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Procedure supplementing SCF interaction energies by dispersion term evaluated in dimer basis set within variation-perturbation approach

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A variation-perturbation procedure for the evaluation of dispersion interaction, originally proposed by Jeziorski and van Hemert, has been reformulated to include basis set extension effects on an equal footing with the SCF interaction energy, corrected for basis set superposition error (BSSE). This approach has been tested for He_2, $(H_2)_2$, $(H_2O)_2$, and $(C_2H_4)_2$ complexes.

Key words: SCF interaction energies — Dispersion terms — Variation-perturbation approach

1. Introduction

The majority of quantum chemical calculations of intermolecular interactions are still performed within the variational SCF approach neglecting the dispersion contribution, which is significant for nonpolar molecules. On the other hand, the dispersion energies evaluated within the classical perturbation approach seem to be seriously underestimated [1-2], especially if the basis set is not sufficiently extended.

In 1976, Jeziorski and van Hemert developed a variation-perturbation procedure [3] for evaluation of induction and dispersion energies overcoming the difficulty of integration over the continuum spectrum of unoccupied molecular orbitals in the perturbation approach. This method has been successfully applied for the

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water dimer yielding results which have been confirmed in independent theoretical [4] and experimental [5] studies. The aim of the present paper is to derive and test an equivalent but somewhat simpler procedure for evaluation of dispersion energy on an equal footing with the remaining contributions included in the SCF interaction energy [6] corrected for basis superposition effects. This approach has been tested on several dimers (i.e., He_2, $(H_2)_2$, $(H_2O)_2$, and $(C_2H_4)_2$) and compared with available experimental and theoretical results. In addition, we attempted to optimize the basis set in order to reduce its size as far as possible.

2. Method

The classical perturbation expression for dispersion energy $E^{(2)}_{\mathrm{DISP}}$ can be formally written as:

$$E^{(2)}_{\mathrm{DISP}} = 4 \sum_{\substack{i=1\\ \mathrm{occ}}}^{M_\mathrm{A}} \sum_{\substack{j=1\\ \mathrm{occ}}}^{M_\mathrm{B}} D(a_i b_j) \tag{1}$$

where

$$D(a_i b_j) = \sum_{\substack{k=M_A+1\\ \mathrm{vac}}}^{\infty} \sum_{\substack{l=M_B+1\\ \mathrm{vac}}}^{\infty} |\langle a_i(1) a_k(1) | r_{12}^{-1} | b_j(2) b_l(2)\rangle|^2 \times (E_i^\mathrm{A} - E_k^\mathrm{A} + E_j^\mathrm{B} - E_l^\mathrm{B})^{-1}$$

a_i, b_j, a_k, b_l, and E_i^A, E_j^B, E_k^A, E_l^B denote Fock eigenvectors and eigenvalues for occupied (occ) and vacant (vac) molecular orbitals determined for isolated A and B molecules in any atomic basis set (i.e., either monomer or dimer basis set). In general, the pair function, $D(a_i b_j)$, representing the dispersion interaction of occupied orbital a_i with occupied orbital b_j may constitute a lower bound for the Hylleraas-type functional [3, 7-8]:

$$\begin{aligned} D(a_i b_j) &\le J_{ij}(\bar{\psi}) \\ &= \int\!\!\int \bar{\psi}(1,2)\mathcal{P}^\mathrm{A}(1)\mathcal{P}^\mathrm{B}(2)[\mathscr{f}^\mathrm{A}(1) + \mathscr{f}^\mathrm{B}(2) - E_i^\mathrm{A} - E_j^\mathrm{B}]\bar{\psi}(1,2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \\ &\quad + 2\int\!\!\int \bar{\psi}(1,2)\mathcal{P}^\mathrm{A}(1)\mathcal{P}^\mathrm{B}(2)|r_{12}^{-1}|a_i(1)b_j(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2 \end{aligned} \tag{3}$$

where $\bar{\psi}(1,2)$ is an arbitrary square integrable real trial function minimizing J functional, $\mathscr{f}^\mathrm{A}$, $\mathscr{f}^\mathrm{B}$ Fock operators and the operators $\mathcal{P}^\mathrm{A}$ and $\mathcal{P}^\mathrm{B}$ project out of the space spanned by occupied orbitals:

$$\mathcal{P}^\mathrm{A} = 1 - \sum_{\substack{i=1\\ \mathrm{occ}}}^{M_\mathrm{A}} |a_i\rangle\langle a_i|. \tag{4}$$

