Gradients for Configuration Interaction Energies with Spin-Orbit Coupling in a Semiempirical Framework

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Abstract: We present a method for the analytical evaluation of the molecular energy gradient for a semiempirical configuration interaction (CI) wavefunction, taking into account the spin-orbit coupling. We show how to proceed in the simplest case where all the wavefunctions belonging to the CI subspace considered are mixed by the spin-orbit interaction, and we develop an original procedure for the more complex case where only a limited number of CI eigenvectors of the spin-free Hamiltonian are mixed.

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Introduction

Intersystem crossing (ISC) processes are frequently important in photochemical reactions. A classical example is provided by Norrish type I reactions[1,2] of carbonyl compounds. Spin-forbidden thermal reactions are also common, expecially when transition metal complexes are involved.[3–5] Taking into account ISC processes in nonadiabatic molecular dynamics simulations requires the evaluation and use of the spin-orbit coupling (SOC): this has been done by several research groups,[6–10] with mixed quantum-classical molecular dynamics methods. However, a general on the fly nonadiabatic molecular dynamics method allowing to include SOC within an arbitrary number of electronic states (with arbitrary spin multiplicities) is still lacking. As a first step in this direction we describe here a formalism for the evaluation of the SOC for configuration interaction (CI) wavefunctions in a semiempirical framework, using the one-electron effective spin-orbit (SO) Hamiltonian defined by Böckmann et al.[11] and with wavefunctions written in terms of Slater determinants. A key feature of the present method is the possibility to evaluate analytical gradients of the energy for the SO mixed CI wavefunctions. This feature is needed in view of the inclusion of the present algorithm in a mixed quantum-classical scheme for nonadiabatic molecular dynamics simulations, such as the Surface-Hopping (SH) algorithm. In fact, in the SH approach, the dynamics is better performed on adiabatic potential energy surfaces. The evaluation of analytical gradients of the molecular energy has been implemented for relativistic wavefunctions, mainly in the DFT framework.[12–14] However, this does not seem the case for nonrelativistic wavefunctions with SO corrections, either in semiempirical or in *ab initio* frameworks. As a test, the present method is applied to geometry optimizations of SO mixed states for the HSiBr molecule.

Spin-Orbit Coupling Matrix Elements for CI Wavefunctions

We shall consider a spin dependent electronic hamiltonian $\hat{\mathcal{H}}_{tot}$, which is the sum of the electrostatic (spin-free) hamiltonian $\hat{\mathcal{H}}_{el}$ and of the spin-orbit interaction $\hat{\mathcal{H}}_{SO}$:

$$\hat{\mathcal{H}}_{tot} = \hat{\mathcal{H}}_{el} + \hat{\mathcal{H}}_{SO}. \tag{1}$$

In principle, two strategies may be considered. The "uncontracted" one consists in diagonalizing $\hat{\mathcal{H}}_{tot}$, projected in a subspace $\mathcal{S}_{CI}$ of Slater determinants or spin-adapted configurations. In the "contracted" alternative one deals with the simultaneous eigenstates of $\hat{\mathcal{H}}_{el}$, $\hat{S}^2$, and $\hat{S}_z$. In this case, one can choose a (small) number N_{mod} of spin multiplets of interest that define a model subspace $\mathcal{S}_{mod}$. The projection of $\hat{\mathcal{H}}_{tot}$ in $\mathcal{S}_{mod}$ is then diagonalized. We shall adopt the contracted strategy, because it allows to define *a priori* the set of electronic states to be included in a molecular dynamics simulation. However, we shall compare this approach with the uncontracted one.

We have implemented the present scheme in our development version of the semiempirical package MOPAC.[15] As the CI in MOPAC is based on Slater determinants, we have kept this feature. The electronic wavefunctions $|n, m_{ref}\rangle$ and energies U_n are obtained by diagonalizing the electrostatic hamiltonian $\hat{\mathcal{H}}_{el}$ in a subspace

$S_{CI}^{m_{ref}} \subset S_{CI}$, where m_{ref} is the $\hat{S}_z$ eigenvalue for all the determinants $\Phi_I^{m_{ref}} \in S_{CI}^{m_{ref}}$ and for the CI states

$$|n, m_{ref}\rangle = \sum_I^{N_{mult}} C_{I,n}^{m_{ref}} |\Phi_I^{m_{ref}}\rangle. \qquad (2)$$

An obvious requirement for the subspace $S_{CI}^{m_{ref}}$ is that it must be closed under the action of $\hat{S}^2$, so that the states $|n, m_{ref}\rangle$ are also eigenstates of $\hat{S}^2$: $\hat{S}^2|n, m_{ref}\rangle = S_n(S_n + 1)|n, m_{ref}\rangle$ (we use atomic units). In the case of energy degeneracy, this property can be enforced by diagonalizing the $\hat{S}^2$ matrix within the degenerate blocks of $|n, m_{ref}\rangle$ states. With an even (odd) number of electrons, a sensible choice for m_{ref} is $m_{ref} = 0$ (respectively, $m_{ref} = 1/2$), in such a way that all the possible spin states can be obtained. In the following, we will formally refer to the full set of spin-orbit coupled components $|n, m_n\rangle$, $m_n = -S_n \ldots S_n$; however, thanks to the Wigner Eckart theorem (see later), only the one with $m_n = m_{ref}$ needs to be explicitly evaluated.

