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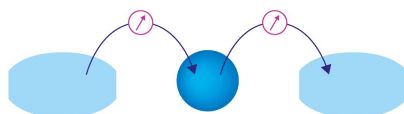
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# Quasidiabatic states described by coupled-cluster theory

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In an attempt to expand the utility of the model Hamiltonian technique developed by Köppel, Domcke, and Cederbaum (KDC) [Adv. Chem. Phys. **57**, 59 (1984)], an *ansatz* for quasidiabatic wave functions is introduced in the framework of equation-of-motion coupled-cluster (EOM-CC) theory. Based on the *ansatz*, the theory for the analytic first derivative of the off-diagonal element of the quasidiabatic potential matrix is developed by extending the theory for the analytic gradient of the EOM-CC energy. This analytic derivative is implemented for EOM-CCSD (singles and doubles approximation) calculations of radicals subject to pseudo-Jahn–Teller and Jahn–Teller interactions. Its applicability in construction of the KDC quasidiabatic model potential is discussed. © 2009 American Institute of Physics. [DOI: [10.1063/1.3127246](https://doi.org/10.1063/1.3127246)]

## I. INTRODUCTION

Phenomena that involve the coupling of electronic and nuclear motion, often called nonadiabatic interaction,<sup>1</sup> play an important role in a variety of chemical and physical processes. In chemistry, nonadiabatic effects are commonly seen in reactive intermediates such as radicals and molecules in electronically excited states, and studies of such nonadiabatic effects constitute a vigorous area of ongoing research.<sup>2–5</sup> This field requires a solid theoretical description of chemical systems that are subject to these effects. Advancement of methods in electronic structure theory as well as molecular dynamics techniques has tremendously helped in this area during the past 30 years.

The outstanding work of Yarkony and co-workers<sup>6,7</sup> in this field pioneered the application of *ab initio* electronic structure calculations based on state-averaged multiconfiguration self-consistent field (SA-MCSCF) wave functions to the study of nonadiabatic interactions. These wave functions, often augmented by configuration interaction, can be constructed so as to treat the coupled states in a balanced way. In the adiabatic representation of the Hamiltonian, usually taken in *ab initio* calculations (see Sec. II A), the coupling of electronic states takes place through derivative couplings. The tremendous progress made in analytic energy derivative methods in quantum chemistry<sup>8</sup> has enormously benefited this area, as Yarkony and co-workers<sup>6,7,9</sup> adapted these methods for analytic calculations of derivative couplings. Application of this technique to a wide range of chemical systems has attested to its value.<sup>10</sup>

In contrast to adiabatic electronic wave functions, which vary dramatically with respect to coupling nuclear coordinates in the vicinity of conical intersections and avoided crossings, diabatic wave functions<sup>11</sup> are smooth functions of the nuclear displacements. The utility of diabatic—or, more precisely, quasidiabatic—representations<sup>12</sup> has been demon-

strated not only by a model Hamiltonian technique due to Köppel, Domcke, and Cederbaum<sup>2</sup> (KDC) but also in many other studies of nonadiabatic phenomena.<sup>4,13,14</sup> Since *ab initio* electronic structure calculations do not directly provide quasidiabatic potential energy surfaces, a number of techniques have been explored for transformation from the adiabatic representation that is readily calculated to quasidiabatic one.<sup>12–17</sup> In the simplest KDC model potential approximation, the coupling strength between two diabatic states—which is, in principle, the first derivative of the off-diagonal matrix element of the electronic Hamiltonian in the quasidiabatic representation—is conveniently evaluated from analysis of the corresponding adiabatic potential energy surfaces.<sup>2</sup> This simple parametrization of the KDC model potential has been found very useful in modeling nonadiabatic dynamics.<sup>18</sup> However, extraction of the information about the diabatic couplings from the adiabatic potentials becomes difficult and/or cumbersome in certain systems. One example is when the couplings involve more than two diabatic states simultaneously, as noted in a recent publication.<sup>19</sup> Ideally, it is desirable to develop an analytic method to evaluate the diabatic coupling strength in constructions of quasidiabatic model potentials. In fact, Yarkony and co-workers recently showed that their existing code for SA-MCSCF/CI calculations of derivative couplings in the adiabatic representation<sup>9</sup> can be utilized to evaluate the coupling constants in their quasidiabatic model Hamiltonian.<sup>20</sup>

We have recently adopted the KDC model potential technique to investigate the manifestation of vibronic coupling in spectra of the benzoquinone radical cation,<sup>21</sup> pyrazolyl (C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>),<sup>22</sup> NO<sub>3</sub>,<sup>23</sup> and cyclopentadienyl (C<sub>5</sub>H<sub>5</sub>)<sup>19</sup> radicals. In these studies, a variant of the equation-of-motion coupled-cluster (EOM-CC) method, known as EOMIP-CC,<sup>24</sup> was employed to parametrize the KDC Hamiltonian. This method has also been utilized recently by a few other groups in studies of nonadiabatic phenomena.<sup>25–27</sup> The present paper outlines a strategy to use this powerful *ab initio* method to directly evaluate the linear diabatic interstate coupling con-

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stants. This strategy was already used in Ref. 19 to analyze the photoelectron spectrum of the cyclopentadienide ion ( $C_5H_5^-$ ).

The theoretical approach employed in this study is delineated in Sec. II. After briefly describing the adiabatic representation in Sec. II A, the quasidiabatic representation of the molecular Hamiltonian, i.e., the KDC diabatic model Hamiltonian, is discussed in Sec. II B. A quasidiabatic *ansatz* is introduced in the framework of EOM-CC theory in Sec. II C. Based on this *ansatz*, the methodology to evaluate the analytic first derivative of the diabatic interstate coupling within EOM-CC theory is developed in Sec. II D. Applications of this methodology to a few molecular systems are presented in Sec. III.

## II. THEORY

At the outset, let us establish some notational conventions and a general framework that will facilitate the subsequent presentation. The foundation for the treatment of nonadiabatic effects is the (admittedly problematic<sup>28</sup>) Born–Huang *ansatz*<sup>29</sup> for the wave function of the vibronic state  $k$ , viz.,

$$\Psi_k(r, R) = \sum_i \psi_i(r; R) \Omega_i^{(k)}(R). \quad (1)$$

Here,  $\psi_i(r; R)$  are elements of an orthonormal set of electronic wave functions that depend explicitly on the electronic coordinates  $r$  and, in general, vary parametrically with the nuclear coordinates  $R$ . In Eq. (1),  $\Omega_i^{(k)}(R)$  is the part of vibrational wave function for state  $k$  that is associated with the electronic wave function  $\psi_i(r; R)$ . Both the electronic wave functions and the vibrational wave functions are, in practice, given in terms of basis set expansions. The former is quite familiar and requires no elaboration here, and the latter can be written as

$$\Omega_i^{(k)}(R) = \sum_m c_m^{(k;i)} \chi_m(R), \quad (2)$$

where  $\chi_m$  is a harmonic oscillator function in terms of some set of nuclear coordinates  $R$ . The vector representation of a finite Born–Huang basis consisting of  $n'$  vibrational basis functions  $\chi_m(R)$  and  $n$  electronic basis functions  $\psi_i(r; R)$  can then be represented as

$$\begin{pmatrix} \psi_1(r; R) \chi_1(R) \\ \psi_1(r; R) \chi_2(R) \\ \vdots \\ \psi_1(r; R) \chi_{n'}(R) \\ \psi_2(r; R) \chi_1(R) \\ \psi_2(r; R) \chi_2(R) \\ \vdots \\ \psi_2(r; R) \chi_{n'}(R) \\ \psi_3(r; R) \chi_1(R) \\ \psi_3(r; R) \chi_2(R) \\ \vdots \\ \psi_n(r; R) \chi_{n'}(R) \end{pmatrix}. \quad (3)$$

Variational approximations to the vibronic energies and wave functions can then be obtained by projecting the molecular Hamiltonian

$$\hat{\mathcal{H}} = \hat{T}_N + \hat{H}_e \quad (4)$$

onto this basis and diagonalizing the resulting matrix. Here,  $\hat{T}_N$  is the nuclear kinetic energy operator and  $\hat{H}_e$  is the electronic Hamiltonian which also includes nuclear repulsion. Eigenvectors of the matrix comprise the coefficients found in Eq. (2) above. Matrix elements of  $\hat{\mathcal{H}}$  can be written as

$$\langle \psi_i(r; R) \chi_j(R) | \hat{\mathcal{H}} | \psi_{i'}(r; R) \chi_{j'}(R) \rangle, \quad (5)$$

which can then be partitioned into contributions from  $\hat{T}_N$  and  $\hat{H}_e$ ,

$$\langle \psi_i(r; R) \chi_j(R) | \hat{T}_N | \psi_{i'}(r; R) \chi_{j'}(R) \rangle \quad (6)$$

and

$$\langle \psi_i(r; R) \chi_j(R) | \hat{H}_e | \psi_{i'}(r; R) \chi_{j'}(R) \rangle. \quad (7)$$

The specific form of these matrix elements depends on the choice of the electronic wave functions  $\psi_i(r; R)$ . Two such choices are discussed now.

### A. Adiabatic representation

In the adiabatic picture, the electronic wave functions are chosen to be those that diagonalize the electronic Hamiltonian at each nuclear configuration  $R$ . This leads to considerable simplification of Eq. (7),

$$\begin{aligned} \langle \psi_i(r; R) \chi_j(R) | \hat{H}_e | \psi_{i'}(r; R) \chi_{j'}(R) \rangle \\ = \langle \psi_i(r; R) \chi_j(R) | V_i(R) | \psi_{i'}(r; R) \chi_{j'}(R) \rangle \\ = \delta_{ii'} \langle \chi_j(R) | V_i(R) | \chi_{j'}(R) \rangle, \end{aligned} \quad (8)$$

where  $V_i(R)$  is the potential energy surface associated with the *adiabatic* electronic state  $i$ . That is, the electronic Hamiltonian is block diagonal in the vibronic (Born–Huang) basis when the adiabatic representation is chosen.

