A General Efficient Implementation of the BSSE-Free SCF and MP2 Methods Based on the Chemical Hamiltonian Approach

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Abstract: We describe some details related to a new, general, and efficient implementation of the BSSE-free SCF and second-order Møller–Plesset perturbation theories of intermolecular interactions, based on the “Chemical Hamiltonian Approach” (CHA). The program is applicable for both open-shell and closed-shell systems and for an arbitrary number of interacting subsystems. With the new program the CHA method is faster than the usual “counterpoise correction” scheme for single point calculations, especially for clusters consisting of several molecules. The numerical results provided by these conceptually different schemes, however, have again found to be very close to each other. The CHA scheme is particularly good for providing truly BSSE-free MP2 data for intermolecular potentials.


Key words: BSSE-free SCF; MP2; Chemical Hamiltonian Approach

Introduction

There has been a decade-long quest (for a survey see ref. 1) for developing methods permitting to tackle the problem of the so-called “basis set superposition error” (BSSE) of intermolecular interactions in an \textit{a priori} fashion, as opposed to the classical \textit{a posteriori} counterpoise correction (CP) scheme of Boys and Bernardi2 (see also the review by van Duijneveldt et al.1). That required a careful analysis for identifying the sources of BSSE at the level of the Hamiltonian, and developing practical computational schemes applicable for the non-Hermitian Hamiltonians (Fockians), which result when the terms responsible for BSSE are excluded. This scheme was given the name “Chemical Hamiltonian Approach” (CHA), referring to the title of the article,4 in which the projection formalism applied was first introduced.

The breakthrough for the SCF theory was achieved in ref. 5, when it was realized that the wave function should be computed with the non-Hermitian BSSE-free CHA Hamiltonian, but then the energy should be calculated as a conventional expectation value of the usual Born–Oppenheimer Hamiltonian; this scheme got the name “CHA with conventional energy,” CHA/CE. The numerical calculations indicated that the CHA and CP results are always very close, and approach each other much faster as the basis set improves, than BSSE disappears from the uncorrected results.1,5

Extending the CHA theory to the MP2 level of electron correlation calculations appeared an extremely hard task. After the failure of the first attempts to produce reasonable results for the helium dimer, we had to check whether the CHA concepts worked at the correlated level at all. The pivoting full CI calculations6 performed for four-electron systems (the He dimer and the H$_2$ dimer) showed that it performs very well; the CHA and CP results were again very close to each other. This motivated us to invest the necessary effort to elaborate the nuances required to obtain the working CHA–MP2 algorithm.7 The crucial point was that one has to build the unperturbed Hamiltonian by using the eigenvectors and eigenvalues of the non-Hermitian Fockian to completely account for the BSSE effects arising at the SCF level of theory. To compute the second-order energy (expectation value of the conventional Hamiltonian, expanded up to second order in perturbation) we had to
introduce a generalized Hylleraas functional\(^8\) applicable for the case of a non-Hermitian unperturbed Hamiltonian. The CHA–MP2 theory developed on this basis was first reported in ref. 7 for closed-shell systems; extension for open-shell ones was described in ref. 9. Again, the CHA and CP results were rather close for any reasonable basis set.

The fact that the numerical results obtained by the conceptually quite different CHA and CP methods corroborate each other completely, motivated us to a theoretical analysis,\(^10\) which could explain this observation in some detail: the apparent additivity of the BSSE effects and true intermolecular interactions, which is behind the success of the CP scheme, could be understood comparing the different components contributing to the CHA/CE and CP energies, at least for the simple model considered in the analytical study.

The aim of the present article is to describe in some detail the new, general, and efficient computer-realization of the CHA-MP2 scheme, some preliminary account of which has been given in ref. 9. The program permits to obtain BSSE free SCF and first-order perturbative wave functions and the corresponding CHA–SCF and CHA–MP2 energies, and is applicable for an arbitrary number of interacting subsystems without any increase in the computational demand when the system is divided in a larger number of subsystems. It can also used for open-shell systems—including ionized species in which the CP method hardly can be applied in an unambiguous manner.

Theoretical Background

**Summary of the CHA–MP2 Formalism**

As it is well known, BSSE is not a physical phenomenon but merely the mathematical consequence of using finite, monomer-centered basis sets. If the basis orbitals \(\chi_\mu\) and \(\chi_\nu\) belong to the monomer \(A\) (we shall denote this assignment as \(\mu, \nu \in A\)), then the functions \(\hat{h}_A \chi_\mu(\vec{r})\) and \(\frac{1}{r_{12}} \chi_\mu(\vec{r}_1) \chi_\nu(\vec{r}_2)\) may be considered to be of intramonomer nature. (Here, \(\hat{h}_A = \frac{1}{2} \Delta + U_A\) is the intramonomer part of the one-electron Hamiltonian, corresponding to the monomer \(A\).) However, if finite basis sets are used, these functions also have components that cannot be expanded by using the monomer basis set—that is, that belong to the orthogonal complement of the monomer basis set. These components are neglected, therefore, when doing free monomer calculations. The components in the orthogonal complement usually have nonzero overlaps with the functions of the partner monomer(s). This means that nonzero matrix elements of the intramonomer Hamiltonian appear between functions that can be expanded in the monomer basis set, and those functions of the other monomers that are in the orthogonal complement to the basis set of the given monomer. Thus, the functions of the other monomers can contribute to the lowering of the intramonomer energy, that is, that cause BSSE. Such an energy lowering is a common effect that occurs for both the “ghost-orbitals” calculations of the individual monomers and within the supermolecule. (“Ghost orbitals” calculations are performed in the CP scheme to correct for BSSE in an *a posteriori* manner.) To avoid the appearance of BSSE, one can omit all the terms in the orthogonal complements and obtain such, BSSE-free, supermolecule wave functions, which keep consistency with the results of the monomer calculations performed in the original free monomer basis sets. However, as already mentioned, the energy corresponding to the CHA wave function obtained in this manner should be calculated as a conventional expectation value of the full Hamiltonian\(^1\)–\(^3\) (CHA/CE scheme).