As mentioned in the introduction, we consider the one-electron effective spin-orbit Hamiltonian defined by Böckmann et al.[11] Using the second quantization formalism, it can be written as

$$\hat{\mathcal{H}}_{SO} = \frac{1}{2} \sum_{i,j} \left(L_{ij}^z (\hat{a}_i^+ \hat{a}_j - \hat{b}_i^+ \hat{b}_j) + L_{ij}^+ \hat{b}_i^+ \hat{a}_j + L_{ij}^- \hat{a}_i^+ \hat{b}_j \right) \qquad (3)$$

where, following Manne and Zerner,[16] $\hat{a}_i$ ($\hat{b}_i$) is an annihilation operator for a spin α (respectively, β) orbital and the summation runs over all the molecular orbitals (MO). L_{ij}^σ ($\sigma = +, -, z$) contains the angular momentum matrix elements and the related atomic effective spin-orbit parameters. In particular, expanding the (real) MOs in terms of the atomic ones: $\varphi_i = \sum_\mu c_{\mu i} \chi_\mu$, we have

$$L_{ij}^\sigma = \sum_\alpha^{atoms} \sum_{\mu, \nu \in \alpha} c_{\mu i} c_{\nu j} \xi_\alpha^{\mu\nu} \langle \chi_\mu | \hat{l}_\sigma^{(\alpha)} | \chi_\nu \rangle \quad \sigma = +, -, z. \qquad (4)$$

where $\hat{\mathbf{l}}^\alpha$ is the angular momentum operator for atom α and $\xi_\alpha^{\mu\nu}$ are the effective spin-orbit parameters. In the above expression, the two center atomic integrals of angular momentum are neglected, considering the short range of the nucleus-electron spin-orbit interaction. This approximation is consistent with the NDO semiempirical ansatz, but can be acceptable also in the *ab initio* framework. The $\hat{l}_\sigma$ operators only mix the atomic orbitals with the same l quantum number. Therefore, with a minimal basis set, as in semiempirical calculations, a given atom α has one effective parameter $\xi_{\alpha,l}$ for each set of basis functions with angular momentum $l > 0$ (for s functions the SO coupling vanishes).

With real MOs we have $L_{ij}^\sigma = -L_{ji}^\sigma$ ($\sigma = +, -, z$), which implies $L_{ii}^\sigma = 0$. Making use of these relations we can recast $\hat{\mathcal{H}}_{SO}$ in this way:

$$\hat{\mathcal{H}}_{SO} = \sum_{q=-1}^{1} \sum_{i<j} (-1)^q L_{ij}^{(-q)} \hat{T}_{ij}^{(q)} \qquad (5)$$

$$\hat{T}_{ij}^{(0)} = \frac{1}{2} \left(\hat{a}_i^+ \hat{a}_j - \hat{b}_i^+ \hat{b}_j - \hat{a}_j^+ \hat{a}_i + \hat{b}_j^+ \hat{b}_i \right) \qquad (6)$$

$$\hat{T}_{ij}^{(1)} = -\frac{1}{\sqrt{2}} \left(\hat{a}_i^+ \hat{b}_j - \hat{a}_j^+ \hat{b}_i \right) \qquad (7)$$

$$\hat{T}_{ij}^{(-1)} = \frac{1}{\sqrt{2}} \left(\hat{b}_i^+ \hat{a}_j - \hat{b}_j^+ \hat{a}_i \right) \qquad (8)$$

where $L_{ij}^{(0)} = L_{ij}^z$, $L_{ij}^{(\pm 1)} = \mp L_{ij}^\pm / \sqrt{2}$. The operators $\hat{T}_{ij}^{(q)}$ with $q = 0, \pm 1$ are the three components of a spin operator that is a spherical tensor of rank one. In fact, they satisfy the following commutation relations:[17]

$$[\hat{S}_z, \hat{T}_{ij}^{(q)}] = q\hat{T}_{ij}^{(q)} \qquad (9)$$

$$[\hat{S}_\pm, \hat{T}_{ij}^{(q)}] = \hat{T}_{ij}^{(q\pm 1)} \sqrt{2 - q(q \pm 1)}. \qquad (10)$$

As observed by Manne and Zerner,[16] $\sum_{i<j} \hat{T}_{ij}^{(q)}$ can be taken as a generalized $\hat{S}^{(q)}$ operator; the generalized one-electron spin density matrices are then

$$\rho_{ij}^{(q)}(n, n'|m_n) = \langle n, m_n | \hat{T}_{ij}^{(q)} | n', m_n - q \rangle. \qquad (11)$$

Since the $\hat{T}_{ij}^{(q)}$ components belong to a spherical spin tensor operator, their matrix elements with spin eigenfunctions must satisfy the Wigner Eckart theorem.[17] In particular, following McWeeny,[18] we have

$$\rho_{ij}^{(q)}(n, n'|m_n) = \rho_{ij}^{(q')}(n, n'|m_{ref}) \begin{bmatrix} S_n & m_n & q \\ S_{n'} & m_{ref} & q' \end{bmatrix} \qquad (12)$$

where the term in square brackets is a shorthand for a ratio of two 3-j symbols

$$\begin{bmatrix} S & m & q \\ S' & m' & q' \end{bmatrix} \overset{def}{=} (-1)^{m'-m} \frac{\begin{pmatrix} S & 1 & S' \\ -m & q & m-q \end{pmatrix}}{\begin{pmatrix} S & 1 & S' \\ -m' & q' & m'-q' \end{pmatrix}}. \qquad (13)$$

