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Elimination of singularities in molecular orbital derivatives: minimum orbital-deformation (MOD) method

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Abstract

We present the minimum orbital-deformation (MOD) method which effectively solves the problem intrinsic to the local approach for calculating the electron correlations. It eliminates the discontinuities in potential energy surfaces (PES) and properties, and hence the singularities of their derivatives which can occur when the localized MOs are used. The present method defines smooth invariant transformation of SCF MOs along the geometrical change, which is similar to the quasidiabatization. We demonstrate the performance of the MOD method for the ground state PES of benzene, for which artificial errors were reported in the analytical energy gradients of the local MP2. © 2002 Published by Elsevier Science B.V.

1. Introduction

The computational costs of conventional electron correlation theories scale as the nth power of system size, n being 6 for CCSD method, for example. One of the strategies to asymptotic linear scaling calculation is to take advantage of the locality of electron correlations. Because the fluctuation potential has short-range nature as shown by Sinanoğlu [1], weak correlations between spatially distant electrons can be safely neglected or treated approximately. Several groups have proposed wavefunctions truncated in the localized MO (LMO) representation [2–12]. This local approach to electron correlations has been implemented at various levels of theory and has successfully reproduced most of the correlation energies. Locality of correlation is also useful for the perturbation selection [13] in the LMO representation.

However, this approach has suffered from a problem; singularities can appear in the derivatives with respect to external parameters, which originate from the breakdown of unitary invariance. Correlation energies obtained by these methods depend on the invariant transformation of SCF MOs; namely transformation within the occupied or unoccupied MO subspaces. This can cause a serious problem in calculating properties defined by the derivatives. Since the localizations are not guaranteed to be smooth functions of the parameters, the energy derivatives in the local methods

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can be unphysical. In fact, the development and application of the derivatives based on the local methods have been very limited, though analytical energy gradients for MP2 [14–16] and QCISD [17] were implemented. Rauhut et al. [15] reported that the artificial errors might occur in calculating the ground state of benzene. Thus, the electronic structure of benzene is one of the good examples illustrating the singularities.

In this communication, we first explain that the invariant transformation of the SCF MOs can be discontinuous when it is defined by only the localization conditions. Second we propose a simple method for eliminating this problematic singularity in the derivatives. The pilot application to the potential energy surface (PES) of benzene is presented.

2. Singularities in molecular orbital derivatives

In this communication, the following conventions are used; occupied spin-orbitals are denoted by i, j, k, l, and unoccupied spin-orbitals by a, b, c, d, and general spin-orbitals by p, q, r, s. Atomic orbitals (AOs) are denoted by Greek letters μ, ν, ρ, σ. The MOs are assumed to be real, orthonormal, and written in the linear combinations of AOs, $\psi_p = \Sigma_\mu \chi_\mu C_{\mu p}$.

We first introduce some notations to express derivatives of the MOs. The first derivatives of the MO coefficients are written in matrix form as [18]

$$\frac{\partial \mathbf{C}}{\partial \alpha} = \mathbf{C}\mathbf{U}^\alpha. \tag{1}$$

All of the $N \times N$ matrix elements (N being number of MOs) of $\mathbf{U}^\alpha$, namely the CPHF coefficients, are not independent due to the orthonormality of MOs. Requiring orthonormality up to first order, we obtain

$$\mathbf{U}^\alpha + \mathbf{U}^{\alpha^\dagger} + \mathbf{S}^\alpha = \mathbf{0}, \tag{2}$$

where

$$\mathrm{S}^\alpha_{pq} = \sum_{\mu\nu} C_{\mu p} C_{\nu q} \frac{\partial \mathrm{S}_{\mu\nu}}{\partial \alpha}, \tag{3}$$

$$S_{\mu\nu} = \langle \chi_\mu \mid \chi_\nu \rangle. \tag{4}$$

Using the anti-symmetric matrix defined by

$$\mathbf{T}^\alpha = \mathbf{U}^\alpha - \mathbf{U}^{\alpha^\dagger}, \tag{5}$$

and $\mathbf{S}^\alpha$, we can express $\mathbf{U}^\alpha$ as

$$\mathbf{U}^\alpha = -\tfrac{1}{2}\mathbf{S}^\alpha + \tfrac{1}{2}\mathbf{T}^\alpha. \tag{6}$$

The anti-symmetric part of the CPHF coefficients $\mathbf{T}^\alpha$ is attributed to α-dependence of unitary transformation of MOs.

