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LETTERS

On the Construction of Diabatic Bases Using Molecular Properties. Rigorous Results in the Vicinity of a Conical Intersection

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Smoothness of a molecular property—achieved by diagonalization of the matrix of the corresponding property operator—is a convenient and frequently used criterion for the construction of an adiabatic to diabatic state transformation. The choice of molecular property has been a matter of considerable discussion. When conical intersections are present, the performance of this approach near that intersection is key since the derivative coupling in the adiabatic basis is singular there. Thus it is desirable to know, a priori, whether use of a particular property will remove the singularity. Here it is shown that diagonalizing the matrix of *any* symmetric (real-valued hermitian) electronic property operator, satisfying only certain limited restrictions, generates a transformation that removes all of the singularity of the derivative coupling at the conical intersection. The result is illustrated by considering the dipole moment operator near a point on the $1^1A'-2^1A'$ seam of conical intersection in HeH_2.

I. Introduction

At a conical intersection, the derivative coupling $f_\tau^{IJ}(\mathbf{R}) \equiv \langle \Psi_I(\mathbf{r};\mathbf{R})|(\partial/\partial\tau)\Psi_J(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}}$ in the adiabatic basis, $\Psi_I(\mathbf{r};\mathbf{R})$, is singular. Here $[H^e(\mathbf{r};\mathbf{R}) - E_I(\mathbf{R})]\Psi_I(\mathbf{r};\mathbf{R}) = 0$, $H^e(\mathbf{r};\mathbf{R})$ is the nonrelativistic electronic Hamiltonian, $\mathbf{r}$ ($\mathbf{R}$) are the electronic (nuclear) coordinates, and τ is an internal nuclear coordinate discussed further below. In order to solve the nuclear Schrödinger equation quantum mechanically, it is desirable to remove this singularity by transforming to a diabatic basis, $\Psi_I^d(\mathbf{r};\mathbf{R})$, for which all $f_{\tau'}^{IJ,d}(\mathbf{R}) = \langle \Psi_I^d(\mathbf{r};\mathbf{R})|(\partial/\partial\tau')\Psi_J^d(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}}$ are small. For this reason interest in the construction of diabatic states has been, and continues to be, intense.[1−3]

Near a conical intersection, the region of interest in this work, the two-state approximation is appropriate and the transformation to diabatic states is given by

$$\begin{pmatrix}\Psi_I^d(\mathbf{r};\mathbf{R})\\ \Psi_J^d(\mathbf{r};\mathbf{R})\end{pmatrix} = \begin{pmatrix}\cos\Phi(\mathbf{R}) & \sin\Phi(\mathbf{R})\\ -\sin\Phi(\mathbf{R}) & \cos\Phi(\mathbf{R})\end{pmatrix}\begin{pmatrix}\Psi_I(\mathbf{r};\mathbf{R})\\ \Psi_J(\mathbf{r};\mathbf{R})\end{pmatrix} \quad (1)$$

where the prescription for $\Phi(\mathbf{R})$ is required. The historical lack of efficient algorithms for the evaluation of the derivative coupling (although this is certainly no longer the case[4]) has stimulated considerable interest in methods to determine $\Phi(\mathbf{R})$ that avoid evaluation of the derivative couplings.[2,3,5−7] Of concern here is the readily implemented and hence popular class of methods that requires smoothness of a molecular property.[8−11] Any of a variety of molecular properties, including a component of the electronic, dipole moment,[9,10] quadrapole moment,[10] or orbital angular momentum[10,12] operators are used for the construction of diabatic bases. Very recently a comparative study of the global performance of several of these approaches has been reported[11] for the $1^1A'$ and $2^1A'$ states of H_2O, which exhibit two seams of conical intersection.

