CALCULATION OF THE VALENCE-REPULSION ENERGY USING APPROXIMATE MOLECULAR ORBITALS FITTED WITH THE INTERMOLECULAR OVERLAP FACTOR*

By K. Pecul

Quantum Chemistry Laboratory, University of Warsaw**

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A new method for the calculation of the valence-repulsion intermolecular interaction energy is proposed. The primary molecular orbital of the interacting molecule is substituted, in respective formulas, by an orbital fitted using a least-square deviation method. The weight factor used in this method depends on the approximate molecular orbital of the other molecule. The valence-repulsion first order exchange energies of the interaction between two H_2 molecules in the linear dimer are in agreement with the results obtained using the primary molecular orbitals.

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1. Introduction and methods

It is known that two kinds of effects can be distinguished in the interaction of two closed-shell molecules namely "long-range interaction", i.e., electrostatic, induction and dispersion, and "short-range" or "valence-repulsion" interaction. The "long-range" effects can be related to some properties of the isolated molecules, i.e., multipole moments, electric charge distribution, static and dynamic polarizabilities. Many simplified methods using these relations have been already proposed [1–5]. However, the valence-repulsion energy cannot be related to any known property of the interacting molecules.

Since conventional ab-initio, e.g., SCF or variation–perturbation [6] methods cannot be effectively applied in the calculation of the valence-repulsion interaction between large polyatomic molecules, some simplified methods have been proposed. However, the problem of the effective calculation of the valence repulsion energy has not been solved, even for the calculation of the first-order exchange "repulsion" energy. Let us discuss some difficul-

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** Address: Pracownia Chemii Kwantowej, Instytut Podstawowych Problemów Chemii, Uniwersytet Warszawski, Pasteura 1, 02-093 Warszawa, Poland.

ties related to this first-order exchange energy problem and propose a simple method which seems to be useful in such calculations.

Let us consider the interaction of two closed-shell systems, A and B. Let the wave functions of these systems be given in the SCF MOLCAO approximation. These wave functions are built of m_a and m_b molecular orbitals (MOs) denoted by a_j and b_k, which are linear combinations of NP_a and NP_b primitive (e.g., simple gaussian) atomic orbitals (AOs), contracted in NC_a and NC_b contracts (groups), respectively. The most time-consuming operation in the evaluation of the "valence-repulsion" first order exchange energy, E_{rep}, is the calculation of the molecular integrals of the type:

$$K(i, j; k, l) = \int dr_1 dr_2 c_i(1) c_j(1) (r_{1,2})^{-1} c_k(2) c_l(2), \tag{1}$$

where the integration is over the spatial coordinates of electrons 1 and 2; $r_{1,2}$ is the inter-electronic distance; $c_i(1)$ is the symbol of the MO of the electron 1, and can be either a_i or b_i MO. In the process of the calculation of the K integrals the number of the molecular integrals approximately proportional to $(NP_a)^2(NP_b)^2$ have to be calculated first. As the second stage, the transformation of the $(NC_a)^2(NC_b)^2$ integrals have to be performed. Both operations require very much computer time and memory for large basis sets, i.e., for large NP and NC numbers.

In order to make these calculations less expensive, several methods of replacing the primary c_i MOs by some shorter expansions have been proposed [6–11, 12, 15–20, 23, 24].

The methods presented e.g. in Refs. [7, 8] consist in forcing the approximate MOs to satisfy some equations fulfilled by the primary MOs. Similar in procedure is the method of Overlap Matched Atomic Orbitals (OMAO) proposed by Cusachs et al. [12] and discussed e.g. by Sokalski and Chojnacki [13, 14]. Since there exists no criterion which can be used for the improvement of the approximate MOs in the methods discussed in Refs. [6–8, 12–14], all these methods are of a limited accuracy. The same can be said about the methods for the calculation of E_{exch} with the simplifications based on the Mulliken [15] or similar approximations [16–19], the most general of them are introduced by Gołębiewski et al. [19].

