The interacting correlated fragments method with non-orthogonal orbitals

J. H. VAN LENTHE and F. DIJKSTRA
Theoretical Chemistry Group, Debye Institute, Utrecht University, Padualaan 14, 3584 CH Utrecht, The Netherlands

(Received 15 April 1998; revised version accepted 19 May 1998)

The interacting correlated fragments (ICF) method proposed by Liu and McLean is employed using non-orthogonal orbital spaces for the interacting fragments. This way orthogonalization schemes may be avoided and the orbitals may be optimized separately at each internuclear distance. This approach is illustrated using a calculation on the He dimer, which is one of the first systems to which ICF was applied. It is found that the use of non-orthogonal orbitals gives a more attractive potential. Although the orbital basis inconsistency is avoided completely, the configuration basis inconsistency still gives rise to a considerable basis set superposition error.

1. Introduction
The interacting correlated fragment (ICF) [1–4] method of Liu and McLean is a multi-reference configuration interaction (MRCI) method intended to describe the interaction between weakly bonded systems. The basis idea is that each monomer (fragment) may be described adequately by a rather small MCSCF or CASSCF function that accounts for the bulk of the intrafragment correlation.

The antisymmetrized product of the individual correlated wavefunctions of the fragments or the complete CI in the corresponding orbital sets [1] is the reference function in the MRCI. To this reference function single excitations are added to allow relaxation of the wavefunction in the dimer and dispersion-type double excitations, which have one hole in the active space of each monomer. By using ever larger reference functions, describing a larger part of the fragment correlation, this procedure may be expected to converge to the full CI limit.

Thus we have the ICF-1 model, which is a single-reference dispersion CI with interacting Hartree–Fock fragments. The next stage is the ICF-2 model, where the monomers are correlated by double excitations to the first empty shell. For He this involves the 2s and 2p orbitals. Since the ICF wavefunction reduces at infinite interfragment distance to an (antisymmetrized) product of fragment wavefunctions, the approach is ‘size consistent’ [5] although, being a variational CI method, it is not ‘size extensive’ [6].

To reduce basis set superposition error (BSSE) [7] the orbitals are kept localized as much as possible, and when using bigger basis sets quite elaborate orthogonalization and counterpoise schemes need to be employed to keep BSSE in check in both orbital and configuration space [8]. Liu and Mclean [1] called the first more common error source orbital basis inconsistency (OBI), whereas the latter, was called configuration basis inconsistency (CBI) by them. They included the error due to both CBI and OBI in the BSSE. One might prefer to call only the error due to OBI BSSE and refer to the CBI error as configuration set superposition error (CSSE) [9]. In this paper we will follow the definition of Liu and Mclean.

The use of non-orthogonal orbitals offers a unique possibility of doing away with localization procedures altogether, by keeping the orbitals strictly localized on their own atoms. This does eliminate the OBI BSSE, but the CBI is still something to be reckoned with.

We have re-investigated the ICF-1 and ICF-2 approaches here using a rather small basis set, C1D2
[10, 11], used by us before, which is just large enough to get the fundamentals of the He dimer interaction right. High accuracy may not be expected from this basis, as a properly counterpoise corrected full CI gives at 5.6\(\sigma_0\) an interaction energy of only \(-9.08\) K, compared with big basis-set results of the order of \(-10.95\) K [1, 12] and the latest result of below \(-11\) K [13, 14].

2. Method
The C1D2 basis is a \((15s3p2d)\rightarrow[6s3p2d]\) Gaussian basis, with spherical harmonic d functions. The ATMOL [15] program INTEGW was used to calculate the integrals. The VB calculations were made with the general valence bond program TURTLE [16–18], which allows completely general wavefunctions without
imposing any orthogonality restrictions. The orbitals in the ICF calculations were optimized in an atomic (MC)SCF calculation. This is equivalent to an atomic CASSCF. We also optimized the orbitals in a non-orthogonal dimer MCSCF, to allow the orbitals in the reference wavefunctions to adapt to the presence of the other atom, without sacrificing the strict local character of the orbitals. Whereas the ICF approach, as published [1], uses a dimer CASSCF function as a reference, we now use a local combined multiconfiguration function, in an attempt to reduce the CBI BSSE. Using a dimer CASSCF the reference space would be equal to that in an orthogonal calculation [8]. Again using local CASSCF functions would give the same ICF wavefunctions.