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As the viability of the molecular properties approach depends on its ability to remove the singularity in the derivative coupling at the conical intersection, it is highly desirable to know, a priori, whether use of a particular property accomplishes this. Although formal discussions of the molecular property based adiabatic to diabatic state transformation exist,[8] an analysis of the effect on the singularity at a general, that is, where symmetry plays no role, conical intersection is lacking. This work reports a rigorous analysis of this question based on a perturbative treatment of a general conical intersection[13] that extended a previous work of Mead.[14] A quite surprising result is obtained. It is shown that in the immediate vicinity of a general conical intersection of states *I* and *J* the transformation determined by the standard property based definition of $\Phi(\mathbf{R}) = \Phi^A(\mathbf{R})$

$$\tan 2\Phi^A(\mathbf{R}) = \frac{2A_{IJ}(\mathbf{R})}{A_{JJ}(\mathbf{R}) - A_{II}(\mathbf{R})} \tag{2}$$

where

$$A_{KL}(\mathbf{R}) = \langle \Psi_K(\mathbf{r};\mathbf{R}) | A^e(\mathbf{r})\, \Psi_L(\mathbf{r};\mathbf{R}) \rangle_{\mathbf{r}} \tag{3}$$

and $A^e(\mathbf{r})$ is a symmetric operator, differs, by a readily computed constant, from the perturbatively determined transformation. Since the later transformation rigorously removes all of the singularity in the $f_\tau^{IJ}(\mathbf{R})$,[13] so must the transformation determined by Φ^A.

Section II presents the analysis of transformation 1 with $\Phi(\mathbf{R}) = \Phi^A(\mathbf{R})$ near a conical intersection. The practical utility of the formal treatment is illustrated using the components of the dipole moment operator near a point of the $1^1A'-2^1A'$ seam of conical intersection in HeH_2. These conical intersections are particularly relevant since a $\Phi(\mathbf{R})$ based exclusively on $f_\tau^{IJ}(\mathbf{R})$ has recently been discussed for this system.[15] Section III summarizes and concludes.

II. Theory and Results

The $\Psi_I(\mathbf{r};\mathbf{R})$ are expanded in a basis

$$\Psi_I(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{CSF}} c_\alpha^I(\mathbf{R})\, \psi_\alpha(\mathbf{r};\mathbf{R}) \tag{4a}$$

where the $\mathbf{c}^I(\mathbf{R})$ satisfy

$$[H(\mathbf{R}) - E_I(\mathbf{R})]\mathbf{c}^I(\mathbf{R}) = 0 \tag{4b}$$

In the numerical treatment below the ψ_α will be configuration state functions (CSFs)[16] constructed from molecular orbitals obtained from a state-averaged multiconfigurational self-consistent field procedure.[4]

A. Wave Functions near a Conical Intersection. Near a point of conical intersection, $\mathbf{R}_x$, of states *I* and *J*, it is convenient to replace the CSF basis with an alternative basis, $\tilde{\psi}_I(\mathbf{r};\mathbf{R})$, analogous to the crude adiabatic basis of Longuet−Higgins[17]

$$\tilde{\psi}_I(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{CSF}} c_\alpha^I(\mathbf{R}_x)\, \psi_\alpha(\mathbf{r};\mathbf{R}) \tag{5a}$$

so that

$$\Psi_I(\mathbf{r};\mathbf{R}) = \sum_{K=I,J} \xi_K^I(\mathbf{R})\, \tilde{\psi}_K(\mathbf{r};\mathbf{R}) + \sum_{K\neq I,J} \Xi_K^I(\mathbf{R})\, \tilde{\psi}_K(\mathbf{r};\mathbf{R}) \tag{5b}$$

ξ and Ξ can be expanded in a power series in displacements $\delta\mathbf{R}$ where $\mathbf{R} = \mathbf{R}_x + \delta\mathbf{R}$ as follows

$$\xi^I(\mathbf{R}) \cong \xi^{0,I}(\theta) + \xi^{1,I}(\mathbf{R}) + \ldots \tag{6a}$$

$$\Xi^I(\mathbf{R}) \cong \Xi^{1,I}(\mathbf{R}) \ldots \tag{6b}$$

where[13]

$$\begin{pmatrix} \tilde{\xi}^{I,0}(\theta) \\ \tilde{\xi}^{J,0}(\theta) \end{pmatrix} = \begin{pmatrix} \cos\lambda(\theta)/2 & \sin\lambda(\theta)/2 \\ -\sin\lambda(\theta)/2 & \cos\lambda(\theta)/2 \end{pmatrix} \begin{pmatrix} \xi^{I,0}(\mathbf{R}_x) \\ \xi^{J,0}(\mathbf{R}_x) \end{pmatrix} \tag{7}$$

