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AB INITIO SIMPLIFIED CALCULATION OF THE INTERMOLECULAR INTERACTION ENERGY*

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The SCF interaction energy between two molecules is approximated by a combination of the first-order perturbation interaction energies between deformed and undeformed interacting molecules. The molecular orbitals used in the undeformed molecules and in the deformation potentials are obtained by the least-square fit approximation to the primary molecular orbitals. Numerical results for the linear configuration of the hydrogen molecule dimer are in a fair agreement with the SCF interaction energies.

1. *Introduction and method*

It is well known that the Self Consistent Field (SCF) interaction energy between two closed-shell molecules, evaluated as the difference of the respective total energies calculated by the SCF method, can be approximated by the sum of the electrostatic, valence-repulsion and induction interaction energies. The accuracy of such an approximation is greater when the molecules are charged or their permanent dipole or quadrupole moments are not very small and when the intermolecular distance is large. The electrostatic and valence-repulsion energies belong to the first-order perturbation energy and can be evaluated by several methods (see e.g. [1–8]). The induction energy can be calculated as the sum of some terms obtained from the variation-perturbation procedure [5], but, as mentioned above, can be in some cases assumed as the difference of the SCF and first-order interaction energies. All the calculations quoted above need the complete number of the molecular integrals used in the SCF dimer calculations. This is probably the reason why the SCF interaction energy calculations rather than the perturbation ones are practised by most of the investigators.

Some simplifications in the calculation of the molecular orbitals used in order to calculate the induction energy were introduced by Piela and Andzelm [6, 9]. They took as these

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orbitals the molecular orbitals (MOs), deformed by the field of other molecules represented by either the exact molecular density calculated with some basis set or the point charges (exact charges in the case of the atomic ions and the Mulliken charges in the case of the water molecule). They calculated the induction energy as the difference of the mean values of the hamiltonian with the wavefunction built of the deformed and undeformed MOs, respectively.

The purpose of the present contribution is to calculate the sum of the first- and second-order interaction energies in a simplified way, using a considerably reduced number of integrals in comparison with the SCF dimer calculations. Our method can be illustrated by some formulas for the interaction energy in the polarization approximation.

Let $F_A(1, \ldots, n_A)$ and $F_B(n_A+1, \ldots, n_A+n_B)$ be the normalized unperturbed wave functions of the molecule A with n_A electrons and of the molecule B with n_B electrons, respectively. Let the normalized wave function of the molecule A deformed by the electrostatic molecular potential of the molecule B be (F_A+f_A) and the respective wave function of the molecule B be (F_B+f_B). In order to simplify our formulas, let us assume that F_A, F_B, f_A and f_B are real. It is well known that $(E^{(1)}+E^{(2)})$, i.e. the sum of the first- and second-order corrections to the energy, is given by

$$E^{(1)}+E^{(2)} = \langle F^{(0)}|V|F^{(0)}+F^{(1)}\rangle, \tag{1a}$$

where V is the hermitian perturbation operator and $F^{(0)}$, $F^{(1)}$ is the unperturbed wave function and its first-order correction, respectively. Let us assume that V is the intermolecular interaction potential for the AB system and that for this system $F^{(0)} = F_AF_B$. If the charge transfer and intermolecular overlap effects are small, the perturbed wave function, $F^{\text{pert}} = F^{(0)}+F^{(1)}$, can be replaced by $(F_A+f_A)(F_B+f_B)$ and the sum $(E^{(1)}+E^{(2)})$ can be replaced in this case by

$$\begin{aligned} E^{\text{int}} = \int d\tau((F_A+f_A)\,(1, \ldots, n_A)\times(F_B+f_B)\,(n_A+1, \ldots, n_A+n_B)\times V \\ \times F_A(1, \ldots, n_A)\times F_B(n_A+1, \ldots, n_A+n_B)), \end{aligned} \tag{1b}$$

or

$$\begin{aligned} E^{\text{int}} = \int d\tau(F_A(1, \ldots, n_A)\times(F_A+f_A)\,(1, \ldots, n_A)\times V \\ \times F_B(n_A+1, \ldots, n_A+n_B)\times(F_B+f_B)\,(n_A+1, \ldots, n_A+n_B)). \end{aligned} \tag{1c}$$

It can easily be proved that, when our assumptions hold, our approximate interaction energy

$$\begin{aligned} E_{\text{a}}^{\text{int}} = \tfrac{1}{2}\int d\tau((F_A(1, \ldots, n_A))^2\times V\times((F_B+f_B)\,(n_A+1, \ldots, n_A+n_B))^2 \\ +(F_B(n_A+1, \ldots, n_A+n_B))^2\times V\times((F_A+f_A)\,(1, \ldots, n_A))^2) \end{aligned} \tag{2a}$$

differs only in third- and higher-order correction terms from E^{int} given by (1c) and that the normalization terms are also third- and higher-order correction ones. We propose to use $E_{\text{a}}^{\text{int}}$ instead of E^{int}.

