

Second-order Møller–Plesset perturbation theory without basis set superposition error. II. Open-shell systems

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The basis set superposition error-free second-order Møller–Plesset perturbation theory of intermolecular interactions, based on the “chemical Hamiltonian approach,” which has been introduced in Part I, is applied here to open-shell systems by using a new, effective computer realization. The results of the numerical examples considered ($\text{CH}_4 \dots \text{HO}$, $\text{NO} \dots \text{HF}$) showed again the perfect performance of the method. Striking agreement has again been found with the results of the *a posteriori* counterpoise correction (CP) scheme in the case of large, well-balanced basis sets, which is also in agreement with a most recent formal theoretical analysis. The difficulties of the CP correction in open-shell systems are also discussed. © 2004 American Institute of Physics.
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I. INTRODUCTION

In Ref. 1 (henceforth Part I) we used the so-called “chemical Hamiltonian approach” (CHA) in order to develop a special second-order Møller–Plesset perturbation theory for treating intermolecular interactions, which is free of the basis set superposition error (BSSE). As is known, BSSE appears when one considers the interaction between two or more molecules (“monomers”) by using finite monomer-centered basis sets, if the latter are not large enough to provide a (nearly) exact description of the *internal* electronic structure of the individual monomers. As the monomer basis is incomplete, the function which one obtains by applying the intramonomer Hamiltonian on the monomer’s wave function also contains components which cannot be expanded by using the monomer basis set. As a consequence, nonzero overlaps and matrix elements of the *intramonomer* Hamiltonian appear between the monomer wave function and some wave functions containing basis functions of the other monomer(s) and lying in the orthogonal complement to the original monomer basis. This leads to some lowering of the *intramonomer* energy, i.e., causes BSSE. Such an energy lowering takes place both in the “ghost-orbitals” calculations of the individual monomers and in the standard calculations performed for the “supermolecule.” The classical “counterpoise correction” (CP) method of Boys and Bernardi² uses the uncorrected total energy of the supermolecule and utilizes the energy lowerings obtained in the ghost orbital calculations to get BSSE-corrected interaction energies.

As opposed to this, the CHA method omits all the terms in the orthogonal complements to the monomer basis sets and obtains in this manner BSSE-free supermolecule wave functions which keep consistency with the results of the monomer calculations performed in the original free mono-

mer basis sets. In other words, instead of correcting the BSSE *a posteriori* by adjusting the monomer energies to the supermolecule problem, in CHA one calculates the wave functions by identifying and omitting those terms of the Hamiltonian which are responsible for BSSE (for a survey see Ref. 3).

The CHA version of the second-order Møller–Plesset (CHA-MP2) method described in Part I had been tested on a number of closed-shell van der Waals complexes and hydrogen bonded systems and exhibited a remarkable agreement with the results of the standard CP scheme: as the basis set improves, the difference between the CHA-MP2 and CP corrected conventional MP2 results diminishes much faster than BSSE disappears from the uncorrected results. (This type of behavior has been observed at other levels of the theory, including pivoting full configuration interaction calculations⁴ as well.)

Comparing these methods from a practical point of view, one may note that CHA is a rather complex theory, while the CP scheme requires several calculations to be performed in order to get a single corrected interaction energy value. For two interacting subsystems the computational costs of the two schemes are roughly comparable, while for clusters consisting of more than two subsystems the number of independent calculations rapidly increases in the CP framework,⁵ while the CHA scheme can be realized in the manner that the computational work is essentially independent of whether the system is considered as consisting of two interacting subsystems or is divided into an arbitrary number of ones.

The calculations described in Part I were performed by a program which had been used for testing the new and new variants of the theory in the more than half decade long quest for the appropriate CHA generalization of the Møller–Plesset perturbation theory. Accordingly, it is neither simple nor effective computationally. In addition, this program can be used for closed-shell systems only. For that reason one of us (P.S.) wrote a new, versatile CHA program which is applicable for open-shell systems, too (CHA-UHF and CHA-

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UMP2 theories) and for any number of interacting fragments. This program uses only two routines of the original one—those which perform the manipulations necessary to use real arithmetics in the CHA-MP2 calculations even if there are some complex CHA-SCF orbitals. The repeated testing of these routines revealed minor inconsistencies with the formulas published in the Appendix of Part I. Fortunately, it was the program containing the correct version and the differences were due to some typing errors in the paper. (The corrected formulas are given here in the Appendix, along with a further equation also corrected for some misprints.)

In Sec. II we shall give a very concise sketch of the most important aspects of the CHA-MP2 theory and discuss very briefly some peculiarities of the new computer realization. Then we are going to discuss the results of the application of the CHA-UMP2 theory to two open-shell systems, CH₄...HO and NO...HF and shall call attention to the fact that in the open-shell case one has to proceed with special care when doing CP corrections. The ghost-orbital calculations for degenerate open-shell fragments should match with that electronic state of the complex, which is actually corrected for BSSE. As the the symmetry of monomer's wave function is lost in the ghost-orbital calculation, this selection is sometimes not trivial. This is especially the case when the complex has two (or more) electronic states of the same symmetry. We have again observed a strikingly good agreement between the results of CHA calculation and those of the usual CP ones; this will be discussed in light of a recent formal theoretical analysis which permitted one to understand how the CHA method can justify the tacit additivity assumption inherent in the CP scheme.