$\chi_K^{I,0}(\mathbf{R}_x) = \delta_{K,I}$, and

$$q(\theta)\cos\lambda(\theta) = g_x \cos\theta$$
$$q(\theta)\sin\lambda(\theta) = h_x \cos\theta + h_y \sin\theta \tag{8a}$$

$$q(\theta)^2 = g_x{}^2 \cos^2\theta + (h_x \cos\theta + h_y \sin\theta)^2 \tag{8b}$$

θ is the polar angle of a generalized cylindrical coordinate system,[13] that is, $x = \rho\cos\theta$ and $y = \rho\sin\theta$, with origin $\mathbf{R}_x$ and axes $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\mathbf{z}^i$, $i = 3 - N^{int}$, where N^{int} is the number of internal coordinates. Here $\hat{\mathbf{x}} = \mathbf{g}^{IJ}(\mathbf{R}_x)/||\mathbf{g}^{IJ}(\mathbf{R}_x)||$, $\hat{\mathbf{y}} = \mathbf{h}^{IJ}(\mathbf{R}_x)^\perp/||\mathbf{h}^{IJ}(\mathbf{R}_x)^\perp||$, $\mathbf{h}^{IJ}(\mathbf{R}_x)^\perp = \mathbf{h}^{IJ}(\mathbf{R}_x) - (\mathbf{h}^{IJ}(\mathbf{R}_x)^\dagger\cdot\hat{\mathbf{x}})\hat{\mathbf{x}}$

$$2g_\tau^{IJ}(\mathbf{R}) = (\mathbf{c}^I(\mathbf{R}_x) - \mathbf{c}^J(\mathbf{R}_x))^\dagger \frac{\partial \mathbf{H}(\mathbf{R})}{\partial\tau}(\mathbf{c}^I(\mathbf{R}_x) + \mathbf{c}^J(\mathbf{R}_x)) \tag{9a}$$

$$h_\tau^{IJ}(\mathbf{R}) = \mathbf{c}^I(\mathbf{R}_x)^\dagger \frac{\partial \mathbf{H}(\mathbf{R})}{\partial\tau}\mathbf{c}^J(\mathbf{R}_x) \tag{9b}$$

and the $\mathbf{z}^i$ are only required to be in the orthogonal complement of the *x*-*y* or *g*-*h* plane. In eqs 8a and 8b, $k_w = \mathbf{k}^{IJ}(\mathbf{R}_x)^\dagger\cdot\hat{\mathbf{w}}$, for $k = g, h$ and $w = x, y$.

The salient feature of this perturbative analysis concerns the derivative coupling in the diabatic basis

$$f_\tau^{IJ,d}(\mathbf{R}) \equiv \left\langle \Psi_I^d(\mathbf{r};\mathbf{R}) \middle| \frac{\partial}{\partial\tau}\Psi_J^d(\mathbf{r};\mathbf{R}) \right\rangle_r = f_\tau^{IJ}(\mathbf{R}) + \frac{\partial}{\partial\tau}\Phi(\mathbf{R}) \tag{10}$$

From first-order perturbation theory $\Phi(\mathbf{R}) = \Phi^{(p1)}(\mathbf{R}) = -\lambda(\theta)/2$. It can be shown[13] that $(1/\rho)(\partial/\partial\theta)\Phi^{(p1)}(\mathbf{R})$ *exactly cancels the only singular part of the derivative coupling*, $(1/\rho)$ $f_\theta^{IJ}(\mathbf{R})$, at $\mathbf{R}_x$.[13,18] The remaining components of the derivative coupling, f_ρ^{IJ} and $f^{IJ}{}_{z^i}$, which are necessarily finite at $\mathbf{R}_x$, turn out to be quite small in all cases studied to date.[13,19,20]