Up to now, we did not obtain any reduction in the number of the molecular integrals in comparison with the SCF dimer calculations. Now, let us approximate F_A, F_B and $E_{\mathrm{a}}^{\mathrm{int}}$ by F_{Aj}, F_{Bj} and $E_{\mathrm{a},j}^{\mathrm{int}}$, respectively, where

$$E_{\mathrm{a},j}^{\mathrm{int}} = \tfrac{1}{2}\int d\tau((F_{Aj}(1, \ldots, n_A))^2 \times V \times ((F_B+f_{Bj})(n_A+1, \ldots, n_A+n_B))^2 \\ +(F_{Bj}(n_A+1, \ldots, n_A+n_B))^2 \times V \times ((F_A+f_{Aj})(1, \ldots, n_A))^2) \tag{2b}$$

and f_{Aj}, f_{Bj} means that these deformation corrections are evaluated by using the molecular potential calculated from F_{Bj} and F_{Aj} wave functions, respectively.

We will discuss hereafter the interaction of the closed-shell molecules and limit ourselves to the one-electron approximation i.e. use Slater determinants as F_A and F_B wave functions. The F_{Aj} and F_{Bj} wave functions will be the Slater determinants built of the MOs being the approximation to the primary MOs, obtained by the least-square fitting. Since e.g. the MOs of F_{Aj} can contain very small number of primitive atomic orbitals in comparison with the MOs of F_A, the number of the molecular integrals used in the calculation of the approximate interaction energy can be considerably reduced, in comparison with the complete number of dimer integrals.

The evaluation of our $E_{\mathrm{a},j}^{\mathrm{int}}$ contains formally the calculation of two first-order electrostatic interaction energies, the first one between the molecules described by F_{Aj} and (F_B+f_{Bj}) wave functions and the second one between the molecules described by F_{Bj} and (F_A+f_{Aj}) wave functions. In order to take into account the exchange effects in the interaction energy, we calculated not only the electrostatic energies mentioned above, but the respective first-order interaction energies with the appropriate antisymmetrization, as proposed by Löwdin [3] and performed e.g. by Andzelm and Piela [6].

In order to test our approximations, we perform calculations of the interaction energy between two hydrogen molecules in the linear dimer. The H_2 dimer has been studied by many investigators (see e.g. [7, 8, 10] and references therein) and the results obtained so far can be used for the comparison. In such a system the charge-transfer effect should be very small. Since the molecular density used in the deformation potential can hardly be replaced by the point charges, the use of the approximate orbitals seems to be useful.

Our primary basis set, used for the calculation of the primary MOs, is given in Table I. It is composed of the simple spherical Gaussian Type Orbitals (GTOs). The symbols in the first row of Table I denote the consecutive number of the GTO, its centre, its exponent and its coefficient in the contract, respectively. All the values, including exponents, are given in atomic units, the GTOs are normalized. The centre H1 denotes one hydrogen nucleus, the centre HCEN denotes the centre (midpoint) of the H_2 molecule. Only the GTOs with the consecutive numbers 4–7 are contracted in one contract, others presented in Table I are uncontracted. The 7 GTOs centered on other hydrogen nucleus, which can be labelled H2, are not given in Table I, but they have the same exponents and coefficients as in the respective GTOs labelled 1–7.

The primary basis set was constructed by one of us (A. L.) as an approximation of the Kołos and Roothaan MO [11]. The description of the used method and the detailed discussion of the basis set was given elsewhere [12, 13]. The energy of the ground state of H_2 molecule obtained with this basis set is $E(H_2) = -1.133378458$.

