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On Basis Set Effects in SCF Calculations of the Interaction Energy between Closed-Shell Atoms*

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The so-called "superposition error" is investigated for different Gaussian basis sets used in the SCF calculations of the interaction energy between neon atoms. The results show that unless the counterpoise method [1] is applied, a qualitatively wrong description of interaction can be obtained. This is observed even for the basis sets which give fairly accurate atomic energies. It is shown that, despite large superposition error, basis sets fitted to the exact density [2] can provide very reasonable results if the counterpoise method is applied.

Key words: Weak atomic interaction

1. Introduction

There is much current interest in the *ab initio* calculations of weak interactions between atomic and molecular systems. Though the interaction energy is in such cases very small, it is of great importance for the explanation of thermodynamic properties of gases and liquids, cohesive energy and structure of crystals, hydrogen-bond energy, etc.

Recently it has been proved that the SCF interaction energy curve is a very good starting point for the inclusion of correlation effects not only in a variational scheme [3–5] but also in a perturbational treatment [6, 7]. However, a serious problem with the SCF approach is the basis set superposition error [4]. The effect was first noted by Kestner [8] in a discussion of early *ab initio* SCF calculations on He_2 [9–11]. The problem may be overcome with the aid of the function counterpoise method proposed by Boys and Bernardi [1]. In this paper we examine the effectiveness of the Boys and Bernardi approach in the case of two interacting neon atoms which may be considered as typical representatives of closed-shell atoms.

2. Method

The Hartree-Fock interaction energy is defined by the formula:

$$E_{\mathrm{int}}^{\mathrm{HF}}(R) = E_{\mathrm{AB}}^{\mathrm{HF}}(R) - (E_{\mathrm{A}}^{\mathrm{HF}} + E_{\mathrm{B}}^{\mathrm{HF}}) \tag{1}$$

where $E_{\mathrm{AB}}^{\mathrm{HF}}, E_{\mathrm{A}}^{\mathrm{HF}}, E_{\mathrm{B}}^{\mathrm{HF}}$ are the exact Hartree-Fock energies of the supersystem and its components respectively. However, these quantities are almost never known exactly, and

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one is forced to deal with the approximate Hartree-Fock functions. As soon as the energies in formula (1) are calculated in finite basis sets the definition is no longer unique.

A common practice is to approximate the Hartree–Fock interaction energy by the formula:

$$E^{\mathrm{I}}_{\mathrm{int}}(R) = E^{\mathrm{SCF}}_{\mathrm{AB}}(R) - (E^{\mathrm{SCF}}_{\mathrm{A}}(\infty) + E^{\mathrm{SCF}}_{\mathrm{B}}(\infty)), \tag{2}$$

where $E^{\mathrm{SCF}}_{\mathrm{AB}}(R)$ is the total SCF energy of the interacting systems A and B at the distance R and $E^{\mathrm{SCF}}_{\mathrm{A}}(\infty)$, $E^{\mathrm{SCF}}_{\mathrm{B}}(\infty)$ denote the SCF energies of the isolated systems A and B respectively. The symbol "∞" means that when calculating the energy $E^{\mathrm{SCF}}_{\mathrm{A}}(\infty)$ the system B is removed to infinity together with its own basis set.

Another way of calculating $E^{\mathrm{HF}}_{\mathrm{int}}$ in a finite basis set has been proposed by Boys and Bernardi [1]. The method consists of approximating $E^{\mathrm{HF}}_{\mathrm{int}}$ by the following formula:

$$E^{II}_{\mathrm{int}}(R) = E^{\mathrm{SCF}}_{\mathrm{AB}}(R) - (E^{\mathrm{SCF}}_{\mathrm{A(B)}}(R) + E^{\mathrm{SCF}}_{\mathrm{B(A)}}(R)). \tag{3}$$

In the above formula the energy of the supersystem as well as the energies of its constituents A and B are calculated with the basis of the whole supersystem AB. The symbol $E^{\mathrm{SCF}}_{\mathrm{A(B)}}(R)$ means that the A energy is to be calculated when B is removed, but the basis set centred on B is still kept at the distance R. Consequently the calculated SCF energies of isolated systems depend (formally) on the intersystem separation. In practice this implies that additional calculations of the SCF energy for the isolated systems A and B have to be performed for each intersystem distance. However, this does not increase computational time considerably, because for calculating the isolated system energies we need the same integral file as for the whole supersystem. Only the SCF procedure has to be repeated.