B. Property Matrices near a Conical Intersection. Using eqs 5 and 7 in eq 3 gives at $\mathbf{R}_x$

$$\mathbf{A}(\rho\to 0, \theta, z^i = 0) \equiv \mathbf{A}^0(\theta) = A^+\mathbf{I} + \boldsymbol{\sigma}_x(A^-\sin\lambda + B^+\cos\lambda + B^-) + \boldsymbol{\sigma}_z(A^-\cos\lambda - B^+\sin\lambda) \tag{11a}$$

where $\boldsymbol{\sigma}_w$, $w = x, z$, are Pauli matrices and

$$A^\pm = (A_{II}(\mathbf{R}_x) \pm A_{JJ}(\mathbf{R}_x))/2 \quad \text{and}$$
$$\mathrm{B}^\pm = (A_{IJ}(\mathbf{R}_x) \pm A_{JI}(\mathbf{R}_x))/2 \tag{11b}$$

For a symmetric matrix $B^- = 0$, whereas if the operator A^e is real-valued and antihermitian only B^- is nonvanishing. For $\rho > 0$ and $z^i \geq 0$, eq 11 provides the lowest order term in the expansion $\mathbf{A}(\mathbf{R}) = \mathbf{A}^0(\theta) + \mathbf{A}^1(\mathbf{R}) + \ldots$. Its numerical utility will be considered below. Note that perturbative evaluation of

$\mathbf{A}^1(\mathbf{R})$ is not computationally efficient since it requires knowledge of $\Xi^{1,J}(\mathbf{R})$, which is about as costly to obtain as the solution to eq 4b.

At $\mathbf{R}_x$, $\mathbf{A}$ is diagonalized by a transformation of the form of eq 1 with $\Phi(\mathbf{R}) = \Phi^{A,0}(\theta)$ given by

$$\tan 2\Phi^{A,0}(\theta) = -\frac{A^- \sin\lambda + B^+ \cos\lambda}{A^- \cos\lambda - B^+ \sin\lambda} = -\frac{\cos\alpha \sin\lambda + \sin\alpha \cos\lambda}{\cos\alpha \cos\lambda - \sin\alpha \sin\lambda} = -\frac{\sin(\alpha+\lambda)}{\cos(\alpha+\lambda)} \quad (12)$$

so that

$$2\Phi^{A,0}(\theta) + \alpha + \lambda(\theta) = n\pi, \quad n = 0, \pm 1, \ldots \quad (13a)$$

where the offset, α, is given by

$$\tan\alpha = B^+/A^- \quad (13b)$$

Equations 12 and 13 fail to define $\Phi^{A,0}(\theta)$ if both B^+ and A^- vanish, that is, if the property operator is degenerate at the conical intersection.[21] While it is possible to construct such operators, using for example functions of the energy,[21] for the usual property operators, dipole moment, quadrapole moment, etc., this is not an issue.

Equation 13 is the promised result. At $\mathbf{R}_x$ $\Phi^A(\mathbf{R})$, the transformation angle that diagonalizes the 2×2 matrix of an arbitrary symmetric property operator A^e differs from the perturbative result $\Phi^{(p1)}(\theta) = -\lambda(\theta)/2$ by a constant, $(\alpha + n\pi)/2$. Thus $(\partial/\partial\theta)\Phi^{A,0}(\mathbf{R}) = (\partial/\partial\theta)\Phi^{(p1)}(\mathbf{R})$ at $\mathbf{R}_x$, and therefore as noted above the transformation generated by Φ^A removes the singularity in the derivative coupling at $\mathbf{R}_x$. Again, $\Phi^{A,0}(\theta)$ is the leading term in the perturbative expansion $\Phi^A(\mathbf{R}) = \Phi^{A,0}(\theta) + \Phi^{A,1}(\mathbf{R}) + \ldots$. However, similar rigorous results are not found at higher order, that is, as one moves away from the conical intersection. See section II.C.