II. METHOD OF CALCULATIONS

To carry out the CHA procedure discussed in Sec. I, one should eventually calculate the wave functions by replacing some one- and two-electron integrals^{3,10} by their “CHA counterparts:”

$$\begin{aligned} \langle \chi_\mu | \hat{h} | \chi_\nu \rangle &= \langle \chi_\mu | \hat{h}_A + \sum_{\substack{B \\ (B \neq A)}} \hat{U}_B | \chi_\nu \rangle \Rightarrow \{ \chi_\mu | \hat{h} | \chi_\nu \} \quad \underline{\nu \in A} \\ &= \langle \chi_\mu | \hat{P}_A \hat{h}_A \chi_\nu \rangle + \langle \chi_\mu | \sum_{\substack{B \\ (B \neq A)}} \hat{U}_B | \chi_\nu \rangle, \end{aligned} \quad (1)$$

$$\begin{aligned} \langle \chi_\rho(1) \chi_\tau(2) | \frac{1}{r_{12}} | \chi_\mu(1) \chi_\nu(2) \rangle &\Rightarrow \{ \rho \tau | \mu \nu \} \quad \underline{\mu, \nu \in A} \\ &= \langle \chi_\rho(1) \chi_\tau(2) | \hat{P}_A(1) \hat{P}_A(2) \frac{1}{r_{12}} \chi_\mu(1) \chi_\nu(2) \rangle, \end{aligned}$$

where $\hat{h}_A = -\frac{1}{2}\Delta + U_A$ is the intramonomer part of the one-electron Hamiltonian, corresponding to the monomer A and \hat{P}_A is the projector

$$\hat{P}_A = \sum_{\kappa, \lambda \in A} | \chi_\kappa \rangle \langle \mathbf{S}_{(A)}^{-1} |_{\kappa\lambda} \langle \chi_\lambda | \quad (2)$$

on the subspace spanned by the basis orbitals of monomer A . In Eq. (2) $\mathbf{S}_{(A)}^{-1}$ is the inverse of the intramonomer overlap matrix.

The CHA integrals are not symmetric with respect to their “bra” and “ket” parts, and if one uses them to set up a Hamiltonian written down in second quantized framework^{3,10} then one gets a non-Hermitian CHA Hamiltonian. From a formal mathematical point of view, this non-Hermiticity is the reason why the energy corresponding to the CHA wave function obtained by its use should be calculated as a conventional expectation value of the full (original) Hermitian Hamiltonian^{3,11}—this is called the “CHA with conventional energy” (CHA/CE) scheme.

We should note that one does not actually compute the CHA integrals over the atomic orbitals (AOs), except the one-electron ones; at the self-consistent field (SCF) level the projectors are adsorbed into a somewhat complex Fock-matrix formula,¹² while for correlated calculations one needs the CHA integrals over the molecular orbitals. The latter can be calculated efficiently by a method based on the scheme described in Ref. 4; the necessary numerical effort exceeds only slightly that of a standard integral transformation.

In the CHA-MP2 theory developed in Part I, the zero-order Hamiltonian is built up on the BSSE-free (but not orthogonal and not necessarily real) *canonic* CHA-SCF orbitals and their orbital energies. Then, as usual, the zero-order energy is the sum of the orbital energies of the occupied CHA orbitals while the sum of the zero- and first-order energies is the expectation value of the total Hamiltonian over the single determinant CHA-SCF wave function $|\Psi_0\rangle$ (the CHA/CE SCF energy). Owing to the non-Hermiticity of the CHA Hamiltonian, biorthogonal perturbation theory is used to obtain the first-order wave function $|\Psi_1\rangle$:

$$|\Psi_1\rangle = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{virt}} \frac{-\{\tilde{a}\tilde{b}||ij\}'}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} |\Psi_{ij}^{ab}\rangle. \quad (3)$$

Here the sums are over the occupied and virtual *spin-orbitals*, and the primes indicate that the integrations include summations over the spins. $|\Psi_{ij}^{ab}\rangle$ denotes the determinant obtained from the unexcited CHA-SCF determinant wave function $|\Psi_0\rangle$ by replacing the occupied spin-orbitals φ_i and φ_j by the virtual spin-orbitals φ_a and φ_b , respectively, and we have introduced a simplified notation for the CHA two-electron integrals over the spin-orbitals with exchange parts:

$$\{\tilde{a}\tilde{b}||ij\}' = \{\tilde{\varphi}_a \tilde{\varphi}_b | \varphi_i \varphi_j\}' - \{\tilde{\varphi}_a \tilde{\varphi}_b | \varphi_j \varphi_i\}'. \quad (4)$$

All integrals are written by using the “1212” convention. In Eq. (4) $\tilde{\varphi}_a$ and $\tilde{\varphi}_b$ are the biorthogonal counterparts of the spin-orbitals φ_a and φ_b , respectively. (They represent the *left* eigenvectors of the non-Hermitian CHA Fockian.)