Matrix elements of the kinetic energy operator are somewhat more complicated. Proceeding in a deliberate fashion, one finds

$$\begin{aligned}
& \langle \psi_i(r;R) \chi_j(R) | \hat{T}_N | \psi_{i'}(r;R) \chi_{j'}(R) \rangle \\
&= \sum_{\alpha} \frac{-\hbar^2}{2M_{\alpha}} \langle \psi_i(r;R) \chi_j(R) | \nabla_{\alpha}^2 | \psi_{i'}(r;R) \chi_{j'}(R) \rangle \\
&= \sum_{\alpha} \frac{-\hbar^2}{2M_{\alpha}} \langle \psi_i(r;R) \chi_j(R) | \psi_{i'}(r;R) \nabla_{\alpha}^2 \chi_{j'}(R) \rangle \\
&\quad + \sum_{\alpha} \frac{-\hbar^2}{M_{\alpha}} \langle \psi_i(r;R) \chi_j(R) | \nabla_{\alpha} \psi_{i'}(r;R) \cdot \nabla_{\alpha} \chi_{j'}(R) \rangle \\
&\quad + \sum_{\alpha} \frac{-\hbar^2}{2M_{\alpha}} \langle \psi_i(r;R) \chi_j(R) | \nabla_{\alpha}^2 \psi_{i'}(r;R) \chi_{j'}(R) \rangle, \quad (9)
\end{aligned}$$

where the summation is taken over all nuclear indices  $\alpha$ , and  $M_{\alpha}$  and  $\nabla_{\alpha}$  represent the corresponding masses and gradients, respectively. Integration over the electronic coordinates gives the following simplified expression:

$$\begin{aligned}
& \langle \psi_i(r;R) \chi_j(R) | \hat{T}_N | \psi_{i'}(r;R) \chi_{j'}(R) \rangle \\
&= \delta_{ii'} \sum_{\alpha} \frac{-\hbar^2}{2M_{\alpha}} \langle \chi_j(R) | \nabla_{\alpha}^2 \chi_{j'}(R) \rangle \\
&\quad + \sum_{\alpha} \frac{-\hbar^2}{M_{\alpha}} \langle \chi_j(R) | g_{ii'}^{\alpha} \cdot \nabla_{\alpha} \chi_{j'}(R) \rangle \\
&\quad + \sum_{\alpha} \frac{-\hbar^2}{2M_{\alpha}} \langle \chi_j(R) | h_{ii'}^{\alpha} \chi_{j'}(R) \rangle, \quad (10)
\end{aligned}$$

where the so-called nonadiabatic coupling matrix elements (in the adiabatic representation)  $g_{ii'}^{\alpha}$  and  $h_{ii'}^{\alpha}$  are defined by

$$g_{ii'}^{\alpha} \equiv \langle \psi_i(r;R) | \nabla_{\alpha} \psi_{i'}(r;R) \rangle \quad (11)$$

and

$$h_{ii'}^{\alpha} \equiv \langle \psi_i(r;R) | \nabla_{\alpha}^2 \psi_{i'}(r;R) \rangle, \quad (12)$$

respectively. The second derivative term above can be written solely in terms of the  $g_{ii'}^{\alpha}$  vectors by noting that

$$\begin{aligned}
\nabla_{\alpha} \cdot g_{ii'}^{\alpha} &= \langle \nabla_{\alpha} \psi_i(r;R) | \cdot \nabla_{\alpha} \psi_{i'}(r;R) \rangle + h_{ii'}^{\alpha} \\
&= \sum_k \langle \nabla_{\alpha} \psi_i(r;R) | \psi_k(r;R) \rangle \\
&\quad \cdot \langle \psi_k(r;R) | \nabla_{\alpha} \psi_{i'}(r;R) \rangle + h_{ii'}^{\alpha} \\
&= - \sum_k \langle \psi_i(r;R) | \nabla_{\alpha} \psi_k(r;R) \rangle \cdot \langle \psi_k(r;R) | \nabla_{\alpha} \psi_{i'}(r;R) \rangle \\
&\quad + h_{ii'}^{\alpha} = - \sum_k g_{ik}^{\alpha} \cdot g_{ki'}^{\alpha} + h_{ii'}^{\alpha}, \quad (13)
\end{aligned}$$

and thus

$$h_{ii'}^{\alpha} = \nabla_{\alpha} \cdot g_{ii'}^{\alpha} + \sum_k g_{ik}^{\alpha} \cdot g_{ki'}^{\alpha}. \quad (14)$$

In deriving Eq. (13), the second step inserts the resolution of the identity

$$1 = \sum_k |\psi_k(r;R)\rangle \langle \psi_k(r;R)| \quad (15)$$

and the next step follows from the orthogonality imposed on the electronic wave functions. The sum runs over the entire spectrum of the basis set Hamiltonian so this is clearly not a practical prescription for calculations. However, it does show that the so-called derivative coupling matrix elements  $g_{ii'}^{\alpha}$  completely govern the mixing between adiabatic states as described by the nonrelativistic molecular Hamiltonian. The wave function gradients are given by

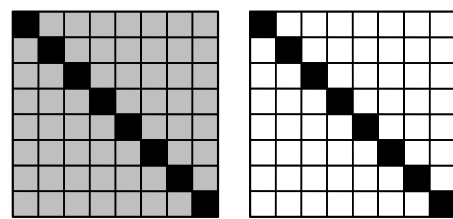
$$\nabla_{\alpha} \psi_i(r;R) = \sum_k' |\psi_k(r;R)\rangle \frac{\langle \psi_k(r;R) | \nabla_{\alpha} \hat{H}_e | \psi_i(r;R) \rangle}{V_i(R) - V_k(R)}, \quad (16)$$

where the prime symbol means that the summation is taken over all states except  $i$ . Substitution of Eq. (16) into Eq. (11) yields

$$g_{ii'}^{\alpha} = \frac{\langle \psi_i(r;R) | \nabla_{\alpha} \hat{H}_e | \psi_{i'}(r;R) \rangle}{V_{i'}(R) - V_i(R)} \quad (17)$$

owing to orthogonality.

A visual representation of the Born–Huang Hamiltonian in the adiabatic representation is thus



$T_N$ 
 $H_e$

(18)

Each block of the matrices above corresponds to the set of vibrational basis functions associated with a particular (adiabatic) electronic function [see Eq. (1)]. The diagonal sub-blocks of the electronic Hamiltonian are the matrix representations of the potential energy functions of the corresponding adiabatic electronic states in the harmonic oscillator basis [Eq. (8)]. The nuclear kinetic energy matrix is diagonally dominant in the electronic basis. The first term in Eq. (10), in which the Laplacian acts directly upon the vibrational basis functions (which depend explicitly on the coordinates  $R$ ), is the largest contribution, and its matrix representation is block diagonal in the electronic basis due to the orthogonality constraint imposed on the electronic basis. In the remaining “derivative coupling” terms, the derivative operators also act on the electronic wave function. These terms are smaller in general (unless the molecule is in the vicinity of conical intersections or avoided crossings), and their effect—which constitutes the entirety of the off-diagonal blocks—is correspondingly represented by a light shade of gray. They also make a contribution to the diagonal elements [the last term in Eq. (10)], which is also usually small; this will be returned to in the following.

When the derivative coupling terms on the off-diagonal blocks of the nuclear kinetic energy matrix are neglected, the Hamiltonian block-diagonalizes into matrix representations of the individual “vibrational” Schrödinger equations

$$[\hat{T}_N(R) + V_i(R)]\Omega_i(R) = E_{\text{vib}}\Omega_i(R). \quad (19)$$

The eigenvalues of Eq. (19) represent the accessible molecular energy levels in the electronic state  $i$ .<sup>30</sup> This approach to the Hamiltonian is known as the adiabatic approximation,<sup>29</sup> in which the wave function is separable into electronic and vibrational parts. This separability holds regardless of whether or not the coupling terms on the diagonal blocks are included in the Hamiltonian. Inclusion of these terms<sup>31</sup> is known as the diagonal Born–Oppenheimer correction (DBOC); its evaluation by quantum chemical methods started with numerical implementations,<sup>32</sup> was later extended to an analytic treatment at the SCF level by Handy *et al.*<sup>33</sup> and subsequently generalized to correlated methods such as multireference configuration interaction,<sup>34</sup> configuration interaction,<sup>35,36</sup> and CC theory.<sup>36</sup> On the other hand, if the coupling terms along the diagonal blocks are also neglected, then this subset of the adiabatic approximation is called the “Born–Oppenheimer” approximation.<sup>37</sup> This approximation is usually taken in quantum chemical calculations of molecular systems with small derivative couplings. An insightful paper by Kutzelnigg<sup>38</sup> suggested that contributions to molecular energy levels arising from the DBOC are comparable to those from the off-diagonal coupling terms, so there is no apparent advantage associated with inclusion of the DBOC alone in the routine calculation of vibrational energy levels. After all, the off-diagonal coupling terms are associated with what is called “nonadiabatic coupling.”

## B. Quasidiabatic representation

When the assumption that the electronic wave function varies slowly with the nuclear coordinates is a good one—and it is for the overwhelming majority of quantum chemical applications—the energy level structure associated with the lowest-lying (adiabatic) electronic state can be determined quite adequately by solving the electronic Schrödinger equation at a high level of theory (such as CC, multireference configuration interaction, quantum Monte Carlo, etc.), constructing the potential energy surface, and then solving Eq. (19). However, the fact is that potential energy surfaces often do cross each other or exhibit avoided crossings, and in these situations the assumption of a slowly varying electronic wave function breaks down. One is then forced to deal with the derivative coupling terms discussed in Sec. II A. In a number of studies of nonadiabatic dynamics, the derivative couplings [Eq. (11)] have been evaluated directly in *ab initio* electronic structure calculations based on multireference configuration interaction methods using state-averaged orbitals.<sup>9</sup> A problem in such calculations is associated with the divergent nature of the derivative couplings at conical intersections [see Eq. (17)]. Such a problem can be avoided by transforming the molecular Schrödinger equation to a diabatic representation.

In an (idealized) diabatic representation, the electronic wave functions in the Born–Huang basis are not those that

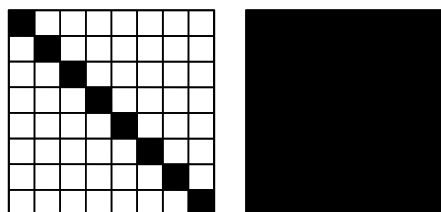
diagonalize the electronic Hamiltonian at each nuclear geometry  $R$ . They are instead those that are not mixed by the nuclear kinetic energy operator, viz.,

$$\langle \psi_i | \hat{T}_N | \psi_j \rangle = \delta_{ij} \hat{T}_N, \quad (20)$$

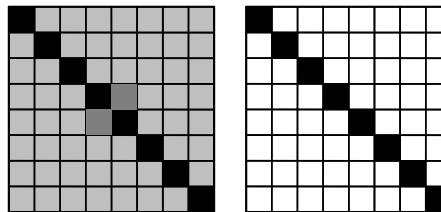
where an orthonormality condition is imposed on the electronic wave functions. The equation above is satisfied exactly in one case, namely, when the diabatic electronic wave functions are chosen to be the set of electronic wave functions obtained at some reference geometry  $R_0$ . It is then readily apparent that all derivative coupling terms vanish. Such an electronic basis, with which is associated the so-called “static Born–Huang” expansion, is pedagogically useful, but clearly not a serious basis for any sort of computational endeavor.<sup>39</sup>

An extremely powerful tool in chemical physics, which—in the authors’ opinion—is somewhat underappreciated in the community, is the quasidiabatic model that has been developed and popularized by Köppel *et al.*<sup>2</sup> and collaborators for over three decades. The KDC model can be discussed from the perspective of the static Born–Huang expansion as follows. At each nuclear configuration, one effects a block diagonalization of the electronic Hamiltonian (which is clearly something of a mess and not diagonally dominant at most geometries  $R$ ) in the static Born–Huang basis that isolates the interacting electronic states. Pictorially, a case of strong coupling, which would resemble the following in the adiabatic representation