Equation 13 can be interpreted as follows. From eq 7, $\Phi^{(p1)} = -\lambda(\theta)/2$ transforms the adiabatic wave functions $\Psi_K(\mathbf{r}; \mathbf{R})$, through first order in energy, "back" to the geometry-independent functions $\Psi_K(\mathbf{r}, \mathbf{R}_x)$, $K = I, J$. For these $\Psi_K(\mathbf{r}, \mathbf{R}_x)$, $\mathbf{A}$ is not diagonal. The goal of $\Phi^{A,0}$, which is the negative of $\lambda/2$ up to a constant, is to take the adiabatic states *back*, for a given ρ and z^i, to a "fixed" pair of states. However, for this pair of states, $\mathbf{A}$ is required to be diagonal and hence the additional rotation provided by the nonzero offset.

Note that if A^e is an antihermitian operator, L, then

$$\mathbf{L}(\rho = 0, \theta, z^i = 0) = \boldsymbol{\sigma}_x B^- \quad (14)$$

that is, near $\mathbf{R}_x$, $\mathbf{L}$ is approximately a constant independent of θ. This observation has practical importance. Sign changes in the off-diagonal matrix element A_{IJ} at neighboring geometries may reflect a change in the overall phase of a Ψ_I or a true change in A_{IJ}. In the vicinity of a conical intersection, the geometry independence of $\mathbf{L}$ can be used to distinquish between these two possibilities.

C. The Electric Dipole Operator near the $1^1A'-2^1A'$ Seam of Conical Intersection in HeH_2. To illustrate the results presented above, the dipole moment operator $\boldsymbol{\mu}(\mathbf{r}) = \sum_i e\mathbf{r}_i$, is considered in the vicinity of a point on the $1^1A'-2^1A'$ seam of conical intersection in HeH_2. Since the two states both have A' symmetry only two components of μ are nonvanishing here, taken as μ_x and μ_y. The configuration interaction (CI) description of the $1^1A'$ and $2^1A'$ states of HeH_2 (denoted I and J, respectively, below) is a second-order CI based on a four-electron in four-orbital active space and has been described in detail previously.[22]

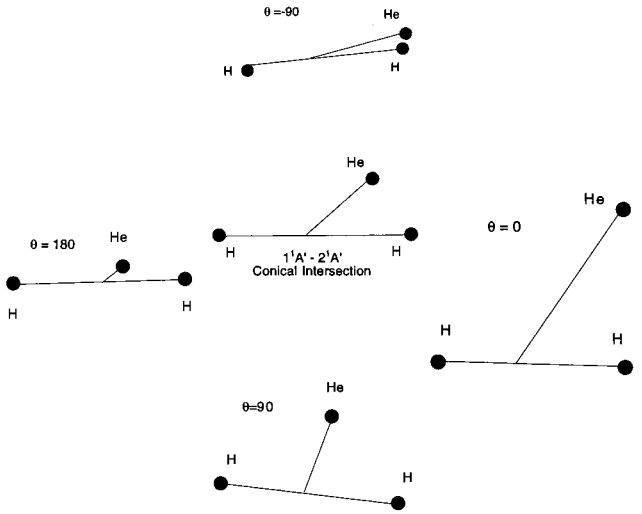

Figure 1. $\mathbf{R}_x = (1.561\,68, 3.729\,43, 44.373\,00°)$, center, as well as $\mathbf{R}$ for $\rho = 0.8$ and $\theta = -90$, 0, 90, 180. Here θ is measured relative to the $\mathbf{h}^{IJ}(\mathbf{R}_x)$.

The point of conical intersection considered is $\mathbf{R}_x = (R = 1.566\,18, r = 3.729\,43, \gamma = 44.373\,00°)$ (Figure 1) where R, r, γ are the standard Jacobi coordinates with $r = R(\mathrm{H-H})$, R the distance from He to the center of mass of H_2, and γ the angle between the r and R line segments with $\gamma = 90°$ corresponding to C_{2v} geometries. The $\mathbf{R}$ dependence of the quantities in question will be investigated for circles in the *g*-*h* plane (see Figure 1). The *g*-*h* plane is essential to the analysis since it contains all the conical part of the potential energy surfaces, so that, for example $f^{IJ}_{z^i}$ is not singular at $\mathbf{R}_x$. The analysis can be extended to different values of z^i by using different points of conical intersection. From the CI wave functions, at $\mathbf{R}_x$, for μ_x, $A^- = 1.725\,20$, $B^+ = 0.215\,57$ so that $\alpha = 7.12°$, and for μ_y, $A^- = -0.100\,47$, $B^+ = -0.518\,93$ so that $\alpha = 259.04°$ (or 79.04°). These quantities plus $\lambda(\theta)$ [and $q(\theta)$] suffice to determine $\mu^0_{w,IJ}$ and $\Phi^{\mu_w,0}$ for $w = x, y$.