Next, we explain the singularities in the derivatives of the canonical MOs (CMOs) [19]. Conditions for occupied CMOs are

$$\left[\mathbf{C}^\dagger \mathbf{F} \mathbf{C}\right]_{ij} = 0 \quad \text{for } i \neq j, \tag{7}$$

where the Fock matrix is denoted by $\mathbf{F}$ in AO representation. Equating derivatives of the left-hand side with zeroes and applying Eqs. (1) and (5), we obtain

$$T^\alpha_{ij} = -\frac{1}{\varepsilon_i - \varepsilon_j}\left\{2\left[\mathbf{C}^\dagger \frac{\partial \mathbf{F}}{\partial \alpha}\mathbf{C}\right]_{ij} - S^\alpha_{ij}(\varepsilon_i + \varepsilon_j)\right\}, \tag{8}$$

where ε_i is the orbital energy. Apparently, the singularity occurs in Eq. (8) at $\varepsilon_i = \varepsilon_j$. Among the degenerate orbitals we cannot define a particular set of MOs without any additional condition. Eq. (8) implies that the derivatives of the degenerate orbitals cannot be defined because the perturbed orbitals do not converge to a unique set of functions in the unperturbed limit. This is not problematic for conventional methods because of the unitary invariance, but can cause serious discontinuities in PES if the wavefunction is truncated by the perturbation selection.

The LMO has advantage in the sense that the singularity in Eq. (8) may be circumvented. Boughton and Pulay compared the Boys [20] and Pipek-Mezey [21] localizations and suggested that the latter method has some advantages for calculating electron correlations [22]. These two localizations can be written in common form

$$\sum_A \sum_i \left|G^A_{ii}\right|^2 = \max, \tag{9}$$

where G^A_{ii} denote diagonal elements of the matrices

$$\{\mathbf{G}^1, \mathbf{G}^2, \mathbf{G}^3\} = \{\langle x \rangle, \langle y \rangle, \langle z \rangle\}$$

and

$$\{\mathbf{G}^1, \mathbf{G}^2, \ldots, \mathbf{G}^{N_A}\} = \{\langle\hat{\rho}_1\rangle, \langle\hat{\rho}_2\rangle, \ldots, \langle\hat{\rho}_{N_A}\rangle\}$$

for the Boys and Pipek-Mezey localizations, respectively. In the latter case, N_A is the number of atoms and

$$\hat{\rho}_A = \frac{1}{2}\sum_{\mu\in A}\sum_{\nu}\{|\chi_\mu\rangle(\mathbf{S}^{-1})_{\mu\nu}\langle\chi_\nu| + |\chi_\nu\rangle(\mathbf{S}^{-1})_{\nu\mu}\langle\chi_\mu|\}. \tag{10}$$

Unfortunately, these localization conditions do not necessarily define uniquely a suitable orbital set as in the case of CMOs. We show this with illustrative example. Three π LMOs of benzene in D_{6h} and D_{3h} are sketched in Fig. 1. Let us imagine two directions of distorting the D_{6h} equilibrium structure to D_{3h} skeletons:

(a) shorten r, three C–C bonds appearing alternately, leaving r_0, the other C—C distances, unchanged,

(b) lengthen r leaving r_0 unchanged.