The procedure outlined above is equivalent to calculating the wave functions by replacing some one- and two-electron integrals by their “CHA counterparts”:

\[
\langle \chi_\mu | \hat{h} | \chi_{\nu} \rangle = \langle \chi_\mu | \hat{h}_A | \chi_{\nu} \rangle + \sum_{B \neq A} \hat{U}_B | \chi_{\nu} \rangle \Rightarrow \langle \chi_\mu | \hat{h} | \chi_{\nu} \rangle = \langle \chi_\mu | \hat{P}_A \hat{h}_A | \chi_{\nu} \rangle + \langle \chi_\mu | \sum_{B \neq A} \hat{U}_B | \chi_{\nu} \rangle;
\]

\[
\langle \chi_\mu(1) | \chi_\nu(2) | \frac{1}{r_{12}} | \chi_\mu(1) | \chi_\nu(2) \rangle \Rightarrow \langle \rho \tau | \mu \nu \rangle \Rightarrow \langle \rho \tau | \mu \nu \rangle_{\mu, \nu \in A} = \langle \chi_\mu(1) | \hat{P}_A \hat{h}_A | \chi_\nu(2) \rangle + \frac{1}{r_{12}} \langle \chi_\mu(1) | \hat{U}_B | \chi_\nu(2) \rangle.
\]

where \(\hat{P}_A\) is the projector

\[
\hat{P}_A = \sum_{k, \lambda \in A} | \chi_k \rangle \langle \chi_\lambda | (S_{(A)}^{-1})_{k, \lambda} | \chi_k \rangle
\]

on the subspace spanned by the basis orbitals of monomer \(A\). In eq. (2), \(S_{(A)}^{-1}\) is the inverse of the intramonomer overlap matrix. Here and further on, curly brackets denote the “CHA integrals” in which the projectors are inserted as shown in eq. (1).

In the case when the indices \(\mu\) and \(\nu\) in the “ket” part correspond to two different subsystems (i.e., the condition \(\mu, \nu \in A\) is not fulfilled) then the “CHA integral” coincides with the usual one. Furthermore, due to the Hermiticity of the projector \(\hat{P}_A\), the “CHA integrals” (1) differ from the original ones only if \(\mu \neq A\) in the one-electron case and if \(\rho \neq A\) and \(\tau \neq A\) in the two-electron one. (For the explicit expressions of the CHA integrals in the case of bimolecular complexes we refer to ref. 6.) The calculation of the CHA counterparts \(|\psi\rangle |\hat{h}|\psi\rangle\) and \(|\psi\rangle |\hat{p}|\psi\rangle\) of the integrals over the molecular orbitals \(\psi\) is performed in the new code by generalizing the scheme described in refs. 6 and 7, making it applicable for more than two interacting subsystems.

Owing to the asymmetry of expressions (1) with respect to the “bra” and “ket” functions, one has \(\langle \chi_\mu | \hat{h} | \chi_{\nu} \rangle \neq \langle \chi_{\nu} | \hat{h} | \chi_{\mu} \rangle\) if \(\nu \in A\) and \(\mu \neq A\). For the integrals over the molecular orbitals one also has, in general, \(\langle \psi | \hat{h} | \psi \rangle \neq \langle \psi | \hat{p} | \psi \rangle\), and similar inequalities hold for the two-electron integrals, as well. As a consequence, the CHA Hamiltonian\(^4\)—which can be written down explicitly by using second quantization—is not Hermitian, and the same holds for the CHA Fockian, as well. (The CHA Fockian has been derived\(^11\) from the respective generalization of the Brillouin theorem; actually, it can be obtained from the usual one by performing the substitutions (1) for the integrals.)

In the CHA–MP2 theory developed in ref. 7 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). As the exclusion of BSSE makes the problem non-Hermitian, the biorthogonal perturbation theory is used to obtain the first-order wave function $|\Psi_1\rangle$:

$$|\Psi_1\rangle = \sum_{i<j} \sum_{a<b} \frac{\langle \hat{\alpha} - \hat{b} | i | j \rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} |\Psi_{ab}\rangle. \quad (3)$$

Here, the sums are over the occupied and virtual spin-orbitals, and the primes indicate that the integrations include summations over the spins. $|\Psi_{ab}\rangle$ denotes the determinant obtained from the unexcited CHA–SCF determinant wave function $|\Psi_0\rangle$ by replacing the occupied spin-orbitals $\phi_i$ and $\phi_j$ by the virtual spin-orbitals $\psi_a$ and $\psi_b$, respectively. (They represent the left eigenvectors of the non-Hermitian CHA Fockian.) The second-order energy is again calculated by using the conventional Hermitian Hamiltonian, in accord with the CHA/CE recipe.\textsuperscript{1,5} For that reason a generalized Hylleraas functional\textsuperscript{6} is used, which guarantees the second-order energy to be real even in the case of complex CHA–SCF orbitals:

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

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 matrix elements entering the generalized Hylleraas functional are calculated by transforming all wave functions, creation, and annihilation operators to an auxiliary orthonormalized spin-orbital basis related to the molecular spin-orbitals by a nonsingular linear transformation as

$$\phi_p = \sum_l K_{pl} \theta_l; \quad \theta_p = \sum_l (K^{-1})_{pl} \phi_l. \quad (6)$$