The trial function $\bar{\psi}(1,2)$ has been assumed in [3] to be spanned by the AB supermolecule atomic orbital set $\{\chi^{\mathrm{AB}}\}$:

$$\bar{\psi}(1,2) = \sum_{r}^{N_\mathrm{AB}} \sum_{s}^{N_\mathrm{AB}} c_{rs}\chi_r(1)\chi_s(2) \tag{5}$$

where c_{rs} are variational parameters to be optimized. In the general case, this leads to a set of N_{AB}^2 inhomogeneous linear equations. One may significantly reduce computational efforts needed to get all c_{rs} coefficients by applying proper linear transformations on the atomic basis set $\{\chi^{\mathrm{AB}}\}$ to diagonalize the $\mathscr{P}^{\mathrm{A}} f^{\mathrm{A}} \mathscr{P}^{\mathrm{A}}$ and $\mathscr{P}^{\mathrm{B}} f^{\mathrm{B}} \mathscr{P}^{\mathrm{B}}$ operators [9]. In the original approach of Jeziorski and van Hemert [3], this was achieved by means of canonical orthogonalization [10] of the $\mathscr{P}_{\chi}^{\mathrm{B}}$ and $\mathscr{P}_{\chi}^{\mathrm{B}}$ sets and subsequent transformations of the orthogonalized sets to diagonalize Fock operators.

In the present approach, we avoid performing any basis set transformations by assuming the trial function $\bar{\psi}(1,2)$ to be spanned by the *molecular* orbital sets $\{a^{\mathrm{AB}}\}$ and $\{b^{\mathrm{AB}}\}$ obtained for isolated molecules A and B, within the AB *supermolecular* atomic orbital basis set χ^{AB} (in general, any atomic basis set could be assumed):

$$\bar{\psi}(1,2) = \sum_{x}^{N_{\mathrm{AB}}} \sum_{y}^{N_{\mathrm{AB}}} c_{xy} a_x^{\mathrm{AB}}(1) b_y^{\mathrm{AB}}(2). \tag{6}$$

Taking into account the orthonormality of the a^{AB} and b^{AB} sets and substituting (6) into expression (3), one may readily obtain:

$$\begin{aligned} J_{ij}[\bar{\psi}(1,2)] = \sum_{k=M_{\mathrm{A}}+1}^{N_{\mathrm{AB}}} \sum_{l=M_{\mathrm{B}}+1}^{N_{\mathrm{AB}}} & [c_{kl}^2 (E_k^{\mathrm{A(B)}} - E_i^{\mathrm{A(B)}} + E_l^{\mathrm{B(A)}} - E_j^{\mathrm{B(A)}}) \\ & + 2c_{kl} \langle a_i^{\mathrm{AB}}(1) a_k^{\mathrm{AB}}(1) | r_{12}^{-1} | b_j^{\mathrm{AB}}(2) b_l^{\mathrm{AB}}(2) \rangle]. \end{aligned} \tag{7}$$

At the minimum of $J_{ij}[\bar{\psi}(1,2)]$ functional we have:

$$\frac{\partial J_{ij}[\bar{\psi}(1,2)]}{\partial c_{kl}} = 0 \tag{8}$$

so the optimal variational coefficients c_{kl} are:

$$c_{kl} = \langle a_i^{\mathrm{AB}}(1) a_k^{\mathrm{AB}}(1) | r_{12}^{-1} | b_j^{\mathrm{AB}}(2) b_l^{\mathrm{AB}}(2) \rangle (E_i^{\mathrm{A(B)}} - E_k^{\mathrm{A(B)}} + E_j^{\mathrm{B(A)}} - E_l^{\mathrm{B(A)}})^{-1}. \tag{9}$$