Thus we have the following reference functions:

ICF-1:

$$\Psi = (1s^2)_A \otimes (1s^2)_B$$

ICF-2:

$$\Psi = (1s^2 + 2s^2 + 2p_x^2 + 2p_y^2 + 2p_z^2)_A \otimes (1s^2 + 2s^2 + 2p_x^2 + 2p_y^2 + 2p_z^2)_B$$

The coefficients of the configurations are optimized without restrictions.

In the following ICF calculation the dispersion excitations may employ either the virtual atomic orbitals of each monomer or the full dimer set of virtual orbitals. The single excitations are to virtual orbitals on the same atom only. This means that no OBI BSSE can occur, but also that no charge transfer interaction is enabled, which for the He dimer is estimated to be 0.16 K attraction [19].

Non-orthogonally orbitals have been used before to study weakly bonded systems, within a multi-configuration VB context, always with the explicit aim to avoid the BSSE [19–24]. Indeed in these approaches no OBI BSSE occurs.

BSSE due to configuration basis inconsistency cannot be excluded. The proper counterpoise is often difficult to define. In principle one may define the counterpoise monomer calculation as using that monomer wavefunction which, when combined with the corresponding wavefunction for the other monomer and antisymmetrized, yields the zero-order approximation to the dimer wavefunction [9, 25]. For example, if the dimer wavefunction is a simple product of the monomer Hartree–Fock wavefunctions (1s_A^2 1s_B^2), the proper monomer calculation is a monomer full CI using the orbitals 1s_A, 1s_B. Thus, the monomer calculation for monomer A, corresponding to an ICF-1 calculation with strictly local single excitations on A, is the full CI mentioned above, augmented by all local single excitations on A. This gives rise to double excitations in the monomer calculation. This procedure is a configuration state counterpoise procedure, yielding in addition to the BSSE the configuration set superposition error (CSSE) [9], correcting for the configuration basis inconsistency.

For the ICF-2 approach the proper counterpoise is not so easy to define. Various approximate models may be constructed. A definite upperbound is the ICF-1 BSSE. A better estimate of the BSSE may be obtained by combining the ICF-2 reference function with the ICF-1 monomer counterpoise wavefunction and comparing this with the ICF-2 wavefunction. This yields an ICF-2 BSSE as the ICF-1 BSSE in the presence of the ICF-2 wavefunction.

All interaction energies are given in kelvin (K, where 1 hartree = $E_h = 315 777 K$).

3. Results and discussion

The results for an internuclear distance of 5.6 $a_0$, close to the minimum of the potential energy curve, are given in table 1. The interaction energies labelled OBI corrected are corrected only for orbitals basis inconsistency. The other results are corrected for all BSSE. As a comparison we collected the results of various orthogonal (MO) calculations using the same basis set. The BSSE in these calculations ranges from 0.2 K to 2.0 K.

The VB calculations do not suffer from OBI, so all BSSE is due to CBI. This BSSE may be as large as 1.42 K for the ICF-1 model. This is consistent with the CBI BSSE found earlier in the orthogonal ICF-1 calculations [8]. The BSSE of the full CI (1.05 K) is even less than that of ICF-1, because the He monomer is much better described in its own configuration and orbital basis.

Table 1. Interaction energies for He_2 (in K) at 5.6 $a_0$ using various models and using the C1D2 basis set (monomer basis atomic Hartree–Fock energy $2.861 679 12 E_h$; full CI energy $-2.901 534 97 E_h$; atomic correlation energy (monomer) $\approx 0.04 E_h \approx -12 585 K$).