The determination of the single matrix element $\rho_{ij}^{(q')}(n, n'|m_{ref})$ amounts to knowing the full set of spin density matrix elements $\rho_{ij}^{(q)}(n, n'|m_n)$ with $q = 0, \pm 1$ and $m_n = -S_n \ldots S_n$ connecting the two spin multiplets n and n'. The choice $q' = 0$, i.e., to compute explicitly $\rho_{ij}^{(0)}(n, n'|m_{ref})$, guarantees that the components of the spin multiplets with $m_n \neq m_{ref}$ do not need to be generated. Unfortunately, with an even number of electrons, setting $q' = 0$ and $m_{ref} = 0$ we face a problem when $S_n = S_{n'}$; we have in fact

$$\begin{bmatrix} S & m & q \\ S & m_{ref} & 0 \end{bmatrix} = \frac{1}{m_{ref}} \left(m(1 - |q|) - q\sqrt{\frac{(S - qm + 1)(S + qm)}{2}} \right). \qquad (14)$$

In this case we can formally keep $m_{ref} = 0$ by setting, for instance, $q' = -1$: we have then to evaluate explicitly $\rho_{ij}^{(-1)}(n, n'|0)$, and this can be done by first applying $\hat{S}_+$ to $|n', 0\rangle$, as follows:

Table 1. Rules for the Evaluation of Generalized Spin Density Matrix Elements.

$|\Phi'\rangle$	$\langle\Phi|\hat{T}_{cd}^{(0)}|\Phi'\rangle$	$\langle\Phi|\hat{T}_{cd}^{(-1)}\hat{S}_+|\Phi'\rangle$	$\langle\Phi'|\hat{T}_{cd}^{(-1)}\hat{S}_+|\Phi\rangle$
$|\Phi\rangle$	$\dfrac{\delta_{ci}\delta_{di}(n_i^\alpha - n_i^\beta)}{2}$	$\dfrac{\delta_{ci}\delta_{di}n_i^\beta(1-n_i^\alpha)}{\sqrt{2}}$	$\dfrac{\delta_{ci}\delta_{di}n_i^\beta(1-n_i^\alpha)}{\sqrt{2}}$
$\hat{a}_i^+\hat{a}_j|\Phi\rangle, i \neq j$	$\dfrac{\delta_{cj}\delta_{di}}{2}$	$\dfrac{-\delta_{cj}\delta_{di}n_j^\beta}{\sqrt{2}}$	$\dfrac{-\delta_{ci}\delta_{dj}n_i^\beta}{\sqrt{2}}$
$\hat{b}_i^+\hat{b}_j|\Phi\rangle, i \neq j$	$\dfrac{-\delta_{cj}\delta_{di}}{2}$	$\dfrac{\delta_{cj}\delta_{di}(1-n_i^\alpha)}{\sqrt{2}}$	$\dfrac{\delta_{ci}\delta_{dj}(1-n_j^\alpha)}{\sqrt{2}}$
$\hat{a}_i^+\hat{a}_j\hat{b}_k^+\hat{b}_l|\Phi\rangle\; i \neq j, k \neq l$	0	$\dfrac{-\delta_{cl}\delta_{di}\delta_{kj}}{\sqrt{2}}$	$\dfrac{-\delta_{ck}\delta_{dj}\delta_{li}}{\sqrt{2}}$

$|\Phi\rangle$ and $|\Phi'\rangle$ are Slater determinants belonging to $\mathcal{S}_{CI}^{m_{ref}}$. Only the matrix elements of $\hat{T}_{cd}^{(0)}$, and, in some circumstances, of $\hat{T}_{cd}^{(-1)}$, need to be evaluated [see eq. (15)]. n_i^σ is the occupation number (0 or 1) of MO φ_i with spin σ. Note that diagonal terms give a null contribution to the SOC as $L_{ii}^{(q)} = 0$.

$$\rho_{ij}^{(-1)}(n, n'|0) = \frac{\langle n, 0|\hat{T}_{ij}^{(-1)}\hat{S}_+|n', 0\rangle}{\sqrt{S_{n'}(S_{n'}+1)}}. \quad (15)$$

Rules for the explicit evaluation of the needed spin density matrix elements are given in Table 1. The matrix elements of $\hat{\mathcal{H}}_{SO}$ are finally computed as

$$\langle n, m_n|\hat{\mathcal{H}}_{SO}|n', m_n - q\rangle$$
$$= (-1)^q \sum_{i<j} L_{ij}^{(-q)}\rho_{ij}^{(q')}(n, n'|m_{ref})\begin{bmatrix} S_n & m_n & q \\ S_{n'} & m_{ref} & q' \end{bmatrix} \quad (16)$$

where, as above, $q = 0, \pm 1$.

In the contracted approach we assume that the $\hat{\mathcal{H}}_{SO}$ matrix elements are evaluated within the N_{mod} spin multiplets of the model space, that contains $\sum_{n=1}^{N_{mod}}(2S_n + 1)$ states. By diagonalization of $\hat{\mathcal{H}}_{tot}$ within the model space we get the SO corrected energies E_A and wavefunctions $|A\rangle$:

$$|A\rangle = \sum_n^{N_{mod}} \sum_{m_n} D_{n,m_n}^A |n, m_n\rangle \quad (17)$$

$$E_A = \sum_n^{N_{mod}} U_n \sum_{m_n} |D_{n,m_n}^A|^2 + \sum_q \sum_{i<j}(-1)^q L_{ij}^{(-q)}\rho_{ij}^{(q)}(A) \quad (18)$$

$$\rho_{ij}^{(q)}(A) = \sum_{n,n'}^{N_{mod}} \rho_{ij}^{(q')}(n, n'|m_{ref}) \sum_{m_n}\left(D_{n,m_n}^A\right)^*$$
$$\times D_{n',m_n-q}^A\begin{bmatrix} S_n & m_n & q \\ S_{n'} & m_{ref} & q' \end{bmatrix}, \quad (19)$$

where U_n are the SO uncorrected energies of the $|n, m_{ref}\rangle$ model states. The first term of the RHS of eq. (18) is E_A^{el}, the electrostatic contribution to E_A, while the second term is the SO contribution, E_A^{SO}. In eq. (18) the sum on MO indices is extended to the