Static Born-Huang Basis



Adiabatic Basis



$T_N$

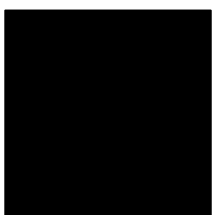
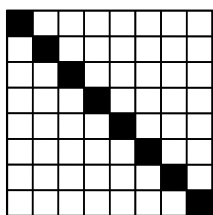
$H_e$

(21)

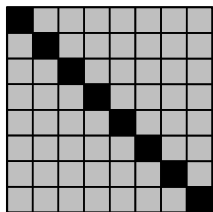
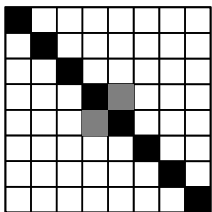
(the relatively darker shading in the off-diagonal blocks of the nuclear kinetic energy matrix indicates two electronic states that are mixed by appreciable derivative coupling in the adiabatic basis), takes on the character



## Static Born-Huang Basis



## Quasidiabatic Basis

 $T_N$  $H_e$ 

(22)

in the KDC quasidiabatic representation. The block diagonalization of the two interacting states against the remainder of the static Born–Huang electronic basis effectively builds in the “following the nuclei” sort of behavior that should be obeyed by the electronic wave functions, but which is, of course, completely lacking in the static electronic basis. However, the rapid variation of wave functions which results from strong interaction and/or quasidegeneracy can be avoided if the set of isolated states comprises all those that are effectively decoupled from the remainder of the spectrum. This choice of basis—as described by this pedagogical model—represents an exact unitary transformation of the adiabatic electronic basis (one requirement usually associated with a true diabatic basis), but the nuclear kinetic energy operator is only approximately diagonal in this basis. Hence the term quasidiabatic, first applied to this choice by Cederbaum *et al.* in Ref. 40. It is presumed in this model that the off-diagonal (and diagonal) derivative coupling terms that remain after the block diagonalization is done can be safely neglected, just as in the usual case in which the Born–Oppenheimer model is applied to calculate molecular energy levels associated with well-isolated electronic states.

Recall that, in the simple Born–Oppenheimer case, the vibrational energy levels are the solutions to Eqs. (19). One way to parametrize the potential energy surface of an electronic state  $i$  is by means of a Taylor expansion in reduced normal coordinates  $q_i$ , viz.,

$$V_i(q) = V_0 + \sum_i \kappa_i q_i + \frac{1}{2} \sum_i \kappa_{ij} q_i q_j + \frac{1}{6} \sum_{ijk} \kappa_{ijk} q_i q_j q_k + \frac{1}{24} \sum_{ijkl} \kappa_{ijkl} q_i q_j q_k q_l + \cdots, \quad (23)$$

where it is (purposely) not assumed that the energy is stationary at the coordinate system origin. The vibrational Schrödinger equation associated with this electronic state is simply the sum of two corresponding darkly shaded blocks in Eq. (18), where the (presumed small) derivative coupling that spoils the diagonal nature of the complete molecular Hamiltonian is neglected.

In the quasidiabatic representation, the situation is similar, except that the equation that must be solved corresponds to nontrivial subblocks of the molecular Hamiltonian. In the simplest case, involving only two coupled quasidiabatic states (designated as  $A$  and  $B$ ), it becomes

$$\left[ \begin{pmatrix} T_N^{AA}(q) & 0 \\ 0 & T_N^{BB}(q) \end{pmatrix} + \begin{pmatrix} V^{AA}(q) & V^{AB}(q) \\ V^{AB}(q) & V^{BB}(q) \end{pmatrix} \right] \begin{pmatrix} \Omega_A(q) \\ \Omega_B(q) \end{pmatrix} = E_{vr} \begin{pmatrix} \Omega_A(q) \\ \Omega_B(q) \end{pmatrix}. \quad (24)$$

The matrix elements of the nuclear kinetic energy operator in the vibrational (harmonic oscillator) basis are straightforward, and those contributions that act on the electronic functions are—provided the choice of electronic basis is wise—negligible. The potential energy matrix is therefore the important part of an effective treatment of the coupling of vibrational and electronic motion in the quasidiabatic representation, just as the nuclear kinetic energy matrix plays a similar role in the adiabatic representation. The quasidiabatic representation, however, offers the advantage that the coupling between states in the potential (perhaps most appropriately termed the “diabatic coupling,” as it is the coupling between diabatic states) is generally a well-behaved function of the nuclear coordinates, even in the vicinity of regions where the corresponding adiabatic potential energy surfaces touch or interact strongly.

The potential matrix in the quasidiabatic representation is a generalization of the potential energy surface, and can again be represented by Taylor series in the coordinates  $q$ . The simplest such model (which will be that used throughout the remainder of this manuscript) is the so-called linear vibronic coupling (LVC) model,<sup>2,41</sup> in which the potential matrix is assumed to be suitably approximated by

$$\begin{pmatrix} V^{AA}(q) & V^{AB}(q) \\ V^{AB}(q) & V^{BB}(q) \end{pmatrix} = \begin{pmatrix} V_0^A + \sum_i \kappa_i^A q_i + \frac{1}{2} \sum_i \omega_i q_i^2 & \sum_i \lambda_i^{AB} q_i \\ \sum_i \lambda_i^{AB} q_i & V_0^B + \sum_i \kappa_i^B q_i + \frac{1}{2} \sum_i \omega_i q_i^2 \end{pmatrix}, \quad (25)$$

where  $V_0^A$  and  $V_0^B$  are the electronic energies of states  $A$  and  $B$  at the origin of the nuclear coordinate system  $q_0$ , one of which is usually chosen to be zero.

While the polynomial representation of the potential matrix used in the KDC-LVC model imposes an approximation, the procedure discussed thus far is in principle equivalent to the block diagonalization of the electronic Hamiltonian in the static Born–Huang basis. However, such a calculation is clearly impossible, and one must make additional assumptions about the nature of the quasidiabatic electronic states  $\psi(r; q)$ . Only then can the parameters in Eq. (25), which are defined by

$$\kappa_i^A = \frac{\partial}{\partial q_i} \langle \psi_A(r; q) | \hat{H}_e | \psi_A(r; q) \rangle |_{q_0}, \quad (26)$$

$$\omega_i^A = \frac{\partial^2}{\partial q_i^2} \langle \psi_A(r; q) | \hat{H}_e | \psi_A(r; q) \rangle |_{q_0}, \quad (27)$$

$$\lambda_i^{AB} = \frac{\partial}{\partial q_i} \langle \psi_A(r; q) | \hat{H}_e | \psi_B(r; q) \rangle |_{q_0}, \quad (28)$$

be deduced.

Let us now restrict our discussion to the following case: the two states  $A$  and  $B$  are the only two which interact with one another, and further that these two states have different electronic symmetries at  $q_0$ . An additional (simplifying, but unnecessary) assumption will be that the system will be described in terms of a point group of order two, having irreducible representations  $\Gamma_1$  and  $\Gamma_2$ . In such a case, it should be clear that, within the nuclear configuration space that retains the nontrivial element of symmetry, the exact (adiabatic) eigenfunctions of the electronic Hamiltonian do not mix the two states  $\psi_A(r; q)$  and  $\psi_B(r; q)$ . Thus, the block diagonalization of the Hamiltonian that yields the quasidiabatic states will lead to the precise equivalence of adiabatic and quasidiabatic states *for geometries that retain this element of symmetry*. This means that all parameters in the quasidiabatic potential energy matrix that pertain only to the totally symmetric subspace of nuclear configurations are given by the corresponding values in the adiabatic basis. In other words, the parameters  $\kappa_i$ , so-called linear intrastate coupling constants, are given by the analytic first derivatives of the adiabatic potential energy surfaces along the totally symmetric coordinates  $q_i$ .<sup>42</sup> Along nonsymmetric coordinates (those that transform as  $\Gamma_2$ ), the first derivatives at  $q_0$  necessarily vanish in both adiabatic and diabatic representations. Similarly, the second derivatives (harmonic frequencies) are exactly those of the associated adiabatic basis *for the totally symmetric coordinates*.

The only two types of parameters in the LVC Hamiltonian that cannot be obtained by straightforward quantum chemical calculation are thus the diabatic harmonic frequencies for the nonsymmetric modes, and the corresponding linear diabatic interstate coupling constants  $\lambda_i^{AB}$ . Analytic diagonalization of the potential matrix (the eigenvalues of which are the adiabatic energies), followed by differentiation of the upper and lower eigenvalues with respect to the coordinates that transform as  $\Gamma_2$  yields the relations

$$\left. \frac{\partial^2 V^+}{\partial q_i^2} \right|_{q_0} = \omega_i + \frac{2[\lambda_i^{AB}]^2}{\Delta_0}, \quad (29)$$

$$\left. \frac{\partial^2 V^-}{\partial q_i^2} \right|_{q_0} = \omega_i - \frac{2[\lambda_i^{AB}]^2}{\Delta_0}, \quad (30)$$

$$\left. \frac{\partial^2 V^+}{\partial q_i \partial q_j} \right|_{q_0} = \frac{2\lambda_i^{AB} \lambda_j^{AB}}{\Delta_0}, \quad (31)$$

$$\left. \frac{\partial^2 V^-}{\partial q_i \partial q_j} \right|_{q_0} = -\frac{2\lambda_i^{AB} \lambda_j^{AB}}{\Delta_0}, \quad (32)$$

where  $V^+$  and  $V^-$  represent the upper and lower adiabatic potential energy surfaces, respectively, and  $\Delta_0 = V_0^B - V_0^A > 0$ . Thus, *to the extent that the model potential is able to describe the adiabatic states*, the harmonic frequencies of the quasidiabatic states and the coupling constants can be obtained from

$$\omega_i = \frac{1}{2} \left( \frac{\partial^2 V^+}{\partial q_i^2} + \frac{\partial^2 V^-}{\partial q_i^2} \right)_{q_0}, \quad (33)$$

$$\lambda_i^{AB} = \frac{1}{2} \left[ \Delta_0 \left( \frac{\partial^2 V^+}{\partial q_i^2} - \frac{\partial^2 V^-}{\partial q_i^2} \right)_{q_0} \right]^{1/2}. \quad (34)$$

This and other related strategies have long been used in conjunction with various quantum chemical procedures to determine parameters of the LVC Hamiltonian.<sup>2,41</sup> Some discussion of minutiae follows.