Since the localization of three π orbitals occurs in the shorter three bonds, the different patterns of localization are obtained for the cases (a) and (b). In D_{6h} unperturbed limit, they do not converge to the same unique set as shown by the arrows. This is due to the existence of 'degenerate' three π LMOs; different linear combinations of them can give equal value for the function defined by Eq. (9) in D_{6h}. The π LMOs of benzene change their shapes discontinuously with respect to r and thus, the PES becomes discontinuous and the derivatives have the singularities at D_{6h}. It should be noted that this kind of 'degeneracy' can also occur accidentally even in non-degenerate symmetry.

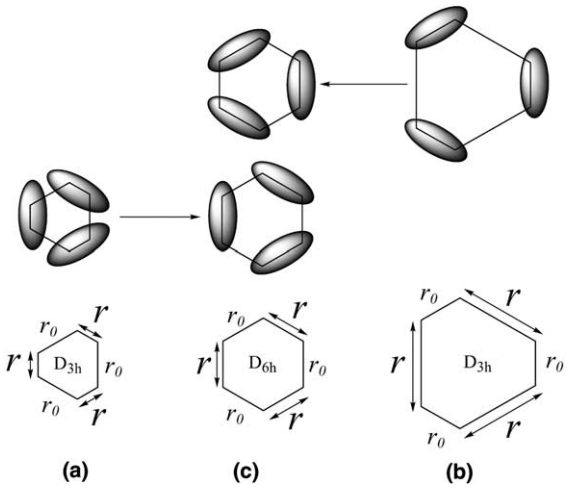

Fig. 1. Three π LMOs of benzene in D_{3h} and D_{6h} are shown for regions: (a) $r < r_0$; (b) $r > r_0$; and (c) the D_{6h} equilibrium structure, $r = r_0$. As the three π LMOs are localized into the shorter three bonds, different patterns of the localization are obtained for regions (a) and (b). In D_{6h} limit (c), they do not converge to unique set of the MOs.

Linear equation to determine T_{ij}^{α} for the Pipek-Mezey localization was proposed by El Azhary et al. [14]. Recently we implemented these linear equations to analytical energy gradients [23,24] of the SAC/SAC-CI method [25–28] in which the perturbation selection is available in LMO representation [29], and we found that the solution of the linear equation does not exist in particular systems. Rauhut et al. [15] had also suggested that some additional conditions should be introduced to the Pipek-Mezey localizations to overcome the degeneracy problem [15], but it has not yet been solved to the best of our knowledge.

3. Minimum orbital-deformation (MOD) method

We now consider how we can define the derivatives of the invariant transformations of SCF MOs without singularity. Let us examine three π LMOs of benzene again. The localization criterion naturally cannot select either of the two sets of π LMOs at D_{6h} as 'more localized'. But, the singularity-free method must choose one set of LMOs to connect the perturbed orbitals in D_{3h} smoothly to their unperturbed limit in D_{6h}. Defining the perturbed MOs as those most similar to the unperturbed MOs is one possibility to satisfy this requirement. For the infinitesimal perturbations, the minimum change in orbital shape may be expressed by $\mathbf{T}^{\alpha} = \mathbf{0}$, because $\mathbf{T}^{\alpha}$, anti-symmetric component of $\mathbf{U}^{\alpha}$, represents the infinitesimal unitary transformation induced by the perturbation. For example, assuming the perturbation to affect only unitary transformation$\mathbf{W} = \mathbf{W}^{\dagger^{-1}}$, namely $\partial\mathbf{S}/\partial\alpha = \mathbf{0}$, we can replace Eq. (1) with

$$\frac{\partial \mathbf{C}}{\partial \alpha} = \mathbf{C}_0 \frac{\partial \mathbf{W}}{\partial \alpha} = \tfrac{1}{2}\mathbf{C}\mathbf{T}^{\alpha} = -\tfrac{1}{2}\mathbf{C}\mathbf{T}^{\alpha\dagger}. \tag{11}$$

The matrix $\mathbf{T}^{\alpha}$ is anti-symmetric as

$$\mathbf{T}^{\alpha} = 2\mathbf{W}^{\dagger}\frac{\partial \mathbf{W}}{\partial \alpha} = -2\frac{\partial \mathbf{W}^{\dagger}}{\partial \alpha}\mathbf{W}. \tag{12}$$

Since most perturbations affect also the AO part, the general expression of $\mathbf{U}^{\alpha}$ has not only anti-symmetric $\mathbf{T}^{\alpha}$ part, but also symmetric $\mathbf{S}^{\alpha}$ part.

