= e^{i(\theta_I-\theta_J)}\left\langle\psi_I\middle|\hat{A}\middle|\psi_J\right\rangle.
\end{aligned} \tag{3}$$

Since COLUMBUS only uses real wavefunctions, the arbitrary phase is limited to ±1, but it will still require careful deliberation, especially as the DCTs change sign (e.g., a nonsmooth "bounce" off an axis may indicate that the DCT actually smoothly traverses the axis).

In addition to the arbitrary phase angle, there will also be an arbitrary mixing angle between degenerate wavefunctions. Due to Kramer's theorem, odd-electron systems will always have doubly degenerate wavefunctions. In order to work within the formalism of Yabushita et al.,[24] a noninteracting ghost electron is added to odd-electron systems in COLUMBUS, doubling the degeneracy again, creating a quadruple-degeneracy. Radial derivative couplings will only occur between states such that the z-component of the total spin, m_j, and the z-component of the ghost electron's spin, $m_{s\,ghost}$, are preserved. Nevertheless, due to the degeneracy, the four electronic wavefunctions that COLUMBUS converges upon for either surface will be an arbitrary mixture of the four pure states, which do not mix those quantities,

$$\left|\Sigma_{1/2}^i\right\rangle = \sum_{j=1}^{4}\left|\Sigma_{1/2}'^j\right\rangle\left\langle\Sigma_{1/2}'^j\middle|\Sigma_{1/2}^i\right\rangle \tag{4}$$

(with a symmetric definition for the $\left|\Pi_{1/2}^i\right\rangle$ states), where the unprimed wavefunctions are the arbitrary mixtures with $1 \leq i \leq 4$ and the primed wavefunctions are the pure *canonical* states, each j representing a specific pairing of m_j and $m_{s\,ghost}$. Because of this mixing, a given calculated DCT, $\left\langle\Sigma_{1/2}^i\middle|\frac{\partial}{\partial R}\middle|\Pi_{1/2}^j\right\rangle$, does not carry all the information about the canonical DCT, $\left\langle\Sigma_{1/2}'^i\middle|\frac{\partial}{\partial R}\middle|\Pi_{1/2}'^i\right\rangle$. We can nevertheless obtain the true DCT in the following manner. Consider the sum square of all DCTs involving the electronic wavefunction $\left|\Sigma_{1/2}^i\right\rangle$,

$$\begin{aligned}
&\sum_j\left\|\left\langle\Sigma_{1/2}^i\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}^j\right\rangle\right\|^2 \\
&= -\sum_j\left\langle\Sigma_{1/2}^i\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}^j\right\rangle\left\langle\Pi_{1/2}^j\middle|\tfrac{\partial}{\partial R}\middle|\Sigma_{1/2}^i\right\rangle \\
&= -\sum_{j,k,l,m,n}\left\langle\Sigma_{1/2}^i\middle|\Sigma_{1/2}'^k\right\rangle\left\langle\Sigma_{1/2}'^k\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}'^l\right\rangle\left\langle\Pi_{1/2}'^l\middle|\Pi_{1/2}^j\right\rangle \\
&\quad\times\left\langle\Pi_{1/2}^j\middle|\Pi_{1/2}'^m\right\rangle\left\langle\Pi_{1/2}'^m\middle|\tfrac{\partial}{\partial R}\middle|\Sigma_{1/2}'^n\right\rangle\left\langle\Sigma_{1/2}'^n\middle|\Sigma_{1/2}^i\right\rangle.
\end{aligned} \tag{5}$$

Since the pure states only have DCTs when m_j and $m_{s\,ghost}$ are preserved, this collapses the sums over l and n,

$$\begin{aligned}
&\sum_j\left\|\left\langle\Sigma_{1/2}^i\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}^j\right\rangle\right\|^2 \\
&= -\sum_{j,k,m}\left\langle\Sigma_{1/2}^i\middle|\Sigma_{1/2}'^k\right\rangle\left\langle\Sigma_{1/2}'^k\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}'^k\right\rangle\left\langle\Pi_{1/2}'^k\middle|\Pi_{1/2}^j\right\rangle \\
&\quad\times\left\langle\Pi_{1/2}^j\middle|\Pi_{1/2}'^m\right\rangle\left\langle\Pi_{1/2}'^m\middle|\tfrac{\partial}{\partial R}\middle|\Sigma_{1/2}'^m\right\rangle\left\langle\Sigma_{1/2}'^m\middle|\Sigma_{1/2}^i\right\rangle.
\end{aligned} \tag{6}$$