The methods that fit the approximate MOs to the primary ones by minimizing of the square deviation functional, which can be used as a criterion for comparison of different fits, offer in principle the possibility for a desirable improvement in the approximation. The square deviation functional can be defined as:

$$SDF = \int dr (f_c(\mathbf{r}, A) - g_c(\mathbf{r}, A))^2 W(\mathbf{r}), \tag{2}$$

where the $W(\mathbf{r})$ is a non-negative weight function; the meaning of other symbols is given in the Appendix. The applicability of the approximate orbital, g_c, to the concrete problem, depends on the choice of the W function.

The most natural choice of $W(\mathbf{r})$ appears to be $W = 1$. Such an approximation was applied to determine the AOs used in the SCF calculations [20–22] and recently to determine the MOs used in the perturbational calculation of the intermolecular interaction energy ([11] quoted hereafter as Paper I). The methods of Clementi [23] and Ahlrichs [24] are also special cases of this approximation. The interaction energies presented in Paper I for

the linear H_2 dimer were in good agreement with the SCF results, but it seems that this agreement is not so good when first- and second-order exchange effects are more important than "classical" electrostatic and induction interaction energies, e.g., in the interaction of the rare-gas atoms. The MOs fitted with $W = 1$ should reproduce well the intramolecular overlap density, $a_i a_j$, but not the intermolecular overlap density, $a_i b_j$, for great intermolecular distance. The same can be said about the truncation of contracts performed by Gołębiewski et al. [19], who retained in their contracts the terms with the biggest absolute values of the linear coefficients.

An interesting choice of the W was proposed by Leś [9, 10] who assumed $W = (rf_c)^{-2}$ where r is the distance from the centre of the system. The MOs determined in such a way were successfully used in the calculation of the interatomic interaction energy [9, 25]. The exponents of their AOs were also used for the construction of the basis set in the SCF calculations ([26] and Paper I). However, this method is not free from some fundamental shortcomings, which have not been discussed until now. Namely, if $W = (rf_c)^{-2}$ is inserted in formula (2), the integrand can have singularities in all the points, where $f_c = 0$. Moreover, when r tends to infinity, the integrand either tends to infinity, whenever g_c/f_c tends to infinity, or to a constant value, if this is not the case. Therefore, if formula (2) is strictly applied, it is impossible to find the minimum of *SDF*, unless g_c and f_c have the same asymptotic behaviour, which does not hold in general. In order to avoid the problems mentioned above, the integration is limited to some finite area. The size of this area is not uniquely defined, and this introduces some arbitrariness into the method. The method gives good results when the primary MOs are close to the $1s$ atomic orbitals or contain a factor close to the $1s$ AO, e.g., the $2p$ orbitals of the Ne atom. For molecules, especially when they do not have high symmetry, the results can be unreliable.

In order to obtain a good approximation to the intermolecular overlap density, we propose to approximate the a_i MO using formula (2) and assuming $W = (F_d(B))^2$, i.e., the weight function is the second power of some approximation to the b_j MO. The justification of such a choice of the W function is given in the Appendix.

The a_i MO approximated in such a way depends somewhat on the orbitals of the B molecule. A similar dependence exists in the OMAO method [12], and also in the method of Murrell and Varandas [27], who propose to replace, in formula (1), the MOs of isolated molecules by some maximum overlap hybrids. It should be noted, however, that their method helps to reduce the number of K integrals, but not the time needed for the calculation of each K integral. The presence of the intermolecular overlap factor in formula (2) offers the possibility to obtain the maximum accuracy of the f_c (e.g., a_i) MO fit in the region of its maximum overlap with the MO of the other molecule (e.g., b_j), that is needed for the proper reproduction of the $a_i b_j$ intermolecular overlap density.