CI-active MOs (hereafter labelled $i, j, \ldots$, while we use $a, b, \ldots$ to indicate any kind of MO). Using the relation $\rho_{ij}^{(q)}(n, n'|m_n) = (-1)^{1-q}\rho_{ij}^{(-q)}(n', n|m_{n'})$ (for real spin density matrices) we can rewrite E_A^{SO} in a form more appealing from the computational point of view

$$E_A^{SO} = \sum_{i<j}\sum_{n<n'}^{N_{mod}} \rho_{ij}^{(q')}(n, n'|m_{ref})G_{ij}^{(q')}(n, n'), \quad (20)$$

where

$$G_{ij}^{(q')}(n, n') = \sum_q (-1)^q L_{ij}^{(-q)} \sum_{m_n}\left\{\left(D_{n,m_n}^A\right)^* D_{n',m_n-q}^A\begin{bmatrix} S_n & m_n & q \\ S_{n'} & m_{ref} & q' \end{bmatrix}\right.$$
$$\left. + (-1)^{1-q}\left(D_{n',m_n+q}^A\right)^* D_{n,m_n}^A\begin{bmatrix} S_n & m_n & -q \\ S_{n'} & m_{ref} & q' \end{bmatrix}\right\}. \quad (21)$$

As explained earlier, we can always choose $q' = 0$ except for $m_{ref} = 0$, when $S_n = S_{n'}$. However, in both cases (i.e., either with $q' = 0$ or with $q' = \pm 1$ and $S_n = S_{n'}$) we have, for the real spin density matrices: $\rho_{ij}^{(q')}(n, n'|m_{ref}) = -\rho_{ij}^{(q')}(n', n|m_{ref})$. This allows to recast eq. (20) in a more symmetric form, written here for later reference

$$E_A^{SO} = \sum_{i<j}\sum_{\substack{n,n' \\ n \neq n'}}^{N_{mod}} \rho_{ij}^{(q')}(n, n'|m_{ref})\tilde{G}_{ij}^{(q')}(n, n') \quad (22)$$

where we used the shorthand

$$\tilde{G}_{ij}^{(q')}(n, n') = \begin{cases} \dfrac{1}{2}G_{ij}^{(q')}(n, n') & \text{for } n < n' \\ -\dfrac{1}{2}G_{ij}^{(q')}(n', n) & \text{for } n > n'. \end{cases} \quad (23)$$

Derivatives of the SO Corrected Energy

In the formulation of the analytical gradient we refer to our previous work,[19] where we applied the Z-vector technique for the evaluation of gradients for semiempirical CI eigenfunctions of the spin-free hamiltonian $\hat{\mathcal{H}}_{el}$. A non standard feature of our approach is that the MOs are obtained by a floating occupation number SCF (FOMO-CI).[20] The FOMO-CI technique is an alternative to State-Averaged CASSCF that has been also applied in the *ab initio* context,[21–23] and allows to represent correctly homolytic dissociations and state degeneracies.[24] As in ref. 19, only the CI-active MOs are allowed to have floating occupation numbers. In the following, R_α shall indicate a nuclear coordinate.

The quantity E_A to be derived is given by eq. (18) above. In particular we focus here on E_A^{SO} [the second term in the RHS of eq. (18)], which is also rewritten in eq. (22). The derivatives of the coefficients D_{n,m_n}^A give a null contribution to $\partial E_A/\partial R_\alpha$; however, the derivatives of the CI coefficients of the model states $|n, m_n\rangle$ have, in general, to be considered (this is not necessary only when the model space spans the whole CI vector subspace taken into account).

The gradient can be partitioned in a "static" and a "response" term.[19] The response gradient of E_A^{SO} contains the derivatives of the MO and CI coefficients. With constant $\xi_{\alpha,l}$ parameters, the matrices $L_{ij}^{(q)}$ depend on the nuclear coordinates only through the MO coefficients. Then, the static contribution to the derivative of $L_{ij}^{(q)}$ is zero:

$$\frac{\partial E_A^{SO}}{\partial R_\alpha}\bigg|_{static} = 0. \qquad (24)$$

We shall now focus on the response term. In the case of geometry dependent $\xi_{\alpha,l}$ SO coefficients, one should simply add a static contribution containing their derivatives.

Uncontracted Strategy: Diagonalization of $\hat{\mathcal{H}}_{tot}$ in the $\mathcal{S}_{CI}$ Subspace

This approach can be seen as the limiting case of the contracted one, with $\mathcal{S}_{mod} = \mathcal{S}_{CI}$ i.e., $N_{mod} = N_{mult}$. Of course, in this case a more efficient procedure is to avoid the unnecessary diagonalization of the $\hat{\mathcal{H}}_{el}$ matrix, by using spin-adapted configurations instead of the $|n, m_{ref}\rangle$ states; in this way, however, the relationship with the spin-orbit uncoupled states is lost. The uncontracted strategy is conceptually simpler then the contracted one: as the $|n, m_{ref}\rangle$ states span the whole CI subspace $\mathcal{S}_{CI}^{m_{ref}}$, the derivatives of the CI coefficients and of the related $\rho^{(q)}$ density matrices do not contribute to the gradient.

