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Evaluation of first- and second-order nonadiabatic coupling elements from large multiconfigurational self-consistent-field wave functions

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An efficient method is proposed for evaluating first- and second-order nonadiabatic matrix elements of the form $\langle \psi_i(q;Q) | \delta\psi_j(q;Q)/\delta Q \rangle$ and $\langle \psi_i(q;Q) | \delta^2\psi_j(q;Q)/\delta Q^2 \rangle$, where $\psi_i(q;Q)$ and $\psi_j(q;Q)$ denote multiconfigurational self-consistent-field electron wave functions. The method is based on a finite-difference procedure and requires the numerical computation of symmetric overlaps of the type $\langle \psi_i(q,Q_0-x) | \psi_j(q,Q_0+x) \rangle$. It gives an accuracy which is quadratic in the nuclear displacement x for both the first- and second-order nonadiabatic coupling constants. The wave functions are separately optimized for each state and obtained through the direct second-order MCSCF method. The biorthogonal scheme of Malmquist is implemented that expresses $\psi_i(q;Q)$ and $\psi_j(q:Q)$ in an orthogonal common basis. The method is applied for the calculation of the nonadiabatic coupling elements and the Born-Oppenheimer corrections to the two lowest $^2\Sigma^+$ states of NaLi^+, relevant for analyzing the asymmetric charge exchange in the ion-atom collision $\mathrm{Na}+\mathrm{Li}^+ \rightarrow \mathrm{Na}^+ + \mathrm{Li}$.

I. INTRODUCTION

The Born-Oppenheimer (BO) approximation is one of the concepts in quantum chemistry that remains as fundamental as its breakdown. The description of electronically nonadiabatic processes has become a challenging subject for theoreticians and experimentalists. Unimolecular decay,[1–3] charge-transfer phenomena,[4–10] ion-atom collisions,[11,4] quenching phenomena, and radiationless transitions represent just a few examples where Born-Oppenheimer-based analyses become inadequate. In charge-transfer processes the occurrence of "surface hopping" between adiabatic states[12,13] is directly related to the transition probabilities among the outcoming channels for the electron distribution in the products. In molecular spectroscopy the breakdown of the BO approximation is manifested in various vibronic coupling phenomena, such as symmetry breaking and intensity borrowing.[14,15]

A great deal of effort has been devoted to the formal representation of nonadiabatic electronic bases,[16–18] and a variety of "diabatic" molecular representations have been proposed, most of them starting out from electronic eigenstates. Nonadiabatic corrections have been analyzed at different levels of sophistication[19–21] and several models have been proposed where the interaction is assumed to be dominant near the curve-crossing (or avoided-crossing) region and gradually vanishing in the asymptotic limit.[6,22] The relevant nonadiabatic coupling constants have mostly been obtained semiclassically, by means of the Landau-Zener approximation, while quantum mechanically it is rather recently that attempts have been made with *ab initio* approaches to obtain such constants. This is linked to the requirements for accurate wave functions over a larger region of nuclear conformations, especially for charge-transfer states at avoided crossings where the states are close lying in energy, giving rise to root-flipping problems, and where they drastically change character over small nuclear displacements.

Previous *ab initio* methods were based on numerical differentiation of configuration-interaction (CI), or on multiconfiguration self-consistent-field (MCSCF) wave functions with state-averaged orbitals.[24] These approaches are based on an asymmetric displacement of the nuclear coordinates, which gives a first-order coupling constant that is correct to first order in this displacement. Other approaches have been based on the Hellmann-Feynman theorem,[25] which, however, is valid only for exact wave functions. Recently, Lengsfield *et al.*[26] derived an analytical method for obtaining first- and second-order coupling constants from a state-averaged set of MCSCF orbitals. This method contains intrinsically the same technique to solve the coupled perturbed MCSCF equations for the nuclear differentiation as is used in current codes for analytical energy gradient calculations.

An analytical approach to the nonadiabatic coupling constants, such as the one of Lengsfield *et al.*,[26] has great merits when there are many degrees of freedom for the nuclear motion. The potential and accuracy of numerical differentiation using the MCSCF wave functions has, however, not been exploited hitherto. With the possibility to apply second-order and step-restricted MCSCF wave functions the numerical differentiation revives, since optimization to the correct electronic state (correct Hessian index) can now be fully controlled which eliminates the root-flipping problem, and sharp convergence can be achieved for small differential steps. With the present method we also obtain the additional advantages of using separate state-optimized orbitals and of getting both first-and second-order coupling elements at the same computational expense. In Sec. II we outline our method which gives first- and second-order nonadiabatic coupling elements that are correct to second order in the nuclear displacement. In Sec. II we describe a numerical application for the NaLi$^+$ system, and in Sec. IV we discuss the numerical results and the merits of the proposed method.

II. METHOD

The method outlined in the present paragraph applies to a physical situation for which the Born-Oppenheimer (BO) separability of nuclear and electronic motion breaks down. Let us consider a total molecular wave function written as

$$\phi(q,Q)=\sum_i X_i(Q)\psi_i(q;Q)\ , \tag{1}$$

where q and Q denote the two sets of electronic and nuclear coordinates and X and ψ denote the nuclear and the BO electronic wave functions, where the latter depend parametrically on Q. We consider the internal Hamiltonian for a diatomic molecule, separated from the translational center-of-mass motion, given as[18]

$$\hat{H}=\hat{T}_N+\hat{H}_{\text{el}}\ , \tag{2}$$

$$\hat{T}_N=-(\tfrac{1}{2}M)\nabla_Q^2\ , \tag{3}$$

where $\hat{T}_N$ denotes the nuclear kinetic energy and M is the reduced mass of the system. $\hat{H}_{\text{el}}$ is the electronic Hamiltonian.