Though it is hard to calculate the MOs satisfying the condition $\mathbf{T}^{\alpha} = \mathbf{0}$ for arbitrary geometry, we can introduce a simple but good-approximate method. Using a given set of unperturbed orbitals, we define

$$\mathbf{M} = \mathbf{C}_0^{-1}\mathbf{C}, \tag{13}$$

which represents the transformation of MOs in the perturbed region. Subscript 0 denotes unperturbed matrix. Truncating the Taylor expansion of $\mathbf{M}$ up to the first order of perturbation α, we obtain

$$\mathbf{M} \simeq \mathbf{1} + \left.\frac{\partial \mathbf{M}}{\partial \alpha}\right|_{\alpha=0} \alpha = \mathbf{1} + (-\tfrac{1}{2}\mathbf{S}^{\alpha} + \tfrac{1}{2}\mathbf{T}^{\alpha})\alpha, \tag{14}$$

We require that $\mathbf{M}$ is symmetric with respect to *ij* and *ab* index pairs as

$$\begin{aligned} &M_{ij} - M_{ji} = 0 \quad \text{for all } i, j \quad \text{and} \\ &M_{ab} - M_{ba} = 0 \quad \text{for all } a, b, \end{aligned} \tag{15}$$

so that $T^{\alpha}_{ij} = 0$ and $T^{\alpha}_{ab} = 0$ are approximately satisfied for all *i*, *j* and for all *a*, *b*, respectively, for small α. The condition $\mathbf{T}^{\alpha} = \mathbf{0}$ is obtained by inserting Eq. (14) into Eq. (15), which is correct in the limit $\alpha \to 0$. The approximation of Eq. (14) is justified for geometry optimization since the calculations are performed only in the neighborhood of the initial geometry.

Using a given set of initial orbitals $\tilde{\mathbf{C}}$, we can calculate the MOs satisfying the conditions of Eq. (15) as

$$\mathbf{C} = \tilde{\mathbf{C}}\left(\tilde{\mathbf{M}}^{\dagger}\tilde{\mathbf{M}}\right)^{-1/2}\tilde{\mathbf{M}}^{\dagger}, \tag{16}$$

where $\tilde{\mathbf{M}}$ denotes *ij* or *ab* block of the matrix obtained by substituting $\tilde{\mathbf{C}}$ for $\mathbf{C}$ in Eq. (13). Note that the occupied and unoccupied MOs are transformed separately.

We call the present scheme approximately satisfying $\mathbf{T}^{\alpha} = \mathbf{0}$ as *minimum orbital-deformation* (MOD) method because it is characterized as keeping the orbital shape against the perturbation. The MOD method is conceptually similar to the quasidiabatization employed in the studies of diabatic electronic states [30,31].

4. Test calculation

The PES of the ground state of benzene with respect to aforementioned coordinate *r* was calculated to examine the performance of the MOD method. The perturbation selection [13,29,32] was performed for the double excitation operators of CISD in the LMO representation. We used 10^{-6} hartree as the energy threshold and the Hartree–Fock determinant as the zeroth order wavefunction. The minimum basis set of STO-3G was adopted to see clearly the problematic singularity, though the MOD method is applicable and effective for arbitrary basis set. The D_{6h} equilibrium geometry was optimized by the full (conventional) CISD. We fixed r_0, the length of three C—C bonds appearing alternately, to be the optimized value of 1.4068 Å and also the C—H lengths to be the optimized one, 1.0981 Å. The PES was calculated as the function of *r*, the other three C—C bond lengths, from 1.3868 to 1.4268 Å ($-0.02 < \Delta r = r - r_0 < 0.02$ Å). The perturbation selection was performed at $\Delta r = -0.02$ Å (D_{3h}) and the set of selected operators was used throughout the PES.