The auxiliary basis $\{\theta_l\}$ is constructed in such a manner that the first $N$ orthonormalized spin-orbitals $\theta_l$ span the same one-electron subspace as do the occupied CHA–SCF orbitals $\phi_l$. That means that one has first to orthogonalize the occupied orbitals between themselves and then orthogonalize the virtual orbitals to the occupied ones and to each other. Using this basis, one can obtain the explicit expression

$$J_2 = \text{Re} \left\{ \sum_{k<l} t(|kl| |k|) \sum_{i<j} y(|ij| |ij|') \right. + \sum_{i<j} \left( \sum_r \sum_l t(|lr| |lk|') \sum_j y(|jr| |jk|') - 2(\theta_l | \hat{F} | \theta_k)' \right) - \sum_{k<l} \sum_{p<q} t(|pq| |kl|') \left[ 2[|pq| |kl|'] - y(|pq| |kl|') \right] \right\} \quad (7)$$

where the primes again indicate that all quantities are in terms of spin-orbitals. Here $[|pq| |kl|']$ is the conventional two-electron integral over the spin-orbitals (with exchange part, in “1212” convention), $\hat{F}$ is the conventional Fock operator corresponding to the occupied CHA–SCF orbitals, while the coefficients $y(|pq| |kl|')$ and $t(|pq| |kl|')$ are defined through the two-electron CHA integrals, $K$-matrix and the CHA orbital energies as

$$y(|pq| |kl|') = \sum_{i,j} \sum_{a,b} K_{pa}K_{qb} \langle \hat{\alpha} + \hat{b} | i | j \rangle (K^{-1})_{a|} (K^{-1})_{|b}. \quad (8)$$

and

$$t(|pq| |kl|') = \sum_{i,j} \sum_{a,b} K_{pa}K_{qb} \langle \hat{\alpha} | i | j \rangle (K^{-1})_{a|} (K^{-1})_{|b}. \quad (9)$$

If the Fock matrix is real, then the eigenvalues and eigenvectors either are real or occur in complex conjugate pairs. The occupied orbitals should be orthogonalized to build up the $P$-matrix (density matrix) necessary to start the next iteration. If the components of each complex conjugate pair are either occupied or both are left empty, then the $P$-matrix is real and, if real basis orbitals are used, the Fock matrix of the next iteration will again be real. The second-order energy correction (generalized Hylleraas functional) is necessarily real according to eq. (5); the individual terms of the expansion (7), however, can be complex. One can avoid the use of complex arithmetic in calculations by combining the complex conjugate terms analytically.

**Computer Realization**

The CHA–SCF and CHA–MP2 methods have been implemented as independent FORTRAN-77 codes interfaced with a slightly modified HONDO-8 package\textsuperscript{12} from which the one- and two-electron integrals are extracted. (HONDO–8, from MOTECC–91, contributed and documented by M. Dupuis and A. Farazdel, IBM Corporation, Center for Scientific & Engineering Computations, Kingston, 1991.) (The modifications were necessary to provide not only the overall one-electron Hamiltonian matrix but also the one-electron Hamiltonian and potential energy integrals corresponding for the individual monomers.) Obviously, any other integral package could be used without any significant difficulty. Here we are
going to briefly discuss the actual implementation, focusing mainly on the changes with respect to the codes used previously.

The main goal was to design efficient CHA–SCF and, especially, CHA–MP2 programs, which are applicable for the general case of an arbitrary number of interacting fragments, as well as for open-shell systems: the existing codes were intended only for closed-shell molecules (except the simplified “CHA/F” variant of the CHA–SCF theory\(^\text{(12)}\)) and, as already noted, the original “exploratory” CHA–MP2 code was not intended to be used for production.

**Efficient Implementation of the CHA–SCF Method**

Considerable improvements have been achieved at the SCF level, and now the CHA–SCF procedure is only marginally more time-consuming than a conventional (disk-based) SCF procedure with no BSSE corrections. (No direct SCF algorithm has been realized as yet for the CHA theory.)

It has been first observed in ref. 13 that the CHA Fockian can be obtained from the conventional one simply by replacing the conventional two-electron integrals by the “1212” convention used for the CHA SCF procedure. (No direct SCF algorithm has been realized as yet for the CHA theory.) The main goal was to design efficient CHA–SCF and, especially, CHA–MP2 programs, which are applicable for the general case of an arbitrary number of interacting fragments, as well as for open-shell systems: the existing codes were intended only for closed-shell molecules (except the simplified “CHA/F” variant of the CHA–SCF theory\(^\text{(12)}\)).

On may observe that all the integrals in the first sum pertain to (at least) two monomers. At the same time, the two sums in the second parentheses contain only “intramonomer” integrals, that is, such ones, all indices of which correspond to the same monomer. These two classes of integrals need to be treated separately.

In the first case, no big change is necessary compared to the building of a conventional Fock matrix. The only peculiarity is the following. There are up to eight integrals that have equal numerical values (if real basis orbitals are used) and differ only in the order of their indices, for example, \([\mu\sigma|\nu\rho]\) is equal to \([\mu\rho|\nu\sigma]\), \([\nu\sigma|\mu\rho]\), and so on. One should simply discard all those of them in which the indices in the “ket” happen to correspond to the same monomer, in accord with the assumption \(v \in A; \rho \notin A\) under which eq. (11) has been obtained. For instance, in case that \(v \in A\) and \(\sigma, \mu, \rho \in B\), the integral \([\nu\sigma|\mu\rho]\) is discarded, but \([\mu\sigma|\nu\rho]\), which is equal to it numerically, must be taken into account.