In order to test our approximation, we have performed calculations of the "valence repulsion", i.e., the first-order exchange interaction energy between two hydrogen molecules in the linear dimer. 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 numbers of the GTO, their centres, their exponents and their coefficients in the contract. All the values,

TABLE I

Primary basis set

N	Centre	Exp	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

TABLE II

Valence-repulsion energies in 10^{-4} a.u.

d	8.5	7.5	7.0	6.5	5.5
17/11+17/11	0.060	0.420	1.095	2.830	18.096
17/11+6/6(2)	0.059	0.418	1.095	2.837	18.182
6/6(2)+6/6(2)	0.058	0.414	1.093	2.837	18.243
17/11+6/6(1)	0.057	0.392	1.056	2.789	18.204
17/11+3/3(1)	0.044	0.370	1.004	2.657	17.137
17/11+6/6(6n)	0.029	0.267	0.766	2.238	15.506

quoted hereafter, are in atomic units, unless otherwise stated; a value of 1.4 is assumed for the internuclear distance in the H_2 molecule; 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 numbered of 4–7 are contracted in one contract while the others presented in Table I are uncontracted. Seven GTOs centered on the 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 Leś using his method [9, 10], as an approximation of the Kołos and Roothaan MO [28]. The energy of the ground state of the H_2 molecule obtained with this basis set is $E(H_2) = -1.133378458$.

Our approximate MOs are linear combinations of 3 or 6 GTOs. In the first case one GTO is centered on each hydrogen nucleus and on the midpoint of the molecule, in the second case two GTOs are centered in such a way. Since such approximated MOs have no physical meaning, they are not presented here. Some details of the calculation of each approximated MO are given with the description of Table II. The first-order exchange interaction energy is calculated using the program written by Andzelm. This program was applied previously to investigate the LiF crystal [29, 30] and in calculations for the interaction energy in the H_2 dimer, presented in Paper I.

2. Results and discussion

The calculated valence-repulsion or the first-order exchange interaction energies, given in 10^{-4} a.u., are presented in Table II. The symbol on the left hand side of the first row, d, denotes the distance between the centres (midpoints) of the H_2 molecules in the linear dimer. The values of d are given in the first row, the interaction energies for a given d are in other rows. The remaining symbols in the first column denote the MOs used in the calculations. In order to test better the accuracy of the approximations, in some instances the primary MO denoted by 17/11 (i.e., 17 simple GTO contracted into 11 groups-contracts) is assumed for the A monomer and some approximate for the B one. The symbol 17/11 +6/6(2) denoted that the primary MO is used for the A monomer and the approximate (fitted) MO, which is the linear combination of 6 contracts, each being only one simple GTO, is used for the B monomer. The index (2) in the symbol 17/11+6/6(2) denotes the number of non-linear parameters, which are fitted in order to minimize the SDF. The fit is obtained as follows.

1. At first, the approximate 6-term MO is obtained from formula (2) with the "natural" weight $W = 1$ and the minimization of all six non-linear parameters, which are in this case the GTO exponents. For each set of non-linear parameters, the coefficients at GTOs are fitted as linear parameters in the classical least-square fit [17, 18]. The approximate MO found in such a way is denoted in Table II as 6/6(6n). It is presented in Paper I.

2. The new 3-term and 6-term MOs for the monomer A are calculated from formula (2) with $W = (F_d(B))^2$ and $F_d(B)$ being the 6/6(6n) MO for the monomer B. All the GTO exponents are the 6/6(6n) exponents multiplied by a common factor, which is only one non-linear parameter. The linear parameters are fitted similarly as those in stage 1. These MOs are denoted as 3/3(1) and 6/6(1), respectively.

3. The improved MO for the manomer A is obtained in a similar way, as in stage 2, but the new $F_d(B)$ is the 6/6(1) MO calculated for $d = 5.5$, being the smallest d assumed in our calculations. In this stage a new non-linear parameter is introduced, namely the GTO exponent, being the smallest one in the 6-term orbital, is fitted independently of the others. This MO is denoted as 6/6(2).

