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Modification of Guest and Saunders open shell SCF equations to exclude BSSE from molecular interaction calculations

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Abstract. The self-consistent field (SCF) for molecular-interactions algorithm, particularly devised to compute intermolecular interactions, is extended to the case in which one of the two interacting fragments is an open shell system. The method excludes the basis set superposition error in an a priori fashion. To preserve the simplicity of the standard SCF procedure, Guest and Saunders equations concerning the open shell fragment are modified at the cost of a negligible complication with respect to the usual algorithm.

Key words: Basis set superposition error – Intermolecular interactions – Restricted open shell Hartree-Fock – Self-consistent field for molecular interactions

1 Introduction

In this paper we concentrate on the problem of avoiding the basis set superposition error (BSSE) in the self-consistent field (SCF) treatment of open shell systems by means of an a priori strategy.

It is well known that the BSSE represents a serious problem and can significantly affect the reliability of intermolecular potentials between weakly interacting systems, such as van der Waals molecules or hydrogen bonded complexes, when a variational approach is employed.

Many attempts have been made during the last 30 years to correct its effects. Among them, the counterpoise method (CP) proposed by Boys and Bernardi [1] is certainly the most widely used for an a posteriori correction of standard SCF results, and was recently reviewed by van Duijnevelt et al. [2].

We have currently proposed the self-consistent field for molecular interactions (SCF-MI) method [3], which prevents the introduction of BSSE in the case of closed shell systems, and it was formulated so as to be easily incorporated into the existing packages which evaluate gradients and force constants.

Here we extend the theory to the case in which one of the two interacting fragments is characterised by an open shell configuration. Also in this case, the SCF-MI wave function is size consistent, and intramolecular relaxation effects are naturally taken into account.

A few systems will be presented as test examples. HeO_2 is a van der Waals molecule which has been intensively studied in spectroscopic and scattering experiments and represents a prototype of van der Waals molecules containing oxygen. In this case the SCF study serves as the necessary starting point for a full ab initio calculation of the intermolecular potential. The other examples considered are the He-Cu and He-Ag systems, where open shell systems interact with a closed shell partner. Since helium diffraction from surfaces is used for surface structure determination, the calculation of a correct ab initio SCF potential can provide the necessary information to define model potentials essential for the application of pairwise additive potential theory. Nevertheless these results are not intended to provide new reliable potentials; this would be achieved by approaching the Hartree-Fock (HF) limit with a high-quality SCF-MI wave function and subsequently adding dispersion terms, which are fundamental in the treatment of non-polar systems such as those considered in the present work.

As a further example of potential application of the SCF level of theory, we considered the complex NO-H_2O. Although the corresponding system involving HF has been already studied [4], no literature is available for the interaction with water.

The difference between the SCF, SCF-CP and the SCF-MI procedures depends exclusively on the basis set employed and must disappear as the basis set is enlarged

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so as to approach the HF limit. While it is accepted that the CP procedure removes all the BSSE in full-CI calculations [2], such a numerical demonstration cannot be given for the SCF wave function. The SCF-MI method is BSSE free by construction and it appears worthwhile to compare the two procedures when truncated basis sets are employed.

2 Theory

In this section the theory is presented in compact form: details of the derivations and general mathematical treatment are available elsewhere [5].

The one-determinant wavefunction Ψ of the supersystem AB – where A is closed shell and B is open shell – is constructed from orbitals which are not assumed to be orthonormal. To avoid the introduction of the BSSE, we set the constraint that the orbitals of fragment A are expanded exclusively in the space of the basis functions centred on A, and that the orbitals of fragment B in the basis functions centred on B. In this way the BSSE is completely avoided in an a priori scheme.

The SCF-MI wave function Ψ for the supersystem AB is:

$$\Psi = (N!)^{-\frac{1}{2}}\mathscr{A}\left[\phi_1^A(1)\bar{\phi}_1^A(2)\ldots\bar{\phi}_{N_A}^A(2N_A)\phi_1^B(2N_A+1)\bar{\phi}_1^B(2N_A+2)\ldots\right.$$
$$\left.\ldots\bar{\phi}_{N_B}^B(2N_A+2N_B)\varphi_1(2N_A+2N_B+1)\ldots\varphi_n(N)\right]$$
$$(1)$$

where $\phi_1^A\ldots\phi_{N_A}^A$ represent the N_A doubly occupied orbitals of fragment A; $\phi_1^B\ldots\phi_{N_B}^B$ are the N_B doubly occupied orbitals of B, while $\varphi_1\ldots\varphi_n$ are the n singly occupied orbitals (with parallel spins) of fragment B. Obviously $N = 2N_A + 2N_B + n$ is the total number of electrons. Each orbital appearing in Eq. (1) is expressed as a linear combination of atomic basis functions χ.

We partition the total basis set $\chi = \{\chi_k\}_{k=1}^M$ into two subsets, $\chi^A = \{\chi_p^A\}_{p=1}^{M_A}$ centred on fragment A and $\chi^B = \{\chi_q^B\}_{q=1}^{M_B}$ centred on fragment $B(M = M_A + M_B)$, and expand the orbitals of the two fragments in the following way:

$$\phi_i^A = \sum_{p=1}^{M_A}\chi_p^A\mathbf{T}_{pi}^A \quad i = 1\ldots N_A$$

$$\phi_j^B = \sum_{q=1}^{M_B}\chi_q^B\mathbf{T}_{qj}^B \quad j = 1\ldots N_B$$

$$\varphi_k = \sum_{r=1}^{M_B}\chi_r^B\mathbf{V}_{rk}^B \quad k = 1\ldots n.$$

In matrix form:

$$\mathbf{\Phi}^A = \chi^A\mathbf{T}^A \quad \mathbf{\Phi}^B = \chi^B\mathbf{T}^B \quad \varphi = \chi^B\mathbf{V}^B.$$

No orthogonality constraints are imposed on the orbitals of different monomers, which are left free to overlap one another.