In Fig. 2, the PES by the CISD with the perturbation selection in which the Pipek-Mezey localization is performed at each geometry is compared with full CISD. Fig. 3 gives the PES by the CISD with the MOD method. In the MOD method, the Pipek-Mezey LMOs at $\Delta r = -0.02$ Å were used as the reference orbitals $\mathbf{C}_0$. The PES in which only the Pipek-Mezey localization is used has distinct discontinuity at $\Delta r = 0$ stemming from the degeneracy of the π LMOs illustrated in Fig. 1. It can be understood as the physically meaningless loss of the correlation energies due to the drastic change of the orbital shapes. Selected excitation operators are not sufficient after the drastic change

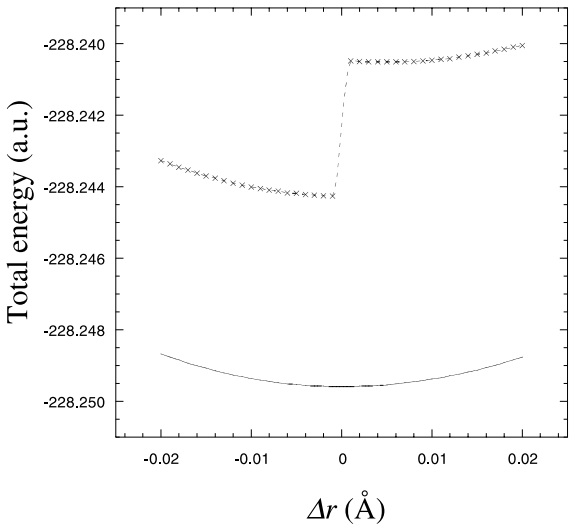

Fig. 2. If the Pipek-Mezey localization is performed at each geometry, the ground state PES of benzene calculated by the CISD with the perturbation selection is discontinuous at D_{6h} (crosses) while full CISD gives continuous PES (solid line). The $\Delta r = r - r_0$ is defined in Fig. 1.

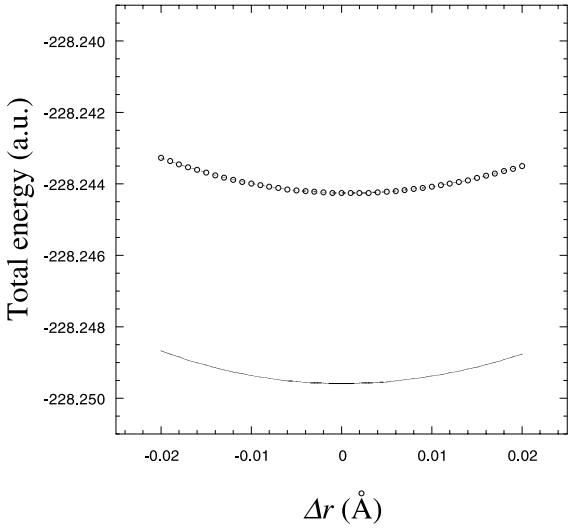

Fig. 3. If the MOD method is used, the ground state PES of benzene calculated by the CISD with the perturbation selection is continuous (circles) as that of full CISD (solid line).

of orbital shapes because they are selected using a reference set of the MOs at particular geometry.

As the energies must be smooth functions of external parameters, it is essential to eliminate the effects of the physically meaningless change of orbital shapes on the energy functions. The MOD method can do this as shown in Fig. 3. The PES calculated using the MOD method behaves correctly over the entire region of the calculation. It is also noted that the energy difference from the full CISD shown together is almost constant throughout the PES.

Thus, the MOD method eliminates the discontinuities in the PES and the related properties and hence the singularities of their derivatives, which can occur when the LMOs are used together with the perturbation selection method. This is very useful in the automatic optimization procedure currently used in the SAC/SAC-CI program.

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