As can be seen in Table II, the valence-repulsion energies, E_{rep}, calculated with the 6/6(2) MO, are in very good agreement with E_{rep} calculated for the primary MO at all the d values investigated in the vicinity of the van der Waals minimum, which is probably close [31] to 7.0. This agreement holds also when the 6/6(2) MOs are assumed for both monomers. This assumption results in a great reduction in the computation time. The absolute value of the relative difference does not exceed in this case 2 percent, except at $d = 8.5$, where the valence-repulsion energy is small compared to the Coulomb electrostatic energy and therefore is not so important.

The agreement for the 6/6(1) and 3/3(1) MOs appears not so good, but it remains considerably better than for the 6/6(6n) MO. This indicates that the present choice of the W function results in a better accuracy of the calculated E_{rep} than the choice of $W = 1$.

Our method can also be used to calculate the molecular integrals needed to investigate second-order or non-additive exchange effects. It can give better results when combined

with the method of Murrell and Varandas [27], whenever the respective procedures are part of the interaction energy calculation programs. It holds also when the orbitals, a_i and b_j, are strongly overlapping and the results are in this case probably better than when the overlap is weak. It seems that the rational use of this method can reduce the computer time needed for the valence-repulsion energy calculation by two orders of magnitude.

In order to save computation time, our fitting procedure should not need many non--linear parameters, because it requires the calculation of many overlap integrals and has to be repeated for each non-equivalent geometrical configuration of the interacting systems. The present calculations suggest that it is possible to obtain good results with a very limited number of non-linear parameters. Therefore, the method seems to be very useful.

APPENDIX

Choice of the weight function

Our aim is to approximate the primary reference molecular orbitals, (MOs), e.g., $_c(\boldsymbol{r}, A)$, by some approximate MOs, $g_c(\boldsymbol{r}, A)$. The symbol, $\boldsymbol{r}$, denotes here the spatial coordinates, the index, c, the type of the MO (e.g., the H_2 MO), the symbol, A, the label of the MO if there are identical MOs in the investigated system (e.g., the H_2 number 2 in the H_2 dimer). Our approximation should reproduce the product of the MOs taken from different molecules. Let us try to fit our approximate MOs in order to minimize the square deviation functional given by (A1), where the argument $\boldsymbol{r}$ is omitted

$$SDF = \int d\boldsymbol{r}(f_c(A)f_d(B) - g_c(A)g_d(B))^2. \tag{A1}$$

Using the identity:

$$f_c(A)f_d(B) - g_c(A)g_d(B) = ((f_c(A) - g_c(A))(f_d(B) + g_d(B)) + (f_d(B) - g_d(B))(f_c(A) + g_c(A))/2 \tag{A2}$$

we can write the SDF functional as the integral over the sum of 3 terms as:

$$SDF = 0.25 \int d\boldsymbol{r}((f_c(A) - g_c(A))^2 (f_d(B) + g_d(B))^2 + (f_d(B) - g_d(B))^2 (f_c(A) + g_c(A))^2 + 2((f_c(A))^2 - (g_c(A))^2)((f_d(B))^2 - (g_d(b))^2)). \tag{A3}$$

As can easily be seen, the first 2 terms of the integrand in (A3) are positive, but the last one oscillates around the zero value. Therefore, the contribution of the last term in the integral can be neglected.

If no new simplifications were made in (A3), the $g_c(A)$ and $g_d(B)$ orbitals should be fitted simultaneously. Such a procedure would be very time-consuming. It appears, however, that numerical results of sufficient accuracy can be obtained when the $(f_d(B) + g_d(B))^2$ and $(f_c(A) + g_c(A))^2$ factors in (A3) are replaced by some functions such as $(F_d(B))^2$ and $(F_c(A))^2$, respectively. The $F_d(B)$ and $F_c(A)$ functions can be some approximate MOs of lower accuracy than our $g_d(B)$ and $g_c(A)$. Finally, the $g_c(A)$ orbital is calculated from the formula:

$$\int d\boldsymbol{r}(f_c(A) - g_c(A))^2 (F_d(B))^2 = \text{minimum} \tag{A4}$$

and a similar formula is used for $g_d(B)$.

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