Collecting the doubly occupied molecular orbitals in a single row vector $\mathbf{\Phi} = [\mathbf{\Phi}^A\mathbin{:}\mathbf{\Phi}^B]$, we may write

$$\mathbf{\Phi} = \chi\mathbf{T}.$$

It is also possible to write

$$\varphi = \chi\mathbf{V}.$$

In order to write the energy expression for the Slater determinant (1) it is useful to orthonormalise its orbitals so as not to alter the wave function. To this aim, the N^c doubly occupied orbitals of the closed shell system must first be orthonormalised within themselves:

$$\mathbf{\Phi} \to \mathbf{\Phi}' = \chi\mathbf{T}'$$

where

$$\mathbf{T}' = \mathbf{T}(\mathbf{T}^\dagger\mathbf{S}\mathbf{T})^{-\frac{1}{2}}.$$

The closed shell density matrix $\mathbf{R}^c$ takes the form:

$$\mathbf{R}^c = \mathbf{T}(\mathbf{T}^\dagger\mathbf{S}\mathbf{T})^{-1}\mathbf{T}^\dagger$$

Successively, the single occupied orbitals φ are orthogonalized to the $\mathbf{\Phi}'$, and these orbitals within themselves.

$$\varphi \to \varphi' = \chi\mathbf{V}'$$

$$\mathbf{V}' = (1 - \mathbf{R}^c\mathbf{S})\mathbf{V}[\mathbf{V}^\dagger(\mathbf{S} - \mathbf{S}\mathbf{R}^c\mathbf{S})\mathbf{V}]^{-\frac{1}{2}}.$$

It is then possible to define the open shell density matrix $\mathbf{R}^\circ$ as:

$$\mathbf{R}^o = (1 - \mathbf{R}^c\mathbf{S})\mathbf{V}[\mathbf{V}^\dagger(\mathbf{S} - \mathbf{S}\mathbf{R}^c\mathbf{S})\mathbf{V}]^{-1}\mathbf{V}^\dagger(1 - \mathbf{S}\mathbf{R}^c).$$

$\mathbf{S}$ is the overlap matrix over the atomic basis set:

$$S_{pq} = \langle\chi_p|\chi_q\rangle = \int\chi_p^*(r)\chi_q(r)\,\mathrm{d}v \quad p,q = 1\ldots M.$$

The energy expression may be written in the form:

$$E = 2\{\mathrm{Tr}\mathbf{H}\cdot\mathbf{R}^c + \mathrm{Tr}(\mathbf{R})^c\cdot\mathbf{G}\mathbf{R}^c\}$$
$$+ \{\mathrm{Tr}\mathbf{H}\cdot\mathbf{R}^o + \tfrac{1}{2}\mathrm{Tr}\mathbf{R}^o\cdot\mathbf{G}'(\mathbf{R}^o)\} + 2\mathrm{Tr}\mathbf{R}^c\cdot\mathbf{G}(\mathbf{R}^o)$$

where

$$H_{pq} = \langle\chi_p|\mathrm{h}|\chi_q\rangle = \int\chi_p^*(r)h\chi_q(r)\,\mathrm{d}v$$

$$G_{pq}(\mathbf{X}) = \sum_{r,s=1}^M X_{sr}(\langle pr|qs\rangle - \frac{1}{2}\langle pr|sq\rangle)$$

$$G'_{pq}(\mathbf{X}) = \sum_{r,s=1}^M X_{sr}(\langle pr|qs\rangle - \langle pr|sq\rangle).$$

$$\langle pr \mid qs\rangle = \langle\chi_p\chi_r \mid \chi_q\chi_s\rangle$$
$$= \int\chi_p^*(r_1)\chi_r^*(r_2)\frac{1}{|r_1 - r_2|}\chi_q(r_1)\chi_s(r_2)\,\mathrm{d}r_1\,\mathrm{d}r_2$$

with $p,q,r,s = 1\ldots M$.

The variation of the energy may be expressed as the sum of two terms, one depending on the variation of the $\mathbf{T}$ matrix, and the second on the variation of the $\mathbf{V}$ matrix:

$$\delta E = \delta E_T + \delta E_V \tag{3}$$

with

$$\delta E_T = \mathrm{Tr}\delta \mathbf{T}^\dagger \left[(1 - \mathbf{SR}^c)\mathbf{F}^T\mathbf{T}(\mathbf{T}^\dagger\mathbf{ST})^{-1} \right] + \mathrm{c.c.}$$

$$\delta E_V = \mathrm{Tr}\delta \mathbf{V}^\dagger$$
$$\left[(1 - \mathbf{SR}^c - \mathbf{SR}^o)\mathbf{F}^o(1 - \mathbf{R}^c\mathbf{S})\mathbf{V}[\mathbf{V}^\dagger(\mathbf{S} - \mathbf{SR}^c\mathbf{S})\mathbf{V}]^{-1} \right] + \mathrm{c.c.}$$