To get the second-order energy corresponding to the first-order wave function (3) in the CHA/CE framework, one has to expand the expectation value of the energy by keeping the terms up to second order, and taking into account the non-Hermitian character of the unperturbed Hamiltonian; this is accomplished by the generalized Hylleraas-functional¹³ which guarantees the second-order energy to be real even in the case of complex CHA-SCF orbitals:

$$J_2 = \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} [\langle \Psi_1 | \hat{V} - E_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}^\dagger - E_1^* | \Psi_1 \rangle + \text{Re}(\langle \Psi_1 | \hat{H}^0 - E_0 | \Psi_1 \rangle)]. \quad (5)$$

Here \hat{H}^0 , E_0 , and E_1 , respectively, are the Møller–Plesset-type zero-order Hamiltonian, zero- and first-order energies mentioned above, while \hat{V} is the difference between the total Born–Oppenheimer Hamiltonian \hat{H} and the zero order \hat{H}^0 .

The explicit evaluation of the matrix elements entering the generalized Hylleraas functional was possible by transforming all wave functions, creation and annihilation operators to an auxiliary orthonormalized spin-orbital basis related to the canonic molecular orbitals by a nonsingular linear transformation of some special type. We refer the reader to Part I for the details; the final expression of J_2 is reproduced here in the Appendix with the aim of correcting some misprints. (As the derivation in Part I was given in terms of spin-orbitals, the working equations remain valid in the open-shell case, too.)

The new, effective implementation of the CHA-SCF and CHA-MP2 methods is based on the observation that one can combine the adjoints of the rectangular matrices corresponding to the projectors (2) for individual subunits into a single square matrix

$$\mathbf{A} = (\mathbf{A}^1, \mathbf{A}^2, \dots, \mathbf{A}^N) \quad (6)$$

permitting one to perform all the projections simultaneously. It can be shown that this matrix \mathbf{A} is nothing else than matrix \mathbf{R} first introduced in a somewhat different context.^{3,14} Then one can form the block-diagonal projected (effective) intramonomer density matrices (σ stands for spin α or β) \mathbf{B}^σ ,

$$\begin{pmatrix} \mathbf{B}^{\sigma 1} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{B}^{\sigma 2} & \mathbf{0} & \dots & \mathbf{0} \\ \dots & \dots & \dots & \dots & \dots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \mathbf{B}^{\sigma N} \end{pmatrix}, \quad (7)$$

the elements of which are expressed with those of the conventional density matrix \mathbf{P}^σ and those of matrix \mathbf{A} as

$$B_{\rho\lambda}^{\sigma A} = \sum_{\sigma} P_{\rho\sigma}^\sigma A_{\sigma\lambda}^A \quad (\rho, \lambda \in A). \quad (8)$$

When forming the CHA Fock matrix, integrals of intermonomer type¹⁵ should be treated as in the conventional unrestricted Hartree–Fock (UHF) case. The contributions arising from the integrals of intramonomer type will have the form of the matrix product $\mathbf{A}\mathbf{X}^\sigma$, where matrix \mathbf{X}^σ has the elements

$$X_{\tau\nu}^\sigma = \sum_{\lambda,\rho} B_{\rho\lambda}^\sigma [\tau\lambda|\nu\rho] + \sum_{\lambda,\rho} B_{\rho\lambda}^\beta [\tau\lambda|\nu\rho]. \quad (9)$$

As the process is driven by the intramonomer integrals, no multiplications with the zero off-diagonal B-matrix elements will take place.

After the CHA Fockian is obtained, one can use a somewhat formal trick of obtaining the CHA solutions with full machine accuracy by using an artificially Hermitized effective Fock matrix.¹⁶ This permits one to avoid the costly di-

agonalization of nonsymmetric matrices. However, after the convergence has been achieved, one has to perform a single cycle in which the true non-Hermitian Fock matrix is directly diagonalized, as the success of CHA-MP2 scheme relies on the fact that the BSSE effects appearing at the SCF level manifest in the non-Hermiticity of the CHA Fockian and on the distinction of its right and left eigenvectors.

The CHA integrals over the molecular orbitals can again be effectively computed by using the distinction between the AO integrals of the intra- and intermonomer type. While the latter contribute to a CHA two-electron integral exactly as in the conventional integral transformation, the integrals of the intramonomer type contribute to the integral over the molecular orbitals (MOs) by replacing the matrix $\tilde{\mathbf{C}}$ of the biorthogonal MO coefficients by the projected matrix $\mathbf{D} = \tilde{\mathbf{C}}\mathbf{A}$.

The use of the combined projection matrix \mathbf{A} permits the CPU requirement of the CHA procedure to be practically independent of the number of subunits in which the overall system is divided. At the same time, the CPU time required for a CP calculation—even if the simplest Turī–Dannenberg scheme⁶ is used—increases sharply with the number of subunits, as one should perform a complete integral transformation and MP2 calculation for each subsystem, by using the whole supermolecule basis. Further details of the new implementation and applications to clusters of increasing size will be described elsewhere.¹⁷

III. RESULTS AND DISCUSSION

We present UMP2-CHA results for two open-shell complexes, namely, NO...HF and CH₄...OH. For the former we discuss both radial and angular PES for two different basis sets and for two electronic states (²A' and ²A''). For the later, full numerical geometry optimization of two conformations was carried out and have been compared with the CP-optimized structures obtained with analytical gradients.