Success of the LVC treatment in the simulation of spectra is clearly predicated on the assumptions upon which the model is based. To some degree, the suitability of the treatment can be judged by checking whether eigenvalues of the model potential matrix approximate the corresponding quantum chemical adiabatic potentials. Several such checks are apparent. First, if there is more than one coupling mode, rotation of the adiabatic Hessian to the normal coordinate representation being used in the LVC treatment is instructive. Specifically, the off-diagonal terms in the transformed Hessian should be reasonably approximated by Eqs. (31) and (32). It should also be noted that the sign of the coupling constants, which cannot be deduced from Eq. (34), can be deduced (up to an overall phase factor) from the signs of the off-diagonal Hessian terms. A second (and somewhat less satisfying) check is to make sure that the diabatic force constants take on “reasonable” values. It is an empirical truth that the diabatic force constants for coupling modes are usually close to those that correspond to the same mode in a nearby (and closed-shell) reference state of the molecule. For example, in the  $\text{NO}_2$  radical, the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  electronic states are coupled by the asymmetric  $\nu_3$  stretching motion. The diabatic force constant for these two states is then expected to be “close” to the asymmetric stretching frequency of the  $\text{NO}_2$  anion, which is a well-behaved closed-shell molecule [see discussion in Sec. III below]. Another check that requires somewhat more tedium in its evaluation is based on the values of the anharmonic (cubic and quartic) force con-

stants associated with the adiabatic states. Again, by diagonalizing the diabatic potential, force constants such as the  $\kappa_{jjjj}$ ,  $\kappa_{ijj}$ ,  $\kappa_{jjj'j'}$ , etc. ( $i$  here refers to totally symmetric coordinates, and  $j$  those transforming as  $\Gamma_2$ ) can be calculated from the LVC model. These can then be compared with the *ab initio* adiabatic quantities. Finally, transition states for pseudorotation, the positions and relative energies of minima on the potential surfaces, etc., can be calculated from the eigenvalues of the LVC potential and compared to the corresponding *ab initio* points.

In the context of the above, it should be noted that the potential constants associated with symmetric nuclear configurations are very simply obtained from *ab initio* calculations, and all vibronic effects (which are manifest in several ways in *ab initio* calculations, such as symmetry breaking of the orbitals) play no role in their calculation. Thus, just about any correlated electronic structure treatment, in conjunction with an adequate basis set, can predict these parameters with some reliability. The situation is different for the coupling parameters and force constants for asymmetric motion, however, as it is possible—even likely—that many quantum chemical methods based on a reference function that has strong overlap with the final adiabatic states of interest will encounter problems in this area of the sort generally characterized as “symmetry breaking.”<sup>43</sup> Thus, while using a method such as MP2, or density functional theory, or even CCSD(T) is a good choice for the symmetric parameters, the results can range from acceptable to catastrophic when they are used to evaluate parameters associated with the coupling modes. This was realized long ago by Cederbaum *et al.*,<sup>41</sup> who used a Green’s function approach<sup>44</sup> to calculate these parameters. In this approach, the reference state is based on the molecule with one more (or one fewer) electron than the state of interest. These reference states have zero overlap with the final states, and—in general—are not prone to symmetry breaking problems. However, even with an appropriate method such as Green’s function approach, parametrization of some quasidiabatic model potentials requires more complicated analysis of the adiabatic potential energy surfaces than Eq. (34). One class of examples, which we have encountered recently in our research,<sup>19</sup> is when an electronic state of interest interacts with more than one other state along the same modes.

At this point, it is appropriate to point out that both the quadratic diabatic constants and the linear coupling constants  $\lambda_i^{AB}$  are defined by Eqs. (27) and (28), respectively, and are thus—in principle—subject to direct computation. Before continuing, we note that there is an assumption in the LVC model that seems to us a rather dubious one in many circumstances: the assumed equivalence of the diabatic harmonic force constants for the states  $A$  and  $B$  [see Eq. (25)]. While it is true that the totally symmetric force constants (where the adiabatic and diabatic constants are coincident) are usually rather close to each other, this seems to be a plausible first assumption to relax when trying to increase the quantitative accuracy of the KDC model. Such differences are included in what is termed the quadratic vibronic coupling model,<sup>22,45,46</sup> and this causes little complication whatsoever for the symmetric modes. However, when one allows for the possibility

that the diabatic force constants for the coupling modes can differ, then Eq. (34) cannot be used to calculate the linear coupling constants. Indeed, there is no way to uniquely fit the three independent parameters  $\lambda_i^{AB}$ ,  $\omega_i^A$ , and  $\omega_i^B$  to the curvature of the two adiabatic potential energy surfaces.

It should be clear at this juncture that there is some merit to the direct and analytic calculation of the diabatic coupling constants in the KDC model Hamiltonian, as well as the upper and lower state force constants. Note, however, that evaluating either of these quantities enables both of them to be determined, if the adiabatic potentials are available. While the adiabatic states are uniquely defined and the definition of derivative couplings is unambiguous, one must make an *ansatz* for the diabatic electronic states before setting about to evaluate equations such as Eqs. (27) and (28). One such *ansatz*, based on CC theory, is introduced in the next section and then applied to calculate couplings between the resulting quasidiabatic states analytically.

### C. Quasidiabatic ansatz

In this section, the quasidiabatic representation of electronic wave functions is discussed in the framework of EOM-CC theory.<sup>24,47–49</sup> It has been shown that EOM-CC methods are—analogue in the spirit to Green’s function method—capable of providing a qualitatively correct description of adiabatic potential energy surfaces in the vicinity of a conical intersection between states of different symmetry,<sup>50</sup> unlike standard single-reference CC theory, which is subject to artifacts associated with the zeroth-order reference function.<sup>43,51</sup> Here, it is demonstrated how analytic energy derivative techniques in EOM-CC theory<sup>24,48,52,53</sup> can be utilized to construct the off-diagonal elements of a KDC diabatic model potential matrix.

The reference wave function for EOM-CC is usually that of an  $n$ -electron, closed-shell state,<sup>54</sup> which is described by the standard parametrization of CC methods,

$$|\psi_{\text{CC}}\rangle = \exp(T)|0\rangle. \quad (35)$$

Here,  $|0\rangle$  refers to a Slater determinant that typically is constructed of the Hartree–Fock SCF orbitals, and  $T$  is the cluster operator

$$T \equiv T_1 + T_2 + \cdots, \quad (36)$$

where

$$T_n = \frac{1}{n!} \sum_{\substack{ijk\cdots \\ abc\cdots}} t_{ijk\cdots}^{abc\cdots} a^\dagger i b^\dagger j c^\dagger k \cdots. \quad (37)$$

The strings of creation and annihilation operators in  $T_n$  are all those that generate  $n$ -fold excited determinants (with respect to  $|0\rangle$ ), each of which carries an overall weight, or amplitude  $t_{ijk\cdots}^{abc\cdots}$ . The usual convention is followed here for the orbital designation:  $i, j, k, \cdots$  represent orbitals that are occupied in the reference determinant, while  $a, b, c, \cdots$  represent unoccupied orbitals. While Eq. (35) is in a form that can be used to parametrize the exact (full configuration interaction, or FCI) wave function, practical considerations dictate that the  $T$  operator be truncated. The most common among



truncated CC methods are CCSD<sup>55</sup> ( $n=2$ ) and CCSDT<sup>56–58</sup> ( $n=3$ ). Intermediate methods such as the ubiquitous CCSD(T)<sup>59</sup> also exist, but this paper considers only “full” models such as CCSD and CCSDT. The amplitudes are most easily obtained by insertion of the wave function ansatz into the Schrödinger equation, followed by premultiplication with  $\exp(-T)$  and projection onto well-defined sets of Slater determinants as follows:

$$\langle 0 | \exp(-T) \hat{H}_e \exp(T) | 0 \rangle = E_{CC}, \quad (38)$$

$$\langle \phi_i^a | \exp(-T) \hat{H}_e \exp(T) | 0 \rangle = 0$$

$$\langle \phi_{ij}^{ab} | \exp(-T) \hat{H}_e \exp(T) | 0 \rangle = 0 \quad (39)$$

⋮

where  $\phi_{ijk}^{abc\dots}$  represents all determinants that are obtained by promoting  $n$  electrons from orbitals occupied in  $|0\rangle$  to unoccupied orbitals. The homogeneous and nonlinear “CC equations” [Eq. (39)] are solved for all excitation levels up to  $n$ , the highest level of excitation included in the truncated  $T$  operator. A very convenient shorthand notation is

$$\langle 0 | \bar{H} | 0 \rangle = E_{CC}, \quad (40)$$

$$\langle p | \bar{H} | 0 \rangle = 0, \quad (41)$$

where the similarity transformation of the Hamiltonian  $\exp(-T) \hat{H}_e \exp(T)$  is designated by  $\bar{H}$ , and  $p$  represents the set of determinants that lie in the projection space of Eqs. (39).

EOM-CC theory, which is equivalent to CC linear response theory<sup>60</sup> for the energies of “full” CC methods such as CCSD and CCSDT, can be derived, justified, explained and otherwise developed in several different ways. One such approach is to note that the correlated reference state energy  $E_{CC}$  can be viewed as the solution to the eigenvalue problem

$$\bar{H} | 0 \rangle = E_{CC} | 0 \rangle. \quad (42)$$

In other words, one eigenvector of  $\bar{H}$  in the Slater determinant basis  $g \equiv |0\rangle \cup p$  is simply the unit vector that projects along the reference determinant.  $\bar{H}$  is not Hermitian, so its right- and left-hand eigenvectors are not the same. Thus, the left-hand eigenvector corresponding to the reference state is not a unit vector but rather defines a linear combination of the determinants in  $g$ . The rest of the spectrum of  $\bar{H}$  are the EOM-CC energies of the system, each parametrized in terms of right ( $\mathcal{R}$ ) and left ( $\mathcal{L}$ ) eigenvectors which necessarily obey the biorthogonality condition

$$\langle \mathcal{L}_i | \mathcal{R}_j \rangle = C \delta_{ij}, \quad (43)$$

where  $C$  can be chosen to be unity.

The approach described above defines the EOM-CC method that is appropriate for excitation energies (EOMEE-CC),<sup>47,48</sup> other variants are obtained when the  $\bar{H}$  operator is projected onto spaces of determinants that have a different number of electrons (like Green’s function methods mentioned earlier<sup>44</sup> or electron propagator methods<sup>61</sup>). The

most common of these are the so-called EOMIP-CC method<sup>24</sup> (one less electron in the diagonalization space than in the reference state) and the EOMEA-CC method<sup>49</sup> (one more electron). The discussion below, however, is general and applies to all three.

Matrix elements of  $\bar{H}$  in the basis of EOM-CC final states obey the relations<sup>62</sup>

$$\langle 0 | \mathcal{L}_A \bar{H} \mathcal{R}_A | 0 \rangle = E_A, \quad (44)$$

$$\langle 0 | \mathcal{L}_B \bar{H} \mathcal{R}_B | 0 \rangle = E_B, \quad (45)$$

$$\langle 0 | \mathcal{L}_A \bar{H} \mathcal{R}_B | 0 \rangle = 0, \quad (46)$$

$$\langle 0 | \mathcal{L}_B \bar{H} \mathcal{R}_A | 0 \rangle = 0, \quad (47)$$

which can be rewritten in terms of the electronic Hamiltonian

$$\langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) \mathcal{R}_A | 0 \rangle = E_A, \quad (48)$$

$$\langle 0 | \mathcal{L}_B \exp(-T) \hat{H}_e \exp(T) \mathcal{R}_B | 0 \rangle = E_B, \quad (49)$$

$$\langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) \mathcal{R}_B | 0 \rangle = 0, \quad (50)$$

$$\langle 0 | \mathcal{L}_B \exp(-T) \hat{H}_e \exp(T) \mathcal{R}_A | 0 \rangle = 0. \quad (51)$$

These forms allow identification of left- and right-hand EOM-CC wave functions, viz.,

$$\langle \tilde{\psi}_i^{\text{EOM-CC}}(q) | \equiv \langle 0 | \exp[-i\kappa(q)] \mathcal{L}_i(q) \exp[-T(q)], \quad (52)$$

$$| \psi_i^{\text{EOM-CC}}(q) \rangle \equiv \mathcal{R}_i(q) \exp[T(q)] \exp[i\kappa(q)] | 0 \rangle, \quad (53)$$

where the orbital dependence of the wave functions is made explicit with an orbital rotation operator,  $\kappa(q)$ . These wave functions represent, of course, adiabatic wave functions in EOM-CC theory.