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta E_{\text{interaction}}$</th>
<th>$\Delta E$ (OBI corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full CI</td>
<td>-9.08</td>
<td>-10.13^b</td>
</tr>
<tr>
<td>MO-ICF-1</td>
<td>-9.73</td>
<td>-11.16</td>
</tr>
<tr>
<td>MO-ICF-2 (model B)</td>
<td>-9.88</td>
<td>-9.07 (model E)</td>
</tr>
<tr>
<td>MO-ICF-2 (model E)</td>
<td>-9.07</td>
<td>-8.60 (local dispersion)</td>
</tr>
<tr>
<td>VB-ICF-1 (local dispersion)</td>
<td>-10.75</td>
<td>-12.17</td>
</tr>
<tr>
<td>VB-ICF-2</td>
<td>-9.75</td>
<td>-9.91</td>
</tr>
</tbody>
</table>

^ Reference [29], as quoted in [30].

This is the uncorrected full CI result; the difference between CBI and OBI is not clear at the full CI level.

^ MO-ICF in the same basis taken from [8].
All the ICF-1 calculations predict a rather deep minimum. This result, even after applying the counterpoise correction, may be rationalized by realizing, that the ICF-1 results do not contain any intra-atomic correlation, which gives a repulsive contribution to the interaction energy. Also the dispersion energy is overestimated in the ICF-1 model, which is a single configuration dispersion CI [26, 27]. The ICF-1 calculations marked ‘local dispersion’ use only local excitations to generate the dispersion configurations. This truncates the virtual space available for dispersion interactions too severely.

As in the MO calculations the ICF-2 is significantly less attractive than the ICF-1. The interaction is still a lot deeper than the full CI limit. Partly this may be due to an inadequate counterpoise calculation. In the ICF-2 dimer calculation a minor part of the configurations 2s^2, 2p^2, 2p^2, 2p^0 on B are not accessible to A, and thus should be accessible to A in the counterpoise monomer. If one would add these configurations to the monomer wavefunction in the ICF-2 counterpoise calculation, a BSSE of 0.81 would be obtained, yielding an interaction energy of ~9.10 K, fortuitously close to the full CI. Where this is a definite overestimate, the real result must be a compromise between the two BSSE estimates.

The VB ICF interaction energies are considerably more attractive than those of the MO-ICF. This is due partly to the fact that the VB uses only the monomer basis set, which is not good enough for a proper description of the exchange repulsion. The Hartree–Fock exchange is improved greatly by using a dimer basis description of the monomers [9, 28]. However, this is not the most important effect. The overlap between the monomers may introduce some extra attraction, which is not present in the MO calculations. This requires further investigation. Since the ICF-2 function does use some more diffuse functions (2s and 2p), which overlap with the other monomer, the difference with the MO-ICF is less pronounced.

There is no exact correspondence between the MO and the VB ICF-2 wavefunctions, so the correspondence between the OBI corrected MO-ICF-2 (model-B) and the uncorrected VB-ICF-2 may be fortuitous.

Optimizing the orbitals proved to be superfluous (< 0.01 K), vindicating the approximations made in the orthogonal ICF calculations [1, 8]. For a distance of 4.0_\text{a_0} the effect is of course more noticeable, but still only 4 K of the 400 K interaction energy.

4. Conclusion

The use of non-orthogonal orbitals does yield an ICF method which is free of the orbital part of the basis set superposition error (OBI). The configuration basis inconsistency still gives rise to a considerable BSSE.

After correcting for this BSSE, the results of the ICF calculations are more comparable with the earlier orthogonal ICF calculations, but the minima are still too deep.

We thank F. B. van Duijneveldt for helpful discussions.

This paper is dedicated to the memory of Bowen Liu and to Doug McLean.

References

[25] van Duijneveldt, F. B., 1997, Basis Set Superposition Error: Molecular Interactions From van der Waals to