The NO...HF complex has been previously studied from both experimental¹⁸ and computational^{19,20} points of view. It has been found that the H atom can form a hydrogen bond with either O or N atoms, presenting a planar geometry (C_s) that breaks the degeneracy of the ²Π state of the NO molecule into A' and A'' states. In the A' case, we have studied the conformation depicted in Fig. 1. We have optimized the structure at the UMP2 (no frozen-core) level with the 6-31++G** basis set. A minimum has been found for a NO...H angle of 134.7° and practically linear hydrogen bond arrangement (FHO angle 179.75°), in good agreement with the previous studies. For the A'' state, the minimum is found for a collinear arrangement ($C_{\infty v}$), where the two A' and A'' states “collapse” into the ²Π state.

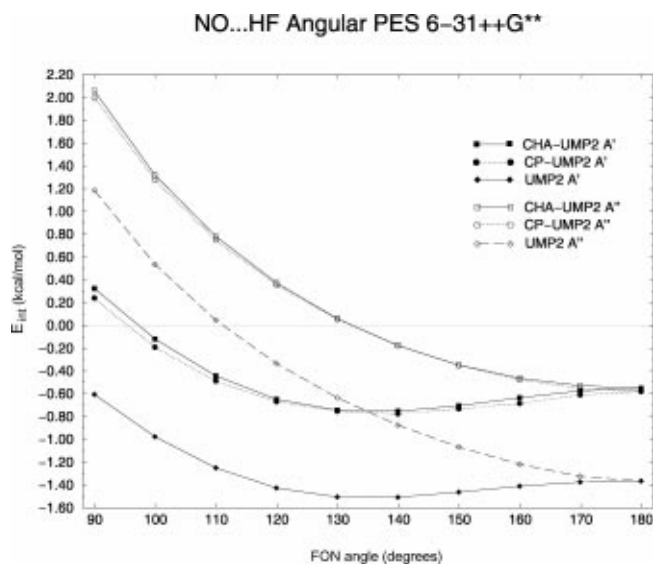
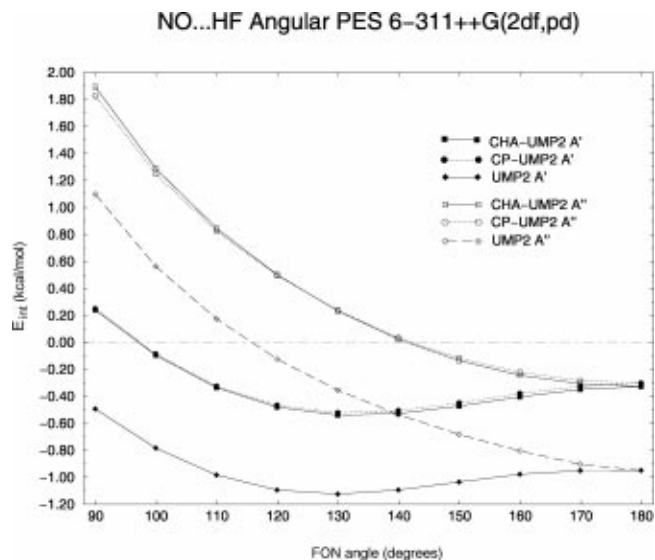
Figures 2 and 3 show the angular PESs computed with the 6-31++G** and 6-311++G(2df,pd) basis sets, respectively, obtained by using the previously optimized structure and varying only the NO...H angle from 90° to 180°. The two A' and A'' states are computed at the uncorrected, CP-corrected and CHA-UMP2 levels of theory. It can be seen that, even with the larger basis set, there is a significant BSSE (exceeding the uncorrected interaction energy), which is roughly independent of the NO...H angle. (That indepen-



FIG. 1. Geometry of the planar NO...HF complex.

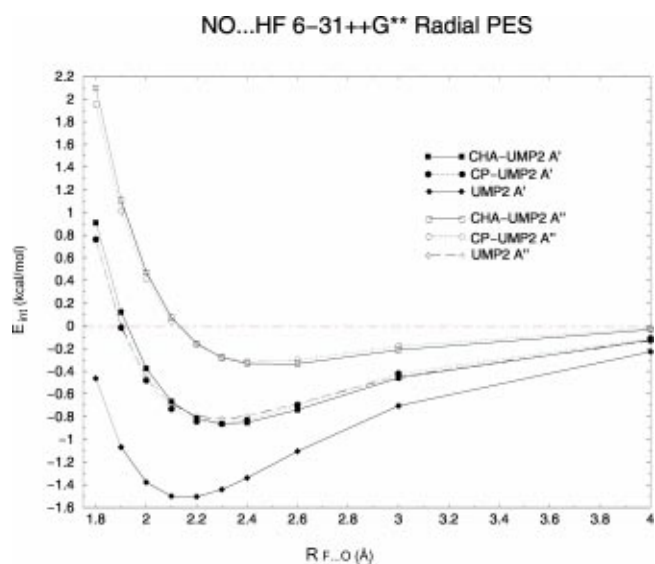
dence prevents an inversion of the relative stability of the two states as a consequence of BSSE.) At the same time, the CP and CHA methods give extremely close results, even with the modest 6-31++G** basis set.