Equations (48) and (49) can be differentiated to give expressions for derivatives of the energies of EOM-CC final states with respect to an arbitrary perturbation, as was first done in Ref. 48. When these perturbations are totally symmetric nuclear displacements, the corresponding first derivatives give the linear terms on the diagonal blocks of the LVC model potential [see Eqs. (25) and (26)], i.e., the equivalence of the adiabatic and quasidiabatic energies at symmetric nuclear configurations discussed in Sec. II B.

Due to the way that the EOM-CC wave function is parametrized, coupling of the target states of interest is manifest entirely at the stage of the calculation in which  $\bar{H}$  is diagonalized. The other wave function parameters—the molecular orbital coefficients and the cluster amplitudes—are those of a noninteracting reference state [Eq. (35)]. Thus, they exhibit the qualitatively necessary “following the nuclei” behavior, and impart electron correlation effects to the final state description, to the extent that these are transferable. This suggests the following *ansatz* for the quasidiabatic wave functions in the vicinity of the high-symmetry region

of nuclear configuration space (in our example, where coordinates transforming as  $\Gamma_2$  are small):

$$\langle \tilde{\psi}_i^{\text{EOM-CC-QD}}(q) | \equiv \langle 0 | \exp[-i\kappa(q)] \mathcal{L}_i(q \in \Gamma_1) \times \exp[-T(q)], \quad (54)$$

$$| \psi_i^{\text{EOM-CC-QD}}(q) \rangle \equiv \mathcal{R}_i(q \in \Gamma_1) \exp[T(q)] \exp[i\kappa(q)] | 0 \rangle, \quad (55)$$

where the coordinate variation of the left- and right-hand wave functions includes the full relaxation of the molecular orbitals and the cluster amplitudes  $T$ . Along the coordinates that transform as  $\Gamma_1$ , eigenvectors of  $\bar{H}$  are also permitted to relax [and hence the equivalence of adiabatic and diabatic wave functions at symmetric geometries; see Eqs. (52) and (53)]. However, the eigenvector elements are *not* allowed to vary as the nuclei move along the coupling coordinates.<sup>63</sup>

### D. Analytic evaluation of quasidiabatic coupling strength

Given the ansatz that leads to Eqs. (54) and (55), the linear coupling constants corresponding to the *nonsymmetric* coupling coordinate  $q_i$  between the two states of different symmetry ( $A$  and  $B$ ) is given by

$$\begin{aligned} \lambda_i^{AB} &= \frac{\partial}{\partial q_i} \langle \tilde{\psi}_A^{\text{EOM-CC-QD}} | \hat{H}_e | \psi_B^{\text{EOM-CC-QD}} \rangle_{q_0} \\ &= \frac{\partial}{\partial q_i} \langle \tilde{\psi}_A^{\text{EOM-CC}} | \hat{H}_e | \psi_B^{\text{EOM-CC}} \rangle_{\mathcal{R}, \mathcal{L}, q_0}, \end{aligned} \quad (56)$$

the rightmost form of which can be subjected in a straightforward way to standard EOM-CC gradient theory.

Following Ref. 48, straightforward differentiation in Eq. (56) gives

$$\begin{aligned} \lambda_i^{AB} &= \langle 0 | \mathcal{L}_A \exp(-T) \frac{\partial \hat{H}_e}{\partial q_i} \exp(T) \mathcal{R}_B | 0 \rangle \\ &+ \langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) \frac{\partial T}{\partial q_i} \mathcal{R}_B | 0 \rangle \\ &- \langle 0 | \mathcal{L}_A \exp(-T) \frac{\partial T}{\partial q_i} \hat{H}_e \exp(T) \mathcal{R}_B | 0 \rangle, \end{aligned} \quad (57)$$

where terms involving derivatives of the eigenvectors have been omitted due to the ansatz used for the quasidiabatic electronic states. In Eq. (57) and expressions laid out below, it is implicitly understood that all the derivatives are taken at the coordinate origin. The first term on the right-hand side of Eq. (57) is easily evaluated by contracting derivatives of the one- and two-electron integrals with the reduced one- and two-particle (transition) density matrices that correspond to left-hand state  $A$  and right-hand state  $B$ . The last two terms, which involve derivatives of the cluster amplitudes, are best analyzed by inserting the resolution of the identity ( $g$  and  $q$  now designate determinants that lay inside and outside the diagonalization space, respectively, while  $p$  is again  $g$  exclusive of the zeroth-order reference<sup>64</sup>)

$$1 = |g\rangle\langle g| + |q\rangle\langle q| \quad (58)$$

into each contribution, giving

$$\begin{aligned} &\langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) | g \rangle \langle g | \mathcal{R}_B \frac{\partial T}{\partial q_i} | 0 \rangle \\ &+ \langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) | q \rangle \langle q | \mathcal{R}_B \frac{\partial T}{\partial q_i} | 0 \rangle \\ &- \langle 0 | \mathcal{L}_A \frac{\partial T}{\partial q_i} | g \rangle \langle g | \exp(-T) \hat{H}_e \exp(T) \mathcal{R}_B | 0 \rangle, \end{aligned} \quad (59)$$

where the fact that  $\mathcal{R}$  and  $T$  commute has also been used in the first two terms. Note that the  $q$  space inner projection corresponding to the third term vanishes since  $T$  acting on  $q$  remains in  $q$  and  $\langle 0 | \mathcal{L}_A | q \rangle = 0$ . Using the eigenvalue conditions, the three terms above reduce to

$$\begin{aligned} &\langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) | q \rangle \langle q | \mathcal{R}_B \frac{\partial T}{\partial q_i} | 0 \rangle \\ &+ (E_A - E_B) \langle 0 | \mathcal{L}_A \mathcal{R}_B \frac{\partial T}{\partial q_i} | 0 \rangle, \end{aligned} \quad (60)$$

which can be conveniently rewritten as

$$[(E_A - E_B) \langle 0 | \mathcal{L}_A \mathcal{R}_B | p \rangle + \langle 0 | \Xi | p \rangle] \langle p | \frac{\partial T}{\partial q_i} | 0 \rangle, \quad (61)$$

where matrix elements of the operator  $\Xi$ —which is a standard part of existing EOM-CC gradient theory<sup>24,48,52,53</sup>—are defined by

$$\langle 0 | \Xi | p \rangle \equiv \langle 0 | \mathcal{L}_A \exp(-T) \hat{H}_e \exp(T) | q \rangle \langle q | \mathcal{R}_B | p \rangle. \quad (62)$$

Thus, the linear diabatic interstate coupling constant can be written as

$$\begin{aligned} \lambda_i^{AB} &= \langle 0 | \mathcal{L}_A \exp(-T) \frac{\partial \hat{H}_e}{\partial q_i} \exp(T) \mathcal{R}_B | 0 \rangle \\ &+ [(E_A - E_B) \langle 0 | \mathcal{L}_A \mathcal{R}_B | p \rangle + \langle 0 | \Xi | p \rangle] \langle p | \frac{\partial T}{\partial q_i} | 0 \rangle. \end{aligned} \quad (63)$$

Equation (63) can be converted to a computationally efficient form by inserting the linear equations obeyed by the  $T$  amplitude derivatives,<sup>65</sup> viz.,

$$\begin{aligned} \langle p | \frac{\partial T}{\partial q_i} | 0 \rangle &= -[\langle p | (\bar{H} - \langle 0 | \bar{H} | 0 \rangle) | p \rangle]^{-1} \\ &\times \langle p | \exp(-T) \frac{\partial \hat{H}_e}{\partial q_i} \exp(T) | 0 \rangle, \end{aligned} \quad (64)$$

to yield

$$\begin{aligned} \lambda_i^{AB} &= \langle 0 | \mathcal{L}_A \exp(-T) \frac{\partial \hat{H}_e}{\partial q_i} \exp(T) \mathcal{R}_B | 0 \rangle \\ &+ \langle 0 | Z \exp(-T) \frac{\partial \hat{H}_e}{\partial q_i} \exp(T) | 0 \rangle, \end{aligned} \quad (65)$$

where matrix elements of the de-excitation  $Z$  operator are

given by solutions to the perturbation-independent linear equations

$$\langle 0|Z|p\rangle \equiv -\langle 0|\Xi + (E_A - E_B)\mathcal{L}_A\mathcal{R}_B|p\rangle \times [\langle p|(\bar{H} - \langle 0|\bar{H}|0\rangle)|p\rangle]^{-1}. \quad (66)$$

Given that one has a working computer program for the analytic evaluation of EOM-CC energy derivatives, extension to evaluate the first derivative of the diabatic interstate coupling is both straightforward and not laborious. The following steps must be followed:

- (1) Routines to calculate the one- and two-particle  $\Xi$  amplitudes (which involve  $\mathcal{L}$  and  $\mathcal{R}$  vectors associated with a single state) must be generalized to work with left and right vectors from two different states.
- (2) The  $\Xi$  amplitudes must then be augmented with the contribution  $\langle 0|\mathcal{L}_A\mathcal{R}_B|p\rangle$  (multiplied by the appropriate energy difference), which is however very simple. For example, for the EOMEE-CCSD, EOMIP-CCSD, and EOMEA-CCSD methods, these are

$$\begin{aligned} \langle 0|\mathcal{L}_A\mathcal{R}_B|p\rangle_{\text{EOMEE-CCSD}} = & \sum_{ia} (\mathcal{R}_B)_i^a (\mathcal{L}_A)_{ab}^{ij} \\ & + (\mathcal{R}_B)_0 [(\mathcal{L}_A)_a^i + (\mathcal{L}_A)_{ab}^{ij}], \end{aligned} \quad (67)$$

$$\langle 0|\mathcal{L}_A\mathcal{R}_B|p\rangle_{\text{EOMIP-CCSD}} = \sum_i (\mathcal{R}_B)_i (\mathcal{L}_A)_{ab}^{ij}, \quad (68)$$

$$\langle 0|\mathcal{L}_A\mathcal{R}_B|p\rangle_{\text{EOMEA-CCSD}} = \sum_a (\mathcal{R}_B)^a (\mathcal{L}_A)_{ab}^i. \quad (69)$$

- (3) Routines to calculate the one- and two-particle reduced densities must be generalized to work with left and right vectors from two different states.<sup>66</sup>

Steps 1 and 3 require only some simple logic, in which the two vectors corresponding to different states are passed to the standard routines instead of those associated with one state, and step 2 is very simple. One then has a code for calculating linear diabatic coupling constants, as defined by the ansatz made in this work.