Using the relations

$$\langle\psi_i\,|\,\hat{H}_{\text{el}}\,|\,\psi_j\rangle=\delta_{ij}V_i(Q)\ , \tag{4}$$

$$\langle\psi_i\,|\,\psi_j\rangle=\delta_{ij}\ , \tag{5}$$

we evaluate the internal Hamiltonian matrix elements resulting from the time-independent Schrödinger equation, integrated over the electronic coordinates,

$$\sum_j\{\delta_{ij}[-(1/2M)\nabla_Q^2-E+V_i(Q)]+J_{ij}/M-(\Gamma_{ij}/M)\nabla_Q\}X_j(Q)=0\ , \tag{6}$$

where

$$\Gamma_{ij}=\langle\psi_i\,|\,\nabla_Q\,|\,\psi_j\rangle \tag{7}$$

and

$$J_{ij}=\langle\psi_i\,|\,(-\tfrac{1}{2})\nabla_Q^2\,|\,\psi_j\rangle\ . \tag{8}$$

Our goal is to perform an efficient and reliable calculation of the two crucial quantities in this expression,

$$N_{ij}^{(1)}(Q_0)=\left\langle\psi_i(q;Q)\,\middle|\,\frac{\delta\psi_j}{\delta Q}(q;Q)\right\rangle_{Q=Q_0}\ , \tag{9}$$

$$N_{ij}^{(2)}(Q_0)=\left\langle\psi_i(q;Q)\,\middle|\,\frac{\delta^2\psi_j}{\delta Q^2}(q;Q)\right\rangle_{Q=Q_0}\ , \tag{10}$$

which constitute the first- and second-order radial coupling constants. For $i\neq j$ these quantities represent the nonadiabatic coupling between the BO electronic eigenstates i and j at a given nuclear coordinate Q_0. For $i=j$ the second-order constant represents the BO correction to the eigenstate i. We obtain ψ_i and ψ_j as MCSCF wave functions which account for the contributions to the nonadiabatic coupling constants from many-electron interactions.

Equations (9) and (10) play a fundamental role in ion-atom collision problems and scattering models in general. The description of charge-transfer processes is essentially based upon the various induced transitions that can occur during the electron rearrangement. In the impact-parameter approach, for example, where the electrons are described quantum mechanically and the nuclei are assumed to follow classical orbits (Bates and Williams, Ref. 27), perturbation theory is applied to determine the probability that a transition from one electronic state to another occurs. In this model the nuclear wave function is of semiclassical type and the trajectory of the incident ion follows a straight line, which is a reasonable assumption for large collision energies (>100 eV). It is common to assume that in this regime the change in electronic energy is small in comparison with the collision energy, e.g.,

$$E\gg V_i(Q)-V_i(\infty)\ . \tag{11}$$

The nuclear wave function can then be written as

$$X_i(Q)=a_i(z)\exp\left[i\int_{-\infty}^{z}k_i(z')dz'\right]\ , \tag{12}$$

where $z^2+b^2=Q^2$ and b is the impact parameter. k_i denotes the momentum of the incoming atom in terms of the ith molecular electronic state,

$$k_i=2M[E-V_i(Q)]^{1/2}\ . \tag{13}$$

Substitution of Eq. (12) into Eq. (6) leads to

$$d^2a_i/dz^2+2ik_ida_i/dz-[(iM/k_i)(dV_i/dz)+2J_{ii}]a_i=\sum_{j\,(\neq i)}[2J_{ij}a_j-2\Gamma_{ij}k_ja_j-2\Gamma_{ij}(da_j/dz)]\exp[i(A_i-A_j)]\ , \tag{14}$$

where

$$A_j(z)=\int_{-\infty}^{z}k_i(z')dz'\ . \tag{15}$$

Formula (14) coincides with the set of coupled equations derived by Melius and Goddard [Eq. (8) in Ref. 5] when neglecting terms of order $1/M$ compared to $1/m_e$ and assuming that $K_i=K_j\approx Mv$ (v is a constant velocity given in terms of the collision energy), e.g.,

$$da_i(z)/dz=-\sum_j\Gamma_{ij}(z)a_j(z)\exp[-i\omega_{ij}(z)]\ , \tag{16}$$

where

$$\omega_{ij}(z)=(1/v)\int_{-\infty}^{z}(V_j-V_i)dz'\ , \tag{17}$$

The solution of the coupled system appearing in expression (14) yields the transition probabilities from state i to state j for a given impact parameter or, more specifically, $|a_i|^2$ measures the probability of remaining in the ith electronic state. The integration of all probabilities at a given channel for all impact parameters considered provides the cross section for electron transfer. It is clear from these equations that the driving force for inducing transitions amongst the various molecular states is given by the first-order $[\Gamma_{ji}(z)]$ and second-order $[J_{ji}(z)]$ couplings, the calculation of which is the object of the present study. The calculations concern the numerical nuclear differentiation of accurate MCSCF wave functions that account for orbital state specific correlation and relaxation effects. Accordingly, the present nonadiabatic corrections represent a significant improvement over methods that resort to approximate molecular states with state averaged or frozen orbitals, or with pseudopotential approximations.

The MCSCF wave functions are separately optimized for each state and parametrized as

$$\psi(q;Q)=\exp\left[-\sum_{\substack{r,s\\(r>s)}}\kappa_{sr}(\hat{E}_{sr}-\hat{E}_{rs})\right]\left[\sum_i c_i\,|\Theta_i\rangle\right], \quad (18)$$

where $\hat{E}_{sr}=\sum_\sigma \hat{a}^\dagger_{s\sigma}\hat{a}_{r\sigma}$ are the orthogonal unitary generators for orbital rotation and

$$|\Theta_i\rangle=P\sum_{K=1}^{N}\hat{a}^\dagger_{K\sigma}\,|\text{vac}\rangle \quad (19)$$

denote the configuration-state functions (CSF's) which are projected for a least linear combination of symmetry- and spin-adapted determinants of molecular orbitals (MO's). The MO's are expanded in linear combinations of atomic functions centered at Q:

$$\varphi_i(q;Q)=\sum_k d^i_k\xi_k(q;Q)\ . \quad (20)$$

The configuration-state amplitudes c_i and orbital rotation parameters κ are optimized by the minimization of the energy functional involving the Born-Oppenheimer nonrelativistic Hamiltonian.

In the numerical differentiation procedure for obtaining $N^{(1)}_{ij}(Q_0)$ and $N^{(2)}_{ij}(Q_0)$ we employ the matrix elements

$$K_{ij}(Q_0,x)=\langle\psi_i(q;Q_0-x)\,|\,\psi_j(q;Q_0+x)\rangle\ . \quad (21)$$

This matrix element is thus symmetrically expanded around the point for the coupling. The use of such elements for the calculation of nonadiabatic coupling constants has been suggested by Halkjaer and Linderberg.[28] For a two-state problem there are several such elements to be evaluated. In the following we restrict ourselves to one nuclear dimension; the two-atomic internuclear distance, the generalization to the many-dimensional case is straightforward. Using the orthogonality condition between BO states,

$$\langle\psi_i(q;Q_0)\,|\,\psi_j(q;Q_0)\rangle=\delta_{ij}\ , \quad (22)$$

one finds by direct differentiation

$$\langle\psi'_i\,|\,\psi_j\rangle+\langle\psi_i\,|\,\psi'_j\rangle=0 \quad (23)$$

and

$$\langle\psi''_i\,|\,\psi_j\rangle+\langle\psi_i\,|\,\psi''_j\rangle+2\langle\psi'_i\,|\,\psi'_j\rangle=0\ . \quad (24)$$