The radial PESs presented in Figs. 4 and 5 were obtained starting from the optimized structure of the A' state and

FIG. 2. Angular dependence of the stabilization energy of the NO...HF complex at the UMP2/6-31++G** level of theory for states $2A'$ and $2A''$.FIG. 3. Angular dependence of the stabilization energy of the NO...HF complex at the UMP2/6-311++G(2df, pd) level of theory for states $2A'$ and $2A''$.

varying the O...H distance. The same conclusions can be drawn as for the angular PES. The BSSE is very important at bonding distances of 2.0–2.4 Å, but the two BSSE-corrected methods give practically indistinguishable results.²¹ The results found with the large basis set show that after BSSE correction the A'' PES essentially becomes repulsive. The modest 6-31++G** basis set cannot reproduce this effect even after removing BSSE.

In order to obtain a state-specific energy for both the uncorrected or the CHA methods, one has simply to choose the proper initial guess for the orbitals in the SCF procedure. In the case of the CP method, the situation is different because one has to choose what state of the open-shell fragment (in our case of the NO radical) is to be computed by using the whole supermolecule basis set for calculating the BSSE

FIG. 4. Radial dependence of the stabilization energy of the NO...HF complex at the UMP2/6-31++G** level of theory for states $2A'$ and $2A''$.

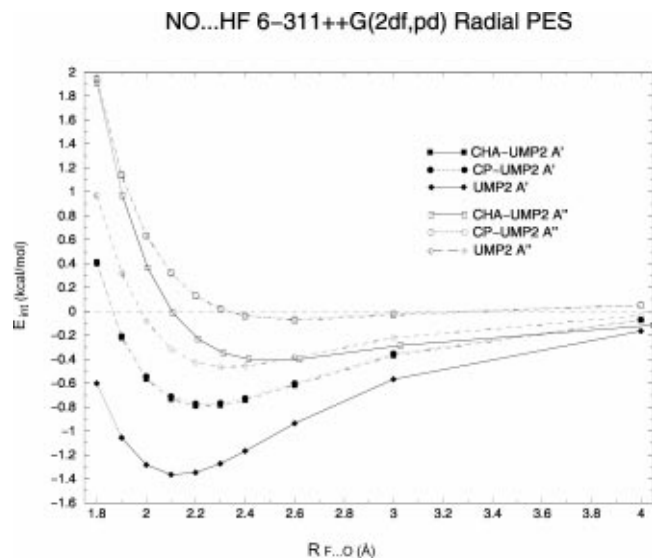


FIG. 5. Radial dependence of the stabilization energy of the NO...HF complex at the UMP2/6-311++G(2df,pd) level of theory for states $2A'$ and $2A''$.

correction to the energy of a given supermolecule electronic state. (For instance, the orientation of the unpaired electron in the space is irrelevant for a free monomer, but not in the ghost orbitals calculations.) In principle, following the CP recipe, one should try to perform a ghost-orbital calculation with the respective orbitals resembling those of the actual electronic state of the complex. Since the symmetry of the individual fragments is usually lost in the ghost-orbital calculation, this selection is sometimes not trivial. In closed-shell systems the loss of the symmetry usually does not cause problems because the ground and excited electronic states are well separated in the energetic sense. However, when one is dealing with degenerate open-shell fragments that can form several supermolecule electronic states of the same symmetry, then there can be several ghost-orbitals solutions which should be considered.

We had not experienced any problem with the selection of the ghost orbitals solutions for the NO...HF complex, since we were dealing with C_s geometries and A' and A'' states, so we could easily select the proper ghost-orbital reference calculation by using the symmetry. However, many different UHF solutions for the NO fragment exist in the ghost orbitals calculations, especially in the vicinity of the collinear configuration, as the in-plane and out-of-plane AOs can also mix. Hence, if the C_s symmetry of the complex were broken, then getting a proper reference ghost-orbital NO energy would be a difficult task. No such problem would arise in the CHA case, however.

Another application has been carried out for the $\text{CH}_4\dots\text{OH}$ complex. It has recently been studied^{22,23} as a possible entrance channel complex for the hydrogen abstraction reaction $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$.

Two configurations of C_{3v} symmetry have been considered, namely methane acting as a proton donor to form a C-H...O type hydrogen bond (Fig. 6, complex B) and the H atom of the OH interacting with the center of a tetrahedral face of the methane moiety (Fig. 6, complex A). The results

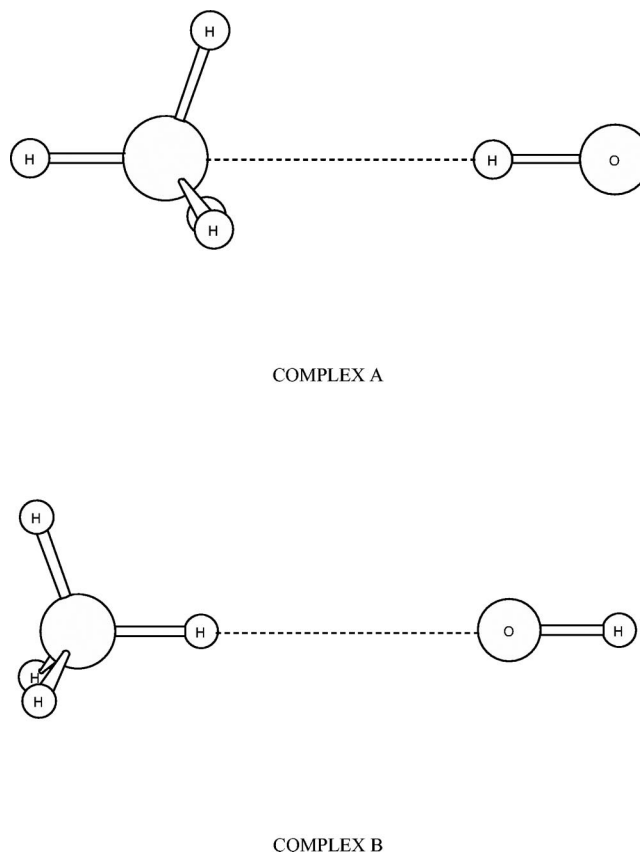


FIG. 6. Geometries of the two $\text{CH}_4\dots\text{OH}$ complexes considered.