Finally, it should be remarked that a well-known consequence of the non-Hermitian nature of CC theory is that interstate properties of the sort discussed here (transition moments, spin-orbit coupling, etc.) are not symmetric. That is, in the current context,  $\lambda_i^{AB} \neq \lambda_i^{BA}$ . These become equal only in the FCI limit, but are very slightly different at the EOM-CCSD level, as shown in Sec. III where numerical examples are presented.

### III. APPLICATIONS

In this section, the utility of the analytic calculation of the linear diabatic interstate coupling constants is discussed with a few molecular systems that are subject to vibronic coupling as examples. Electronic structure calculations have been carried out with the CFOUR program system.<sup>67</sup> A program code to analytically evaluate the diabatic coupling constants, as described in Sec. II D, has been implemented in the current version of the CFOUR.

The ground state of the BNB radical has been a subject of experimental as well as theoretical studies in recent years. Neumark and co-workers<sup>68</sup> made an important contribution to the understanding of its electronic structure. They measured the photoelectron spectrum of the BNB anion and ana-

TABLE I. The linear diabatic interstate coupling constants for the BNB, C<sub>3</sub>N<sub>2</sub>H<sub>3</sub>, and NO<sub>2</sub> radicals at the equilibrium geometries of the corresponding anions, evaluated with the EOMIP-CCSD/DZP method.

BNB <sup>-</sup>			BNB						
Mode	Symmetry	Harmonic frequency (cm <sup>-1</sup> )	<i>Ab initio</i> quadratic force constant (cm <sup>-1</sup> )			Energy gap (eV)	λ (eV) [Eq. (34)]	Analytic λ (eV)	
ν <sub>3</sub>	σ <sub>u</sub> <sup>+</sup>	1807	$\tilde{A}^2\Sigma_g^+$	$\tilde{X}^2\Sigma_u^+$	Average	0.7469	λ <sup>AX</sup>	λ <sup>XA</sup>	(λ <sup>AX</sup> λ <sup>XA</sup> ) <sup>1/2</sup>
			4165	−590	1788	0.3318	0.3334	0.3321	0.3328
C <sub>3</sub> N <sub>2</sub> H <sub>3</sub> <sup>-</sup>			C <sub>3</sub> N <sub>2</sub> H <sub>3</sub>						
ν <sub>14</sub> ν <sub>15</sub> ν <sub>16</sub> ν <sub>17</sub> ν <sub>18</sub>	b <sub>2</sub>	1448	$\tilde{X}^2A_2$	$\tilde{A}^2B_1$	Average	0.0595	λ <sup>XA</sup>	λ <sup>AX</sup>	(λ <sup>AX</sup> λ <sup>XA</sup> ) <sup>1/2</sup>
		1411	9287	−6208	1540	0.1691	0.1698	0.1699	0.1698
		1177	5057	−2220	1418	0.1159	0.1157	0.1153	0.1155
		1045	4385	−1929	1228	0.1079	0.1087	0.1074	0.1080
		912	4257	−2073	1092	0.1081	0.1076	0.1081	0.1078
			1839	51	945	0.0574	0.0577	0.0571	0.0574
NO <sub>2</sub> <sup>-</sup>			NO <sub>2</sub>						
ν <sub>3</sub>	b <sub>2</sub>	1364	$\tilde{A}^2B_2$	$\tilde{X}^2A_1$	Average	0.9529	λ <sup>AX</sup>	λ <sup>XA</sup>	(λ <sup>AX</sup> λ <sup>XA</sup> ) <sup>1/2</sup>
			402	763	582	NA	0.0783	0.0799	0.0791
			$\tilde{\alpha}^2B_2$	$\tilde{X}^2A_1$		6.8789	λ <sup>αX</sup>	λ <sup>Xα</sup>	(λ <sup>αX</sup> λ <sup>Xα</sup> ) <sup>1/2</sup>
			1398	763	1080	0.3680	0.4655	0.4628	0.4642
			$\tilde{\beta}^2A_1$	$\tilde{A}^2B_2$		5.3719	λ <sup>BA</sup>	λ <sup>Aβ</sup>	(λ <sup>BA</sup> λ <sup>Aβ</sup> ) <sup>1/2</sup>
			2749	402	1576	0.6251	0.5934	0.5986	0.5960

lyzed the vibronic features in the spectrum with diabatic coupling between the  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$  states of the BNB radical taken into account. Their analysis can also explain the matrix IR spectrum of  $\tilde{X}^2\Sigma_u^+$  BNB, measured by Andrews *et al.*<sup>69</sup> A few studies were subsequently carried out to assess the quality of several theoretical methods in their applications to this vibronically coupled system.<sup>70</sup>

The two states interact along the asymmetric stretching coordinate  $q_3$ . The strength of the diabatic coupling of the two states was analytically evaluated with the EOMIP-CCSD method<sup>24</sup> at the equilibrium geometry of the  $\tilde{X}^1\Sigma_g^+$  BNB anion. Analytic energy gradient calculations<sup>71</sup> were performed to determine the equilibrium geometry of the BNB anion with the CCSD method.<sup>55</sup> The Huzinaga–Dunning double-zeta plus polarization (DZP) basis set<sup>72,73</sup> was employed in the calculations. Analytic second derivatives of energy<sup>74</sup> were calculated for the BNB anion at this geometry to obtain a set of reduced normal coordinates, one of which is  $q_3$ .<sup>75</sup>

The analytic values of the  $\lambda$  constant for the coupling between  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$  BNB are given in Table I. The values of  $\lambda_3^{XA}$  and  $\lambda_3^{AX}$  [see Eq. (56)] are not identical owing to the non-Hermiticity of  $\bar{H}$  when  $T$  is truncated, but the difference is very small (0.4%). These values are comparable to a value, 0.287 eV, reported in Ref. 68, which was derived from fitting of eigenstates of a model potential to the vibronic levels observed in the photoelectron spectrum.<sup>76</sup> The diabatic coupling constant was also evaluated through Eq.

(34), and it agrees with the analytic values very well, as shown in Table I. While this agreement apparently supports the validity of the analytic method of  $\lambda$  evaluation, it also indicates that the assumptions, based on which Eq. (34) is established, are good in this system; the  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$  states are well decoupled from the rest of the BNB states, and the two diabatic states have very similar values of quadratic force constants for the  $\nu_3$  mode.

This notion is illustrated in Fig. 1. The CCSD calculations were performed for the  $\tilde{X}^1\Sigma_g^+$  BNB anion along the  $q_3$  coordinate around its equilibrium geometry, and the results are shown at the bottom of the figure. The potential energy curve was fit to a polynomial function by interpolating through the quadrature points that cover the range of  $q_3$  displayed in the figure. It is clearly shown that the polynomial function fits the *ab initio* potential energies of the anion very well. As mentioned in Sec. II C, the anion state is expected to be quasidiabatic, and it could be relevant to approximate the force constants of the diabatic states of the BNB radical with those of the anion, which is a usual approximation adopted in the KDC-LVC model at the harmonic level.<sup>2</sup> Indeed, Table I shows that the average of the *ab initio* quadratic force constants of  $\tilde{X}$  and  $\tilde{A}$  BNB states is very close to the harmonic frequency of the anion [see also Eq. (33)]. In this case, for the  $\tilde{X}$  and  $\tilde{A}$  BNB states, the diabatic model potential of Eq. (25) with respect to  $q_3$  can be expressed as

$$\begin{pmatrix} \frac{1}{2}\kappa_{3,3}q_3^2 + \frac{1}{24}\kappa_{3,3,3,3}q_3^4 + \cdots & 0 \\ 0 & \frac{1}{2}\kappa_{3,3}q_3^2 + \frac{1}{24}\kappa_{3,3,3,3}q_3^4 + \cdots \end{pmatrix} + \begin{pmatrix} 0 & \lambda_3 q_3 \\ \lambda_3 q_3 & \Delta \end{pmatrix}, \quad (70)$$

where the energy of the  $\tilde{X}$  state is set to zero while that of the  $\tilde{A}$  state is  $\Delta$  at the coordinate origin. Note that the common diagonal terms that contain force constants of the anion are separated out from the remaining terms of the potential matrix, which can be easily diagonalized to obtain the corresponding adiabatic potential energies,

$$V^\pm = \frac{1}{2}\kappa_{3,3}q_3^2 + \frac{1}{24}\kappa_{3,3,3,3}q_3^4 + \cdots + \frac{1}{2}[\Delta \pm (\Delta^2 + 4\lambda_3^2 q_3^2)^{1/2}]. \quad (71)$$

This adiabatic model potential of Eq. (71) is parametrized with (a) the force constants obtained from the polynomial fit of the anion potential energy curve, (b) the geometric mean of analytic  $\lambda_3^{XA}$  and  $\lambda_3^{AX}$  as  $\lambda_3$ , and (c) the EOMIP-CCSD energy difference at the reference geometry as  $\Delta$ . This model potential is plotted against the EOMIP-CCSD energies of the  $\tilde{X}$  and  $\tilde{A}$  adiabatic states along  $q_3$  in the upper part of Fig. 1. Excellent agreement between the model potential and *ab initio* potential energies is evident.<sup>77</sup> Thus, these model calculations of the BNB system demonstrate that the quasidiabatic ansatz and analytic evaluation of the diabatic coupling con-

stants proposed in the present study are sound such that the diabatic model potential can well reproduce the adiabatic potential energies in the vicinity of the reference geometry within the EOMIP-CCSD framework.<sup>78</sup>

Analytic  $\lambda$  calculations were also carried out for the couplings between the  $\tilde{X}^2A_2$  and  $\tilde{A}^2B_1$  states of the  $C_3N_2H_3$  radical.<sup>22</sup> These two nearly degenerate states are vibronically coupled along  $b_2$  coordinates. Table I shows that the analytic  $\lambda$  values are again in excellent agreement with the values derived from Eq. (34).<sup>79–81</sup> These results are consistent with the fact that the simulation based on the diabatic model Hamiltonian successfully reproduces the vibronic features observed in the photoelectron spectrum of the pyrazolide- $d_3$  ion.<sup>22</sup>