Rearranging, we have

$$\begin{aligned}
&\sum_j\left\|\left\langle\Sigma_{1/2}^i\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}^j\right\rangle\right\|^2 \\
&= -\sum_{k,m}\left\langle\Sigma_{1/2}'^k\middle|\tfrac{\partial}{\partial R}\middle|\Pi_{1/2}'^k\right\rangle\left\langle\Pi_{1/2}'^m\middle|\tfrac{\partial}{\partial R}\middle|\Sigma_{1/2}'^m\right\rangle \\
&\quad\times\left\langle\Sigma_{1/2}^i\middle|\Sigma_{1/2}'^k\right\rangle\left\langle\Sigma_{1/2}'^m\middle|\Sigma_{1/2}^i\right\rangle\sum_j\left\langle\Pi_{1/2}'^k\middle|\Pi_{1/2}^j\right\rangle\left\langle\Pi_{1/2}^j\middle|\Pi_{1/2}'^m\right\rangle.
\end{aligned} \tag{7}$$

This last sum over j is replaced with $\delta_{k,m}$, leaving us with

$$
\sum_j \left\| \left\langle \Sigma_{1/2}^i \left| \frac{\partial}{\partial R} \right| \Pi_{1/2}^j \right\rangle \right\|^2
$$

$$
= - \sum_k \left\langle \Sigma_{1/2}'^k \left| \frac{\partial}{\partial R} \right| \Pi_{1/2}'^k \right\rangle \left\langle \Pi_{1/2}'^k \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}'^k \right\rangle
$$

$$
\times \left\langle \Sigma_{1/2}^i \middle| \Sigma_{1/2}'^k \right\rangle \left\langle \Sigma_{1/2}'^k \middle| \Sigma_{1/2}^i \right\rangle
$$

$$
= \sum_k \left\| \left\langle \Sigma_{1/2}'^k \left| \frac{\partial}{\partial R} \right| \Pi_{1/2}'^k \right\rangle \right\|^2 \left\langle \Sigma_{1/2}^i \middle| \Sigma_{1/2}'^k \right\rangle \left\langle \Sigma_{1/2}'^k \middle| \Sigma_{1/2}^i \right\rangle. \quad (8)
$$

With nothing in the Hamiltonian to discriminate otherwise, we assert that the DCTs between any pair of electronic wavefunctions from these two spaces, which preserve m_j and m_{sghost} must be of equal magnitude (the example below will serve to bolster this assertion). Then, Eq. (8) tells us that

$$
\sqrt{\sum_j \left\| \left\langle \Sigma_{1/2}^i \left| \frac{\partial}{\partial R} \right| \Pi_{1/2}^j \right\rangle \right\|^2} = \sqrt{\left\| \left\langle \Sigma_{1/2}'^k \left| \frac{\partial}{\partial R} \right| \Pi_{1/2}'^k \right\rangle \right\|^2}, \quad (9)
$$

that is, the norm of the canonical DCT is the root sum square of the mixed DCTs, involving any single electronic wavefunction $\left| \Sigma_{1/2}^i \right\rangle$ with all electronic wavefunctions $\left| \Pi_{1/2}^j \right\rangle$ (the argument is equally valid for the DCTs of a single wavefunction $\left| \Pi_{1/2}^i \right\rangle$ with all $\left| \Sigma_{1/2}^j \right\rangle$).

From the four $\left| \Pi_{1/2} \right\rangle$ wavefunctions to the four $\left| \Sigma_{1/2} \right\rangle$ wavefunctions, there are a total of 16 different DCTs, represented within the matrix,

$$
\mathbf{p} = \begin{pmatrix}
\left\langle \Pi_{1/2}^1 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^1 \right\rangle & \left\langle \Pi_{1/2}^1 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^2 \right\rangle & \left\langle \Pi_{1/2}^1 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^3 \right\rangle & \left\langle \Pi_{1/2}^1 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^4 \right\rangle \\
\left\langle \Pi_{1/2}^2 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^1 \right\rangle & \left\langle \Pi_{1/2}^2 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^2 \right\rangle & \left\langle \Pi_{1/2}^2 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^3 \right\rangle & \left\langle \Pi_{1/2}^2 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^4 \right\rangle \\
\left\langle \Pi_{1/2}^3 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^1 \right\rangle & \left\langle \Pi_{1/2}^3 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^2 \right\rangle & \left\langle \Pi_{1/2}^3 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^3 \right\rangle & \left\langle \Pi_{1/2}^3 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^4 \right\rangle \\
\left\langle \Pi_{1/2}^4 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^1 \right\rangle & \left\langle \Pi_{1/2}^4 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^2 \right\rangle & \left\langle \Pi_{1/2}^4 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^3 \right\rangle & \left\langle \Pi_{1/2}^4 \left| \frac{\partial}{\partial R} \right| \Sigma_{1/2}^4 \right\rangle
\end{pmatrix}. \quad (10)
$$