Here we have dropped the variable specification $(q;Q_0)$ for brevity and used primes and double primes to denote wave functions differentiated with respect to the nuclear coordinates Q one and two times, respectively. From Eq. (23) follows

$$N^{(1)}_{ij}(Q_0)=-N^{(1)}_{ji}(Q_0)\ , \quad (25)$$

and consequently

$$N^{(1)}_{ii}(Q_0)=0\ . \quad (26)$$

For the second derivatives we define the symmetric combination

$$\begin{aligned}N^{(2S)}_{ij}(Q_0)&=\tfrac{1}{2}[N^{(2)}_{ij}(Q_0)+N^{(2)}_{ji}(Q_0)]\\&=\tfrac{1}{2}(\langle\psi_i\,|\,\psi''_j\rangle+\langle\psi''_i\,|\,\psi_j\rangle)=-\langle\psi'_i\,|\,\psi'_j\rangle\ ,\end{aligned} \quad (27)$$

where Eq. (24) has been used to reach the last equality, and the antisymmetric combination

$$\begin{aligned}N^{(2A)}_{ij}(Q_0)&=\tfrac{1}{2}[N^{(2)}_{ij}(Q_0)-N^{(2)}_{ji}(Q_0)]\\&=\tfrac{1}{2}(\langle\psi_i\,|\,\psi''_j\rangle-\langle\psi''_i\,|\,\psi_j\rangle)=\frac{dN^{(1)}_{ij}}{dQ}(Q_0)\ ,\end{aligned} \quad (28)$$

where again Eq. (24) has been used. For a two-state problem the different non-Born-Oppenheimer elements are thus $N^{(1)}_{12},N^{(2)}_{11},N^{(2)}_{22}$ and either $N^{(2)}_{12},N^{(2)}_{21}$ or $N^{(2S)}_{12},N^{(2A)}_{12}$. In order to obtain the nonadiabatic coupling constants we Taylor-expand the wave functions over the nuclear displacement

$$\psi_i(Q_0+x)=\psi_i(Q_0)+x\psi'_i(Q_0)+\tfrac{1}{2}x^2\psi''_i(Q_0)+\cdots\ . \quad (29)$$

If one inserts this expression in Eq. (21) for each displacement, one obtains the K overlap

$$\begin{aligned}K_{ij}(Q_0,x)=\langle\psi_i(q;Q_0-x)\,|\,\psi_j(q;Q_0+x)\rangle&=\delta_{ij}+x[\langle\psi_i(Q_0)\,|\,\psi'_j(Q_0)\rangle-\langle\psi'_i(Q_0)\,|\,\psi_j(Q_0)\rangle]\\&\quad+\tfrac{1}{2}x^2[\langle\psi''_i(Q_0)\,|\,\psi_j(Q_0)\rangle+\langle\psi_i(Q_0)\,|\,\psi''_j(Q_0)\rangle-2\langle\psi'_i(Q_0)\,|\,\psi'_j(Q_0)\rangle]+\cdots\ .\end{aligned} \quad (30)$$

Making a similar expansion for $K_{ji}(Q_0,x)$ and combining the K_{ij} and K_{ji} elements one finds after some straightforward algebra

$$K_{ij}(Q_0,x)+K_{ji}(Q_0,x)=2\delta_{ij}-4x^2N^{(2S)}_{ij}(Q_0)+O(x^4) \quad (31)$$

and

$$K_{ij}(Q_0,x)-K_{ji}(Q_0,x)=-2xN^{(1)}_{ij}(Q_0)+O(x^3)\ , \quad (32)$$

which leads to the first order and the symmetric second-order coupling elements

$$N_{ij}^{(1)}(Q_0)=(\tfrac{1}{4}x)[K_{ij}(Q_0,x)-K_{ji}(Q_0,x)]-O(x^2)\ , \tag{33}$$

$$N_{ij}^{(2S)}(Q_0)=(\tfrac{1}{4}x^2)[K_{ij}(Q_0,x)+K_{ji}(Q_0,x)-2\delta_{ij}]-O(x^2)\ . \tag{34}$$

To calculate $N_{ij}^{(1)}(Q_0)$ and $N_{ij}^{(2S)}(Q_0)$ with quadratic accuracy in the displacement x, we thus need to obtain converged solutions for the $\psi_i(q,Q_0-x)$, $\psi_i(q,Q_0+x)$, $\psi_j(q,Q_0-x)$, and $\psi_j(q,Q_0+x)$ wave functions. However, $N_{ij}^{(2A)}(Q_0)$ (and thus the separate $N_{ij}^{(2)}(Q_0)$ and $N_{ji}^{(2)}(Q_0)$ elements) cannot be obtained from the two geometries Q_0-x and Q_0+x, we also need converged solutions for the $\psi_i(q,Q_0)$ in the midpoint Q_0, requiring a total of five wave functions. With $\psi_i(q,Q_0)$ we can also obtain $N_{ij}^{(2A)}$ to quadratic accuracy because we can find $N_{ij}^{(2)}$ to the same accuracy. To see this we use Eq. (29) twice to get

$$\begin{aligned}\langle\psi_i(Q_0)\,|\,\psi_j(Q_0+x)\rangle&=K_{ij}(Q_0+x/2,x/2)\\&=\delta_{ij}+x\langle\psi_i\,|\,\psi_j'\rangle+(x^2/2)\langle\psi_i\,|\,\psi_j''\rangle+(x^3/6)\langle\psi_i\,|\,\psi_j^{(\mathrm{iii})}\rangle+(x^4/24)\langle\psi_i\,|\,\psi_j^{(\mathrm{iv})}\rangle+\cdots\ ,\end{aligned} \tag{34a}$$

$$\begin{aligned}\langle\psi_i(Q_0)\,|\,\psi_j(Q_0-x)\rangle&=K_{ij}(Q_0-x/2,-x/2)\\&=K_{ji}(Q_0-x/2,x/2)\\&=\delta_{ij}-x\langle\psi_i\,|\,\psi_j'\rangle+(x^2/2)\langle\psi_i\,|\,\psi_j''\rangle-(x^3/6)\langle\psi_i\,|\,\psi_j^{(\mathrm{iii})}\rangle+(x^4/24)\langle\psi_i\,|\,\psi_j^{(\mathrm{iv})}\rangle-\cdots\ ,\end{aligned} \tag{34b}$$

and add these two overlap elements

$$K_{ij}(Q_0+x/2,x/2)+K_{ji}(Q_0-x/2,x/2)=2\delta_{ij}+x^2N_{ij}^{(2)}(Q_0)+O(x^4)\ . \tag{35}$$