All the integrals of second type may be treated on equal footing, by introducing a “combined” square projection matrix \(A\), built up of the rectangular matrices \(A^\mu\) of the individual monomers:

\[
A = (A^1, A^2, \ldots, A^N).
\]

This matrix may be best constructed in the following manner. One defines the block-diagonal matrix \(S_0\) obtained from the overlap matrix \(S\) by zeroing all the intermonomer overlap integrals. Its inverse \(S_0^{-1}\) is also block-diagonal and contains the inverses of the individual monomer overlap matrices \(S^{-1}_A\) along its main diagonal. Then one can easily check that the matrix product

\[
S S_0^{-1} = \begin{pmatrix}
S_{11} & S_{12} & \cdots & S_{1N} \\
S_{21} & S_{22} & \cdots & S_{2N} \\
\vdots & \vdots & \ddots & \vdots \\
S_{N1} & S_{N2} & \cdots & S_{NN}
\end{pmatrix}
\times
\begin{pmatrix}
S_1^{-1} & 0 & \cdots & 0 \\
0 & S_2^{-1} & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & S_N^{-1}
\end{pmatrix}
\]

is nothing else than matrix \(A\) defined in eq. (13). (It was denoted matrix \(R\) in a somewhat different context\(^\text{1,12}\)).

Now one can combine the respective blocks of the density matrices \(P^\sigma (\sigma = \alpha or \beta)\) with matrices \(A^\lambda\), to form the square “projected density matrices” \(B^\rho\), the elements of which are defined as

\[
B^\rho_{\rho\lambda} = \sum_{\sigma} p^\rho_{\rho\sigma} A^\lambda_{\sigma\lambda} \quad (\rho, \lambda \in A).
\]

Matrices \(B^\rho\) can be collected in a block-diagonal matrix \(B\)

\[
\begin{pmatrix}
B^1 & 0 & \cdots & 0 \\
0 & B^2 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & B^N
\end{pmatrix}
\]

and using one may form the auxiliary matrix \(X\) following the usual scheme of building up a Fock matrix, properly taking into account
that the matrices $B^{\sigma A}$ (contrary to the usual density matrix) are not Hermitian:

$$X^{\alpha\tau}_{\rho\nu} = \sum_{\lambda,\rho} B_{\rho\lambda}^{\alpha} [\tau \lambda] \nu \rho + \sum_{\lambda,\rho} B_{\rho\lambda}^{\beta} [\tau \lambda] \nu \rho. \quad (17)$$

As the process is driven by the intramonomer integrals, no multiplications with the zero off-diagonal B-matrix elements will take place. Finally, the part of the Fockian eq. (11) containing the intramonomer integrals is obtained by a further multiplication with matrix $A$; thus, the overall two-electron contribution to the CHA Fockian is the sum of the result of processing the two-center contributions discussed above with matrix $AX^0$.

One often starts the CHA–SCF orbitals from the conventional SCF ones; the latter are usually also calculated anyway. If one is not interested in comparisons with the uncorrected SCF results, then it is worth first to perform a few cycles of calculations with the conventional Fockian and then switch to the CHA one. The simple iterative SCF procedure is usually convergent in the CHA framework, but sometimes slowly. At the same time, if one wishes to use the CHA–SCF orbitals to include further electron correlation, then rather tight convergence criteria should be used. The usual error vector for the well-known SCF convergence acceleration technique of DIIS could not be applied, due to the non-Hermitian nature of the CHA Fockian, which does not commute with the density matrix upon convergence, in contrast to the behavior of the conventional Fockian. However, one of us generalized the DIIS technique by using a biorthogonal formalism for non-Hermitian problems (details will be published elsewhere$^{14}$), which permitted to reduce the number of necessary cycles to that usual in the conventional SCF case.

Quite recently we have adapted in our program the new scheme of the Hermitization of the CHA Fockian.$^{15}$ That represents a somewhat formal trick of obtaining the CHA solutions with full machine accuracy by using an artificially Hermitized effective Fock matrix. This permits avoiding the costly diagonalization of nonsymmetric matrices in the process of searching the SCF solutions. (An orbital

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**Figure 1.** Algorithm for the determination “on the fly” of the two-electron part of the CHA Fockian (unrestricted version).
Efficient Implementation of the CHA–MP2 Method

The key point for an efficient implementation of the CHA–MP2 algorithm is to compute for each conventional integral \([\mu \nu | \lambda \sigma]\) of the AO basis all its contributions to the different CHA-transformed integrals \(\{\tilde{a}\tilde{b}|ij\}\) in the CHA MO basis. That is, the CHA-transformed integrals \(\{\tilde{a}\tilde{b}|ij\}\) over the AOs are never computed explicitly, but the CHA integrals for the MOs are determined directly. In the particular case of the open shell, these CHA-transformed integrals in the MO basis should be obtained for each of the alpha, beta, and alpha–beta contributions, but that is the case in the conventional UMP2 theory also.

Similar to building the CHA Fockian, the four-index integral transformation is again based on distinguishing intermonomer and intramonomer contributions.

For the the subset of AO integrals \([\mu \nu | \lambda \sigma]\), the indices \(\lambda\) and \(\sigma\) of whose correspond to AOs assigned to different fragments, (i.e., for pure intermolecular two-electron integrals) we have to use the original MO coefficients of the left and right eigenvectors of the CHA Fockian, forming rows of matrix \(\tilde{C}\) and columns of matrix \(C\), respectively. Thus, each such integral contributes to every CHA integral \(\{\tilde{a}\tilde{b}|ij\}\) in a manner that can be denoted symbolically as

\[
\{\tilde{a}\tilde{b}|ij\} \leftarrow \tilde{C}_{\mu\nu}\tilde{C}_{\lambda\lambda}\mu\nu | \lambda\sigma C_{\sigma j} C_{\sigma j} \quad \lambda \in A, \sigma \in B, A \neq B.
\]

(Here again we should properly distinguish between up to eight integrals having equal numerical values, and discard those of the “kets” of which contain orbitals assigned to the same monomer.) Obviously, the calculations in (18) should be performed in four consecutive steps, as it is usual for doing integral transformations.