The matrixes $\mathbf{F}^T$, $\mathbf{F}^c$, $\mathbf{F}^o$ and $\mathbf{P}$ are defined as follows:

$$\mathbf{F}^T = 2\mathbf{F}^c + \mathbf{P}^\dagger\mathbf{F}^o\mathbf{P} - \mathbf{F}^o\mathbf{P} - \mathbf{P}^\dagger\mathbf{F}^o$$

$$\mathbf{F}^c = \mathbf{H} + 2\mathbf{G}(\mathbf{R}^c) + \mathbf{G}(\mathbf{R}^o)$$

$$\mathbf{F}^o = \mathbf{H} + 2\mathbf{G}(\mathbf{R}^c) + \mathbf{G}'(\mathbf{R}^o)$$

$$\mathbf{P} = (1 - \mathbf{R}^c\mathbf{S})\mathbf{V}[\mathbf{V}^\dagger(\mathbf{S} - \mathbf{SR}^c\mathbf{S})\mathbf{V}]^{-1}\mathbf{V}^\dagger\mathbf{S}.$$

$\mathbf{F}^T$, $\mathbf{F}^c$ and $\mathbf{F}^o$ are hermitian matrices and c.c. means the complex conjugate.

We emphasise that in these expressions for E and δE, $\mathbf{T}$, $\mathbf{V}$, $\delta\mathbf{T}$ and $\delta\mathbf{V}$ are arbitrary matrices.

We impose now on the matrices $\mathbf{T}$, $\mathbf{V}$ and on their variations – $\delta\mathbf{T}$ and $\delta\mathbf{V}$ – the following block structures:

$$\mathbf{T} = \begin{bmatrix} \mathbf{T}^A & 0 \\ 0 & \mathbf{T}^B \end{bmatrix} \quad \mathbf{V} = \begin{bmatrix} 0 \\ \mathbf{V}^B \end{bmatrix}$$

$$\delta\mathbf{T} = \begin{bmatrix} \delta\mathbf{T}^A & 0 \\ 0 & \delta\mathbf{T}^B \end{bmatrix} \quad \delta\mathbf{V} = \begin{bmatrix} 0 \\ \delta\mathbf{V}^B \end{bmatrix} \tag{4}$$

In order to specialise the expression of $\delta\mathbf{E}$ when the matrices $\mathbf{T}$, $\delta\mathbf{T}$, $\mathbf{V}$ and $\delta\mathbf{V}$ have the block diagonal structure given above, we define the two matrices $\mathbf{R}^A$ and $\mathbf{R}^B$:

$$\mathbf{R}^A = \mathbf{T}^A(\mathbf{T}^{A\dagger}\mathbf{S}^{AA}\mathbf{T}^A)^{-1}\mathbf{T}^{A\dagger}$$

$$\mathbf{R}^B = \mathbf{T}^B(\mathbf{T}^{B\dagger}\mathbf{S}^{BB}\mathbf{T}^B)^{-1}\mathbf{T}^{B\dagger} \tag{5}$$

where the overlap matrix $\mathbf{S}$ is written in partitioned form:

$$\mathbf{S} = \begin{bmatrix} \mathbf{S}^{AA} & \mathbf{S}^{AB} \\ \mathbf{S}^{BA} & \mathbf{S}^{BB} \end{bmatrix} = \begin{bmatrix} \langle \chi^A \mid \chi^A \rangle & \langle \chi^A \mid \chi^B \rangle \\ \langle \chi^B \mid \chi^A \rangle & \langle \chi^B \mid \chi^B \rangle \end{bmatrix}.$$

$\delta\mathbf{E}$ may be put in a very compact form by imposing the following orthonormality conditions:

$$\begin{aligned}
\mathbf{T}^{A\dagger}\boldsymbol{\Sigma}^A\mathbf{T}^A &= \mathbf{1}^{(N_A)} \\
\mathbf{T}^{B\dagger}\boldsymbol{\Sigma}^B\mathbf{T}^B &= \mathbf{1}^{(N_B)} \\
\mathbf{V}^{B\dagger}\boldsymbol{\Sigma}^B\mathbf{V}^B &= \mathbf{1}^{(n)} \\
\mathbf{V}^{B\dagger}\boldsymbol{\Sigma}^B\mathbf{T}^B &= \mathbf{0}^{(n \cdot N_B)}
\end{aligned} \tag{6}$$

with

$$\boldsymbol{\Sigma}^A = \mathbf{S}^{AA} - \mathbf{S}^{AB}\mathbf{R}^B\mathbf{S}^{BA}$$

$$\boldsymbol{\Sigma}^B = \mathbf{S}^{BB} - \mathbf{S}^{BA}\mathbf{R}^A\mathbf{S}^{AB} \tag{7}$$