Thus,

$$N_{ij}^{(2)}(Q_0)=(1/x^2)[K_{ij}(Q_0+x/2,x/2)+K_{ji}(Q_0-x/2,x/2)-2\delta_{ij}]+O(x^2) \tag{36}$$

and the other coupling element can be obtained to quadratic accuracy using Eqs. (27), (34), and (36)

$$N_{ji}^{(2)}(Q_0)=2N_{ij}^{(2S)}(Q_0)-N_{ij}^{(2)}(Q_0)\ . \tag{37}$$

One can also show

$$\begin{aligned}N_{ij}^{(2A)}(Q_0)&=\frac{dN_{ij}^{(1)}}{dQ}(Q_0)\\&=[N_{ij}^{(1)}(Q_0+x/2)-N_{ij}^{(1)}(Q_0-x/2)]/x\\&\quad+O(x^2)\end{aligned} \tag{38}$$

but the use of Eq. (36) as well as the above expression directly for $N_{ji}^{(2)}(Q_0)$ requires convergence of the sixth wave function $\psi_j(q,Q_0)$.

Alternatively, we may obtain the values of

$$N_{ij}^{(2A)}(Q_0)=\frac{dN_{ij}^{(1)}}{dQ}(Q_0)$$

in an indirect way. We propose, for a diatomic molecule, to make a spline fit through the values obtained for $N_{ij}^{(1)}(Q_0)$ at different geometries and use the latter relation. In doing so one has the advantage of obtaining the first- and second-order coupling constants with the same set of wave function optimizations.

The evaluation of the coupling constants thus requires four MCSCF calculations, for two states at two slightly displaced geometries. The separate optimization of all variables involved in the coupling gives additional flexibility and accuracy over previous frozen-orbital and state-average approaches. A small price has to be paid in terms of non-orthogonality between the states. Typical overlap elements between $\psi_i(q,Q)$ and $\psi_j(q,Q)$ in the present application on NaLi$^+$ are 10^{-2}. Symmetric orthogonalization which, as numerically verified below, varies smoothly with the nuclear geometry, serves as a simple alleviation of this problem. In the following we denote the Q_0-x geometry by α and the Q_0+x geometry by β. We define the symmetrically orthogonalized state as

$$(X_i,X_j)=(\psi_i,\psi_j)(\underline{K}^{\alpha\alpha})^{-1/2}\ , \tag{39}$$

with

$$\underline{K}^{\alpha\alpha}=\begin{bmatrix}1 & K_{ij}^{\alpha\alpha}\\ K_{ji}^{\alpha\alpha} & 1\end{bmatrix}\ , \tag{40}$$

where $K_{ji}^{\alpha\alpha}$ is defined by Eq. (30), but denoting the overlap elements between the two states evaluated at the same geometry α. After some straightforward algebra one finds

$$\begin{aligned}2xN_{ij}^{(1)}&=\langle X_i^\alpha\,|\,X_j^\beta\rangle-\langle X_j^\alpha\,|\,X_i^\beta\rangle\\&=X_{ij}^{\alpha\beta}-X_{ji}^{\alpha\beta}\\&=(c_{ii}^\alpha c_{ji}^\beta-c_{ji}^\alpha c_{ii}^\beta)(K_{ii}^{\alpha\beta}-K_{jj}^{\alpha\beta})\\&\quad+(c_{ii}^\alpha c_{jj}^\beta-c_{ji}^\alpha c_{ij}^\beta)(K_{ij}^{\alpha\beta}-K_{ji}^{\alpha\beta})\end{aligned} \tag{41}$$

and similarly

$$\begin{aligned}(4x^2)N_{ij}^{(2S)}&=\langle X_i^\alpha\,|\,X_j^\beta\rangle+\langle X_j^\alpha\,|\,X_i^\beta\rangle\\&=(c_{ii}^\alpha c_{ji}^\beta+c_{ji}^\alpha c_{ii}^\beta)(K_{ii}^{\alpha\beta}+K_{jj}^{\alpha\beta})\\&\quad+(c_{ii}^\alpha c_{jj}^\beta+c_{ji}^\alpha c_{ij}^\beta)(K_{ij}^{\alpha\beta}+K_{ji}^{\alpha\beta})\ ,\end{aligned} \tag{42}$$

where

$$\begin{aligned}c_{ii}^\alpha=c_{jj}^\alpha&=\tfrac{1}{2}[1/(1+K_{ij}^{\alpha\alpha})^{1/2}+1/(1-K_{ij}^{\alpha\alpha})^{1/2}]\ ,\\c_{ii}^\beta=c_{jj}^\beta&=\tfrac{1}{2}[1/(1+K_{ij}^{\beta\beta})^{1/2}+1/(1-K_{ij}^{\beta\beta})^{1/2}]\ ,\end{aligned} \tag{43}$$

$$\begin{aligned}c_{ij}^\alpha=c_{ji}^\alpha&=\tfrac{1}{2}[1/(1+K_{ij}^{\alpha\alpha})^{1/2}-1/(1-K_{ij}^{\alpha\alpha})^{1/2}]\ ,\\c_{ij}^\beta=c_{ji}^\beta&=\tfrac{1}{2}[1/(1+K_{ij}^{\beta\beta})^{1/2}-1/(1-K_{ij}^{\beta\beta})^{1/2}]\ .\end{aligned} \tag{44}$$

Thus each pair of coupling constants $N_{ij}^{(1)}$ and $N_{ij}^{(2)}$ requires the evaluation of six overlap elements $K_{ij}^{\alpha\beta}$, $K_{ji}^{\alpha\beta}$, $K_{ij}^{\alpha\alpha}$, $K_{ij}^{\beta\beta}$, $K_{ii}^{\alpha\beta}$, and $K_{jj}^{\alpha\beta}$.