The intramonomer integrals, all four indices of which correspond to the same monomer, contribute to the CHA integrals in a projected fashion:

\[
\{\tilde{a}\tilde{b}|ij\} \leftarrow \tilde{C}_{\rho\nu}C_{\tau\tau}A^{A}_{\rho\mu}A^{A}_{\tau\nu} \mu\nu | \lambda\sigma C_{\lambda j} C_{\sigma j} \quad \mu, \nu, \lambda, \sigma \in A.
\]

To convert this transformation into a usual four-index one, we may project the virtual orbitals (left eigenvectors) by forming rows of the matrices \(D^{A}\):

\[
D^{A}_{\nu} = \sum_{\mu \in A} \tilde{C}_{\rho\mu}A^{A}_{\mu\nu} \quad \nu \in A; \forall i.
\]

The rectangular matrices \(D^{A}\) may be combined in a single square matrix \(D\) that can be calculated very simply by using matrix \(A\) in eq. (13):

\[
D = \tilde{C}A.
\]

Thus, for integrals of the pure intramonomer type one should use the rows of the matrix \(D\) instead of the virtual orbitals. Otherwise, this part of the procedure differs from a usual four-index transformation.

\[\text{Figure 2. Relative CPU time vs. the number of monomers for a linear hydrogen fluorine chain at the MP2/6-31G level of theory (H–F distance: 1.0 Å, F...F distance 3.0 Å).}\]
only by skipping the integrals that are not strictly intramolecular ones.

Finally, the two types of contributions are summed to obtain the CHA integrals $\{\tilde{a}_{\tilde{b}ij}\}$ over the MOs. As each nonzero AO integral contributes only to one component above, the CHA integral transformation is more expensive than a conventional one by some 10 to 20%, and this is practically independent of the number of fragments in which the system is divided. We also need a complete conventional integral transformation for the orthogonalized auxiliary basis $\{\vartheta_i\}$ to get integrals $[pq|kl]$, as well as the CHA integrals (with and without the energy denominators) should also be subjected to a four-index transformation by using matrices $K$ and $K^{-1}$ to get quantities $y(pq|kl)$ and $t(pq|kl)$. The latter are relative cheap, as two transformation indices are related to the occupied subspace only.

Thus, all the integral transformations that are necessary in the CHA case require about three times more CPU time than one conventional integral transformation. The same factor is valid for a CP calculation for a supersystem consisting of two monomers. In the CP case, however, the increase of the number of subsystems of which the supersystem is formed leads to an increase of the number of necessary integral transformations while this number stays constant in the CHA theory. The first two sums on the right-hand side of eq. (7) reflect the fact that—due to the overlap of the canonical CHA orbitals—the first-order CHA wave function contains some nonzero unexcited and mono-excited contributions in terms of the orthogonalized auxiliary basis. The contribution of these terms to the second order energy has been found negligible in all cases studied to date, so their omission would represent a reasonable approximation, permitting to reduce the calculation of the quantities $y(pq|kl)$ and $t(pq|kl)$ to the cases when both $p$ and $q$ correspond to the virtual subspace. However, we did not apply this approximation, as it would not reduce dramatically the computational cost of the method.

Figures 2 and 3 display the necessary CPU time relative to the single uncorrected MP2 calculation for a linear neutral HF chain and its charged counterpart having one additional electron, with the increase of the number of HF units, treated by using the 6-31G basis set. (The same unoptimized geometry has been used in each case.) As can be seen on Figure 2, for systems consisting of two closed-shell subsystems, the cost of the CHA calculation is about three times larger than that of a conventional uncorrected one, and this ratio does not depend on the length of the chain. For as HF dimer the CPU requirement of a single-point CP calculation is practically the same as that of the CHA method, but the CP method shows a linear increase of that ratio, because the number of subsystems to be treated by using the whole supermolecule basis increases linearly. (The simplest scheme of CP correction has been utilized.)

For an open-shell system the CHA calculation is about 3.5 times more time-consuming than an uncorrected one, and this ratio is independent of the length of the chain (see Fig. 3). In contrast to this, the CP method is only ca. 2.5 more time-consuming than the uncorrected one for the HF dimer (only one of the subsystems should be treated by the more expensive UMP scheme, another is a closed-shell one), but sharply increases with the number of the the HF units, and above five HF units becomes more expensive than CHA. If we would consider a system consisting of only open-shell subsystems, a behavior similar to Figure 2 would again be obtained. In our opinion,

![Figure 3](image_url). Relative CPU time vs. the number of monomers for a negatively charged linear hydrogen fluorine chain at the UMP2/6-31G level of theory.
the above behavior makes the CHA method particularly suitable for dealing with the BSSE problem in clusters.

In the present implementation, everything is stored in memory. A single-step (fully in-core, without “passes”) implementation requires, besides the $M^3N^2$ words for the conventional transformation, $2(M - N)^2N^2$ extra words for the storage of the several transformed integrals. (Here, $M$ is the number of the basis orbitals and $N$ is that of the occupied SCF ones.)

To test the open-shell part of the code, we have repeated several closed-shell calculations as if they were open-shell ones and tested against our old program. For crosschecking the treatment of pairs of complex eigenvalues of the Fock matrix in a truly open-shell problem, an artificial example has been considered, consisting of a hydrogen atom (standard 6-31G basis) and an He dimer with a [10/5s,3p,1d] basis for which the He dimer alone exhibited complex roots. Figure 4 shows the resulting CHA–UMP2 potential curve, obtained by keeping fixed at 2 a.u. the distance between the hydrogen and one of the He atoms and varying the He–He distance.