Equation 3 now reads

$$\delta E = \delta E_{T^A} + \delta E_{T^B} + \delta E_{V^B}$$

where

$$\delta E_{T^A} = \mathrm{Tr}\delta\mathbf{T}^{A\dagger}\left(\mathbf{1}^{(M_A)} - \boldsymbol{\Sigma}^A\mathbf{T}^A\mathbf{T}^{A\dagger}\right)\left[\mathbf{1}^{(M_A)} - \mathbf{S}^{AB}\mathbf{R}^B\right]\mathbf{F}^T$$
$$\times \begin{bmatrix} \mathbf{1}^{(M_A)} \\ \cdots \\ -\mathbf{R}^B\mathbf{S}^{BA} \end{bmatrix}\mathbf{T}^A + \mathrm{c.c.}$$

$$\equiv \mathrm{Tr}\delta\mathbf{T}^{A\dagger}\left(\mathbf{1}^{(M_A)} - \boldsymbol{\Sigma}^A\mathbf{T}^A\mathbf{T}^{A\dagger}\right)\mathbf{F}^{T^A}\mathbf{T}^A + \mathrm{c.c.}$$

$$\delta E_{T^B} = \mathrm{Tr}\delta\mathbf{T}^{B\dagger}\left(\mathbf{1}^{(M_B)} - \boldsymbol{\Sigma}^B\mathbf{T}^B\mathbf{T}^{B\dagger}\right)\left[-\boldsymbol{\Sigma}^{BA}\mathbf{R}^A\vdots\mathbf{1}^{(M_B)}\right]\mathbf{F}^T$$
$$\times \begin{bmatrix} -\mathbf{R}^A\mathbf{S}^{AB} \\ \cdots \\ \mathbf{1}^{(M_B)} \end{bmatrix}\mathbf{T}^B + \mathrm{c.c.}$$

$$\equiv \mathrm{Tr}\delta\mathbf{T}^{B\dagger}\left(\mathbf{1}^{(M_B)} - \boldsymbol{\Sigma}^B\mathbf{T}^B\mathbf{T}^{B\dagger}\right)\mathbf{F}^{T^B}\mathbf{T}^B + \mathrm{c.c.}$$

$$\delta E_{V^B} = \mathrm{Tr}\delta\mathbf{V}^{B\dagger}\left(\mathbf{1}^{(M_B)} - \boldsymbol{\Sigma}^B\mathbf{T}^B\mathbf{T}^{B\dagger} - \boldsymbol{\Sigma}^B\mathbf{V}^B\mathbf{V}^{B\dagger}\right)$$
$$\times \left[\mathbf{S}^{BA}\mathbf{R}^A\vdots\mathbf{1}^{(M_B)}\right]\mathbf{F}^o \begin{bmatrix} -\mathbf{R}^A\mathbf{S}^{AB} \\ \cdots \\ \mathbf{1}^{(M_B)} \end{bmatrix}\mathbf{V}^B + \mathrm{c.c.}$$

$$\equiv \mathrm{Tr}\delta\mathbf{V}^{B\dagger}(\mathbf{1}^{(M_B)} - \boldsymbol{\Sigma}^B\mathbf{T}^B\mathbf{T}^{B\dagger} - \boldsymbol{\Sigma}^B\mathbf{V}^B\mathbf{V}^{B\dagger})\mathbf{F}^{V^B}\mathbf{V}^B + \mathrm{c.c.}$$

The minimisation of the energy E is performed by an iterative procedure in which the elementary step consists of two simultaneous rotations in the two spaces of the fragments A and B, respectively. The stationary condition $\delta E_{T^A} = 0$ to be satisfied by an arbitrary variation $\delta\mathbf{T}^A$ implies the solution of the "pseudo secular" system:

$$\begin{cases} \mathbf{F}^{T^A}\mathbf{T}^A = \boldsymbol{\Sigma}^A\mathbf{T}^A\mathbf{D}^A \\ \mathbf{T}^{A\dagger}\boldsymbol{\Sigma}^A\mathbf{T}^A = \mathbf{1}^{(M_A)} \end{cases}$$

where $\mathbf{D}^A$ is a diagonal matrix.

As far as fragment B is concerned, it is convenient to introduce the matrix $\mathbf{Z}^B$ of the virtual orbitals of order $M_B \times (M_B - N_B - n)$. $\mathbf{Z}^B$ is subject to orthonormality constraints so that the $(M_B \times M_B)$ matrix $\mathbf{Y} = [\mathbf{T}^B\vdots\mathbf{V}^B\vdots\mathbf{Z}^B]$ satisfies the condition $\mathbf{Y}^\dagger\mathbf{S}^B\mathbf{Y} = \mathbf{1}^{(M_B)}$. Following Guest and Saunders [6], the elementary step – which guarantees $\delta E_{T^B} < 0$ and $\delta E_{V^B} < 0$ at first order – consists in the unitary transformation $\mathbf{Y} \to \mathbf{Y}' = \mathbf{YU}$, where $\mathbf{U}$ is the matrix of the eigenvectors of the matrix $\mathbf{H}$ defined as

$$\mathbf{H} = \begin{bmatrix} \mathbf{T}^{B\dagger}\mathbf{F}^{T^B}\mathbf{T}^B & \mathbf{T}^{B\dagger}\mathbf{F}^{T^B}\mathbf{V}^B & \mathbf{T}^{B\dagger}\mathbf{F}^{T^B}\mathbf{Z}^B \\ \mathbf{V}^{B\dagger}\mathbf{F}^{T^B}\mathbf{T}^B & \mathbf{V}^{B\dagger}\mathbf{F}^{V^B}\mathbf{V}^B + \alpha\mathbf{1}^n & \mathbf{V}^{B\dagger}\mathbf{F}^{V^B}\mathbf{Z}^B \\ \mathbf{Z}^{B\dagger}\mathbf{F}^{T^B}\mathbf{T}^B & \mathbf{Z}^{B\dagger}\mathbf{F}^{V^B}\mathbf{V}^B & \mathbf{Z}^{B\dagger}\mathbf{F}^{V^B}\mathbf{Z}^B + \beta\mathbf{1}^{M_B-N_B-n} \end{bmatrix}$$

where α and β are empirical level shifting parameters.