Thus,

$$\begin{aligned} D(a_i b_j) \leq \sum_{\substack{k=M_{\mathrm{A}}+1 \\ \mathrm{vac}}}^{N_{\mathrm{AB}}} \sum_{\substack{l=M_{\mathrm{B}}+1 \\ \mathrm{vac}}}^{N_{\mathrm{AB}}} & \langle a_i^{\mathrm{AB}}(1) a_k^{\mathrm{AB}}(1) | r_{12}^{-1} | b_j^{\mathrm{AB}}(2) b_l^{\mathrm{AB}}(2) \rangle^2 \\ & \times (E_i^{\mathrm{A(B)}} - E_k^{\mathrm{A(B)}} + E_j^{\mathrm{B(A)}} - E_l^{\mathrm{B(A)}})^{-1}. \end{aligned} \tag{10}$$

This equation (10) is quite similar to the classical Møller-Plesset perturbational expression (11), but the summation over the continuous set of virtual orbitals in (2) has been replaced by a sum over discrete orbital energies in (11)

$$\begin{aligned} D(a_i b_j) = \sum_{k=M_{\mathrm{A}}+1}^{N_{\mathrm{A}}} \sum_{l=M_{\mathrm{B}}+1}^{N_{\mathrm{B}}} & \langle a_i^{\mathrm{A}}(1) a_k^{\mathrm{A}}(1) | r_{12}^{-1} | b_j^{\mathrm{B}}(2) b_l^{\mathrm{B}}(2) \rangle^2 \\ & \times (E_i^{\mathrm{A}} - E_k^{\mathrm{A}} + E_j^{\mathrm{B}} - E_l^{\mathrm{B}})^{-1}. \end{aligned} \tag{11}$$

Using monomer atomic basis sets $\{a^{\mathrm{A}}\}$ and $\{a^{\mathrm{B}}\}$ for isolated monomers in (6), the dispersion energy obtained from (10) will be equivalent to the classical

Table 1. Dispersion energy for interaction of two hydrogen molecules (rectangular geometry, $R = 5.5$ a.u.) in [kcal/mol]

		A3 basis plus 1*s* bond orbital with α exponent				Other results for a dispersion energy calculation
	A3 basis	0.05	0.1	0.2	0.4	
$E_{\mathrm{DISP}}{}^{a}$	−0.1783	−0.1975	−0.1987	−0.1929	−0.1748	-0.1776^{c}
$E_{\mathrm{DISP}}{}^{b}$	−0.2178	−0.2327	−0.2336	−0.2300	−0.2162	
						$-0.2614^{c,d}$
						-0.2855^{d}
						-0.251^{d}

[a] Classical perturbational formula (11) (monomer in monomer basis set)
[b] Variation-perturbation formula (10) (monomer in dimer basis set)
[c] Ref. [12]
[d] Epstein-Nesbet formula [16]

perturbational expression (11) (Møller-Plesset). However, any extension of the atomic basis set beyond monomer set size will result in an increase in the number of discrete virtual states providing a better estimate of dispersion energy. From the viewpoint of computational economy, the dimer basis set $\{\chi^{AB}\}$ may provide the optimal choice. The time consuming two electron integrals have to be calculated within the dimer basis set to evaluate the remaining SCF interaction energy contributions corrected by Boys' counterpoise method [11]. So, using (10) at quite little expense, one may significantly improve dispersion energy estimates over the classical perturbation approach (11). Thus, the method based on equation (10) seems to supplement in a natural way the SCF interaction energy corrected for basis set superposition effects [6] by means of the counterpoise correction [11] where monomer energies and wave functions have to be calculated in dimer basis set also.

$$\Delta E_{\mathrm{SCF}} = E_{\mathrm{AB}} - E_{\mathrm{A(B)}} - E_{\mathrm{B(A)}} = E^{(1)}_{\mathrm{EL}} + E^{(1)}_{\mathrm{EX}} + E^{(R)}_{\mathrm{IND}} \tag{12}$$

$E^{(1)}_{\mathrm{EL}}$ denotes the first order electrostatic
$E^{(1)}_{\mathrm{EX}}$ – first order exchange and
$E^{(R)}_{\mathrm{IND}}$ – higher order induction energy.