The adiabatic corrections to the Born-Oppenheimer states are obtained in the symmetrically orthogonalized basis (X) as

$$2MB_{ii}^{(2)}=\left\langle \psi_i(q;Q_0) \left| \frac{\delta^2\psi_i}{\delta Q^2}(q;Q) \right.\right\rangle$$
$$=c_{ii}^{\alpha}c_{ii}^{\beta}K_{ii}^{\alpha\beta}+c_{ij}^{\alpha}c_{ii}^{\beta}K_{ji}^{\alpha\beta}+c_{ii}^{\alpha}c_{ij}^{\beta}K_{ij}^{\alpha\beta}+c_{ij}^{\alpha}c_{ij}^{\beta}K_{jj}^{\alpha\beta} . \tag{45}$$

Separate state optimization introduces in general a nonorthogonality problem in the evaluation of transition-state properties. Although efficient schemes for cofactor evaluation have been developed,[29,30] the explicit calculation of determinant-determinant overlap elements becomes cumbersome and slow for large wave functions if the state optimized sets of orbitals are mutually nonorthogonal. One way to avoid this problem, which has been adopted in previous *ab initio* approaches for nonadiabatic coupling constants, is to use state averaged or frozen orbitals and to recover part of the relaxation error by CI expansions. However, the need for full MO flexibility at avoided crossings where the adiabatic states drastically change character and where the wave function should account for the simultaneous changes in correlation and relaxation effects cannot be underestimated. For complete active-space wave functions one can exploit the invariance property towards orbital rotations in the active space to construct transition matrix elements that can efficiently be calculated. For transition moment calculations this has been achieved[31,32] by means of the corresponding orbital procedure of Amos and Hall[33] which brings the MO overlap matrix to diagonal form. This imposes the restriction that the set of inactive orbitals has to be the same for the two states connected by the transition. The latter restriction means that the inactive orbitals must be truly core orbitals, in which case this restriction has been shown to be numerically well founded.[32] However, for the calculation of overlap matrix elements, $K_{ij}^{\alpha\beta}$ of Eq. (30) generated by geometry displacements, there is an additional complication due to nonzero overlap between active orbitals of one geometry and inactive orbitals of another. This calls for the full diagonalization over all occupied orbitals contained in the $X_{ij}^{\alpha\beta}$ matrix elements [defined by Eq. (41)]. The recently developed biorthogonalization scheme of Malmquist,[34] which transcends the ordinary corresponding orbital procedure, seems to be particularly suitable for this purpose. Below we recapitulate the main steps of the procedure applied to complete active space wave functions that are relevant for the evaluation of $X_{ij}^{\alpha\beta}$-type elements. The $\underline{\chi}^{\alpha\beta}$ overlap matrix is partitioned into four blocks,

$$\underline{\chi}^{\alpha\beta}=\begin{bmatrix} \underline{\chi}_{II}^{\alpha\beta} & \underline{\chi}_{IT}^{\alpha\beta} \\ \underline{\chi}_{TI}^{\alpha\beta} & \underline{\chi}_{TT}^{\alpha\beta} \end{bmatrix} , \tag{46}$$

where the labels I and T denote inactive and active parts, respectively. The main idea is to modify the active-active block ($\underline{\chi}_{TT}^{\alpha\beta}$) before bringing it to diagonal form,

$$\underline{M}_{TT}^{\alpha\beta}=\underline{\chi}_{TT}^{\alpha\beta}-\underline{\chi}_{TI}^{\alpha\beta}\underline{U}_{2I}\underline{D}_{I}^{-1}\underline{U}_{1I}^{\dagger}\underline{\chi}_{IT}^{\alpha\beta} , \tag{47}$$

where $\underline{D}_I$ is the prediagonalized inactive matrix $\underline{\chi}_{II}^{\alpha\beta}$. Both inactive $\underline{\chi}_{II}^{\alpha\beta}$ and modified active $\underline{M}_{TT}^{\alpha\beta}$ parts of $\underline{\chi}^{\alpha\beta}$ are diagonalized by means of the conventional corresponding orbital procedure

$$\begin{aligned} &\underline{U}_{1I}\underline{\chi}_{II}^{\alpha\beta}(\underline{\chi}_{II}^{\alpha\beta})^{\dagger}\underline{U}_{1I}=\underline{D}_{I}^{1/2} , \\ &\underline{U}_{2I}(\underline{\chi}_{II}^{\alpha\beta})^{\dagger}\underline{\chi}_{II}^{\alpha\beta}\underline{U}_{2I}=\underline{D}_{I}^{1/2} , \\ &\underline{U}_{1T}\underline{M}_{TT}^{\alpha\beta}(\underline{M}_{TT}^{\alpha\beta})^{\dagger}\underline{U}_{1T}=\underline{D}_{T}^{1/2} , \\ &\underline{U}_{2T}(\underline{M}_{TT}^{\alpha\beta})^{\dagger}\underline{M}_{TT}^{\alpha\beta}\underline{U}_{2T}=\underline{D}_{T}^{1/2} . \end{aligned} \tag{48}$$

where we have used the fact that both transformation matrices for each block ($\underline{U}_{1I},\underline{U}_{2I}$ and $\underline{U}_{1T},\underline{U}_{2T}$) give the same eigenvalues $\underline{D}_{I}^{1/2}$ and $\underline{D}_{T}^{1/2}$, respectively, in either the inactive and the active case. A new set of orbitals, pseudocorresponding orbitals, are obtained from the original ones by using the transformation matrices $\underline{U}$,

$$\begin{aligned} &|\phi_{1I}^{\alpha}\rangle=\underline{U}_{1I}\,|\psi_{iI}^{\alpha}\rangle , \\ &|\phi_{iT}^{\alpha}\rangle=\underline{U}_{1T}\,|\psi_{1T}^{\alpha}\rangle \end{aligned} \tag{49}$$

and

$$\begin{aligned} &|\phi_{jI}^{\beta}\rangle=\underline{U}_{2I}\,|\psi_{jI}^{\beta}\rangle , \\ &|\phi_{jT}^{\beta}\rangle=\underline{U}_{2T}\,|\psi_{jT}^{\beta}\rangle . \end{aligned} \tag{50}$$

After having obtained new CI vectors $|C_i^{\alpha}\rangle$ and $|C_j^{\beta}\rangle$ pertaining to (φ_i^{α}) and (φ_j^{β}) (very efficiently by means of the algorithm of Malmquist[34] consisting of a sequence of single-orbital transformations of the CI vectors), a scaling procedure is performed such that

$$[C_j^{\beta}(\mu)]''=C_j^{\beta}(\mu)d_t^{n_t(\mu)} , \tag{51}$$

where $n_t(\mu)$ is the occupation of orbital t in CSF μ. d_t denotes the corresponding (diagonal) density-matrix elements. After this scaling, $X_{ij}^{\alpha\beta}$ is obtained as a simple dot product between the two CI vectors

$$X_{ij}^{\alpha\beta}=\sum_{\mu} C_i^{\alpha}(\mu)[C_j^{\beta}(\mu)]'' . \tag{52}$$

From Eqs. (49) and (50) onwards an alternative route was also devised by Malmquist,[34] in which fully biorthogonal orbitals are obtained by means of a nonorthogonal transformation of $(|\phi_i^{\alpha}\rangle,|\phi_j^{\beta}\rangle)$ which preserves the invariance of the CI vectors $|C_i^{\alpha}\rangle$ and $|C_j^{\beta}\rangle$. This route would be necessary for transition matrix elements involving two states with different symmetries and would necessitate the calculation of a transition density matrix. For charge-transfer coupling between two states of identical symmetry, we believe, however, that the calculation of $X_{ij}^{\alpha\beta}$ by means of Eqs. (51) and (52) will be more efficient.