TABLE I

Primary basis set

No	Centre	Exponent	Coefficient
1	H1	0.0948	1.0
2	H1	0.1988	1.0
3	H1	0.4252	1.0
4	H1	1.168	0.1044890
5	H1	3.676	0.0417543
6	H1	15.61	0.0102140
7	H1	143.1	0.0010082
8	HCEN	0.04129	1.0
9	HCEN	0.4958	1.0
10	HCEN	1.895	1.0

The approximate MOs are given in Table II. The meaning of the symbols is the same as in Table I, except of the second index in the first column. In the MO called hereafter F_3 nad being the linear combination of 3 GTOs, the second index in the first column is equal to 3, in the respective F_6 six-term MO it is equal to 6. Our MOs were obtained by the least-square approximation (fit) of the primary MO. The method of the fitting was the same as used by Reeves and Fletcher [14] and continued by other investigators [15–16], but in our case all the integrals are calculated analytically.

TABLE II

Approximate molecular orbitals

No	Centre	Exponent	Coefficient
1, 3	H1	0.98242381	0.28791462
2, 3	H2	0.98242381	0.28791462
3, 3	HCEN	0.17027561	0.61411106
1, 6	H1	2.66603	0.09797368
2, 6	H1	0.400428	0.29767592
3, 6	H2	2.66603	0.09797368
4, 6	H2	0.400428	0.29767592
5, 6	HCEN	0.909846	0.10652628
6, 6	HCEN	0.113396	0.32599211

The induction (or polarization) of one hydrogen molecule ($M1$) by the other ($M2$) is taken into account by calculating the deformation of $M1$ with the primary MO by the field of the $M2$ molecule. The deformed primary MO is calculated as the SCF MO of the $M1$ molecule with the additional electrostatic deformational molecular potential due to the charge distribution in the $M2$ molecule. This charge distribution is calculated using the approximate MO.

In order to evaluate the approximate interaction energy, we calculate the first-order interaction energy between the $M1$ molecule with the deformed primary MO and the $M2$ molecule with the approximate MO. In such an approximation the third- and higher-order effects of intermolecular interaction are not taken into account properly, but, on the other hand, the number of the molecular integrals used is considerably reduced in comparison with the full SCF dimer calculations in the primary basis set.

Both the deformation and first-order interaction energy calculation are performed using the programs written by Andzelm and applied previously in his investigation of the LiF crystal [6, 17]. The SCF interaction energies with the primary basis set are also calculated for the sake of the comparison. In the SCF calculations we apply the counterpoise method of correcting the superposition errors (basis set effect) [18, 8, 19]. In all our calculations the value of 1.4 a.u. for the internuclear distance is assumed for the isolated hydrogen molecule.

2. *Results and discussion*

The values of the interaction energy, given in 10^{-4} a.u., are presented in Table III. The symbol in the first column, d, denotes the distance between the centres (midpoints) of the H_2 molecules in the linear dimer presented also in Fig. 1 of Ref. [8]. The symbols V and V_c denote the variational (SCF) interaction energies for the primary basis set, calculated without and with the counterpoise correction, respectively. The counterpoise corrected SCF interaction energy for Basis V and the uncorrected (but practically equal to the corrected one) for Basis IX of Urban and Hobza [7, 8] are denoted by UHV and UHIX, respectively. Our approximate interaction energies between deformed and undeformed molecules are denoted by EF_6 and EF_3 for F_6 and F_3 approximate MO, respectively. The respective interaction energies between underformed molecules (first-order interaction energies) are denoted by EF_6^1 and EF_3^1.

TABLE III

Interaction energies in 10^{-4} a.u.

d	V	V_c	EF_6	EF_6^1	EF_3	EF_3^1	UHV	UHIX
8.5	0.272	0.328	0.329	0.335	0.344	0.351	—	—
7.5	0.663	0.802	0.781	0.794	0.711	0.729	0.62	0.88
7.0	1.241	1.429	1.420	1.437	1.157	1.185	1.10	1.53
6.5	2.545	2.798	2.920	2.922	2.168	2.202	2.18	2.94
5.5	12.553	13.071	15.686	15.172	11.625	11.339	10.85	13.16

The SCF interaction energies obtained for Basis IX of Urban and Hobza [7, 8], practically equal to those of Jaszuński et al. [10], are probably the most accurate among all such results. Therefore, they are quoted in Table III. The counterpoise corrected results for Basis V are the best among all those corrected and uncorrected for small and intermediate basis sets of Urban and Hobza. The calculations for Basis V need, in our opinion, at least 3 times more computation time than ours using the F_6 MO.