of the geometry optimizations for several basis sets and BSSE correction methods are gathered in Tables I and II. It is found that the complex A is more stable than B and upon BSSE correction the difference is smaller. As pointed out in Ref. 23, very large basis set is necessary to properly describe the dispersion forces responsible for the formation of the complex. This seems to be particularly dramatic for the rather unconventional complex A.

TABLE I. Total energies (a.u.), interaction energies (kcal/mol) and some internuclear distances (Å) of the complex A (see Fig. 6) with several basis sets, with and without BSSE correction.

| | UMP2 | CHA-UMP2 | CP-UMP2 |
|----------------------------|----------------|----------------|----------------|
| 6-31++G** | | | |
| E_{tot} | -115.916 511 9 | -115.915 934 8 | -115.915 938 0 |
| $r(\text{C}\dots\text{O})$ | 3.649 | 3.821 | 3.805 |
| $r(\text{C}\dots\text{H})$ | 2.676 | 2.848 | 2.831 |
| ΔE_{stab} | -0.829 | -0.467 | -0.469 |
| 6-311++G** | | | |
| E_{tot} | -116.005 833 4 | -116.005 433 7 | -116.005 419 6 |
| $r(\text{C}\dots\text{O})$ | 3.644 | 3.757 | 3.762 |
| $r(\text{C}\dots\text{H})$ | 2.793 | 2.787 | 2.793 |
| ΔE_{stab} | -0.772 | -0.520 | -0.512 |
| 6-311++G(3df,pd) | | | |
| E_{tot} | -116.098 449 0 | -116.097 835 0 | -116.097 875 5 |
| $r(\text{C}\dots\text{O})$ | 3.472 | 3.576 | 3.569 |
| $r(\text{C}\dots\text{H})$ | 2.504 | 2.609 | 2.602 |
| ΔE_{stab} | -1.185 | -0.800 | -0.825 |

TABLE II. Total energies (a.u.), interaction energies (kcal/mol) and some internuclear distances (Å) of the complex B (see Fig. 6) with several basis set, with and without BSSE correction.

| | UMP2 | CHA-UMP2 | CP-UMP2 |
|----------------------------|----------------|----------------|----------------|
| 6-31++G** | | | |
| E_{tot} | -115.916 007 5 | -115.915 534 9 | -115.915 525 2 |
| $r(\text{C}\dots\text{O})$ | 3.881 | 4.046 | 4.047 |
| $r(\text{O}\dots\text{H})$ | 2.796 | 2.961 | 2.962 |
| ΔE_{stab} | -0.513 | -0.216 | -0.210 |
| 6-311++G** | | | |
| E_{tot} | -116.005 206 8 | -116.004 938 5 | -116.004 942 7 |
| $r(\text{C}\dots\text{O})$ | 3.931 | 4.061 | 4.049 |
| $r(\text{O}\dots\text{H})$ | 2.842 | 2.972 | 2.960 |
| ΔE_{stab} | -0.378 | -0.210 | -0.213 |
| 6-311++G(3df,pd) | | | |
| E_{tot} | -116.097 265 3 | -116.097 043 4 | -116.097 049 3 |
| $r(\text{C}\dots\text{O})$ | 3.798 | 3.919 | 3.906 |
| $r(\text{O}\dots\text{H})$ | 2.714 | 2.836 | 2.822 |
| ΔE_{stab} | -0.442 | -0.303 | -0.307 |

We have observed also a tiny Jahn–Teller distortion that breaks the C_{3v} symmetry of the complexes, but for the larger basis set it is so small that frequency analysis indicates both the uncorrected and CP-corrected C_{3v} geometries as minima. Therefore we present only the broken symmetry solutions obtained at the conformation of high symmetry.

The PES is so flat that the effect of the BSSE correction on the geometry of the stationary points is considerable. Even with the 6-311++G(3df,pd) basis set, the C...O distance increases in both complexes by 0.1 Å upon BSSE correction.

However, the main point of the results is that both the analytical CP-corrected and the numerical CHA-UMP2 optimizations (very tight convergence criteria) give practically coinciding results in all cases. Thus we have again observed this striking similarity between these methods of completely different philosophy, which is particularly notable bearing in mind the relative large BSSE contents, especially for complex A: the largest difference between the CP-corrected and CHA total energies is 0.025 kcal/mol for the 6-311++G(3df,pd) basis set, while BSSE is 0.385 kcal/mol.