In reality, $\mathbf{p}$ is an off-diagonal submatrix of the entire DCT matrix for all wavefunctions; however, if we are only interested in the coupling between the $\left\{ A^2 \Pi_{1/2}^j \right\}$ space and the $\left\{ B^2 \Sigma_{1/2}^i \right\}$ space, we need to only consider the matrix formed between these eight wavefunctions and their duals, for which the diagonal blocks are zero,

$$
\mathbf{P} = \begin{pmatrix} 0 & \mathbf{p} \\ -\mathbf{p}^\dagger & 0 \end{pmatrix}. \quad (11)
$$

If we assume that $\mathbf{p}$ is not singular, then there exists a similarity transformation by which it may be diagonalized,

$$
\mathbf{p}^d = \mathbf{v}^{-1} \mathbf{p} \mathbf{v}. \quad (12)
$$

It follows that the off-diagonal blocks of the matrix $\mathbf{P}$ can be diagonalized by the transformation

$$
\mathbf{P}' \equiv \begin{pmatrix} 0 & \mathbf{p}^d \\ -\mathbf{p}^{d\dagger} & 0 \end{pmatrix} = \begin{pmatrix} \mathbf{v}^{\dagger-1} & 0 \\ 0 & \mathbf{v} \end{pmatrix}^\dagger \begin{pmatrix} 0 & \mathbf{p} \\ -\mathbf{p}^\dagger & 0 \end{pmatrix} \begin{pmatrix} \mathbf{v}^{\dagger-1} & 0 \\ 0 & \mathbf{v} \end{pmatrix}. \quad (13)
$$

We now find $\mathbf{P}'$ in a new basis in which the original, arbitrarily rotated, and phased wavefunctions have been rerotated to yield the canonical sets of wavefunctions $\left\{ \left| \Pi_{1/2}' \right\rangle \right\}$ and $\left\{ \left| \Sigma_{1/2}' \right\rangle \right\}$. This transformation has reduced the number of DCTs from 16 to 4 (the four eigenvalues of the off-diagonal block), each of which couples only one $\left| \Pi_{1/2}' \right\rangle$ wavefunction to only one $\left| \Sigma_{1/2}' \right\rangle$ wavefunction. Since the wavefunctions in each respective space are, for our purposes, indistinguishable, there should be no distinction of the coupling between any two pairs, and we should expect all four new DCTs to have the same magnitude.

As an example of the preceding discussion, consider the DCTs of the KHe system at 5.0 Å (9.4 bohr). The calculated DCTs are found in the matrix

$$
\mathbf{p} = \begin{pmatrix}
0.0668 & -0.0242 & -1.72 & 511 \\
-510 & 0.163 & -0.0651 & 0.0533 \\
-0.0554 & 10.4 & 511 & 1.75 \\
-0.184 & -511 & 10.4 & 0.0156
\end{pmatrix} \times 10^{-4} \ \text{rad/bohr}, \quad (14)
$$

which is diagonalized by the matrix

$$
\mathbf{v} = \begin{pmatrix}
0.347 - 40.9i & 0.480 + 40.8i & 70.6 & 0.988 - 40.9i \\
0.347 + 40.9i & 48.0 - 40.8i & 70.6 & 0.988 - 40.9i \\
57.8 & 28.9 + 50.0i & 0.102 - 0.734i & -28.9 + 50.0i \\
57.8 & 28.9 - 50.0i & 0.10.2 + 0.734i & -28.9 - 50.0i
\end{pmatrix} \times 10^{-2}. \quad (15)
$$

When the matrix **P** built from the matrix in Eq. (14) is subjected to the transformation in Eq. (13), the resultant DCT matrix is

$$
\mathbf{P'} = \begin{pmatrix}
0 & 0 & 0 & 0 & 51.1 - 0.505i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 51.1 + 0.505i & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -25.5 - 44.3i & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -25.5 + 44.3i \\
-51.1 - 0.505i & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -51.1 + 0.505i & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 25.5 - 44.3i & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 25.5 + 44.3i & 0 & 0 & 0 & 0
\end{pmatrix}
$$