Five different sections may be defined in the distance range of 3 to 5 a.u., corresponding to different number of pairs of complex roots appearing in the CHA–UHF calculation. In sections I and V, there is one pair of complex orbital energies in the alpha part and another for the beta set. Sections II and IV present no complex roots and section III shows one pair complex root in the beta set. It can be observed that the appearance/disappearance of complex roots does not affect the smoothness of the potential curve.

Illustrative Calculations

We have carried out full numerical geometry optimizations at the CHA–MP2 level (all electrons were correlated) for two prototype hydrogen-bonded complexes, namely water dimer and hydrogen fluoride dimer. The interaction energies and optimized geometrical parameters (see Fig. 5) obtained are gathered in Tables 1 and 2, respectively. For comparison, we have also carried out similar calculations with the counterpoise-corrected MP2 method. Uncorrected MP2 results are also given for completeness. The uncorrected and CP-corrected analytical gradient optimizations have been carried out with the standard Gaussian-98 package, as implemented in it by one of us (PS; also see ref. 18). (As the integrals in the CHA case are computed by using the HONDO-8 packages, all basis sets have been used with the six Cartesian $d$-functions, and the 10 $f$-ones.)

The effect of the BSSE correction on the interaction energies and intermolecular distance is well known, and we will discuss it here only superficially. Furthermore, our aim is not to perform state-of-the-art calculations on these well-studied systems, but to compare the performance of both BSSE correction methods at the correlated level. Particularly, we focus on rather small to moderate basis sets (for the size of these particular complexes) that are today regularly used for larger molecular complexes.

As a general trend, the CHA–MP2 energies tend to lie between the MP2 and CP–MP2 ones, but much closer to the latter. The largest discrepancy is obtained for the cc-pVDZ basis set. For both systems,
the CHA–MP2 stabilization energy obtained by using this basis is ca. 0.5 kcal/mol larger (in absolute value) than the CP–MP2 one. This difference is greatly reduced upon inclusion of diffuse functions, as is the BSSE itself.

This general trend of the stabilization energies was observed in practically all cases and any levels of theory (see, e.g., ref. 1) except, maybe, some very peculiar cases. We shall discuss these observations by considering the CHA–MP2 energy value as the reference one, because it gives the energy calculated with the strictly BSSE-free wave function. Then the usual behavior of the CP energies, which we have observed here too, can be best understood by observing that for small basis sets the CP method tends to predict slightly larger BSSE than the CHA one. The analytical study\(^{19}\) showed that the differences between both methods are partly due to the so-called “occupied to occupied” type mixings, which are possible in the “ghost orbitals” calculations but not in the actual supermolecule, while there is another minor contribution of opposite sign. This picture also explains the tendencies we can see concerning the equilibrium intermolecular distances, which are also in line with the general observations: as BSSE is larger when the molecules are closer, the uncorrected curve exhibits too short intermolecular distances; as opposed to this, the small overcorrection characteristic for CP compared with the CHA reference increases the distances somewhat. Thus, in most cases, the CP-corrected distances are slightly larger than the ones predicted by CHA–MP2. It is possible that the “occupied to occupied” delocalizations present in the CP case may appear useful in the sense that they compensate for some defects of Gaussian basis orbitals decreasing too quickly with the distance, which causes underestimated overlap repulsion. We think, however, that correcting BSSE and that of basis set deficiencies should be considered as separate tasks.

As noted in the Introduction, the simple analytical model\(^{10}\) permitted to conclude that the leading terms in the CHA and CP schemes are the same, which explains the rather good agreement, which has always been observed between these dramatically different approaches. The minor differences between the CHA and CP results may be attributed to the fact that the simplifying assumptions assumed in that model are not strictly fulfilled for the real systems. At the same time, the closeness of the results provided by these conceptually different schemes indicates that the CP and CHA methods of excluding BSSE corroborate each other.

Finally, no meaningful differences are found in the anisotropy of the BSSE-corrected interaction. Even in the well-known cases where the angular PES is poorly described by the uncorrected method (such as MP2/6-31G** and MP2/cc-pVDZ for hydrogen fluoride dimer), both BSSE correction methods correct for such pitfall and lead to comparable intermolecular angles. It is demonstrated once again that both BSSE correction methods tend to match each other much faster than the BSSE disappears from the calculation.

The lack of analytical gradient for the CHA–MP2 method is a serious shortcoming. Except for some particular cases (high symmetry, unrelaxed monomers) the exploration of the complete PES by means of the CHA–MP2 method seems to be prohibitive. In the case of the CP method, the analytical gradients are readily available (provided they are available for the uncorrected method, too). Today, several computational chemistry packages allow for analytical gradient optimization on the CP-corrected PES in a straightforward manner, unrelaxed monomers) the exploration of the complete PES by means of the CHA–MP2 method seems to be prohibitive. In the case of the CP method, the analytical gradients are readily available (provided they are available for the uncorrected method, too). Today, several computational chemistry packages allow for analytical gradient optimization on the CP-corrected PES in a straightforward manner.

![Figure 5](image-url) Geometrical parameters of the (H₂O)₂ and (HF)₂ dimers.