The two nearly degenerate states of  $C_3N_2H_3$  correspond to the degenerate ground state of the isoelectronic  $C_5H_5$  radical. The  $\tilde{X}^2E_1''$  state of  $C_5H_5$  is subject to linear Jahn–Teller (LJT) effects along  $e_2'$  coordinates.<sup>19</sup> Consequently, the minimum of the adiabatic potential energy surface is located not in a  $D_{5h}$  geometry but along a (virtually barrierless) pseu-



dorotation path that encircles the  $D_{5h}$  conical intersection point.<sup>19</sup> There are two ways to evaluate the LJT coupling constants in *ab initio* calculations. One is to calculate the analytic energy gradients of the degenerate state at a  $D_{5h}$  geometry along the components of the degenerate coordinates that are symmetric with respect to the  $C_{2v}$  Abelian subgroup (i.e.,  $a_1$ ).<sup>19</sup> The other is to calculate the analytic first derivative of the diabatic coupling between the two orthogonal components of the degenerate states (i.e.,  ${}^2A_2$  and  ${}^2B_1$  in  $C_{2v}$  subgroup) along the asymmetric component of the degenerate coordinates (i.e.,  $b_2$ ). These evaluations of the LJT coupling strength set up a model potential, aside from terms for the diabatic force constants, as

$$\begin{pmatrix} \sum_i \kappa_i^A q_{ix} & \sum_i \lambda_i^{AB} q_{iy} \\ \sum_i \lambda_i^{BA} q_{iy} & \sum_i \kappa_i^B q_{ix} \end{pmatrix}, \quad (72)$$

with respect to the degenerate coordinates,  $q_{ix}$  ( $a_1$ ) and  $q_{iy}$  ( $b_2$ ). Our EOMIP-CCSD calculations find that  $\kappa_i^A = -\kappa_i^B = \lambda_i^{AB} = \lambda_i^{BA}$  for  $\tilde{X}^2E_1''$  C<sub>5</sub>H<sub>5</sub> within the numerical precision, as it should be the case for an LJT system.<sup>82</sup> These results also attest to the validity of the analytic method to evaluate the diabatic coupling strength in EOM-CC theory. It should be

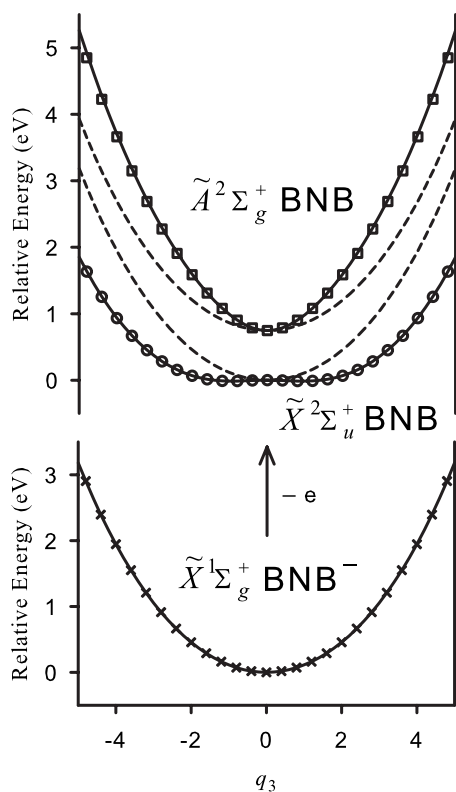


FIG. 1. Plots of the potential energies of the BNB system along the reduced normal coordinate  $q_3$  (asymmetric stretch). The lower part: The CCSD/DZP energies of the anion ground state (crosses), and their polynomial fit (solid line). The upper part: The EOMIP-CCSD/DZP energies of the  $\tilde{X}^2\Sigma_u^+$  (circles) and  $\tilde{A}^2\Sigma_g^+$  (squares) states of the radical, and their corresponding model potential energy curves [solid lines, see Eq. (71)]. The dashed lines represent the potential energy curve of the anion, suitably energy shifted for the radical states.

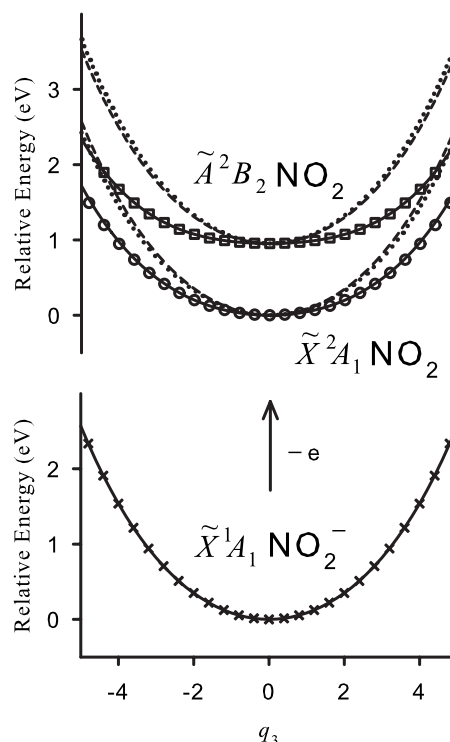


FIG. 2. Plots of the potential energies of the NO<sub>2</sub> system along the reduced normal coordinate  $q_3$  (asymmetric stretch). The lower part: The CCSD/DZP energies of the anion ground state (crosses), and their polynomial fit (solid line). The upper part: The EOMIP-CCSD/DZP energies of the  $\tilde{X}^2A_1$  (circles) and  $\tilde{A}^2B_2$  (squares) states of the radical. The dotted lines represent the model potential energy curves obtained when only the diabatic coupling between the  $\tilde{X}$  and  $\tilde{A}$  states is taken into account. When the diabatic couplings with high-lying states are also included (see the text), the model potential energy curves (solid lines) fit the *ab initio* energies very well. The dashed lines represent the potential energy curve of the anion, suitably energy shifted for the radical states.

noted that the symmetry-enforced degeneracy of the system demands the equality,  $\lambda_i^{AB} = \lambda_i^{BA}$ , in this case.

Finally, vibronic coupling of low-lying states of the NO<sub>2</sub> radical is considered. There are a large number of spectroscopic and theoretical studies of the low-lying states of NO<sub>2</sub> reported in literature. The vibronic coupling between the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states is well known.<sup>83–87</sup> The analytic  $\lambda$  constant for this coupling was calculated at the equilibrium geometry of the  $\tilde{X}^1A_1$  NO<sub>2</sub> anion along the asymmetric stretching coordinate  $q_3$ , and it is given in Table I. The analytic value, 0.0791 eV, is comparable to a value estimated from the analysis of the photoelectron spectrum of the NO<sub>2</sub> anion,  $\sim 0.087$  eV.<sup>85,86</sup> In contrast to the other systems discussed so far, however, the diabatic coupling constant cannot be evaluated from Eq. (34) for the coupling between  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  NO<sub>2</sub>; the quadratic force constant of the upper adiabatic state is less positive than that of the lower state (see Table I).<sup>88</sup> Since Eq. (34) is based on the two-state LVC model, the failure of application of Eq. (34) means at least one of the two assumptions on which the model is founded must be inappropriate for the NO<sub>2</sub> system.

Some light is cast on this question by Fig. 2. The upper part of the figure displays plots of the EOMIP-CCSD adiabatic energies of  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  NO<sub>2</sub> along  $q_3$ . The less

positive quadratic force constant of the upper adiabatic state is apparent in the figure. When the diabatic potential is taken from the polynomial fit of the anion potential, which is shown in the lower part of the figure, and the analytic  $\lambda$  constant for the coupling between the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states is used, the adiabatic model potential of Eq. (71) cannot at all reproduce the *ab initio* potential energies (see the dotted lines in the figure). Our calculations find that the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states are not well decoupled from the other states of  $\text{NO}_2$ . Table I also lists the analytic  $\lambda$  constants for the coupling between the  $\tilde{X}^2A_1$  state and a high-lying  $^2B_2$  state and that between the  $\tilde{A}^2B_2$  state and a high-lying  $^2A_1$  state. Even though these high-lying states are substantially separated in energy from the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states, the strengths of the diabatic couplings with these high-lying states are much greater than that of the coupling between the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states. When terms accounting for these diabatic couplings are added to the model potential of Eq. (71), it reproduces the *ab initio* adiabatic potential energies very well for both the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states (see the solid lines in Fig. 2).<sup>89–91</sup>

These calculations for the low-lying states of  $\text{NO}_2$  highlight the utility of the analytic first derivative of the diabatic interstate coupling. The quadratic force constants of the two lowest adiabatic states of  $\text{NO}_2$  mostly reflect the vibronic couplings with high-lying states, and information about the magnitude of the diabatic coupling between the  $\tilde{X}$  and  $\tilde{A}$  states cannot be obtained directly from a simple two-state model, Eq. (34). On the other hand, the analytic derivative method can be applied even when the corresponding two states are not well decoupled from the other states of the system. Indeed, this advantage of the analytic method has been utilized in modeling the pseudo-Jahn–Teller interactions between the  $\tilde{X}^2E'$  state and high-lying excited states of  $\text{C}_5\text{H}_5$  in our previous study.<sup>19</sup> It should be mentioned that this analytic method is also effective when the other assumption of the two-state LVC model does not hold; i.e., when the diabatic quadratic force constants [Eq. (27)] of the two states are substantially different from each other [cf. Eq. (25)]. The low-lying states of the ethylene radical cation serves as an example.<sup>26,92,93</sup>

## IV. CONCLUSION

There is abundant evidence available in the literature that the KDC quasidiabatic model Hamiltonian technique is very useful in elucidation of nonadiabatic dynamics in molecular systems. One class of parameters, known as intrastate coupling constants, form the diagonal elements of the model potential matrix, and analytic methods to evaluate the linear and quadratic coupling constants exist for various electronic structure theories. On the other hand, diabatic interstate coupling constants that relate to the off-diagonal elements have usually been evaluated indirectly from analysis of the corresponding adiabatic potential energy surfaces. However, depending on the molecular systems at hand, such analysis could be demanding or very difficult. The present paper in-

troduces an *ansatz* of quasidiabatic wave functions within the framework of EOM-CC theory, and describes the analytic first derivative of the off-diagonal elements of the potential matrix in the quasidiabatic representation. This analytic method, which has been developed as an extension of the analytic first derivative of the EOM-CC energy, allows direct *ab initio* evaluation of the linear diabatic interstate coupling constant that parametrizes the KDC model potential. The utility of such parametrization of the model potential has been presented for several molecular systems subject to vibronic couplings.

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<sup>1</sup>In the literature, the term “nonadiabatic” is used to mean several different things. Entirely relevant to this paper is that deviation from strictly diabatic behavior (see Sec. II B) is sometimes termed nonadiabatic. Within the framework of the vibronic coupling models described here, the deviation from Born–Oppenheimer behavior is quantitatively embodied in the difference between the eigenvalues and states obtained by diagonalization of the molecular Hamiltonian, and those obtained when one diagonalizes the potential matrix and assumes that the kinetic energy operator is diagonal. We view some (but certainly not all) nonadiabatic descriptions of molecular spectra as something of a misnomer, when they result only from the inclusion of an off-diagonal term in V. Herzberg–Teller coupling, for example, is not a nonadiabatic effect from this perspective.