One should note that a further increase of theoretical dispersion energy estimates could result from applying Epstein-Nesbet partitioning of the total hamiltonian [12, 13] resulting in shifting of denominators of (10) and (11) by replacing the differences between orbital energies by the differences of the related excitation energies. However, as the Epstein-Nesbet approach is basis set dependent and not strictly bound [12, 13], we use in this study the Møller-Plesset partition of hamiltonian [14] only.

3. Sample test results

In order to evaluate the physical utility of the present approach, the intermolecular interaction energies have been calculated within the SCF method, corrected for

BSSE and supplemented by the dispersion contribution evaluated from the classical perturbation formula (11) and within the variation-perturbation approach (10) utilizing the dimer basis set. Calculations have been performed for hydrogen dimer $(H_2)_2$, which was primarily our numerical test case for equation (11), and for He_2, for which extensive literature data are available. The next two cases: water dimer $(H_2O)_2$ and ethylene dimer $(C_2H_4)_2$ are already in the range of chemists' interests.

Interaction of two hydrogen molecules is quite weak and is dominated by the dispersion term. Results reported in [16] allowed us to test our program, comparing our results from equation (11) with those reported by Kochanski [12]. The rectangular dimer ($R = 5.5$ a.u.) has been examined within the $(4, 1) \rightarrow [2, 1]$ basis set taken from [12] (basis A3 in the nomenclature of Ref. [12]). Extension of this basis by supplementing it by 1*s* bond orbital with optimized exponent brings the dispersion energy closer to the results of Jaszunski, et. al. [15].

He_2 is also a case of very weak physical interaction dominated by dispersion energy. The *s* and *p* part of extended (8, 2, 1, 1) basis set contracted to [1, 2, 1, 1] reported in [16] has been used in this work. Instead of pure *d* orbitals, the lobe representation of it was employed. Each set of *d* orbitals was represented by 12 or 6 symmetrically placed 1*s* lobe functions around each atom. The distance *x* between lobes and nuclei has been determined according to the approximate Whitten rule:

$$x = \frac{(0.3)^{-1/2}}{\alpha}$$

where α denotes *d* orbital exponent [17, 18]. According to previous theoretical studies [16, 19], the dispersion energy is quite strongly dependent on the value of the polarization function exponents. In Table 2, the interaction energy components have been presented as a function of lobe function exponent α. In the case of He_2, the optimal α values reported previously for *d* polarization functions

Table 2. He–He interaction energy components in [kcal/mol] as a function of the lobe polarization function exponent α ($R = 5.6$ a.u.)

	α (12 lobe functions/atom)				α (6 lobes/ atom)	Other results
	0.16	0.21897[c]	0.28	0.48	0.21897	
E_A^{SCF}	−2.859063	−2.859056	−2.859044	−2.859038	−2.859055	
E_{DISP}[a]	−0.0278181	−0.0293121	−0.0292580	−0.0270865	−0.0204885	
E_{DISP}[b]	−0.0285719	−0.0305880	−0.0310766	−0.0290272	−0.0218587	−0.03201[d]
ΔE_{SCF}	0.0194270	0.0189593	0.0184500	0.0162386	0.0189561	0.019333[d]
$\Delta E_{SCF} + E_{DISP}$	−0.0091449	−0.0116288	−0.0126266	−0.0127886	−0.0029036	−0.012698[d]

[a] Dispersion energy obtained from classical formula (11)

[b] Dispersion energy obtained within variational-perturbational approach (10)

[c] Chałasinski and Jeziorski optimal value of α [15]

[d] Ref. [15]

Table 3. Water dimer interaction energy components (geometry from [22]) in kcal/mol for different number and exponent α of ghost orbitals