Parts a and b of Figure 2, respectively, report $2\Phi^{\mu_w}$, $2\Phi^{\mu_w,0}$, λ, $\Delta_w \equiv 2\Phi^{\mu_w} + \lambda + n\pi$, f_θ and $f^{(p1)}_\theta$, and $\mu_{w,IJ}$, $\mu^0_{w,IJ}$, and iL_{zIJ} for $w = x, y$ and $\rho = 0.01$ a_0. Here iL_z is the z component of the real-valued electronic angular momentum operator, an antihermitian operator. Here and below the IJ superscripts on f are omitted for notational convenience. These figures evince the formal results of subsection II.B. Note in Figure 2a that f_θ and $f^{(p1)}_\theta$ are virtually identical reflecting the general result that taking $\Phi = \Phi^{(p1)}$ gives $f^d_\theta = 0$ at $\mathbf{R}_x$. Since $\Delta_w(\theta)$, $w = x, y$, is clearly constant, taking $\Phi = \Phi^{\mu_w}$ also gives $f^d_\theta = 0$ at $\mathbf{R}_x$ as required. It should also be emphasized that while $\Phi^{\mu_x} \neq \Phi^{\mu_y}$, $(\partial/\partial\theta)[\Phi^{\mu_x} - \Phi^{\mu_y}] = 0$ as required since both must yield $f^d_\theta = 0$ at $\mathbf{R}_x$. The transition dipole moment obtained from the CI wave functions, $\mu_{w,IJ}$, and the perturbative result (eq 11), $\mu^0_{w,IJ}$ are also virtually indistinquishable, as expected for $\rho = 0.01$ a_0 (Figure 2b). Consequently, $\Phi^{\mu_w} = \Phi^{\mu_w,0}$. Finally note in Figure 2b that $iL_{z,IJ}(\theta)$ is approximately independent of θ. This enables the relative phase of Ψ_I and Ψ_J at neighboring geometries to be straightforwardedly decided.

Parts a and b of Figure 3, respectively, report $2\Phi^{\mu_w}$, $2\Phi^{\mu_w,0}$, λ, $\Delta_w \equiv 2\Phi^{\mu_w} + \lambda + n\pi$, f_θ and $f^{(p1)}_\theta$, and $\mu_{w,IJ}$, $\mu^0_{w,IJ}$, and iL_{zIJ} for $w = x, y$ and $\rho = 0.2$ a_0. Note that $(1/\rho)f_\theta$ is approximately 1/20th its value at $\rho = 0.01$. At this ρ the agreement between the results of the perturbative treatment and those obtained from