The derivatives of $L_{ij}^{(q)}$ are

$$\frac{\partial L_{ij}^{(q)}}{\partial R_\alpha} = \sum_a \left(B_{ia}^\alpha L_{aj}^{(q)} - L_{ia}^{(q)} B_{aj}^\alpha \right) \qquad \mathbf{B}^\alpha = \frac{\partial \mathbf{c}^+}{\partial R_\alpha} \mathbf{c} \qquad (25)$$

where, as in ref. 19, $\mathbf{B}^\alpha$ is the antisymmetric matrix containing the derivatives of the MO coefficients $\mathbf{c}$. By exploiting the antisymmetry of the real matrix B_{ij}^α and of the complex matrices $L_{ij}^{(q)}$ and $\rho_{ij}^{(q)}$ we have immediately

$$\frac{\partial E_A^{SO}}{\partial R_\alpha}\bigg|_{response} = \sum_{i,a} B_{ia}^\alpha \sum_{q=0,1} (-1)^q \sum_j \Re\{L_{aj}^{(-q)} \rho_{ij}^{(q)}(A)\}(2 - \delta_{q,0}) \qquad (26)$$

where δ is the Kronecker delta and $\Re$ means real part of a complex quantity. At this point the derivative of E_A can be expressed in the compact form of ref. 19, eq. (A10):

$$\frac{\partial E_A}{\partial R_\alpha}\bigg|_{response} = \sum_a \sum_i \left(B_{ia}^\alpha + \frac{\partial \epsilon_i}{\partial R_\alpha}\delta_{ia} \right) \left(q_{ia}^{el} + q_{ia}^{SO} \right) \qquad (27)$$

$$q_{ii}^{SO} = 0 \qquad (28)$$

$$q_{ia}^{SO} = \sum_{q=0,1} (-1)^q \sum_j \Re\{L_{aj}^{(-q)} \rho_{ij}^{(q)}(A)\}(2 - \delta_{q,0})$$

$$(for\ i \neq a) \quad (29)$$

$$q_{ii}^{el} = \Delta_{ii}(A) - O_i - \frac{1}{2}\sum_{jkl} \beta_{ki}\langle lj||kk\rangle(\Delta_{lj}(A) - \delta_{lj}O_l) \qquad (30)$$

$$q_{ia}^{el} = 4\sum_{jkl} \Gamma_{ijkl}(A)\langle aj|kl\rangle - \sum_{jk} \Delta_{ij}(A)O_k\langle kk||aj\rangle$$

$$- \sum_{jk} \Delta_{jk}(A)O_i\langle ai||jk\rangle + \sum_j O_iO_j\langle ai||jj\rangle$$

$$(for\ i \neq a) \quad (31)$$

$$\beta_{ki} = f_k(\epsilon_F)\left(\frac{f_i(\epsilon_F)}{\sum_j f_j(\epsilon_F)} - \delta_{ik} \right) \qquad (32)$$

where, as usual, $\langle ij||kl\rangle = 2\langle ij|kl\rangle - \langle ik|jl\rangle$ and ϵ_i, O_i are, respectively, energy and occupation number of the i-th MO. $f_i(\epsilon)$ is a gaussian function of the i-th orbital energy such that $O_i = \int_{-\infty}^{\epsilon_F} f_i(\epsilon)d\epsilon$ where ϵ_F, the Fermi energy, is found by imposing that the sum of the occupation numbers equals the total number of active electrons. The $\mathbf{q}^{el}$ terms shown above have been obtained in ref. 19; clearly, in the present case, $\Delta_{ij}(A)$ and $\Gamma_{ijkl}(A)$ represent the spinless one- and two-electron density matrices of state $|A\rangle$, which are real quantities:

$$\Delta_{ij}(A) = \sum_{n \leq n'} \delta_{S_n,S_{n'}} \Delta_{ij}(n,n') \sum_{m_n} \Re\{(D_{n,m_n}^A)^* D_{n',m_n}^A\} \qquad (33)$$

and similarly for $\Gamma_{ijkl}(A)$.

Contracted Strategy: Diagonalization of $\hat{\mathcal{H}}_{tot}$ in the $\mathcal{S}_{mod}$ Subspace

In this case the spin density matrices $\rho_{ij}^{q'}(n, n'|m_{ref})$ have to be differentiated, as the derivatives of the CI coefficients of the $|n, m_{ref}\rangle$ model states do contribute to the gradient of E_A^{SO}. We define the real antisymmetric matrix $\mathbf{d}^{(\alpha)}$

$$d_{nk}^{(\alpha)} = \sum_I^{N_{mult}} \frac{\partial C_{I,n}^{m_{ref}}}{\partial R_\alpha} C_{I,k}^{m_{ref}} \qquad (34)$$