$\times 10^{-3}$ rad/bohr. $\qquad$ (16)

Although each of the DCTs in $\mathbf{P'}$ is complex, we have the option of affecting an arbitrary phase rotation between each pair of wavefunctions, allowing us to remove the imaginary portion of each DCT,

$$
\mathbf{P'} = \begin{pmatrix}
0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0
\end{pmatrix} \times 0.0511 \text{ rad/bohr.}
$$

$\qquad$ (17)

As hypothesized, we see that, in the canonical basis, the DCTs between each distinct pair of wavefunctions are indeed of the same magnitude. From this exercise, we also conclude that we need to only calculate four DCTs, not 16, to find the magnitude of a single canonical DCT. From the four distinct elements of any given row or column of the DCT matrix, we can calculate a Euclidean norm, which is the DCT in the canonical basis. The radial DCT in the canonical basis,
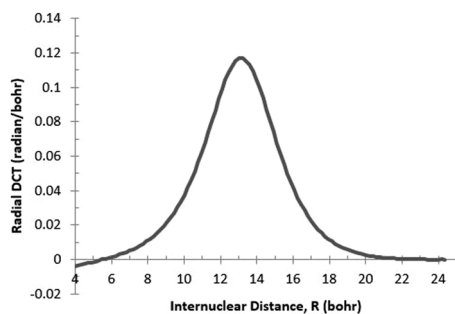
calculated as the norm of the DCTs in the first row of **P**, is shown in Fig. 2.

This exercise has shown that, despite the eight wavefunctions involved, we are effectively seeking the adiabatic mixing angle for only two wavefunctions. That mixing angle is calculated as the integral of the DCTs from $R' = (\infty)$ to $R' = R$. Figure 3 shows the result of that integration for KHe. Figure 4 shows the adiabatic surfaces and the resultant mixed diabatic surfaces. Figure 5 shows the off-diagonal diabatic coupling surface. The strength of the coupling surface depends upon both the size of the coupling angle
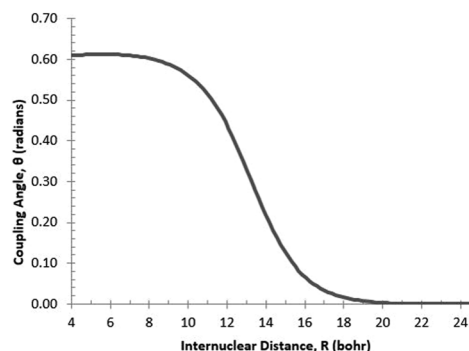
FIG. 3. Radial coupling angle between $\Pi_{1/2}$ and $\Sigma_{1/2}$ states via methods 1 and 2.
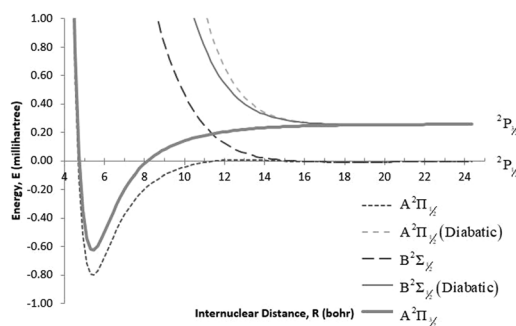
FIG. 2. Radial DCT between $\Pi_{1/2}$ and $\Sigma_{1/2}$ states.

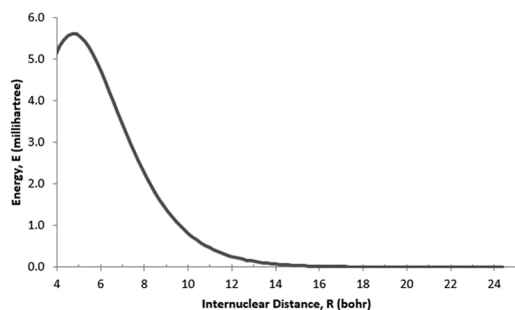FIG. 4. Diabatic vs adiabatic K He surfaces.

FIG. 5. Diabatic K He coupling surface.

and the energy difference between the two adiabatic surfaces; thus, the coupling surface continues to grow well past the area where DCTs are strong, into a region which, for most interactions, would be energetically disallowed.