We have developed an algorithm which, starting from an initial guess, proceeds iteratively. Each cycle comprises the following steps:

1. Guess for $\mathbf{T}^A$ and $\mathbf{Y} = [\mathbf{T}^B\vdots\mathbf{V}^B\vdots\mathbf{Z}^B]$;
2. Evaluation of $\mathbf{R}^A$ and $\mathbf{R}^B$ using (5);

3. Construction of Σ^A and Σ^B using (7);
4. Orthonormalisation of $\mathbf{T}^A$ and $\mathbf{Y}$:

$$\mathbf{T}^A \leftarrow \mathbf{T}^A (\mathbf{T}^{A\dagger} \Sigma^A \mathbf{T}^A)^{-\frac{1}{2}}$$

$$\mathbf{T}^B \leftarrow \mathbf{T}^B (\mathbf{T}^{B\dagger} \Sigma^B \mathbf{T}^B)^{-\frac{1}{2}}$$

$$\mathbf{V}^B \leftarrow \left(\mathbf{1}^{(M_B)} - \mathbf{T}^B \mathbf{T}^{B\dagger} \Sigma^B\right) \mathbf{V}^B$$

$$\mathbf{V}^B \leftarrow \mathbf{V}^B (\mathbf{V}^{B\dagger} \Sigma^B \mathbf{V}^B)^{-\frac{1}{2}}$$

$$\mathbf{Z}^B \leftarrow \left(\mathbf{1}^{(M_B)} - \mathbf{T}^B \mathbf{T}^{B\dagger} \Sigma^B - \mathbf{V}^B \mathbf{V}^{B\dagger} \Sigma^B\right) \mathbf{Z}^B$$

$$\mathbf{Z}^B \leftarrow \mathbf{Z}^B (\mathbf{Z}^{B\dagger} \Sigma^B \mathbf{Z}^B)^{-\frac{1}{2}};$$

5. Evaluation of the density matrixes $\mathbf{R}^c$ and $\mathbf{R}^o$

$$\mathbf{R}^c = \mathbf{T}(\mathbf{T}^\dagger \mathbf{S} \mathbf{T})^{-1} \mathbf{T}^\dagger$$

$$\mathbf{R}^o = (1 - \mathbf{R}^c \mathbf{S}) \mathbf{V} \mathbf{V}^\dagger (1 - \mathbf{S} \mathbf{R}^c)$$

In the expression of $\mathbf{R}^o$ the condition Eq. (6) introduces the simplification

$$\mathbf{V}^\dagger (\mathbf{S} - \mathbf{S} \mathbf{R}^c \mathbf{S}) \mathbf{V} = \mathbf{1};$$

6. Check the convergence of the density matrix elements;
7. Evaluation of E;
8. Construction of the matrixes $\mathbf{F}^{\mathbf{T}^A}$, $\mathbf{F}^{\mathbf{T}^B}$ and $\mathbf{F}^{\mathbf{V}^B}$;
9. Solution of the "pseudo secular" Eq. (8) for fragment A;
10. Solution of $\mathbf{HU} = \mathbf{UD}$, with $\mathbf{D}$ diagonal and $\mathbf{U}^\dagger \mathbf{U} = \mathbf{1}$;
11. $\mathbf{Y} \leftarrow \mathbf{YU}$;
    Go back to 2

3 Results

In order to test the algorithm and its general applicability, we have studied the Hartree-Fock contribution to the interaction potential of He with a series of important partners such as O_2, Cu and Ag. The system NO-H_2O, where the strong dipole of water interacts with the small dipole of the NO radical, represents a good test example for which the HF level of theory is expected to be already acceptable. For this system a rather complete comparison between the SCF, SCF-CP and SCF-MI results for a series of basis sets is presented.

3.1 He-O_2

Figures 1 and 2 show the two paths of approach of He to O_2 considered in this work. For the basis set employed see van Lenthe and van Duijneveldt [7]. The interatomic distance of O_2, r_{O-O}, was maintained at the experimental value of 2.282 a.u.

In Tables 1 and 2 we report the SCF-MI energies and the CP corrected SCF values computed using the GAMESS-UK suite of programs [8]. All the curves are repulsive. The SCF-MI results turn out very close to the
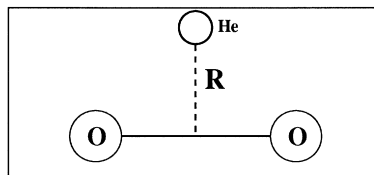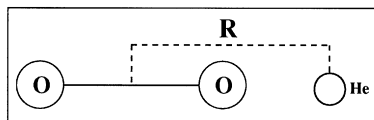

Fig. 1. He—O_2: perpendicular path of approach

Fig. 2. He—O_2: collinear path of approach

Table 1. SCF-MI, CP corrected SCF, and SCF interaction energies for He-O_2, perpendicular path of approach. Basis set of Ref. [7] (distances in a.u. and energies in mhartree)

R (He-O_2)	ΔE_{SCF-MI}	ΔE_{CP}	ΔE_{SCF}
12.0	0.00	0.00	0.00
8.0	0.00	0.00	0.00
7.0	0.01	0.01	0.00
6.0	0.11	0.11	0.08
5.5	0.33	0.31	0.28
5.0	0.99	0.93	0.89
4.5	2.90	2.68	2.64
4.0	8.26	7.63	7.57