Note that $d_{nk}^{(\alpha)} = 0$ if $S_n \neq S_k$ and/or $m_n \neq m_k$; moreover the $d_{nk}^{(\alpha)}$ are independent on m_n (i.e., we would obtain the same result by using $C_{I,n}^{m_n}$, with $m_n \neq m_{ref}$). This is due to the obvious fact that all the $2S_n + 1$ components $|n, m_n\rangle$ change in the same way as the nuclear geometry changes (in particular, they keep S_n and m_n unchanged). The real numbers $d_{nk}^{(\alpha)}$ are the "CI contribution" to the derivative couplings $\langle n, m_n|\partial/\partial R_\alpha|k, m_n\rangle$. As such, they can be obtained using the Hellmann-Feynman theorem: we have $d_{nn}^{(\alpha)} = 0$ and, for $n \neq k$

$$d_{nk}^{(\alpha)} = (U_n - U_k)^{-1} \sum_{I,J} C_{In}^{m_{ref}} \frac{\partial\langle\Phi_I^{m_{ref}}|\hat{\mathcal{H}}_{el}|\Phi_J^{m_{ref}}\rangle}{\partial R_\alpha} C_{Jk}^{m_{ref}}$$

$$= \sum_{ij} \frac{\Delta_{ij}(n,k)}{U_n - U_k} \frac{\partial \varepsilon_{ij}^+}{\partial R_\alpha} + \sum_{ijkl} \frac{\Gamma_{ijkl}(n,k)}{U_n - U_k} \frac{\partial\langle ij|kl\rangle}{\partial R_\alpha} \qquad (35)$$

where (see ref. 19)

$$\varepsilon_{ij}^+ = \varepsilon_i \delta_{ij} - \frac{1}{2} \sum_k \langle ij || kk \rangle O_k. \tag{36}$$

Analogously to $L_{ij}^{(q)}$, the derivatives of the transition spin density matrices are

$$\frac{\partial \rho_{ij}^{(q)}(n, n'|m_n)}{\partial R_\alpha} = \sum_k^{N_{mult}} \left[d_{nk}^{(\alpha)} \rho_{ij}^{(q)}(k, n'|m_n) + d_{n'k}^{(\alpha)} \rho_{ij}^{(q)}(n, k|m_n) \right]. \tag{37}$$

We can write at this point the derivative of E_A^{SO}, using the expression of eq. (22)

$$\frac{\partial E_A^{SO}}{\partial R_\alpha} = \sum_{a,i} B_{ia}^\alpha q_{ia}^{SO}$$
$$+ \sum_{i<j}^{N_{mod}} \sum_{\substack{n,n' \\ n \neq n'}} \tilde{G}_{ij}^{(q')}(n, n') \sum_k^{N_{mult}} \left[d_{nk}^{(\alpha)} \rho_{ij}^{(q')}(k, n') + d_{n'k}^{(\alpha)} \rho_{ij}^{(q')}(n, k) \right] \tag{38}$$

where the first term of the RHS comes from the derivative of $L_{ij}^{(q)}$, see eq. (27). In the above equation and in the rest of this section we omit, for notational simplicity, the m_{ref} argument from the transition spin density matrices. By inserting eq. (35) in eq. (38) we get

$$\frac{\partial E_A^{SO}}{\partial R_\alpha} = \sum_{a,i} B_{ia}^\alpha q_{ia}^{SO} + \sum_{ij} \frac{\partial \varepsilon_{ij}^+}{\partial R_\alpha} \tilde{\Delta}_{ij} + \sum_{ijkl} \frac{\partial \langle ij|kl \rangle}{\partial R_\alpha} \tilde{\Gamma}_{ijkl} \tag{39}$$

where

$$\tilde{\Delta}_{ij} = \sum_k^{N_{mult}} \sum_{\substack{n \\ n \neq k}}^{N_{mod}} \Delta_{ij}(n, k) \frac{R(n, k)}{U_n - U_k} \tag{40}$$

$$\tilde{\Gamma}_{ijkl} = \sum_k^{N_{mult}} \sum_{\substack{n \\ n \neq k}}^{N_{mod}} \Gamma_{ijkl}(n, k) \frac{R(n, k)}{U_n - U_k} \tag{41}$$

$$R(n, k) = \sum_{i<j} \left[\sum_{n'=1}^{n-1} G_{ij}^{(q')}(n', n) \rho_{ij}^{(q')}(n', k) \right.$$
$$\left. + \sum_{n'=n+1}^{N_{mod}} G_{ij}^{(q')}(n, n') \rho_{ij}^{(q')}(k, n') \right]. \tag{42}$$

The response derivative of E_A^{el} can be formally obtained as the weighted sum of the SO uncorrected energies U_n with the state mixing coefficients $|D_{n,m_n}^A|^2$. Therefore, the evaluation of $\partial E_A / \partial R_\alpha$ can proceed in the same way outlined in ref. 19. In particular, for the

Table 2. Evaluation of Some SO Semiempirical Atomic Parameters from Ground State Atomic Terms.