B. Method 2: Direct calculation of the coupling angle from the electronic eigenvalues

We now explore an alternative method that directly approximates the coupling angle $\alpha(R)$ for a two-state $C_{\infty v}$ system, without the need to calculate DCTs directly. This method is based on Nikitin's 3×3 matrix description of the coupling between the Σ and Π surfaces.[18] For comparison with method 1, DCTs can then be calculated as $\partial \alpha(R)/\partial R$.

For the systems of interest to DPALs, M + Ng with the valence electron of M excited to the p-manifold, the only allowable angular momentum values are 1 for the orbital angular momentum and 1/2 for spin. Therefore, before relativistic considerations, the space we are interested in is spanned by the wavefunctions

$$\left\{ \left| \begin{matrix} l & s \\ m_l & m_s \end{matrix} \right\rangle \right\} = \left\{ \left| \begin{matrix} 1 & 1/2 \\ 1 & \pm 1/2 \end{matrix} \right\rangle, \left| \begin{matrix} 1 & 1/2 \\ 0 & \pm 1/2 \end{matrix} \right\rangle, \left| \begin{matrix} 1 & 1/2 \\ -1 & \pm 1/2 \end{matrix} \right\rangle \right\}. \tag{18}$$

The electronic Hamiltonian has the form

$$\mathbf{H}(R) = \mathbf{H_0}(R) + \mathbf{H_{so}}(R), \tag{19}$$

$$\mathbf{H_{so}} \equiv a(R) \hat{l} \cdot \hat{s} = a(R) \left(\hat{j}^2 - \hat{l}^2 - \hat{s}^2 \right), \tag{20}$$

where $\hat{j}$, $\hat{l}$, and $\hat{s}$ represent the total, orbital, and spin angular momentum, respectively, and $\mathbf{H_0}(R)$ is the nonrelativistic electronic Hamiltonian, which is diagonal in the basis,

$$\mathbf{H_0}(R) = \begin{pmatrix} \Pi & 0 & 0 \\ 0 & \Pi & 0 \\ 0 & 0 & \Sigma \end{pmatrix}, \tag{21}$$

where we have, and will continue to suppress dependence on R within matrix representations, unless emphasis is necessary. Without the spin-orbit operator, $\mathbf{H_{so}}(R)$, each pair of wavefunctions is degenerate. The addition of the spin-orbit operator encourages a change from the $l - s$ basis to total angular momentum, j basis,

$$\left\{ \left| \begin{matrix} j \\ m_j \end{matrix} \right\rangle \right\} = \left\{ \left| \begin{matrix} 3/2 \\ \pm 3/2 \end{matrix} \right\rangle, \left| \begin{matrix} 3/2 \\ \pm 1/2 \end{matrix} \right\rangle, \left| \begin{matrix} 1/2 \\ \pm 1/2 \end{matrix} \right\rangle \right\}. \tag{22}$$

Although $\mathbf{H_{so}}(R)$ is diagonal in this basis, with elements

$$\left\langle \begin{matrix} j' \\ m_j' \end{matrix} \right| \mathbf{H_{so}}(R) \left| \begin{matrix} j \\ m_j \end{matrix} \right\rangle = \delta_{j',j} \delta_{m_j',m_j} [a(R)(j(j+1) - l(l+1) - s(s+1))], \tag{23}$$

now $\mathbf{H_0}(R)$ is not, with elements

$$\left\langle \begin{matrix} j' \\ m_j' \end{matrix} \right| \mathbf{H_0}(R) \left| \begin{matrix} j \\ m_j \end{matrix} \right\rangle = \sum_{m_l,m_l',m_s,m_s'} \left(l m_l' s m_s' | l s j' m_j' \right) \left(l m_l s m_s | l s j m_j \right) \left\langle \begin{matrix} l & s \\ m_l' & m_s' \end{matrix} \right| \mathbf{H_0}(R) \left| \begin{matrix} l & s \\ m_l & m_s \end{matrix} \right\rangle$$

$$= \sum_{m_l,m_l',m_s,m_s'} \left(l m_l' s m_s' | l s j' m_j' \right) \left(l m_l s m_s | l s j m_j \right) W_{m_l,m_s} \delta_{m_l',m_l} \delta_{m_s',m_s}$$

$$= \delta_{m_j',m_j} \sum_{m_l,m_s} \left(l m_l' s m_s' | l s j' m_j' \right) \left(l m_l s m_s | l s j m_j \right) W_{m_l,m_s}, \tag{24}$$