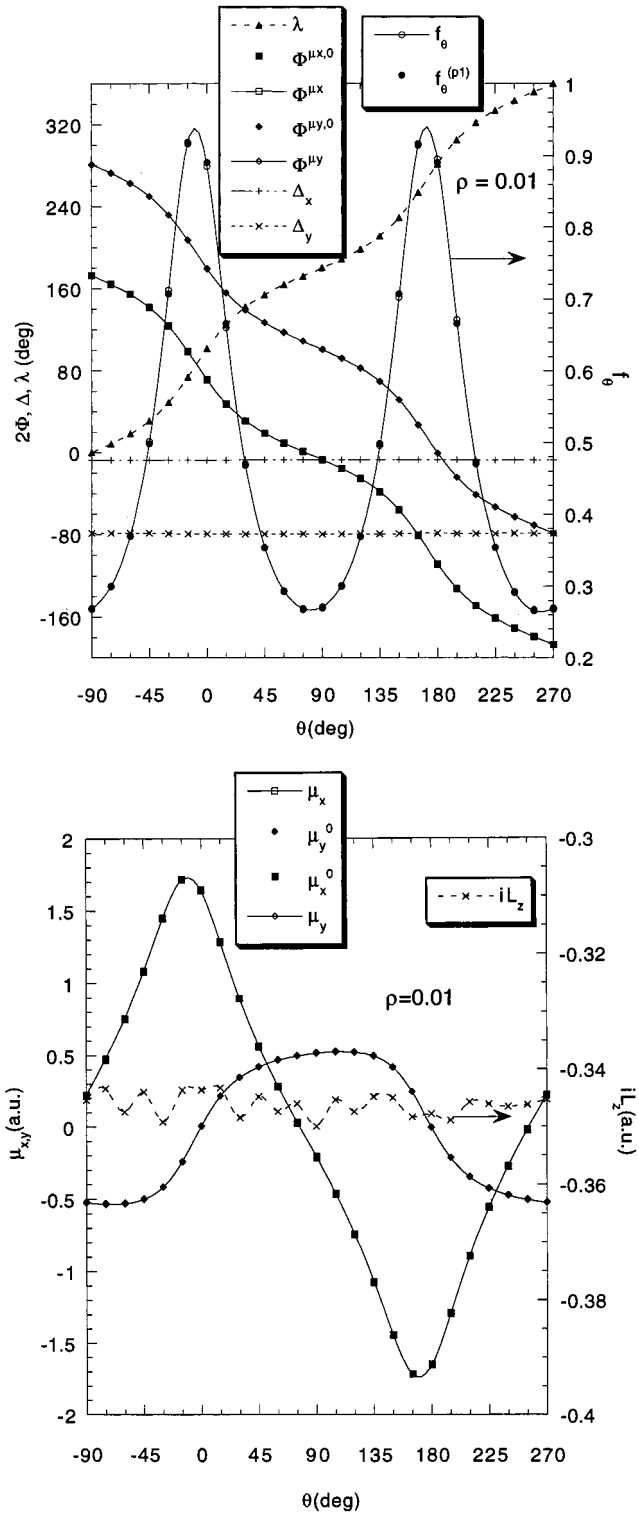

Figure 2. (a, top) $2\Phi^{\mu_w}$, $w = x$ (filled squares), y (filled diamonds) $2\Phi^{\mu_w 0}$, $w = x$ (open squares), y (open diamonds), Δ_w, $w = x$ (pluses), y (crosses), λ (filled triangles), f_θ (open circles) and $f_\theta^{(p1)}$ (filled circles) at $\rho = 0.01$. (b, bottom) $\mu_{w,IJ}$, $w = x$ (filled squares), y (filled diamonds) μ^0_{wIJ}, $w = x$ (open squares), y (open diamonds), and iL_{zIJ} (crosses) at $\rho = 0.01$.

the CI wave functions has deteriorated somewhat although it is surprisingly good, suggesting the preeminence of the θ dependence in characterizing μ. Thus the significant geometry dependence of μ in the region of the conical intersection is readily understood in terms of the perturbative analysis. Using numerical differentiation $(\partial/\partial\theta)\Phi^{\mu_w}$ is found to be within ±10% of the exact result, f_θ supporting the utility of this property-based approach for finite ρ. Finally note that iL_{zIJ} exhibits a larger θ dependence, as expected, but is still useful in assigning phase of $\mu_{w,IJ}$ at neighboring geometries.