III. COMPUTATIONAL

A computer program that implements the formalism derived above has been written and interfaced to SIRIUS, the direct second-order MCSCF program recently developed by two of us.[35] Energies and wave functions were calculated for the two first $^2\Sigma^+$ states of NaLi$^+$ for internuclear distances between 6.00 and 18.00 a.u. In all calculations the origin was chosen at the center of mass. This choice has some numerical and formal advantages for calculations at very large internuclear separations.[5] For each pair of (first- and second-order) coupling elements, four MCSCF optimizations are carried out; for the two states at two symmetrically displaced geometries from the point of the coupling. Sharp convergence criteria were enforced, 10^{-9} in energy gradient, and integral thresholds were put to 10^{-13}. The numerical stability of the second-order coupling constants was found to be crucially dependent on low thresholds. NaLi$^+$ at large distances has previously been shown to provide a problematic case for MCSCF convergence. In test calculations we found that the full account of the configurational-orbital part in the Hessian coupling block was necessary for obtaining convergence of the second state at large internuclear separation.

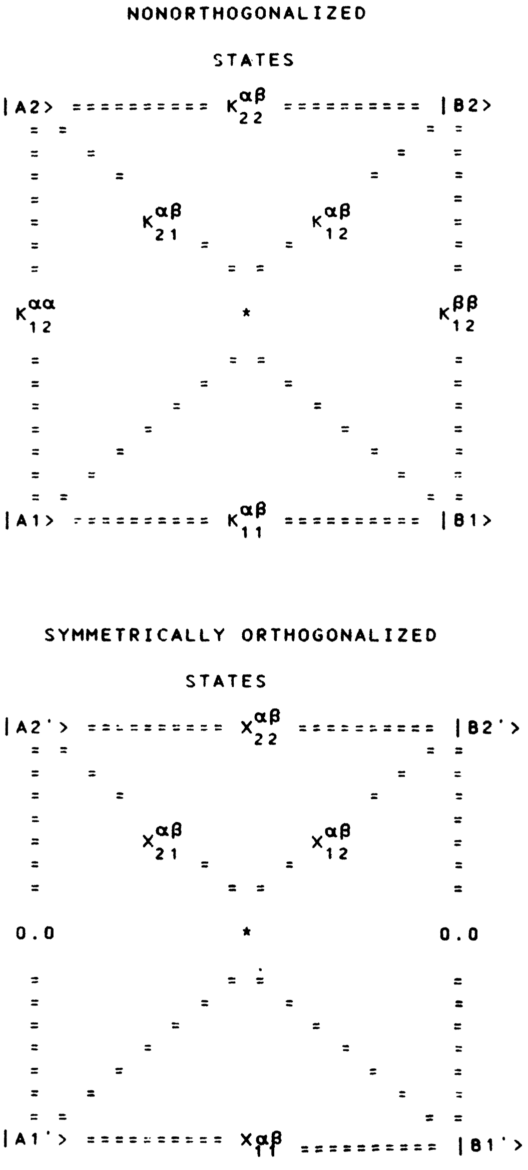

FIG. 1. Diagram illustrating the various wave-function overlaps in the nonorthogonalized and symmetrically orthogonalized cases, respectively.

The flow of the calculation is illustrated in Fig. 1. Each pair of coupling elements $N_{ij}^{(1)}$ and $N_{ij}^{(2)}$, requires the calculation of six overlap elements; $K_{ij}^{\alpha\beta}$, $K_{ij}^{\beta\alpha}$, $K_{ij}^{\alpha\alpha}$, $K_{ij}^{\beta\beta}$, $K_{ii}^{\alpha\beta}$, and $K_{ji}^{\beta\beta}$. Each such element is processed by means of a sequence of a biorthogonalization, two CI vector transformations, and one scaling procedure as described by Eqs. (46)–(52). The computational effort in these last transformations is of the order of a few seconds and is thus fully negligible compared to the MCSCF wave-function optimizations. The calculation of the "symmetrically orthogonalized" elements are therefore in practice not more costly than that of the "bare" elements. The wave functions obtained are undetermined with respect to their phases, and this would have caused problems if the transformed CI vectors were determined in new CI calculations. These problems are completely avoided with Malmquist's algorithm[34] for explicit transformations using single orbital transformations, as we then are ensured that any wave functions $[\psi_i(q,Q_0-x)$, $\psi_i(q,Q_0+x)$, $\psi_j(q,Q_0-x)$, or $\psi_j(q,Q_0+x)]$ has the same phase in all the three overlaps with the other three wave functions (cf., Fig. 1).

The wave functions were of complete active-space type (CAS), with an active space consisting of the 3*s*, 4*s*, 5*s*, 6*s*, 7*s*, 1π, and 2π orbitals, and with an inactive space comprising the core (Na 1*s* and Li 1*s*) orbitals. (2308 CSF's and 207 rotational parameters were generated.) A Huzinaga (10*s*6*p*/5*s*2*p*) basis set[36] was used for Na and augmented with two *s* Gaussians ($\alpha=0.1,0.01$) and three *p* Gaussians ($\alpha=0.1,0.05,0.01$). One set of *d* functions was also included ($\alpha=0.1$). For Li a (11*s*6*p*1*d*/5*s*3*p*1*d*) contracted basis set was constructed from Huzinaga's 10*s* set augmented with one diffuse *s* function ($\alpha=0.01$). The basis set is very similar to the one used by Orel *et al.*,[37] with the inclusion of diffuse functions that meet the requirements for correctly describing the molecular asymptotic behavior.