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  - <sup>35</sup> E. F. Valeev and C. D. Sherrill, *J. Chem. Phys.* **118**, 3921 (2003).
  - <sup>36</sup> J. Gauss, A. Tajti, M. Kállay, J. F. Stanton, and P. G. Szalay, *J. Chem. Phys.* **125**, 144111 (2006).
  - <sup>37</sup> Here we adhere to the nomenclature used by Kutzelnigg (see Ref. 28), rather than that suggested by Worth and Cederbaum in Ref. 3. The former convention is certainly more commonly followed in the chemical physics literature, at least for the “Born–Oppenheimer approximation,” while the latter authors prefer that the DBOC be included in this picture. Since thousands of quantum chemical Born–Oppenheimer calculations have been published that do not include the DBOC, the convention of Ref. 28 is at least pragmatic even if one does not agree with us that it is intrinsically superior.
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  - <sup>39</sup> This “set of electronic wavefunctions” need not be eigenfunctions of the electronic Hamiltonian, as any unitary transformation of the exact eigenfunctions at the reference geometry will suffice. The only important condition is that they are orthonormal and “frozen.” There is a famous and widely cited argument [C. A. Mead and D. G. Truhlar, *J. Chem. Phys.* **77**, 6090 (1982)] that no rigorously exact diabatic basis [in the sense of satisfying Eq. (20)] exists, but the frozen Born–Huang electronic basis used in this discussion is undeniably rigorous in this sense.
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  - <sup>41</sup> L. S. Cederbaum, W. Domcke, H. Köppel, and W. von Niessen, *Chem. Phys.* **26**, 169 (1977).
  - <sup>42</sup> This parametrization is termed “vertical parametrization;” see Ref. 22. The other type of parametrization, “adiabatic parametrization,” is not considered in the present paper.
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  - <sup>45</sup> H. Müller, H. Köppel, and L. S. Cederbaum, *J. Chem. Phys.* **101**, 10263 (1994).
  - <sup>46</sup> While there are a number of studies reported in the literature that derive quadratic coupling constants at the “vertical” geometry, the adiabatic parametrization discussed in Ref. 22 yields quadratic coupling constants that appropriately account for Duschinsky rotation effects and is more suitable for quantitative predictions of the vibronic level energies observed in spectroscopy. See Ref. 22 for a detailed discussion.
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  - <sup>49</sup> M. Nooijen and R. J. Bartlett, *J. Chem. Phys.* **102**, 3629 (1995).
  - <sup>50</sup> J. F. Stanton, *J. Chem. Phys.* **115**, 10382 (2001).
  - <sup>51</sup> T. D. Crawford, J. F. Stanton, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **107**, 10626 (1997).
  - <sup>52</sup> J. F. Stanton and J. Gauss, *J. Chem. Phys.* **100**, 4695 (1994).
  - <sup>53</sup> J. F. Stanton and J. Gauss, *Theor. Chim. Acta* **91**, 267 (1995).
  - <sup>54</sup> The EOM-CC approach is quite general, and permits the use of any single determinant as a zeroth-order reference function. However, closed-shell reference functions are only very rarely affected by symmetry breaking issues and other qualitative problems such as spin contamination. Therefore, discussion in this paper—which assumes that the zeroth-order reference state is immune from such problems—is best presented in terms of a closed-shell reference state.
  - <sup>55</sup> G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
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  - <sup>58</sup> J. D. Watts and R. J. Bartlett, *J. Chem. Phys.* **93**, 6104 (1990).
  - <sup>59</sup> K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
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  - <sup>61</sup> J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Wiley, Hoboken, 2004); J. V. Ortiz, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski (World Scientific, Singapore, 1997), Vol. 2, pp. 1–61.
  - <sup>62</sup> Equations (44) and (45) indicate that  $C$  in Eq. (43) has been chosen to be unity.
  - <sup>63</sup> In contrast, in Ref. 20, quasidiabatic wavefunctions are defined by “freezing” CI vectors for *all* coordinates in their expansions in a basis of configuration state functions.



- <sup>64</sup>For EOMEE-CC, these are the same as the corresponding spaces in the reference state CC equations, but differs in EOMIP-CC and EOMEA-CC.
- <sup>65</sup>E. A. Salter, G. W. Trucks, and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).
- <sup>66</sup>As in the energy derivative calculations, the reduced one-particle transition density matrix also accounts for the response of the molecular orbital coefficients to the perturbation (see Ref. 48). The orbital relaxation treatment is based on the “symmetric connection,” i.e., on the assumption that the occupied-occupied and virtual-virtual blocks of the coupled-perturbed Hartree–Fock coefficients are expressed in terms of the corresponding overlap matrix derivatives (see, for example, Ref. 71).
- <sup>67</sup>CFour, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Q. Christiansen, M. Heckert, O. Heun, C. Huber, J. Jusélius, K. Klein, W. J. Lauderdale, D. Matthews, T. Metzroth, D. P. O’Neill, D. R. Price, E. Prochnow, K. Rudd, F. Schiffmann, S. Stopkiewicz, A. Tajti, M. E. Varner, J. Vázquez, F. Wang, and J. D. Watts, and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
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- <sup>74</sup>J. Gauss and J. F. Stanton, *Chem. Phys. Lett.* **276**, 70 (1997).
- <sup>75</sup>While a normal coordinate  $Q_3$  is determined automatically by symmetry in this case, a reduced normal coordinate  $q_3$  depends on the corresponding harmonic frequency and, therefore, has to be “calculated.”
- <sup>76</sup>Determination of this value in Ref. 68 depends on an assumption of the frequency of the corresponding mode of the anion. Use of the adiabatic energy difference, instead of the vertical energy difference, in the one-dimensional model potential in Ref. 68 seems to slightly alter the diabatic coupling constant.
- <sup>77</sup>When Eq. (71) is expanded, Eqs. (29) and (30) can be easily derived. This expansion also allows comparison of higher-order force constants between the model potential and *ab initio* potential energies, which was alluded to in Sec. II B.
- <sup>78</sup>Analytic expressions of the second derivative of energies in EOM-CC theory have been given in J. F. Stanton and J. Gauss, *J. Chem. Phys.* **103**, 8931 (1995); when a so-called symmetric expression is applied to the derivative with respect to the asymmetric coordinate  $q_3$ , it becomes
- $$\partial^2 V_X / \partial q_3^2|_{q_3=0} = \langle 0 | \mathcal{L}_X (\partial^2 \tilde{H} / \partial q_3^2) \mathcal{R}_X | 0 \rangle|_{q_3=0} + \langle 0 | Z (\partial^2 \tilde{H} / \partial q_3^2) | 0 \rangle|_{q_3=0} + 2 \langle 0 | \mathcal{L}_X (\partial \tilde{H} / \partial q_3) (\partial \mathcal{R}_X / \partial q_3) | 0 \rangle|_{q_3=0}.$$
- According to the quasidiabatic ansatz given in Sec. II C, the first two terms on the right-hand side represent the derivatives of the quasidiabatic state [see Eqs. (27), (54), and (55)]. In the KDC-LVC model, they are usually approximated by those of the closed-shell reference state [e.g., the BNB anion in Eq. (70)]. The perturbed adiabatic wavefunction in the last term can be expressed in a usual manner;
- $$(\partial \mathcal{R}_X / \partial q_3) | 0 \rangle|_{q_3=0} = \sum_k \mathcal{R}_k | 0 \rangle [ \langle 0 | \mathcal{L}_X \frac{\partial \tilde{H}}{\partial q_3} \mathcal{R}_X | 0 \rangle / (V_X - V_k) ]|_{q_3=0}.$$
- For the BNB system where the two-state model holds well, it is sufficient to consider only the  $\tilde{A}$  state in the summation. Insertion of the second equation into the first one makes it clear that there is an exact correspondence between the quasidiabatic model potential and *ab initio* adiabatic potential energies in EOM-CC theory up to second order.
- <sup>79</sup>One of the  $b_2$  modes is characterized as asymmetric C–H stretching motion. The  $\tilde{X}$  and  $\tilde{A}$  states of  $C_3N_2H_3$  couple only very weakly along this  $b_2$  coordinate, and this mode is not included in Table I.
- <sup>80</sup>Note in Table I that the potential energy of  $\tilde{X}^2A_1$   $C_3N_2H_3$  is higher than that of the  $\tilde{A}^2B_1$  state at the equilibrium geometry of the  $C_3N_2H_3$  anion.
- <sup>81</sup>Unlike Eq. (34), the analytic calculations directly reveal the relative signs of the diabatic coupling constants (see discussion in Sec. II B). Note that the phases of the reduced normal coordinates are chosen here such that all  $\lambda$  values are positive (see Table I).
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- <sup>88</sup>In Ref. 86, the  $\lambda$  constant for the coupling between  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$   $NO_2$  was evaluated by means of Eq. (34) in *ab initio* calculations based on Green’s function method. This theoretical method should be able to account for nonadiabatic phenomena very well. It is unclear to us why our EOMIP-CCSD calculations yield results that are drastically different from those of the calculations using Green’s function approach.
- <sup>89</sup>The high-lying  $^2B_2$  state discussed here is characterized as a one-hole state with respect to the reference determinant of the  $NO_2$  anion state. This  $^2B_2$  state should not be confused with the  $\tilde{D}^2B_2$  state which has been a subject of a number of spectroscopic and theoretical studies reported in literature. This  $\tilde{D}^2B_2$  state is mainly a two-hole, one-particle state, and it cannot be well described with the EOMIP-CCSD method employed in the present study. Since the  $\tilde{D}^2B_2$  state can be created with a single-electron transition from the  $\tilde{X}^2A_1$  state, it is possible that the  $\tilde{X}^2A_1$  state is significantly affected by the vibronic coupling with the  $\tilde{D}^2B_2$  state.
- <sup>90</sup>Our value of the  $\lambda$  constant for the diabatic coupling between  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$   $NO_2$ , 638  $cm^{-1}$ , is significantly different from a value determined from the fit of a number of vibronic levels observed in the high-resolution spectroscopic studies through a model Hamiltonian, 332  $cm^{-1}$ , reported in Ref. 84. Perhaps, an important factor that contributes to the difference between these two values is associated with the dependence of the diabatic coupling on the symmetric stretching coordinate. According to our calculations, the strengths of the diabatic coupling are 21 and 723  $cm^{-1}$  at the equilibrium geometries of the  $\tilde{X}^2A_1$  and  $\tilde{A}^2B_2$  states, respectively. This dependence on the symmetric stretching coordinate is even larger than that reported in Ref. 87 (but, see also Ref. 88). The diabatic coupling constant determined in Ref. 84 may represent an “averaged” value over the symmetric stretching coordinate. In contrast, our calculations show only a weak dependence of the diabatic coupling on the bending coordinate.
- <sup>91</sup>It should be noted that, when the higher excited states that have the same spatial symmetries as the lower states at the reference geometry are included in the model Hamiltonian of the  $NO_2$  radical, the equivalence of the adiabatic and quasidiabatic potential energy surfaces along totally symmetric coordinates, which was alluded to in Sec. II B for the two-state model systems, does not hold, although the present approach could



be generalized to handle such cases.

<sup>92</sup>The  $\tilde{X}^2B_{3u}$  and  $\tilde{A}^2B_{3g}$  states of the ethylene radical cation couple along the  $a_u$  torsion coordinate. Compared to the other systems discussed in the present study, a higher-order term (i.e., cubic interstate coupling term) plays a much more important role in the diabatic coupling along the

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<sup>93</sup>Numerical evaluation of the diabatic coupling constants in Ref. 26 is based on the same ansatz of quasidiabatic wavefunctions as that adopted in the present study. See also Ref. 16.