where $(l m_l s m_s | l s j m_j)$ are the Clebsch-Gordon coefficients. Replacing these coefficients with the Wigner 3j-matrices, $\mathbf{H_0}(R)$ becomes

$$\left\langle \begin{matrix} j' \\ m_j' \end{matrix} \right| \mathbf{H_0}(R) \left| \begin{matrix} j \\ m_j \end{matrix} \right\rangle = \delta_{m_j',m_j} \left[(2j'+1)(2j+1) \right]^{1/2} \sum_{m_l,m_s} \begin{pmatrix} l & s & j' \\ m_l & m_s & -m_j \end{pmatrix} \begin{pmatrix} l & s & j \\ m_l & m_s & -m_j \end{pmatrix} W_{m_l,m_s}. \tag{25}$$

As we are only interested in the p-manifold for the M + Ng system, we can enumerate those states with $l = 1$,

$$\left\langle \begin{matrix} j' \\ m_j' \end{matrix} \right| \mathbf{H_0}(R) \left| \begin{matrix} j \\ m_j \end{matrix} \right\rangle = \delta_{m_j',m_j} \left[(2j'+1)(2j+1) \right]^{1/2}$$

$$\times \sum_{m_s} \left[\begin{pmatrix} 1 & s & j' \\ 1 & m_s & -m_j \end{pmatrix} \begin{pmatrix} 1 & s & j \\ 1 & m_s & -m_j \end{pmatrix} \Pi + \begin{pmatrix} 1 & s & j' \\ -1 & m_s & -m_j \end{pmatrix} \begin{pmatrix} 1 & s & j \\ -1 & m_s & -m_j \end{pmatrix} \Pi + \begin{pmatrix} 1 & s & j' \\ 0 & m_j & -m_j \end{pmatrix} \begin{pmatrix} 1 & s & j \\ 0 & m_j & -m_j \end{pmatrix} \Sigma \right] \tag{26}$$

(where we have used the relationship $m_j = m_s$ for a state in which $m_l = 0$). To Eq. (26), we can add zero in the form

$$0 = \begin{pmatrix} 1 & s & j' \\ 0 & m_j & -m_j \end{pmatrix}\begin{pmatrix} 1 & s & j \\ 0 & m_j & -m_j \end{pmatrix}\Pi - \begin{pmatrix} 1 & s & j' \\ 0 & m_j & -m_j \end{pmatrix}\begin{pmatrix} 1 & s & j \\ 0 & m_j & -m_j \end{pmatrix}\Pi,$$

(27)

so that we can now set $\mathbf{H}_0(R)$ equal to

$$\left\langle \begin{matrix} j' \\ m_j' \end{matrix} \middle| \mathbf{H}_0(R) \middle| \begin{matrix} j \\ m_j \end{matrix} \right\rangle = \delta_{m_j',m_j}\Big[\delta_{j',j}\Pi + \big[(2j'+1)(2j+1)\big]^{1/2}(\Sigma - \Pi)$$

$$\times \begin{pmatrix} 1 & s & j' \\ 0 & m_j & -m_j \end{pmatrix}\begin{pmatrix} 1 & s & j \\ 0 & m_j & -m_j \end{pmatrix}\Big],$$

(28)

or, in the matrix form in the j, m_j basis,

$$\mathbf{H}_0(R) = \frac{1}{3}\begin{pmatrix} 3\Pi & 0 & 0 \\ 0 & 2\Sigma + \Pi & \mp\sqrt{2}(\Sigma - \Pi) \\ 0 & \mp\sqrt{2}(\Sigma - \Pi) & \Sigma + 2\Pi \end{pmatrix}.$$

(29)

With the addition of $\mathbf{H}_{so}(R)$ from Eq. (23), we have

$$\mathbf{H}_0(R) + \mathbf{H}_{so}(R) = \frac{1}{6}\begin{pmatrix} 6\Pi + 3a & 0 & 0 \\ 0 & 4\Sigma + 2\Pi + 3a & \mp 2\sqrt{2}(\Sigma - \Pi) \\ 0 & \mp 2\sqrt{2}(\Sigma - \Pi) & 2\Sigma + 4\Pi - 6a \end{pmatrix}.$$

(30)