When discussing the adequacy of the above approach it is important to point out an inconsistency which appears in formula (2). In computing $E^{\mathrm{SCF}}_{\mathrm{AB}}(R)$ one reproduces the energies of the isolated systems A and B and the interaction energy between them. The reproduction of the energies A and B takes place in the full basis of the supersystem AB, rather than in the bases of its components. According to formula (2) we subtract the energies of isolated systems A and B obtained with a poorer basis set, i.e. basis of constituent systems only. As a result, particular components in formula (2) are calculated at a different level of accuracy. Since $E^{\mathrm{HF}}_{\mathrm{int}}$ is a few orders smaller than the quantities in formula (2), it is possible that the error caused by a poor basis set may be of the same order of magnitude as the interaction energy.

When formula (3) is used, an extra destabilization correction appears, caused by the extension of the basis set for the isolated systems. The effect is known in the literature as a basis set superposition error [4]. It is always positive and will be further denoted as

$$\Delta\epsilon(R) = E^{II}_{\mathrm{int}}(R) - E^{I}_{\mathrm{int}}(R) \tag{4}$$

The magnitude of $\Delta\epsilon$ may serve as a useful criterion of completeness of the basis set used. If one uses the counterpoise method, the $\Delta\epsilon$ correction is included in the interaction energy.

The above remarks cannot be considered as a rigorous theoretical justification of the inadequacy of formula (2). More conclusive are the results of practical applications of both formulae. It was shown [12] that application of formula (2) can even lead to a quantitatively wrong description of the interaction.

However, in the literature one can find only a few examples of the application of the counterpoise method on SCF level [12–17]. Recently Urban and Hobza [15] reported an interesting analysis of the influence of the superposition error on the SCF interaction energy and its components in the case of two H_2 molecules. It is noteworthy that in all the above calculations, independently of basis shortcomings, a considerable improvement has been achieved, with a trend to overcorrecting the SCF interaction energy.

It is interesting to know how formulae (2) and (3) work in the case of very weakly interacting systems, e.g. rare gas atoms. In this case the interaction energy is very small due to the lack of permanent multipole moments. The $E_{\text{int}}^{\text{HF}}$ is thus dominated by the first-order repulsion which decreases exponentially with R. Thus one can expect that the E_{int}^{I} could be of the magnitude of the superposition error. The calculations have been performed for the system of two neon atoms, since neon is the rare gas atom including p-type orbitals which do not saturate as rapidly as s-type orbitals.

While investigating the SCF interaction energy between two closed-shell atoms the problem appears of how to construct an effective Gaussian basis set for the calculation of interaction energy. The basis set for AB is commonly built as a sum of two basis sets for A and B plus, in some cases, a few polarization functions. The basis for the isolated atom is optimized to give the lowest atomic energy. Recently Kołos and Leś [2] proposed another choice of basis set for the isolated systems. The functions of Kołos and Leś are optimized to give the best density[1]. Their results for the first-order interaction energy have shown that the periphery of wave function is also of great importance for correct reproduction of the interaction energy [19–21]. Hence, it would be interesting to compare the usefulness of the basis sets "optimized on energy" and those "fitted to density" in the SCF calculations.

3. Results and Discussion

In this paper the "optimized on energy" basis sets of Duijneveldt [22] and those "fitted to density" of Leś [23] have been used. The basis sets and the atomic energies obtained using these basis sets are specified in Table 1.

The values of the SCF interaction energy obtained using formula (2) with all basis sets under consideration have been displayed in the first part of Table 2. For the uncontracted basis sets (A, B, C) a minimum on the energy curve has been obtained. For the remaining basis sets (D, E, F) the interaction energies are not so unrealistic, but in the van der Waals minimum region there is still poor agreement with the accurate energies, even for the best bases used.

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[1] The density was calculated with the Hartree–Fock limit wave function of Clementi [18], and the fit was done by the least squares method.

If one performs calculations according to formula (3) (see the second part of Table 2) then for bases *A*, *B*, *C* the minimum disappears and for bases *D*, *E*, *F* a quantitative disagreement is corrected and the values of the SCF interaction energy, especially those for Leś' bases, agree quite well with the most accurate SCF results [24, 25]. In Ref. [24] only one figure is reported near the van der Waals minimum region, but more recent results of Reinsch and Meyer [25] obtained with the basis set ($11s/6p/2d/1f$) contracted to [$7s/5p/2d/1f$] are in very good agreement with ours.