### Table 1. Interaction Energies (in kcal/mol) and Geometrical Parameters (Å and Degrees, see Fig. 5) of the (H₂O)₂ Complex with Several Basis Sets at the MP2, CP–MP2, and CHA–MP2 Levels of Theory.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Method</th>
<th>Δ_{E_{int}}</th>
<th>r_{O—O}</th>
<th>α</th>
<th>β</th>
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<td>134.6</td>
</tr>
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<td>125.0(^b)</td>
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</table>

\(^a\)Ref. 20.\(^b\)Ref. 21.
manner. It is sometimes argued that the CP-corrected optimization is too computationally demanding, and thus BSSE is still often corrected only for the total energy at the geometry corresponding to the minimum of the uncorrected potential surface. However, starting the CP-corrected optimization from an uncorrected converged structure usually leads to the BSSE-corrected geometry in a few steps. Whereas for very large basis sets the difference between the BSSE-corrected energies at the uncorrected and BSSE-corrected stationary points are indeed often negligible, this is not the case for small to moderate basis sets. The BSSE-corrected total energy computed on the uncorrected PES is an upper limit of the BSSE-corrected energy. This fact often leads to the wrong impression that the CP method overcorrects for BSSE to a much larger extent than the CHA method. Accordingly, this method is especially interesting in the case of molecular clusters. The study of such clusters is critical to obtain n-body information to be incorporated into intermolecular potential energy functions. Most often, such potentials are obtained from n-th dimensional accurate \textit{ab initio} PES. Together with the basis set and method, the BSSE removal is one of the key points when constructing a potential. Notice that the situation is not generally improved using inherently BSSE-free symmetry adapted perturbation theory (SAPT) potentials because they are constructed with unrelaxed monomers. The theoretically really correct “hierarchical” CP energy correction scheme is hardly practicable beyond three interacting subsystems except, maybe, for very symmetric clusters.

In accord with this, in recent articles dealing with water clusters it has been pointed out that the calculation of a completely counterpoise-corrected PES is computationally prohibitive, especially for asymmetric structure clusters. In these cases, the BSSE is either ignored or its effect is estimated according to the values for symmetric structures, where the number of fragment calculations can be reduced. We believe that in this case the CHA–MP2 method could be the most appropriate method to provide BSSE-free \textit{ab initio} data to build accurate potentials.

The water clusters have been extensively studied both theoretically and experimentally and the importance of the BSSE has been pointed out. Wieczorek et al. have recently shown that a residual BSSE (counterpoise-corrected) of 0.23 kcal/mol is still present in a MP2(FC)/aug-cc-pVQZ calculation for the water dimer. Nielsen et al. also found a 0.22 kcal/mol CP-correction for a single-point MP2 calculation for the water trimer with the aug-cc-pV6Z basis set. In the case of the water hexamer, Xantheas et al. showed that the BSSE still amounts 1.1 kcal/mol at the MP2/aug-cc-pV5Z level of theory. Unfortunately, up to six isomers lie between 1kcal/mol so the BSSE correction is more than justified in this case. Recently, some authors have proposed the use of accurate DFT methods.

Table 2. Interaction Energies (in kcal/mol) and Geometrical Parameters (Å and Degrees, See Fig. 5) of the (HF)₂ Complex with Several Basis Sets at the MP2, CP–MP2, and CHA–MP2 Levels of Theory.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>Method</th>
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</table>

\textsuperscript{a}Ref. 20. \textsuperscript{b}Ref. 21.

In the light of the results of Tables 1 and 2 and in accord with the accumulated experience, the CHA energies and optimum geometries are very close the CP ones. Thus, it can be a reasonable strategy to explore the PES with the CP method and then carry out single-point CHA calculation at the stationary points to obtain a BSSE-corrected wave function. In general, only properties depending on the total energy can be determined with the CP method in a straightforward manner, whereas charges, spin-densities, and other quantities, the calculation of which requires explicit use of the wave function, should be calculated with the CHA method.

There are few but important cases where the CHA–MP2 method can clearly outperform the CP–MP2. As stated above, the CHA methodology can be implemented in such a way that the computational cost of a single-point calculation is independent of the number of fragments composing the system, in sharp contrast with the CP method. In accord with this, the method is especially interesting in the case of molecular clusters. The study of such clusters is critical to obtain n-body information to be incorporated into intermolecular potential energy functions. Most often, such potentials are obtained from n-th dimensional accurate \textit{ab initio} PES. Together with the basis set and method, the BSSE removal is one of the key points when constructing a potential. Notice that the situation is not generally improved using inherently BSSE-free symmetry adapted perturbation theory (SAPT) potentials because they are constructed with unrelaxed monomers. The theoretically really correct “hierarchical” CP energy correction scheme is hardly practicable beyond three interacting subsystems except, maybe, for very symmetric clusters.

In accord with this, in recent articles dealing with water clusters it has been pointed out that the calculation of a completely counterpoise-corrected PES is computationally prohibitive, especially for asymmetric structure clusters. In these cases, the BSSE is either ignored or its effect is estimated according to the values for symmetric structures, where the number of fragment calculations can be reduced. We believe that in this case the CHA–MP2 method could be the most appropriate method to provide BSSE-free \textit{ab initio} data to build accurate potentials.

The water clusters have been extensively studied both theoretically and experimentally and the importance of the BSSE has been pointed out. Wieczorek et al. have recently shown that a residual BSSE (counterpoise-corrected) of 0.23 kcal/mol is still present in a MP2(FC)/aug-cc-pVQZ calculation for the water dimer. Nielsen et al. also found a 0.22 kcal/mol CP-correction for a single-point MP2 calculation for the water trimer with the aug-cc-pV6Z basis set. In the case of the water hexamer, Xantheas et al. showed that the BSSE still amounts 1.1 kcal/mol at the MP2/aug-cc-pV5Z level of theory. Unfortunately, up to six isomers lie between 1kcal/mol so the BSSE correction is more than justified in this case. Recently, some authors have proposed the use of accurate DFT methods.

Figure 6. Isomers of the water trimer and tetramer.
to the study of water clusters, on the basis of a lower computational cost and lesser BSSE contamination. (Although their results seems to agree with those from more involved post-Hartree–Fock methods, this will not probably be the case for van der Waals or weaker interactions.)