This similarity can be qualitatively understood if one reconsiders carefully the tacit assumptions behind the CP correction scheme and clarifies the precise meaning of the BSSE-corrected (BSSE-free) interaction energy.²⁴ In the CP scheme one usually deals with the BSSE-corrected *interaction energy* which for the case of two interacting subsystems A and B is given as

$$\Delta E_{AB}^{\text{CP}} = E_{AB}(AB) - E_A(AB) - E_B(AB), \quad (10)$$

where the notation “(AB)” indicates that every energy value is computed in the same supermolecule (AB) basis set. However, at the infinite AB distance there is no interaction and no BSSE, so the total energy of the system is $E_{AB}(\infty) = E_A(A) + E_B(B)$ and this permits one to convert the CP corrected interaction energy (10) into the CP corrected *total energy* $E_{AB}^{\text{CP}} = E_{AB}(\infty) + \Delta E_{AB}^{\text{CP}} + E_A(A) + E_B(B)$. By using Eq. (10) one gets

$$\begin{aligned} E_{AB}^{\text{CP}} &= E_{AB}(AB) + [E_A(A) - E_A(AB)] + [E_B(B) - E_B(AB)] \\ &= E_{AB}(AB) - \delta E_{\text{BSSE}}. \end{aligned} \quad (11)$$

Thus the CP scheme is equivalent to the use of a total energy which is corrected by the amount $-\delta E_{\text{BSSE}}$, where

$$\delta E_{\text{BSSE}} = E_A(AB) - E_A(A) + E_B(AB) - E_B(B) \quad (12)$$

is the energy lowering obtained in the “ghost orbitals” calculations with respect to the free monomer energies calculated in the respective monomer basis sets. The equivalence of Eqs. (11) and (10) means that there is no need to assign any physical significance to the monomer wave functions calculated in the supermolecule basis, but one has simply to consider the energy lowering obtained in such a calculation as an *estimate* of the lowering of the monomer’s internal energy taking place within the supermolecule. Obviously, one may use such an estimate only by making the (tacit) assumption that BSSE is independent of the actual physical interactions of the systems. i.e., BSSE and true interactions represent additive effects. This additivity assumption needs to be justified; it does not follow directly from the fact that in the CP scheme “all quantities are computed by using the same basis set.”

In fact, there is no *full* additivity. The major BSSE effects, however, can be proven additive, by using the “CHA/CE principle.” To see this, we shall consider the following simplified analytical model²⁴ using second-order perturbation theory.

Let us assume that we consider a system described with the Hermitian Hamiltonian \hat{H} that can be written as the sum of the unperturbed Hamiltonian \hat{H}^0 , containing no interaction and no BSSE, and of the perturbation \hat{V} :

$$\hat{H} = \hat{H}^0 + \hat{V}. \quad (13)$$

Let us also assume that the unperturbed Hamiltonian \hat{H}^0 is also Hermitian, and that it has a ground state eigenfunction $|\Psi_0^0\rangle = |\Psi_0\rangle$ with the unperturbed energy E_0^0 . We shall further decompose the perturbation \hat{V} as

$$\hat{V} = \hat{W} + \hat{B}, \quad (14)$$

where \hat{W} is responsible for the true physical interactions in the system and \hat{B} is that part of the Hamiltonian which gives rise to BSSE. (Neither \hat{W} nor \hat{B} are assumed Hermitian, but their sum, \hat{V} , is Hermitian.)

The first-order energy is given by $\langle \Psi_0 | \hat{V} | \Psi_0 \rangle$ in any variants of the theory. The second-order uncorrected energy will be a sum of terms containing $|V_{0i}|^2$ where i denotes an excited unperturbed state. Owing to Eq. (14), this sum will contain terms which are quadratic in matrix elements of either \hat{W} or \hat{V} as well as “cross terms” containing products of matrix elements of \hat{W} and \hat{V} . The presence of these cross terms causes that the total second-order energy cannot be presented as a sum of pure “physical” and “BSSE-type” contributions; this was considered as an indication of a non-additivity²⁵ before the CHA/CE concept emerged.¹¹ However, in the CHA/CE frame the second-order energy

should be calculated by using the Hylleraas functional (*vide supra*). Owing to the stationary properties of the Hylleraas functional,²⁶ the difference between the uncorrected and the CHA/CE second-order energies should be *quadratic* in the difference $|\Psi_{\text{unc}}^{(1)}\rangle - |\Psi_{\text{CHA}}^{(1)}\rangle$ of the respective first-order wave functions, i.e., in the matrix elements of the operator $\hat{V} - \hat{W}$; actually this energy difference reads²⁴ in terms of the reduced resolvent²⁶ \hat{R}^0 ,

$$E_{\text{unc}}^{(2)} - E_{\text{CHA/CE}}^{(2)} = -\langle \Psi_0 | \hat{B}^\dagger \hat{R}^0 \hat{B} | \Psi_0 \rangle, \quad (15)$$

which is nothing other than the second-order energy corresponding to the BSSE operator \hat{B} alone.²⁷ This is the quantity the CP method tries to estimate by performing the “ghost orbitals” calculations.