Table 2. SCF-MI, CP corrected SCF, and SCF interaction energies for He-O_2, linear path of approach. (Basis set of Ref [7]). (distances in a.u. and energies in mhartree)

R (He-O_2)	ΔE_{SCF-MI}	ΔE_{CP}	ΔE_{SCF}
12.0	0.00	0.000	0.00
8.0	0.01	0.01	0.00
7.0	0.07	0.07	0.06
6.0	0.76	0.72	0.70
5.5	2.40	2.25	2.23
5.0	7.38	6.92	6.88
4.5	22.19	20.78	20.68
4.0	65.52	60.70	60.44

SCF values of van Lenthe and van Duijneveld and to the CP corrected results at long distance; at short distances, however, they differ and become more repulsive. This is to be ascribed to limitations of the basis set employed, which was not optimised for the SCF-MI procedure, and to the BSSE affecting the standard SCF results, which is not completely removed by the CP correction. The depth of the potential well for the C_{2v} approach, as appearing in the ESMSV potential of Faubel et al. [9], which probably remains the most reliable potential known so far, is of the order of 0.1 mH, a value which in itself emphasises the importance of a correct treatment of the BSSE.

Our SCF value for O_2 is lower than that reported by van Lenthe and van Duijneveld [7], because these authors used spherical harmonic d functions, while in the present calculation sets of six d functions are employed. Agreement with the standard SCF open shell procedure

Table 3. SCF-MI, CP corrected SCF, and SCF interaction energies for He-Cu. The basis set is reported in Table 4 (distances in a.u. and energies in mhartree)

R (He-Cu)	$\Delta E_{\text{SCF-MI}}$	ΔE_{CP}	ΔE_{SCF}
12.0	0.00	0.00	0.00
8.0	0.19	0.16	0.15
7.0	0.59	0.52	0.50
6.0	1.78	1.59	1.51
5.5	2.99	2.74	2.58
5.0	4.94	4.63	4.41
4.5	8.07	7.70	7.42
4.0	13.24	12.67	12.34
3.5	22.23	21.25	20.80

Table 4a. He basis set for the He-Cu system

Orbital	Exponent	Coefficient
s	4840.888547	0.000059
	723.108918	0.000463
	164.299706	0.002422
	46.636262	0.009995
s	15.277787	0.034249
	5.526897	0.096302
s	2.132879	1.0
s	0.849674	1.0
s	0.343643	1.0
s	0.138709	1.0
s	0.055989	1.0
p	5.526897	0.040963
	2.132879	0.145166
	0.849674	0.375520
p	0.343643	1.0
p	0.138709	1.0
p	0.055989	1.0
d	2.132879	0.099399
	0.849674	0.407386
d	0.343643	1.024217
	0.138709	0.864263
d	0.055989	1.0
d	0.022560	1.0
f	0.055989	1.0

incorporated into the GAMESS-UK program [8] is confirmed.

3.2 He-Cu

We have performed all electron calculations (Table 3) using a basis set derived from that employed by Toennies et al. [10] and by Bagus et al. [11] on Cu and one derived from Matías et al. [12] on He (Tables 4a and b). The results show that SCF, SCF-CP and SCF-MI procedures converge to the same final result.

3.3 He-Ag

As a more significant test, as far as the total number of the electrons involved is concerned, we have considered the He-Ag system. Also in this case we have performed all electron calculations (Table 5) using a basis set of reasonable extension. For He we employed the same set

Table 4b. Cu basis set for the He-Cu system

Orbital	Exponent	Coefficient
s	337200.0	0.000277
	50072.9	0.002169
	11373.4	0.011216
	3239.82	0.044615
	1071.97	0.138363
	395.099	0.312543
	158.399	0.410608
	67.3591	0.214510
	22.2983	0.017655
s	158.399	−0.076904
	67.3591	−0.053763
	22.2983	0.521222
	9.39357	0.542653
	2.57848	0.052418
s	9.39357	−0.111324
	2.57848	0.618728
	0.964080	0.493372
s	0.964080	−0.101389
	0.150003	0.156472
s	0.079035	1.0
s	0.031927	1.0
s	0.012897	1.0
s	0.004299	1.0
p	2245.29	0.002255
	532.106	0.018408
	172.195	0.086463
	65.3239	0.254486
	27.0551	0.434210
	11.7435	0.333857
	4.69382	0.061723
p	27.0551	−0.022188
	11.7435	0.023927
	4.69382	0.420277
	1.90667	0.628484
p	0.711445	1.0
p	0.141340	1.0
p	0.030833	1.0
p	0.010278	1.0
d	53.65	0.025972
	15.07	0.141029
	5.104	0.347976
	1.727	0.448865
d	0.5283	1.0
d	0.1491	1.0
d	0.0421	1.0
d	0.01403	1.0
f	1.0	1.0
f	0.28220	1.0
f	0.07970	1.0
g	0.1	1.0

Table 5. SCF-MI, CP corrected SCF, and SCF interaction energies for He-Ag. The basis set is reported in Tables 4a and 6 (distances in a.u. and energies in mhartree)