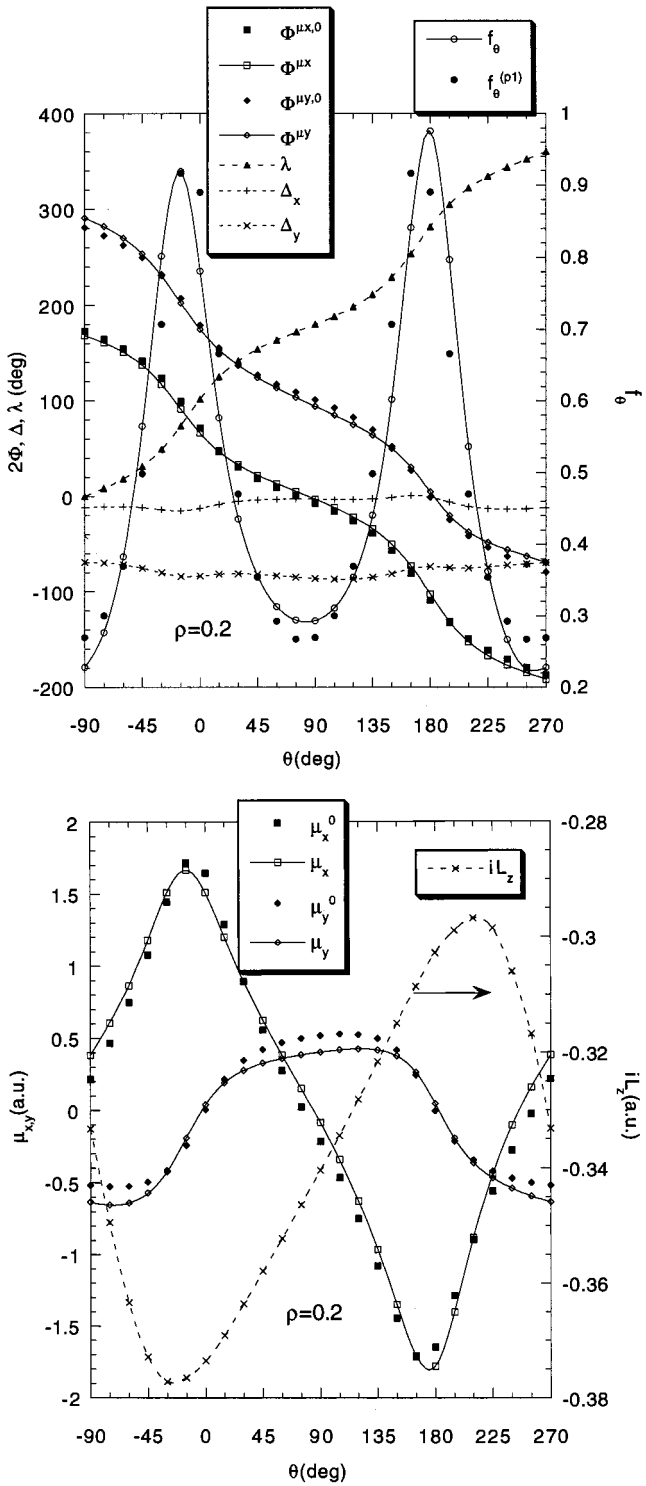

Figure 3. (a, top) Same as Figure 2a for $\rho = 0.2$. (b, bottom) Same as Figure 2a for $\rho = 0.2$.

III. Summary and Conclusions

It is shown that diagonalizing the matrix of *any* symmetric (real-valued hermitian) electronic property operator, satisfying only certain limited restrictions, generates an orthogonal transformation that removes all of the singularity of the derivative coupling at a conical intersection. Hence property-based

diabatizations, as defined in the Introduction, necessarily provide a potentially viable diabatic basis for states exhibiting conical intersections. A perturbative estimate of the matrix elements of the property operator is provided. The analysis is illustrated using the components of the dipole moment operator in the vicinity of a point on the $1^1A'-2^1A'$ seam of conical intersection in HeH_2. As expected, the choice of the (not identically vanishing) component of the dipole moment function is seen to be immaterial as far as removing the singularity in the derivative coupling is concerned. The analysis provides a clear explanation for the rapid changes in the transition moment function in the vicinity of the conical intersection.

The present analysis, which has by design focused on the singular component of the derivative coupling, provides strong support for the use of this easily implemented approach for obtaining approximate diabatic states in the immediate vicinity of a conical intersection. In a future work the present analysis will be used as part of a more complete numerical study of the approximate diabatic basis generated by the dipole moment operator in "tube" surrounding the $1^1A'-2^1A'$ seam of conical intersection in H_2S.

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