This result indicates that the additivity assumption inherent in the CP scheme can be justified if (and only if) one accepts that the correct BSSE-free energy is to be calculated as the expectation value of the BSSE-free wave function over the total Hamiltonian, i.e., that it is the CHA/CE energy. In this case all the cross terms between operators \hat{W} and \hat{B} , contained in the uncorrected energy $E_{\text{unc}}^{(2)}$ are absorbed in the BSSE-free conventional energy $E_{\text{CHA/CE}}^{(2)}$. We may conclude, therefore, that the CHA and CP schemes corroborate each other not only numerically but also conceptually.²⁸

Owing to the presence of (nearly) degenerate monomer states, the potential surfaces of open-shell systems are expected to exhibit numerous “avoided crossings.” In this respect the question arises whether one has to perform the BSSE correction according to the adiabatic or for the diabatic state of the complex. Thus, Alexander²⁹ proposed, for the B...H₂ system, the transformation of both the ghost-orbital (of the B atom) and the complex energies to diabatic ones. He defined a diabatic→adiabatic rotation angle for the mixing of the two diabatic electronic states of the complex and transformed the ghost-orbital energies in the same way, in order to obtain the CP-corrected diabatic interaction potential. Contrary to this, Klos *et al.*³⁰ have recently performed approximate counterpoise correction to adiabatic states for the two *A'* states of the Cl...HCl van der Waals complex. They rotated the ghost-orbital orbitals of the Cl atom as to get the same orientation of the singly occupied orbital which it has in the complex, and obtained adiabatic CP-corrected interaction energies.

Equations (11) and (12) indicate that the true meaning of the CP correction is to estimate the BSSE content in the supermolecule total energy. BSSE is determined by the actual electronic state of the monomers *within* the supermolecule, that is by the diabatic state of the system. The derivation sketched above also indicates that the CP correction performed for the diabatic state is that which is expected to agree well with the CHA solution, not that for the adiabatic one. The authors of Ref. 30 are right by referring to the fact that only the adiabatic states diagonalize the total Hamiltonian, but do not properly take into account that the BSSE is due to the use of approximate wave functions. The errors in the description of the monomers within the supermolecule is governed by their actual state and are independent on the question to what states the given adiabatic PES dissociates

after (several) avoided crossings. (The above point stresses again that the argumentation justifying the CP method by referring to the use of the same basis set everywhere is not sufficient.³¹)

The complications connected with the use of diabatic states could make it rather difficult to perform a geometry optimization on the CP corrected PES of some systems. In that case not just the ghost-orbital calculations themselves but also the free monomer (“monomer centered basis set”) calculations³⁵—and possibly gradients of both^{36,37}—should be properly transformed to (approximately) match the corresponding description of the complex.

Finally, let us mention that one can also imagine other situations where the application of the CP method is not straightforward, like an even-electron dimer made up of two open-shell interacting fragments. We believe that the CHA method can be used more safely in all problematic cases. Furthermore, its *a priori* nature allows one to obtain not only energy corrections but also BSSE-corrected MO orbitals and hence the charge and spin densities and other quantities the calculation of which requires explicit use of the wave function.

IV. SUMMARY

The BSSE-free second-order Møller–Plesset perturbation theory of intermolecular interactions, based on the “chemical Hamiltonian approach,” which has been introduced in Part I is applied here to open-shell systems by using a new, effective computer realization. The results of the numerical examples considered (CH₄...HO, NO...HF) showed again the perfect performance of the method. Striking agreement has again been found with the results of the *a posteriori* counterpoise correction scheme in the case of large, well-balanced basis sets. This is also in agreement with a most recent formal theoretical analysis which is also briefly summarized, and used to discuss that the CP correction for the diabatic surfaces should be preferred to the adiabatic ones.

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APPENDIX: ERRATA TO PART I

(1) In Eq. (62) the summation indices in the first term should be corrected. The correct equation reads:

$$\begin{aligned}
 J_2 = & \operatorname{Re} \left\{ \sum_{k < l}^{\text{occ}} t(kl \| kl)' \sum_{i < j}^{\text{occ}} y(ij \| ij)' \right. \\
 & + \sum_r^{\text{virt}} \sum_k^{\text{occ}} \sum_l^{\text{occ}} t(lr \| lk)' \left[\sum_j^{\text{occ}} y(jr \| jk)' \right. \\
 & \left. \left. - 2 \langle \vartheta_r | \hat{F} | \vartheta_k \rangle' \right] - \sum_{k < l}^{\text{occ}} \sum_{p < q}^{\text{virt}} t(pq \| kl)' [2[pq \| kl]' \right. \\
 & \left. \left. - y(pq \| kl)' \right] \right\}.
 \end{aligned}$$

(2) In Eq. (A10) factors A multiply only the immediately following term, not the whole sum.

(3) In Eq. (A11) notations B and C are interchanged.

(4) In the expression of B (former C) the factor η^2 in the numerator should be replaced by η .

(5) In Eq. (A12), the term $+ \eta_b^2$ should be replaced by $- \eta_b^2$.

(Only the first and last corrections are relevant for the open-shell case.)

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²⁸Real systems differ from our simplified model, leading to some differences between the CHA/CE and CP results, especially if small basis sets are used. This problem is, however, out of our present scope.

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³¹It is only the case of binary complexes with no avoided crossings for which it is immaterial whether one uses Eq. (10) or Eq. (11). Some more complex cases in which Eq. (11) is clearly preferable have been mentioned in Ref. 3. A further advantage of the interpretation based on Eq. (11) is that it allows for a straightforward analytical definition of any CP-corrected quantity that depends on the total energy or its derivatives—Refs. 32, 33 (gradients, dipole moments, vibrational frequencies, polarizabilities, etc.) as it is realized by one of us in the recent version of the GAUSSIAN program system (Ref. 34).

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