Accordingly, to test the CHA–MP2 method for clusters, we have also carried out CHA–MP2 single-point calculations at both the uncorrected and CP-corrected geometries of two isomers for each of the water trimer and tetramer (see Fig. 6). (We could not apply the complex “hierarchical” scheme of Turi and Dannenberg\textsuperscript{16} to agree with those from more involved post-Hartree–Fock methods, this will not probably be the case for van der Waals or weaker interactions.)

The results obtained for the 6-311++G** and 6-311++G(2df,2p) basis sets are gathered on Tables 3 and 4. The global minimum of the water trimer has been characterized as a cyclic structure containing three almost coplanar H-bonds, and three O—H free bonds, one of which is oriented opposite to the other two with respect to the plane defined by the three O atoms. This geometry is often referred as uud (up down). Slightly higher in energy, in the case of the uuu structure all free O—H bonds are oriented to the same direction, and hence the three water molecules are equivalent (C\textsubscript{3} symmetry). Our results for both the uud and uuu isomers are consistent with these findings. For both basis sets, the uud isomer is more stable than the uuu by less than 1 kcal/mol. The BSSE correction is quite similar at both geometries, leading to an estimate 0.7 kcal/mol difference between both isomers. Oddly, at the MP2/6-311++G** level, the uncorrected energetic difference is somewhat closer to the BSSE-corrected result of the large basis set. This is fortuitous, because the uncorrected energy difference for the 6-31G** basis set is 1.62 kcal/mol. The single-point CHA and CP-corrected value drops to 1.18 and 1.19 kcal/mol, respectively, and the further relaxation to the respective CP-corrected stationary points lead to 1.01 and 0.96 kcal/mol, in better agreement with the best estimate. The differences between the CHA–MP2 and CP–MP2 corrected energies oscillate between 0.2–0.3 kcal/mol, and are pretty much independent of the geometry. Thus, the isomerization

Table 3. Geometrical Parameters (in Å and Degrees), Interaction, and Isomerization Energies (in kcal/mol) for the uud and uuu Water Trimer Conformations (see Fig. 6).

<table>
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<th>Geom.</th>
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<th>ΔE\textsubscript{CP} \textsuperscript{iso}</th>
<th>ΔE\textsubscript{CHA} \textsuperscript{iso}</th>
<th>ΔE\textsubscript{unc} \textsuperscript{int}</th>
<th>ΔE\textsubscript{CP} \textsuperscript{int}</th>
<th>ΔE\textsubscript{CHA} \textsuperscript{int}</th>
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Table 4. Geometrical Parameters (in Å and Degrees), Interaction, and Isomerization Energies (in kcal/mol) for the uud and uudd Water Tetramer Conformations (see Fig. 6).

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<th>γ</th>
<th>ΔE\textsubscript{unc} \textsuperscript{iso}</th>
<th>ΔE\textsubscript{CP} \textsuperscript{iso}</th>
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<td>uudd</td>
<td>2.750</td>
<td>8.0</td>
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<td>−29.45</td>
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<td>2.790</td>
<td>8.5</td>
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<tr>
<td>uudd</td>
<td>2.755</td>
<td>8.4</td>
<td>128.3</td>
<td>−28.49</td>
<td>−24.01</td>
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<tr>
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The CHA–MP2 results correspond to single-point calculations at the MP2 and CP–MP2 stationary points (unlabeled and labeled as “CP,” respectively). γ is the dihedral angle defining the nonplanarity of the OH bond not involved in a hydrogen bonding. Numbers in italics represent average values.
energies predicted by both methods differ by 0.07 kcal/mol in the worst case.

The optimum geometry of the water tetramer, \textit{udud}, has also been found cyclic, with \textit{S\textsubscript{4}} symmetry. There are four almost coplanar H-bonds forming a eight-member ring and the free O—H bonds are oriented up and down with respect to the ring alternatively. There is another local minima in the PES of \textit{C\textsubscript{4}} symmetry with a different arrangement of the free O—H bonds, labeled \textit{uudd}. Our calculations are again in agreement with these findings. The \textit{udud} is lower in energy than the \textit{uudd} by 0.9 kcal/mol. For the 6-311+ +G** basis sets, the BSSE still represents about 25% of the binding energy. The differences between the CP and CHA corrected energies are systematically around 0.8 kcal/mol, which represents ca 10% of the BSSE. It may be mentioned that the high symmetry of the molecular clusters has generated a rather practical problem for the CHA calculation, but according to our experience, only in calculations. As mentioned above, complex roots can indeed appear in clusters has generated a rather practical problem for the CHA calculation, but according to our experience, only in.

Two of the eigenvalues of the matrix above are complex conjugate, the imaginary part of them being \( \beta(\beta+\delta) \pm \delta \). It can be easily seen that for \( \delta \neq 0 \) (nonhermitian case) this quantity does not vanish, except for the particular case \( \beta = 0 \), however, then the matrix is nondiagonalizable and there are less eigenvectors than the dimension of the matrix. Therefore, we have been forced to neglect the imaginary part of the degenerate occupied eigenvectors for such highly symmetric arrangements. Fortunately, the values of the imaginary part of the orbital energies were always below 1.0 d–5 a.u. so the error introduced is very small. Indeed, any dramatic effect would have been translated into large differences between the more symmetric \textit{uuu} structure and the respective \textit{uud} isomer.

**Summary**

A new, general, and efficient implementation of the BSSE-free SCF and second-order Møller–Plesset perturbation theories of intermolecular interactions, based on the “Chemical Hamiltonian Approach” (CHA) is described in detail. The program is applicable for both open-shell and closed-shell systems and for an arbitrary number of interacting subsystems. With the new program the CHA method is faster than the usual “counterpoise correction” scheme for single point calculations, especially for clusters consisting of several molecules. The numerical results provided by these conceptually different schemes, however, have again been found to be very close to each other.

**References**

14. Salvador, P. to be published.