Atom	Configuration	Term	J	Level[a]	A[b]	Semiemp. parameter $\xi = 2|A| \min(L, S)$
C	$2s^2 2p^2$	^3P	0	0	14.3	$\xi_{C,p} = 28.6$
			1	16.4		
			2	43.4		
Si	$3s^2 3p^2$	^3P	0	0	74.6	$\xi_{Si,p} = 149$
			1	77		
			2	223		
Br	$4s^2 4p^5$	$^2P^o$	1/2	0	2457	$\xi_{Br,p} = 2457$
			3/2	3685		
Fe	$3d^6 4s^2$	^5D	4	0	−97.7	$\xi_{Fe,d} = 391$
			3	416		
			2	704		
			1	888		
			0	978		

Data in cm^{-1}.
[a]Experimental, from ref. 25.
[b]Fitted on the experimental J levels using the Landé interval rule.

response derivative, we have to sum q_{ia}^{SO} to q_{ia}^{el}, as shown in eq. (27), and to replace $\Delta_{ij}(A)$ and $\Gamma_{ijkl}(A)$ with the following expressions

$$\Delta_{ij}'(A) = \sum_n^{N_{mod}} \Delta_{ij}(n) \sum_{m_n} \left| D_{n,m_n}^A \right|^2 + \tilde{\Delta}_{ij} \tag{43}$$

$$\Gamma_{ijkl}'(A) = \sum_n^{N_{mod}} \Gamma_{ijkl}(n) \sum_{m_n} \left| D_{n,m_n}^A \right|^2 + \tilde{\Gamma}_{ijkl}. \tag{44}$$

Notice that in the evaluation of the static derivative of E_A the tilded terms in the above equations must be omitted.

If compared with the method outlined in "Uncontracted Strategy: Diagonalization of $\hat{\mathcal{H}}_{tot}$ in the $\mathcal{S}_{CI}$ Subspace" section, this procedure is computationally more demanding: one must determine all the eigenvectors in the $\mathcal{S}_{CI}^{m_{ref}}$ subspace, the one and two electron spinless density matrices $\Delta_{ij}(n, k)$ and $\Gamma_{ijkl}(n, k)$, and the one-electron spin density matrices $\rho_{ij}^{(q')}(n, k)$ with $k \in N_{mult}$, $n \in N_{mod}$. It would be, therefore, of very limited utility in most *ab initio* frameworks, but it is quite viable in semiempirical calculations with small CI expansions.

Application to HSiBr

Explicit SOC calculations require the determination of the SO atomic parameters $\xi_{\alpha,l}$. For an atom, the Hamiltonian in eq. (5) strictly fulfils the Landé interval rule: the energy separation between two consecutive J levels of a ^{2S+1}L atomic term is $E(^{2S+1}L_J) - E(^{2S+1}L_{J-1}) = AJ$, with the atomic SO parameter for the relevant set of orbitals given by $\xi_{\alpha,l} = 2|A| \min(L, S)$. Some examples are shown in Table 2. This procedure does not guarantee the correctness of SOC for a molecular system: note for instance that the bielectronic part of the SO interaction has to be accounted for by the semiempirical SO parameters. Nevertheless, it has the advantage to yield the

Table 3. Geometry Optimizations of the First Two Singlet and Two Triplet States of HSiBr.

State optimized	Si-H (Å)	Si-Br (Å)	∠HSiBr (°)	State energies (eV)				SO couplings (cm^{-1})				
				S_0	T_1	T_2	S_1	S_0-T_1	S_0-T_2	S_1-T_1	S_1-T_2	T_1-T_2
Exp[a]	1.518	2.237	93.4	0.13	1.47	2.39	2.57	270.9	82.5	59.4	199.2	232.7
S_0 $^1A'$	1.380	2.227	98.6	0.00	1.22	2.12	2.42	265.0	71.6	55.7	199.6	225.8
T_1 $^3A''$	1.345	2.176	128.3	0.34	0.96	1.56	2.18	227.9	37.5	37.8	222.5	280.0
T_2 $^3A'/^3\Pi$	1.347	2.054	180.0	1.33	1.23	1.23	2.40	42.6	42.6	0.0	329.6	467.1
S_1 $^1A''$	1.367	2.177	132.3	0.42	0.97	1.53	2.17	220.7	32.9	36.1	229.4	295.0

Presented are geometrical parameters, state energies (referred to the S_0 minimum) and SO couplings (absolute value).
[a] S_0 Experimental geometry.[27]

proper couplings at dissociation. If necessary, a compromise solution can be adopted, i.e., a set of parameters that fit as accurately as possible the spin-orbit coupling at the molecular geometries of interest, possibly including some dissociated atoms. An alternative is to resort to internal coordinate dependent $\xi_{\alpha,l}$ parameters (in this last case, the static derivative of E^{SO} has also to be taken into account, see "Derivatives of the SO Corrected Energy" section). Note finally that a compromise solution has anyway to be adopted if, for a given atom, more than one atomic multiplet is considered.

As a test case, we chose HSiBr, a molecule with rather large spin-orbit couplings, that have been accurately determined by Christiansen et al.[26] They performed *ab initio* CCSD response theory calculations at the experimental[27] equilibrium geometry, and found the absolute value of the $S_0(^1A')$-$T_1(^3A'')$ and $S_1(^1A'')$-$T_1(^3A'')$ couplings to be 270.9 and 59.4 cm^{-1}, respectively. We performed CAS-CI calculations using a PM5 semiempirical hamiltonian and an active space of 6 electrons in 5 MOs. The MOs were obtained from a floating occupation number SCF with a gaussian width $w = 0.1$ hartree. The active space comprises three a' and two a'' MOs. The semiempirical parameters were determined by fitting the two SOC evaluated by Christiansen et al. with a quadratic error function (see Table 3). As we have two semiempirical parameters, the fit gave exact results and we obtained: $\xi_{Si,p} = 650.6$ and $\xi_{Br,p} = 796.2$ cm^{-1}. Note that these values of the parameters are quite different from those obtained from the atomic terms (see Table 2), which yield values of 190.0 and 135.6 cm^{-1} for the S_0-T_1 and S_1-T_1 SOC, respectively. However, this is irrelevant if one is not interested in the HSiBr fragmentation. According to the values of the SO semiempirical parameters considered, both Si and Br give an important contribution to the SOC, with the largest one coming from Br, as expected on the basis of the atomic number. We considered a model space of 4 multiplets: S_0, S_1, T_1, and T_2. Geometry optimizations for the uncoupled states are shown in Table 3. The state energies are in qualitative agreement with the *ab initio* results of Christiansen et al., who find 1.63 and 2.76 eV for the vertical S_0-T_1 and S_0-S_1 transitions, respectively. An accurate description of the electronic structure and equilibrium geometries of HSiBr being beyond the scope of this test, we did not proceed to a reparameterization of the semiempirical hamiltonian as in other cases.[24] At the nuclear geometries shown in Table 3, S_1 and T_1 are mainly described as a HOMO → LUMO excitation: their SOC is then small,[28] about one order of magnitude smaller than the S_0-T_1 coupling. The same considerations also apply, to a lesser extent, to the S_0-T_2 coupling: the