IV. RESULTS AND DISCUSSION

In the present work we confine ourselves to the calculations of the nonadiabatic coupling elements and the Born-Oppenheimer corrections for the two lowest $^2\Sigma^+$ states of NaLi$^+$ and we do not consider the scattering part of the problem for obtaining the total charge-transfer cross section. Our main goal in this paper is rather to present an efficient method to obtain the underlying nonadiabatic constants. Results for energies, first ($N_{12}^{(1)}$) and second-order ($N_{12}^{(2)}$),($N_{21}^{(2)}$) coupling constants are shown in Fig. 2. The Born-Oppenheimer corrections (B_{11} and B_{22}) to the states are illustrated in Fig. 3. In Table I we report the numerical results obtained for all quantities discussed in Sec. II, which also form the raw material for Figs. 2 and 3. In order to ensure numerical stability for numerical differentiation a study was performed for the evaluation of the nonadiabatic coupling constants as a function of different step lengths in the internuclear dis-

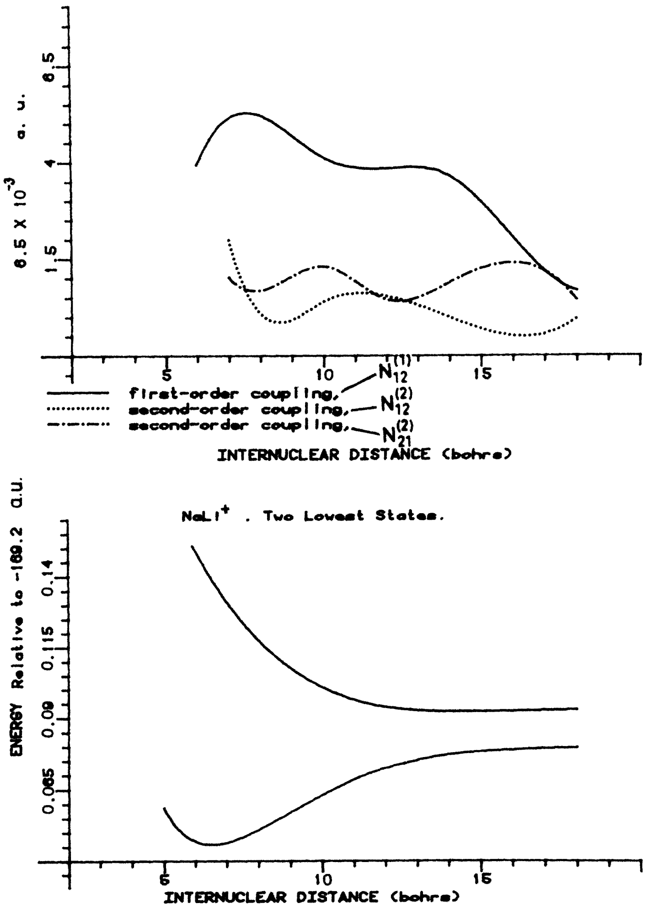

FIG. 2. Progression of the first-order $N_{12}^{(1)}$ and second-order $N_{12}^{(2)}, N_{21}^{(2)}$ coupling constants along the internuclear distance. Potential-energy curves for ground $1\,^2\Sigma^+$ and first excited $2\,^2\Sigma^+$ states.

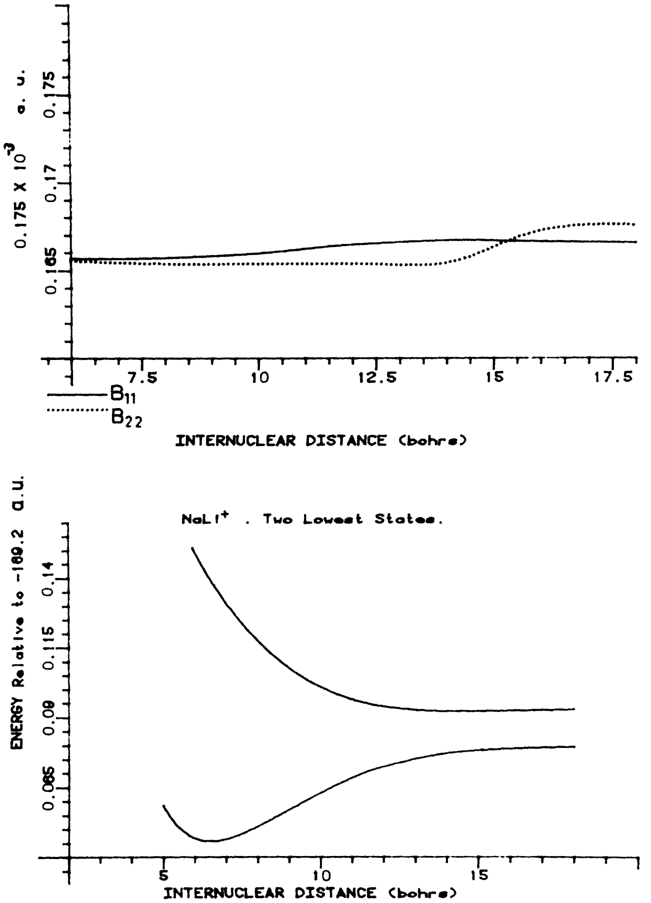

FIG. 3. Born-Oppenheimer corrections to the MCSCF electronic states.

placement. The values for overlap elements, coupling constants, and BO corrections at $R=12.00$ for different step lengths are shown in Table II.

A numerical evaluation of nonadiabatic coupling elements for MCSCF wave functions puts a high demand on the optimization algorithm for safe and fast convergence to the desired states. Low thresholds should be attained if small differential steps are taken. Charge-transfer states and avoided crossings seem to be particularly difficult. Lengsfield *et al.*[26] derived an analytical response method for obtaining first-order nonadiabatic coupling elements employing a state-averaged MCSCF procedure to define a common orbital basis for the states involved. It is based on the coupled MCSCF equations and absorbs much of the analytical molecular energy gradient codes. Hirsch

TABLE I. Nonadiabatic coupling constants evaluated at different internuclear distances (see text). First-order couplings: $(N_{12}^{(1)})^*$ (nonorthogonalized), $N_{12}^{(1)}$ (symmetrically orthogonalized). Symmetric component of the second-order coupling $N_{12}^{(2S)}$. Corrections to the Born-Oppenheimer states, second-order diagonal terms divided by the reduced mass, M. $J_{11}/M=B_{11}$, $J_{22}/M=B_{22}$. The antisymmetric component $N_{12}^{(2A)}$, was estimated by means of a cubic spline. Displacement $2x=0.002$ bohrs has been used throughout. B_{11}^* and B_{22}^* are the scaled Born-Oppenheimer corrections. $B_{11}=fB_{11}^*$, $B_{22}=fB_{22}^*$. f is the conversion factor between electronic and nuclear masses in a.u. f=electron mass/atomic unit mass $=4.48578\times10^{-4}$.