Equation (30) is obtained using a simple form for the spin-orbit coupling where the diabatic coupling surface is given by the 2,3 matrix element. As discussed in Refs. 11 and 25, the diabatic coupling curve is obtained by first diagonalizing equation (30) and identifying the eigenvalues as the MRCI $A^2\Pi_{1/2}(R)$, $B^2\Sigma_{1/2}(R)$, and $A^2\Pi_{3/2}(R)$ adiabatic potential energy curves. Analytic expressions for the eigenvalues in terms of $\Sigma(R)$, $\Pi(R)$, and $a(R)$ are inverted to yield expressions for $\Sigma(R)$, $\Pi(R)$, and $a(R)$ in terms of the MRCI surfaces. As a result, the diabatic coupling curve given by the difference of the $\Sigma(R)$ and $\Pi(R)$ surfaces directly incorporates the full MRCI-level calculation into the simple Hamiltonian given by Eq. (20).

It is interesting to note that the off-diagonal diabatic curve in Eq. (30) is given by the difference between the $\Sigma(R)$ and $\Pi(R)$ surfaces but does not directly depend on the spin-orbit coupling $a(R)$. For KHe, the spin-orbit coupling exhibits a very shallow two-wavenumber well with a minimum at $R \approx 3$ Å and reaching a constant value at $R \approx 9$ Å, and is nearly constant thereafter. Spin-orbit splittings as a function of internuclear separation are shown for K, Rb, and Cs interacting with He, Ne, and Ar in Fig. 3 of Ref. 25.

The full Hamiltonian is now

$$\mathbf{H}(R) = \mathbf{T_N}(R) + \mathbf{H}_0(R) + \mathbf{H}_{so}(R)$$

$$= -\frac{1}{2\mu}\begin{pmatrix} \frac{\partial}{\partial R} & 0 & 0 \\ 0 & \frac{\partial}{\partial R} & p \\ 0 & p & \frac{\partial}{\partial R} \end{pmatrix}^2$$

$$+ \frac{1}{6}\begin{pmatrix} 6\Pi + 3a & 0 & 0 \\ 0 & 4\Sigma + 2\Pi + 3a & \mp 2\sqrt{2}(\Sigma - \Pi) \\ 0 & \mp 2\sqrt{2}(\Sigma - \Pi) & 2\Sigma + 4\Pi - 6a \end{pmatrix},$$

(31)

where we have ignored the angular kinetic part of the Hamiltonian, as it plays no part in the calculation of the radial DCTs. Note that in Eq. (31), we have left p(R) in the kinetic Hamiltonian, as nothing in this derivation guarantees that it is summarily zero. We can compare this form of the Hamiltonian to the adiabatic Hamiltonian on the basis of molecular wavefunctions,

$$\mathbf{H}(R) = -\frac{1}{2\mu}\begin{pmatrix} \frac{\partial}{\partial R} & 0 & 0 \\ 0 & \frac{\partial}{\partial R} & p \\ 0 & p & \frac{\partial}{\partial R} \end{pmatrix}^2 + \begin{pmatrix} \Pi_{3/2} & 0 & 0 \\ 0 & \Sigma_{1/2} & 0 \\ 0 & 0 & \Pi_{1/2} \end{pmatrix}.$$

(32)

When the correct rotation is applied to this Hamiltonian to diagonalize the kinetic energy operator, Eq. (32) transforms to

$$\mathbf{H}(R) = -\frac{1}{2\mu}\begin{pmatrix} \frac{\partial}{\partial R} & 0 & 0 \\ 0 & \frac{\partial}{\partial R} & 0 \\ 0 & 0 & \frac{\partial}{\partial R} \end{pmatrix}^2$$

$$+ \begin{pmatrix} \Pi_{3/2} & 0 & 0 \\ 0 & \Sigma_{1/2}\cos^2\alpha + \Pi_{1/2}\sin^2\alpha & \sin\alpha\cos\alpha(\Sigma_{1/2} - \Pi_{1/2}) \\ 0 & \sin\alpha\cos\alpha(\Sigma_{1/2} - \Pi_{1/2}) & \Pi_{1/2}\cos^2\alpha + \Sigma_{1/2}\sin^2\alpha \end{pmatrix}.$$

(33)

Lewis has demonstrated that the potential energy surfaces in Eq. (31) are exactly equal to those of Eq. (33).[11] From this result, we come to the conclusion that Eqs. (31) and (33) are equivalent, since Eq. (31) is the strictly diabatic representation of the Hamiltonian. Furthermore, we conclude that the off-diagonal potential energy surfaces of (31) and (33) are equivalent, and we therefore have the following formula for the calculation of α, the coupling angle:

$$\alpha(R) = \frac{1}{2}\arcsin\left(\frac{2\sqrt{2}}{3}(\Sigma - \Pi)\Big/\Sigma_{1/2} - \Pi_{1/2}\right),$$