T_2 state is mainly described as a HOMO → LUMO + 1 excitation which, for symmetry reasons, also contributes to S_0.

In Table 4 we show the results of geometry optimizations on the 8 SO mixed states belonging to the model space. The $\hat{S}^2$ eigenstates that contribute to a SO mixed state may have spatial factors belonging to different irreducible representations of the symmetry point group, and the same holds for their spin factors, therefore one must take into account both to assign the global symmetry of a state. For an even number of electrons, the standard point group of the molecular system is appropriate for the spin part too. In particular, in the present case[29] (i.e., for the C_s symmetry group) assuming the z axis as perpendicular to the reflection plane, a spin function with $\hat{S}_z$ eigenvalue m even belongs to the A' irreducible representation, while a spin function with m odd is A''. As one can see by comparing Tables 3 and 4, the modifications of the equilibrium geometries induced by the SO interaction are almost undetectable, with the exception of the T_2 state. In fact, for the SO mixed states 3-A'' and 4-A', a sizeable departure from linearity is evident in Table 4 and Figure 1, showing a considerable interplay between the SO coupling and the Renner-Teller effect. In Figure 1 we show the potential energy curves of the first 7 SO mixed states, obtained by varying the H-Si-Br angle in the range $155°$ − $180°$ and keeping the Si-H and Si-Br bond lengths fixed to 1.347 and 2.053 Å, respectively. As the H-Si-Br angle is opened, the energy of the ground state singlet increases and crosses the two low lying triplet states, giving rise to a quite complicated pattern when the SOC is considered.

Table 4. Geometry Optimizations for HSiBr with SO Mixed States.

State	Energy	$\langle \hat{S}^2 \rangle$	Si-H	Si-Br	∠HSiBr
1-A'	−0.001	0.001	1.380	2.227	98.4
1-A''	0.957	2.000	1.345	2.176	128.4
2-A'	0.957	2.000	1.345	2.176	128.4
3-A'	0.959	1.996	1.345	2.176	128.2
2-A''/1-Π	1.233	2.000	1.347	2.054	180.0
3-A''	1.262	2.000	1.346	2.053	163.9
4-A'	1.262	2.000	1.346	2.053	163.9
4-A''	2.175	0.004	1.367	2.177	132.3

Energies (referred to the minimum of the unmixed S_0 state) in eV, distances in Å, angles in degree, $\hat{S}^2$ expectation values in a.u. The symmetry labels account for both the spin and the spatial parts.
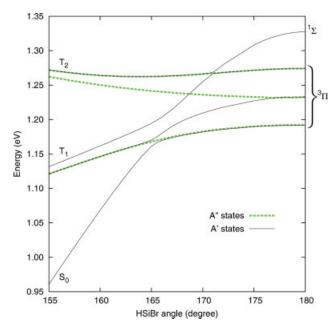
Figure 1. Potential energy curves for SO mixed states of HSiBr near to linearity. Where possible, the (approximate) spin symmetry of the states considered is shown.

The determination of the gradient of the energy for SO mixed states is computationally demanding, especially with the contracted procedure, in comparison with the same calculation for unmixed states. Tests with CI subspaces of increasing size N_{mult} (between 100 and 10,000 Slater determinants, for the same molecular system considered here) show that the CI part of the evaluation of the energy gradient (i.e., the determination of $\mathbf{q}^{el}$ and $\mathbf{q}^{SO}$) is about 10 times slower in the presence of spin-orbit coupling. That step may become the bottleneck of the calculation for CI sizes well above 100 Slater determinants. However, as in semiempiric calculations smaller CI expansions are usually employed, the present method appears to be of concrete practical utility.

Conclusions

As a first step toward the set up of a scheme to perform direct nonadiabatic molecular dynamics simulations, we presented a method to evaluate molecular gradients for a CI wavefunction, taking into account the spin-orbit coupling. A key feature of the present method is that only a limited number of $\hat{S}^2$ CI eigenstates are allowed to mix. This choice is especially suited for use with semiempirical methods: while an *ab initio* calculation taking account the whole SOC matrix should lead to more accurate results, this is not true in the semiempirical framework, because the parameterization of SOC is usually valid only for a small subspace of electronic states. In nonadiabatic

molecular dynamics calculations this way to define the electronic subspace allows to avoid intruder state problems and to use a local diabatization procedure[30] for the evaluation of the dynamic couplings. The price to pay is a CPHF-like procedure for the evaluation of the derivatives of the SO unmixed CI coefficients of the model states, which is however viable in a semiempirical framework.

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