$R(B)$	$(N_{12}^{(1)})^*$	$N_{12}^{(1)}$	$N_{12}^{(2S)}$	$N_{12}^{(2A)}$	B_{11}^*	B_{22}^*
6.00	0.003 857	0.003 919	0.004 762	0.001 932	0.369 319	0.369 043
8.00	0.005 163	0.005 196	0.000 385	−0.000 301	0.369 426	0.368 655
10.00	0.004 089	0.004 100	0.000 847	−0.000 448	0.370 045	0.368 692
12.00	0.003 827	0.003 831	0.000 465	0.000 043	0.371 152	0.368 709
14.00	0.003 616	0.003 616	0.000 430	−0.000 452	0.371 649	0.368 810
16.00	0.002 029	0.002 029	0.000 445	−0.000 936	0.371 395	0.372 855
18.00	0.000 663	0.000 663	0.000 189	−0.000 231	0.371 265	0.373 433

TABLE II. Overlap for the nonorthogonalized states, evaluated at the symmetrically displaced geometries A and B. See caption to Table I. All quantities were calculated at five different displacements $(2x)$ at the internuclear distance $R=12.00$ bohrs.

$2x$	0.10	0.05	0.01	0.004	0.002
$\langle A1 \mid B2 \rangle$	0.041 006	0.042 428	0.042 989	0.043 026	0.043 036
$\langle A2 \mid B1 \rangle$	0.041 757	0.042 812	0.043 066	0.043 057	0.043 051
$\langle A1 \mid B1 \rangle$	0.961 161	0.990 086	0.999 604	0.999 937	0.999 984
$\langle A2 \mid B2 \rangle$	0.961 409	0.990 150	0.999 607	0.999 937	0.999 984
$\langle A1 \mid A2 \rangle$	0.043 718	0.043 381	0.043 112	0.043 071	0.043 058
$\langle B1 \mid B2 \rangle$	0.042 374	0.042 709	0.042 977	0.043 018	0.043 031
$(N_{12}^{(1)})^*$	0.003 756	0.003 849	0.003 825	0.003 827	0.003 827
$N_{12}^{(1)}$	0.003 760	0.003 852	0.003 829	0.003 831	0.003 831
$N_{12}^{(2S)}$	0.000 459	0.000 412	0.000 492	0.000 452	0.000 465
B_{11}^*	0.364 254	0.371 896	0.371 052	0.371 140	0.371 152
B_{22}^*	0.361 917	0.369 507	0.368 609	0.368 697	0.368 709

et al.[23] obtained the coupling matrix as a sum of two parts, one describing a differentiation of CI coefficients and another corresponding to MO derivatives times a transition density matrix. Our method gives both first- and second-order constants at the same expense and utilizing separately optimized MCSCF states. Lengsfield, on the other hand, uses a more general CI wave function, and has the advantage of attaining any nuclear degree of freedom in one calculation.

Potential-energy curves and first-order nonadiabatic coupling constants for $NaLi^+$ have previously been studied by Melius and Goddard[5] (MG) who used Hartree-Fock wave functions with effective core potentials, and who also took into consideration the problem of including traveling phase factors. Orel and Kulander[37] (OK) performed CI calculations on the same system with a first-order wave function with a frozen core and undertook an investigation of coherence effects in $Na\text{-}Li^+$ collisions. They compared the results for the first-order coupling elements from three approaches: first employing the Hellmann-Feynman theorem, second using the Sidis's formula,[38] which is a commutator expansion of the coupling element, and third by means of numerical differentiation of their CI wave function. The results of the two first approaches differed significantly from the third numerical differentiation method, and these authors contended that the first two methods were not accurate enough to be used in the scattering calculations, something which is connected to completeness requirements for the wave functions.

Comparing our results with those of MG and OK we find that the computed potential-energy curves are rather similar; these nearly coincide at the dissociation limit, indicating that the charge transfer can be expected to be most significant in the long-range regime. The first-order coupling displays, however, a rather extensive progression and attains its maximum at about 8.00 a.u. in the internuclear distance and decreases towards the asymptotic and the united atom regions, see Fig. 2. This trend agrees to some extent with the results of OK but does not support the localized character found by MG. The former authors have carried out calculations with different schemes of CI and we accordingly expect to find a better agreement with our MCSCF calculations than the results of MG. Yet the magnitude of the coupling constants obtained both by OK and MG is quite different from the ones here reported. This indicates that the nonadiabatic coupling constants indeed are very dependent on the quality of the underlying wave functions. This was verified at an early stage of the present investigation; e.g., a single-Z, open-shell Hartree-Fock type calculation gave a first-order coupling constant which was 25 times larger than the ones we report in Tables I and II. It also seems that Hartree-Fock—based calculations tend to "overlocalize" the couplings in a small range of internuclear distances.[5] The comparison with previous work indicates that the first-order nonadiabatic coupling has a complex "all-electron" nature. Thus despite the fact that $NaLi^+$ contains a single electron outside two closed-shell noble-gas cores and expectedly should provide an "ideal" Hartree-Fock case, the effect of correlation on the nonadiabatic constant is substantial.

The numerical differentiation of OK and MG was performed with an asymmetric coordinate displacement around the point for the coupling, which is only valid up to first order in the nuclear displacement. This is also the approach of Hirsch *et al.*[23] and of Werner and Meyer.[24] In all these approaches, and in that of Lengsfield *et al.*,[26] a common set of orbitals for the interacting states is used (which are MCSCF state-averaged orbitals in the two latter cases). The validity of an asymmetric expansion in the nuclear coordinate can be derived from Table II, which shows values of the $\langle A1 \mid B2 \rangle$ and $\langle A2 \mid B1 \rangle$ elements for some geometries. These two values are slightly different over the range of chosen displacements and there should not be any preference from one to the other if the asymmetric expansion approximation is used. In the symmetric expansion, Eq. (30), one thus obtains the coupling constant to one higher order in accuracy, and also the second order constant with the same computational effort.

As seen in Table I, the first-order coupling is almost completely independent of symmetric orthogonalization, which is due to the symmetric expansion of the displacement since the nonorthogonal contributions will have the same magnitude and same signs in the two cases. The wave-function overlap has a significant influence on the second-order constant, which, however, effectively is removed after orthogonalization of the involved states, cf., Eq. (42).

The BO corrections, i.e., the diagonal second-order couplings, are also given in Table I and Fig. 3. Being expectation values of the nuclear kinetic energy operator, they give positive corrections to the Born-Oppenheimer energies.[18] Their magnitudes are found to be insignificant.

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