	4 additional lobe functions/oxygen				6 additional lobe functions/oxygen			s, p basis	Other
	0.1	0.278[b]	0.2	0.4[c]	0.1	0.2	0.278	only	results
E_A^{SCF}	−76.0449	−76.0471	−76.0450	−76.0483	−76.0451	−76.0460	−76.0478	−76.0430	−76.0576[e]
E_{DISP}[a]	−0.7125	−0.7605	−0.7748	−0.7314	−0.7636	−0.8824	−0.8724	−0.5518	
E_{DISP}[d]	−1.2437	−1.2738	−1.3976	−1.2122	−1.6500	−1.9545	−1.4819	−0.9547	−1.54[c]
ΔE_{SCF}	−3.3880	−3.1479	−3.1720	−3.1940	−3.3462	−3.0803	−2.9822	−3.8220	−3.87[c]
$\Delta E_{SCF} + E_{DISP}$[d]	−4.6317	−4.4217	−4.5696	−4.4062	−4.9962	−5.0348	−4.4641	−4.7767	−5.41[e]

[a] Classical perturbation formula (11)
[b] Kochanski optimal value Ref. [19]
[c] Jeziorski, van Hemert value Ref. [3]
[d] Variation-perturbation formula (10)
[e] Value estimated in Ref. [20]

of Cartesian Gaussian form are $\alpha = 0.14$ [19] and $\alpha = 0.21897$ [16]. The value of the dispersion energy $E^{(2)}_{\mathrm{DISP}} = -0.03107$ kcal/mole obtained for $R = 5.6$ a.u. with the optimal exponent found in this study ($\alpha = 0.28$) is very close (within 3%) to the value reported by Chałasinski and Jeziorski [16] ($E^{(2)}_{\mathrm{DISP}} = -0.0320$ kcal/mole).

The water dimer and the ethylene dimer represent a wide class of molecular complexes where the role of the dispersion term is still a matter of dispute [2–3, 15, 20]. Up to now, one of the most reliable calculations of dispersion energy for $(H_2O)_2$ has been done within the variation-perturbation method [3] in an extended (11, 7, 2/6, 1)→[4, 3, 2/2, 1] basis set. In the present study, we used only the *sp* part of the above mentioned basis set described in [22]. In addition, we represented polarization functions in two ways: a) by placing symmetrically four 1*s* lobe functions around each oxygen atom in the symmetry plane of the complex at its assumed geometry [22], and (b) by locating symmetrically six 1*s* lobe functions around each oxygen atom. In both cases, we have optimized the exponent of the off-centre lobe function (Table 3). The dispersion energy seems to be very sensitive to the variation of the polarization function exponent, reaching extreme values for very diffuse functions. This could explain quite significant differences between previously reported dispersion energy values for $(H_2O)_2$ ranging from −1.9 to −0.3 kcal/mol [3, 20–22] where the value of the polarization function exponent was more or less arbitrarily assumed to minimize the energy or to reproduce the molecular dipole moment. The use of the dimer basis set in (11) leads to much greater dispersion energies in agreement with the recent study of Kestner et al. [21] where counterpoise correction was applied within Møller–Plesset approach.

The ethylene dimer represents here a new class of molecular $\pi - \pi$ complexes. In this study, we have used a parallel "sandwich" arrangement of ethylene monomers with interplanar distance 5 a.u. (orientation 1 in Ref. 2) and 4-31G basis set. The resulting dispersion energies evaluated in dimer basis set (10) and monomer basis set (11) are −7.334 kcal/mol and −4.209 kcal/mol (in agreement with the value −4.208 kcal/mol reported by Suzuki et al. [2]). As before, the use of the dimer basis set in (10) results in a substantial increase of dispersion energy.

4. Conclusions

The procedure outlined above utilizing dimer basis sets for monomers in the Møller–Plesset formula (10) seems to be an optimal, but still arbitrary, way to evaluate dispersion energy in a way consistent with other interaction energy components evaluated within the SCF approach corrected for BSSE. Additional support for using the dimer basis set may be found in recent papers of Chałasinski [23, 24].

Our calculations, like other post-SCF calculations, emphasize the importance of a proper choice for the basis; a good SCF basis is seldom an optimal post-SCF basis. But the addition of polarization functions to a good SCF basis set is an indispensable first step [24]. This still does not provide a remedy for the problems of an incomplete basis; semiempirical models may then be needed to make up for the deficiencies. It is encouraging that simple atom-atom CR^{-6} potentials are capable to represent dispersion energy correctly [25, 26].

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