(34)

where we emphasize that Π and Σ represent the nonrelativistic electronic eigenvalues, whereas $\Pi_{1/2}$ and $\Sigma_{1/2}$ represent those that include the spin-orbit contribution. The radial DCTs are then computed as the radial derivative of the coupling angle, as stated previously.[7] Figure 6 shows that the KHe radial DCTs computed this way are equivalent to those computed by method 1.
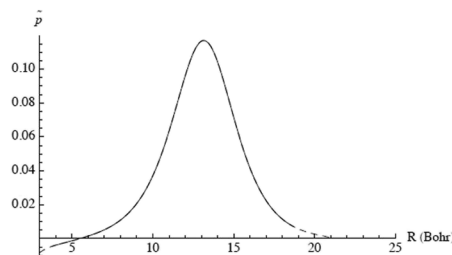

FIG. 6. Comparison of radial DCTs from method 1 (solid) and method 2 (dashed).
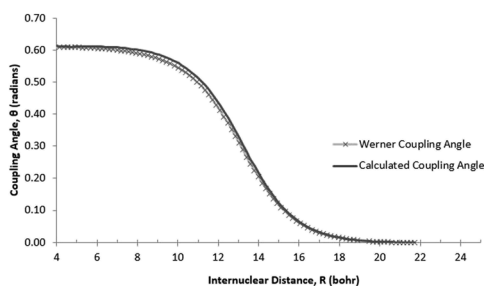
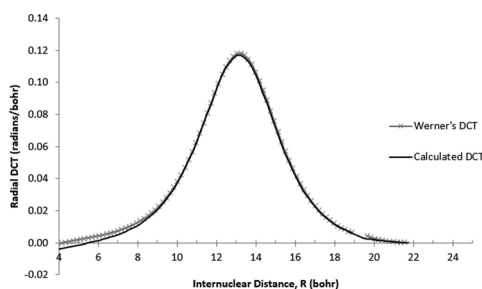**FIG. 7**. Coupling angle as calculated via DCTs vs calculated via CI coefficients.

FIG. 8. DCT as calculated vs derivative of Werner's angle.

C. Method 3: Approximation of the coupling angle from MRCI coefficients

Werner, Follmeg, and Alexander established a method to estimate the coupling angle using the MRCI wavefunction coefficients,[19]

$$\theta_{\Sigma_{1/2} - \Pi_{1/2}} \approx \arcsin\left(\sqrt{\sum_{i \in \Pi_{1/2}} \left(c_i^{\Sigma_{1/2}}\right)^2 \Big/ \sum_i \left(c_i^{\Sigma_{1/2}}\right)^2} \right), \qquad (35)$$

where the Euclidean norm is taken off the coefficients of the $\Sigma_{1/2}$ eigenvector, $c_i^{\Sigma_{1/2}}$, which coincides with CSFs that have $\Pi_{1/2}$ symmetry (for simplicity, only the reference CSFs are considered in an MRCI calculation). We can generalize this method to spin-orbit wavefunctions by using the Euclidean norm of all coefficients pertaining to CSFs whose physical occupation is appropriate. Figure 7 compares the calculated mixing angle from methods 1 and 2 with the angle estimated via the Werner method. Similarly, Fig. 8 compares the radial DCT from methods 1 and 2 with the derivative of Werner's angle. The Werner's angle matches with the angle calculated with the DCTs by less than 0.02 radians, with greater difference at the repulsion wall, an acceptable error, given the parsimonious nature of this approximation.

III. CONCLUSIONS

Code based on COLUMBUS and NWCHEM has been modified to directly calculate analytic energy gradients and DCTs of spin-orbit wavefunctions at the MRCI level. The DCTs, coupling angles, and coupling surfaces calculated with this modified code compare favorably with those calculated using a simple method based on Nikitin's 3×3 matrix formulation, as well as the coupling angle approximation from Werner's method. These favorable comparisons lead us to conclude that we have correctly calculated the radial DCTs for KHe. Cross-section calculations[25] identify that these DCTs are required to properly model the KHe dynamics. Although Lewis' method was specifically derived for M + Ng systems, it may be adaptable for more general situations. Our manipulations to the COLUMBUS and NWCHEM code were not specific to any system or geometry and should be generally applicable should that formalism be incorporated into the production code.

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