It is also important to notice that the Leś' functions yield a very reasonable interaction energy, provided the counterpoise method is used. This implies that an atomic energy criterion is not the only criterion, and not a very sensitive one, of the usefulness of the basis set for investigation of the interaction energy in the supermolecular approach.

Presented results imply the following conclusions:

1) When the SCF interaction energy is to be computed one should always use the counterpoise method.
2) One should not limit oneself only to the bases optimized on energy.
3) It should be strongly emphasized that even the counterpoise method cannot produce reliable results if a poor basis set is used (see basis $(4/2)_D$ in Table 2).

In the above discussion we have limited ourselves to a supermolecular approach on the SCF level only. The same problem, however, appears in other supermolecular methods, such as CI or MCSCF. It was shown [26, 27] that a significant part of the correlation energy might be a result of superposition error.

It is worthwhile to remark on the physically important problem of the investigation of many-body effects. Three- and more-body effects are significantly smaller than two-body ones. Therefore greater accuracy of the calculations and better functions are needed. In this case the system's energies have to be calculated with not only the

Table 1. Comparison of the SCF energies for the Ne atom in various basis sets. The energy is expressed in Hartrees

Basis		E^{SCF}(Ne)	% Deviation from HF Limit
A	$(4/2)_D$	−126.81594	1.3467
B	$(8/4)_D$	−128.49770	0.0384
C	$(4/3/4)_L$	−118.43388	7.8674
D	$(8/4)_D \rightarrow [4/2]$	−128.43097	0.0903
E	$(12/6)_D \rightarrow [8/4]$	−128.54229	0.0037
F	$(6/8/8)_L \rightarrow [8/4]$	−125.54135	2.3382
	$(6/4)_C$ STO (HF limit)	−128.52708	

1. Subscript D denotes Duijneveldt's [22] bases, subscript L denotes Leś' [23] bases, subscript C denotes Clementi's [18] basis assumed as a HF limit.
2. Parentheses are used for uncontracted basis sets, square brackets are used for contracted basis sets.
3. In the case of Leś' bases 1*s* and 2*s* orbitals were expanded on different sets of exponents [23]. The first two figures in the parentheses refer to *s*- and the last to *p*-function.

Table 2. Comparison of the SCF interaction energies calculated with various bases using formulae (2) and (3). The energy and internuclear distance R are expressed in Hartrees and Bohrs (a_0) respectively

	R			
Basis	3.0	4.0	5.0	6.0
		Using formula (2)		
A	5.072 (−2)	3.539 (−4)	−2.482 (−5)	−1.0 (−10)
B	9.734 (−2)	6.385 (−3)	−4.520 (−5)	−2.910 (−5)
C	8.324 (−2)	−1.742 (−3)	−6.810 (−3)	−4.371 (−3)
D	9.570 (−2)	6.632 (−3)	2.621 (−4)	6.002 (−6)
E	1.000 (−1)	8.526 (−3)	6.749 (−4)	3.006 (−5)
F	9.869 (−2)	7.985 (−3)	3.700 (−4)	−1.584 (−4)
		Using formula (3)		
A	8.389 (−2)	1.862 (−3)	4.242 (−6)	1.10 (−8)
B	9.557 (−2)	7.958 (−3)	6.218 (−4)	2.680 (−5)
C	1.055 (−1)	1.006 (−2)	6.501 (−4)	5.853 (−5)
D	9.795 (−2)	7.780 (−3)	5.167 (−4)	1.843 (−5)
E	1.001 (−1)	8.586 (−3)	7.176 (−4)	5.777 (−5)
F	9.978 (−2)	8.660 (−3)	7.441 (−4)	6.374 (−5)
ASCF[a]	9.95 (−2)	8.5 (−3)	7. (−4)	-
RM[b]	-	-	7.427 (−4)	6.34 (−5)

[a] Results from Ref. [24].

[b] Results of Reinsch and Meyer [25] obtained with a basis set $(11s/6p/2d/1f) \rightarrow [7s/5p/2d/1f]$ and also using the counterpoise technique.

"dimer" but also the "trimer" basis set. The influence of this fact on the superposition basis error should be investigated. Work in this direction is in progress in our laboratory.

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