R (He-Ag)	$\Delta E_{\text{SCF-MI}}$	ΔE_{CP}	ΔE_{SCF}
12.0	0.00	0.00	0.00
8.0	0.28	0.24	0.23
7.0	0.81	0.73	0.70
6.0	2.29	2.08	2.04
5.5	3.80	3.47	3.42
5.0	6.29	5.77	5.71
4.5	10.47	9.72	9.65
4.0	18.15	17.07	16.99
3.5	34.73	32.83	32.74

as used for the system He-Cu (Table 4a); for Ag, the basis set is obtained by augmenting the set (17s, 11p, 8d) of ref. [13] by new s, p, d, f and g diffuse functions (Table 6).
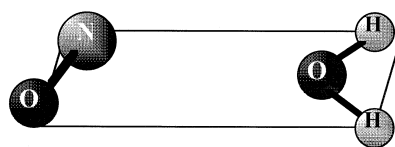
The energy curves turn out again to be fully repulsive, with the SCF-MI values above the SCF ones. The results (Table 5) show that the differences among ΔE_{SCF-MI}, ΔE_{SCF-CP}, and ΔE_{SCF} are sufficiently small and acceptable for this basis set. It is to be emphasised, however, that the only care required by the SCF-MI method is that the basis sets on each fragment be properly balanced and able to describe the long range behaviour of the wave functions of the interacting fragments, by including basis functions with sufficiently small exponents.

3.4 NO-H$_2$O

As a final test, a van der Waals complex involving molecular fragments has been investigated at the HF level of the theory. It is well known that weakly bonded complexes containing open shell molecules are difficult to study and little information is available when hydrogen bonding is involved. However, an important system in this class which has received attention is the complexes of closed shell fragments as confirmed in [14] forthe H$_2$O-HO system [14]. Here we present a series of calculations on the NO-H$_2$O complex performed using several standard and or slightly modified medium size basis sets (Tables 7–9). The polarisation functions used have been optimised to maximise the polariszabilities of

Table 6. Ag basis set for the He-Ag system

Orbital	Exponent	Coefficient
s	782615.55	1.0
s	116697.35	1.0
s	264657.05	1.0
s	7559.2393	1.0
s	2531.3743	1.0
s	954.42758	1.0
s	393.96647	1.0
s	173.46788	1.0
s	67.292480	1.0
s	30.194935	1.0
s	11.102996	1.0
s	5.6412301	1.0
s	2.1374430	1.0
s	1.0945265	1.0
s	0.48011424	1.0
s	0.11787222	1.0
s	0.041876163	1.0
s	0.014875	1.0
p	6116.6742	1.0
p	1426.6642	1.0
p	458.34731	1.0
p	175.50623	1.0
p	74.964904	1.0
p	34.255544	1.0
p	15.808571	1.0
p	7.4193252	1.0
p	3.3942283	1.0
p	1.4640686	1.0
p	0.56583919	1.0
p	0.21866	1.0
p	0.084509	1.0
d	260.66912	1.0
d	77.125699	1.0
d	28.986678	1.0
d	11.892642	1.0
d	5.1018889	1.0
d	2.1332702	1.0
d	0.83680243	1.0
d	0.28806987	1.0
d	0.10133	1.0
d	0.03540	1.0
d	0.01237	1.0
f	1.0	1.0
f	0.33333	1.0
f	0.11111	1.0
f	0.0374	1.0
g	0.5	1.0

Fig. 3. Geometry 1 for the NO—H$_2$O complex
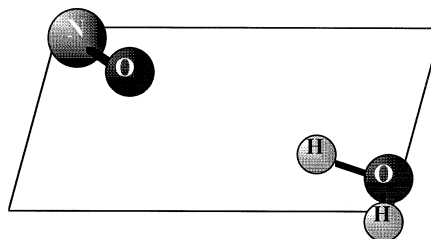
Fig. 4. Geometry 2 for the NO—H$_2$O complex

Table 7. SCF-MI, CP corrected SCF, and SCF interaction energies for geometry 1 of NO-H$_2$O (Fig. 3) (energies in kcal/mol)

Basis set	ΔE_{SCF-MI}	ΔE_{CP}	ΔE_{SCF}
6-311G	−1.59	−1.39 (−1.62)	−1.99
6-31G	−1.62	−1.48 (−1.62)	−2.08
6-31++G	−1.40	−1.42	−2.00
6-31G**	−1.16	−1.20	−2.22
6-31++G**	−1.19	−1.18	−2.64
TZV++	−1.50	−1.60	−1.98
TZV++**	−1.02	−1.18	−1.89

Table 8. SCF-MI, CP corrected SCF, and SCF interaction energies for geometry 2 of NO-H$_2$O (Fig. 4) (energies in kcal/mol)

Basis set	ΔE_{SCF-MI}	ΔE_{CP}	ΔE_{SCF}
6-311G	−1.21	−1.45	−1.87
6-31G	−1.26	−1.45	−1.88
6-31++G	−1.15	−1.15	−2.12
6-31G**	−1.00	−1.16	−2.22
6-31++G**	−1.00	−1.14	−2.10
TZV++	−1.18	−1.12	−1.72
TZV++**	−0.94	−0.97	−1.59

Table 9. SCF-MI and SCF O-O intermolecular distances for geometries 1 and 2 of NO-H_2O (Figs. 3, 4) (distances in angstroms)

Basis set	Geometry 1		Geometry 2	
	SCF-MI	SCF	SCF-MI	SCF
6-311G	3.14	3.14	3.40	3.22
6-31G	3.12	3.11	3.40	3.21
6-31++G	3.21	3.21	3.34	3.18
6-31G**	3.08	3.08	3.26	3.26
6-31++G**	3.29	3.29	3.50	3.22
TZV++	3.31	3.24	3.21	3.21
TZV++**	3.31	3.31	3.44	3.26

several related molecules. For each basis set SCF (ROHF) CP-SCF and SCF-MI wave functions have been calculated, determining also the energy minimum energy geometry. Two equilibrium geometriesy (Figs. 3, 4) of C_s symmetry and comparable stability have been found by all the SCF techniques employed.