The Coulomb and exchange contributions to the approximate interaction energy are presented in Table IV. The symbols CF_6, CF_6^1, CF_3, CF_3^1 denote the Coulomb interaction energies appropriate to the EF_6, EF_6^1, EF_3, EF_3^1, respectively. The EXF_6 and EXF_3 symbols denote the exchange energies defined by $EXF_j = EF_j - CF_j$ where $j = 6,3$. The EF_6^i and EF_3^i energies are defined by $\mathrm{EF}_j^i = CF_j + EXF_j^1$ where $EXF_j^1 = EF_j^1 - CF_j^1$ and $j = 6,3$.

TABLE IV

Coulomb and exchange contributions in 10^{-4} a.u.

d	CF_6	CF_6^1	CF_3	CF_3^1	EXF_6	EXF_3	EF_6^i	EF_3^i
8.5	0.301	0.307	0.333	0.340	0.028	0.011	0.329	0.344
7.5	0.514	0.532	0.591	0.612	0.267	0.120	0.776	0.708
7.0	0.636	0.671	0.771	0.811	0.785	0.368	1.401	1.145
6.5	0.682	0.760	0.936	1.021	2.238	1.232	2.844	2.117
5.5	−0.851	−0.334	0.063	0.585	16.537	11.562	14.655	10.817

As it can be proved from Table III, our EF_6 results are in a good agreement with the counterpoise corrected SCF ones, for large intermolecular distances, where the exchange and higher-order effects are small. The agreement for $R = 5.5$ a.u. is not so good, but for such internuclear distances the relation $EF_6 < EF_6^1$ does not hold. This means that for small R the MOs of the molecule A calculated by minimizing the energy of the molecule A deformed by the electrostatic molecular potential of the molecule B are not close to those MOs of the molecule A which minimize the first order interaction energy, including exchange, between deformed molecule A and undeformed molecule B. The electron density in the deformed molecule A is in such a case too much shifted towards the molecule B. Therefore, the increment of the exchange or valence-repulsion interaction energy is very great, for $R = 5.5$ a.u. even greater than the "pure" induction energy i.e. the increment in the attractive Coulomb energy. On the other hand, it is evident that the induction or deformation effects should reduce the total energy i.e. EF_j should be lesser than EF_j^1, where j labels the approximation used for MOs. Therefore, in order to improve our method, the exchange effects should be taken into account in the deformation calculation. If they were, the increments of the exchange and attractive Coulomb interaction energies should be reduced, in comparison with their present values, in such a way, that the total energy should also be reduced. Therefore, if we denote such improved interaction energy by E_cF_j, we can write

$$EF_j^i < E_cF_j < EF_j^1. \tag{3}$$

As it can be seen from Tables III and IV, the absolute values of the relative differences $(EF_6^1 - V_c)$ and $(EF_6^i - V_c)$ do not exceed 17% for $R = 5.5$ a.u. and 5 % for greater R. This suggests that our method is useful also in the part of the region, where the exchange is important. The V_c (SCF) interaction energies are better approximated by 6-term than by 3-term results, (better agreement of some 3-term results for $R = 5.5$ a.u. is fortuitous) as it should be. We find $EF_6 > EF_3$ and $EF_6^1 > EF_3^1$ for all R, except for $R = 8.5$ a.u. Urban and Hobza [8] also find that their first order interaction energy (approximately equal to our EF_j^1) becomes less repulsive when going from a large basis set to a small one, but they do not comment this effect. The comparison of the exchange energies presented in Table IV suggests that it is due to the underestimation of the exchange interaction energy in the calculations using small basis sets, in our case using the F_3 MOs. When the exchange interaction energy is very small, in our calculations for $R = 8.5$ a.u., this effect is invisible. It is interesting that the "pure" or "polarization" induction energies, $CF_6 - CF_6^1$ and $CF_3 - CF_3^1$, are almost equal. Therefore, the electrostatic molecular potential can be well described by using the least-square fitted MOs, even for relatively short expansions.

The numerical results suggest that it would be possible to calculate the first-order and induction interaction energy, between two closed-shell systems with not very small permanent dipole or quadrupole moments, within an approximation such as ours, instead of using the time-consuming SCF or perturbational methods of calculation.

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