Calculations for geometry 1 (Fig. 3) are summarised in Table 7. In this geometric configuration the water molecule remains of C_{2v} symmetry with the oxygen atom pointing approximately to the centre of the NO bond. Molecular orbital analysis of the SCF-MI wave function shows that the singly occupied orbital of the NO open shell fragment hasis of π symmetry. The computed binding energiesy reported are of the order of 1 kcal/mol. Also in this case, SCF-MI interaction energies are in close accordance with the corresponding CP corrected values. For some basis sets, however, (namely 6-311G and 6-31G) the CP correction procedure overestimates the BSSE magnitude. In these cases the CP interaction energy improves only after a further optimisation of the geometry of the complex with the CP corrected wave function and agrees with the SCF-MI result (Table 7, values in parenthesis) [15].

Calculations for geometry 2 (Fig. 4) are reported in Table 8. This geometric configuration would involve a classical linear hydrogen bond between the fragments. In this case the singly occupied orbital of the open shell NO fragment is of has σ symmetry. Binding energies reported in Table 10 are comparable with the corresponding values calculated for geometry 1. The SCF-MI interaction energies and the CP corrected values are still in close accordance. The OH bond donor donor involved in the hydrogen bond becomes longer than in the free OH of water.

The small gap between SCF-MI and CP corrected values infor both the equilibrium structures can be due to relaxation fragment effects [16] not considered at the SCF-CP level of the theory and to a residual BSSE in the CP procedure [17].

SCF-MI intramolecular parameters remain unchanged with respect to the corresponding SCF values; as expected [15], intermolecular distances result longer, in accordance with BSSE removal [15]. In Table 9 the interfragment O—O distance, is generally longer for both geometries.

All the reported calculations show that the HF interaction for this system is attractive. The inclusion of zero point vibrational energy and the use of a higher level of theory is beyond the aim of this work.

4 Conclusions

We have presented the extension of the SCF-MI algorithm [3] to the more general case of the intermolecular interactions between a closed and an open shell system. As in our previous work, the BSSE is excluded a priori, as the expansion of molecular orbitals of each fragment is permitted only in the basis functions centred on the fragment itself.

The simplicity of the standard SCF procedure has been preserved. Guest and Saunders open shell equations have been modified at the cost of a negligible complication with respect to the usual algorithm.

The method takes naturally into account the geometry relaxation effects in polyatomic fragments. As discussed recently [16], the estimation of the BSSE correction by the CP methods requires, in addition to the SCF calculation on the dimer, CP calculations on the monomers at the geometries of the dimer and the asymptotic monomer. This reduction in computation time will be significantly important for large systems.

The implementation [17] of the closed shell SCF-MI method into the GAMESS-US program [18], comprising standard and direct SCF procedures, gradient and Hessian evaluation features, has been accomplished. Work on its inclusion in other standard packages as one of the available options is in progress.

For all the systems considered we did not observe any convergence difficulty, while the computing time is comparable with that of standard SCF procedures.

The SCF-MI a priori strategy of avoiding BSSE is always correct and the wave function remains size consistent. This becomes important in the case of anisotropic potentials, as the errors in the wave function introduced by the CP procedure – the secondary BSSE – can contribute to alter the resulting physical picture [19].

The program has been tested by means of a code based on an iterative first order Brillouin scheme where the nonorthogonality of the orbitals of the two fragments is directly taken into account by general VB techniques [20].

A possible criticism might concern the fact that the SCF-MI procedure does not allow charge transfer effects to occur. As already discussed previously [3], we call to mind that the constraints on the SCF-MI orbitals, $\Phi^A = \chi^A T^A$, $\Phi^B = \chi^B T^B$ and $\Phi = \chi^B V^B$, do not prevent a certain amount of charge transfer to take place. This can occur because the SCF-MI orbitals Φ^A and Φ^B are not orthogonal but are allowed to *overlap*. In this way the orbitals of A can have tails on B and vice versa, tails which do not originate from unphysical nodes imposed by the orthonormalisation process. This peculiarity is also beneficial to *all* the other terms which are sensitive to the detailed description of the overlap region, as it provides to the SCF-MI orbitals the necessary flexibility and freedom to adapt to the effects of the physical interactions. For this to be true,

it is necessary to employ functions which are not closely localised on the monomers, as required in the study of van der Waals complexes or hydrogen-bonded systems.

The extension of the BSSE free SCF-MI strategy for closed shell systems to include electron correlation effects has already been presented [21] and its application to the study the properties of water turned out to be extremely promising [21–23].

The advantage of starting from a correctly defined BSSE free HF method in the calculation of intermolecular potentials in van der Waals systems can hardly be overemphasised.

For a more complete evaluation of the advantages of the a priori strategy to avoid BSSE see also ref. [24], where spin coupled valence bond calculations for the He-LiH system are reported.

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