

**PERTURBATION TREATMENT OF THE INTERACTIONS
BETWEEN NONPOLAR MOLECULE–NONPOLAR MOLECULE
AND POLAR MOLECULE–POLAR MOLECULE***

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This paper is devoted to the study of the interaction energies for pairs of nonpolar (H_2 , N_2 , F_2), weakly polar (CH_4), and strongly polar molecules (NH_3 , H_2O , HF). The primary goal is the investigation of the utility of semiempirical CNDO/2 and MINDO/2 methods within the framework of the perturbation theory. An attempt has been made to draw some general conclusions about the individual energy terms which contribute to the total interaction energy.

METHODS

Attention is restricted throughout to pairs of identical molecules H_2 , N_2 , F_2 , CH_4 , NH_3 , H_2O , and HF . Expression of the interaction energy is based on the perturbation theory formulated by Murrell and coworkers¹. The actual calculations were carried out according to the CNDO/2 approximation following Fueno and coworkers² and according to the MINDO/2 approximation³. All perturbation calculations were performed for optimized geometries given by the automatic energy minimization⁴ using the variable metric method: the CNDO/2 treatments were based on geometries given by CNDO/2, the MINDO/2 treatments on those given by MINDO/2. Only in treatments of H_2O and NH_3 dimers were we forced to use the experimental geometries⁵ of the isolated systems (with the O–H and N–H bond lengths corrected for the 0.1 and 0.15 offsets) because MINDO/2 fails here to give a satisfactory account of equilibrium geometries, as it predicts H_2O to be linear and NH_3 to be planar⁶. Net charges and charge densities used throughout are those calculated for the optimized geometries.

RESULTS AND DISCUSSION

The interaction energies and their constituents in Tables I–II are calculated at the energy minima. The mutual intermolecular orientations are shown in Figs 1 and 2. In the following we comment on the individual energy terms.

Coulomb energy. The expression for this contribution (see Eq. (4) in ref.²) can be rewritten in terms of atomic net charges, q , as follows

$$E^Q = \sum_{\mu}^R \sum_{\nu}^T q_{\mu} q_{\nu} \gamma_{\mu\nu} - \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} \gamma_{\mu\nu} + E^{CC}, \quad (1)$$

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where $\gamma_{\mu\nu}$ and Z_{μ} are the repulsion integral and the core charge, respectively. Core-core repulsions, E^{CC} , are given by the following two equations^{7,8}

$$E^{CC} = \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} r_{\mu\nu}^{-1}. \quad (2)$$

$$E^{CC} = \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} \gamma_{\mu\nu} + \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} (14 \cdot 399 r_{\mu\nu}^{-1} - \gamma_{\mu\nu}) \exp(-\alpha r_{\mu\nu}). \quad (3)$$

The former applies to CNDO/2, the latter to MINDO/2; r denotes the distance between atoms μ and ν and α an empirical constant. With nonpolar systems, the CNDO/2 and MINDO/2 approximations reduce Eq. (1) to

$$E^Q = \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} (14 \cdot 3986 r_{\mu\nu}^{-1} - \gamma_{\mu\nu}), \quad (4)$$

$$E^Q = \sum_{\mu}^R \sum_{\nu}^T Z_{\mu} Z_{\nu} (14 \cdot 399 r_{\mu\nu}^{-1} - \gamma_{\mu\nu}) \exp(-\alpha r_{\mu\nu}). \quad (5)$$

With both the CNDO/2 and MINDO/2 parametrizations the terms ($const r_{\mu\nu}^{-1} - \gamma_{\mu\nu}$) are positive for all distances.* This implies that in the interaction of two nonpolar systems the Coulomb energy is always repulsive, in accordance with chemical anticipation. However, the predicted MINDO/2 values in some cases are drastically overestimated. Consequently the overall interaction energy (*i.e.* the sum of the Coulomb, dispersion, induction, exchange-repulsion and charge-transfer energies) is repulsive at all distances (Table I).

On passing from nonpolar systems to polar ones, the Coulomb energy is given by Eqs (4) and (5) augmented for the term expressing the interactions among net charges of two systems, *i.e.* for the first term standing in Eq. (1). It is evident that the latter is insignificant for weakly polar molecules such as hydrocarbons. Listed in Table III are the Coulomb energies obtained by retaining and by neglecting interactions of net charges. Although the difference is negligible for the CH₄ dimer, it is significant for the strongly polar molecules NH₃ and H₂O.

The MINDO/2 approach overestimates repulsion for all systems containing hydrogen. If core-core repulsions are not compensated by a strong attraction of net charges (the case with nonpolar or weakly polar systems), the Coulomb energy is repulsive

* In this connection the following warning is noteworthy, *viz.* that in the case of very small energy differences a special attention has to be paid to the accuracy of the conversion factors from a.u. to eV and Å. The following values have been used in this paper: 1 a.u. \rightarrow 27.209936 eV; 1 a.u. \rightarrow 0.529167 Å.

enough for the total interaction energy to be repulsive in the whole range of distances (see results for H_2 and CH_4). With strongly polar systems (NH_3 , H_2O) there is a minimum in the interaction energy but the energy is underestimated considerably and the distance much overestimated (Table II). The preference for configuration 2 of the H_2O dimer is due to interactions between high net charges on hydrogen atoms of one molecule with those of the oxygen of the other molecule. An unrealistic account of the Coulomb energy obtained from MINDO/2 for molecules containing hydrogen is due to the form of the expression of core-core repulsions (Eq. (3)) and empirical parameters involved. One could lower the Coulomb repulsion with a higher values of the one-centre γ_{HH} integrals and the α_{XH} parameters ($X = H, C, N, O$). However, it is not our aim to find the optimal parameter set but rather to examine the utility of semiempirical methods with standard parameter sets. It should be noted that the overestimation of the core-core repulsion explains why MINDO/2 gives incorrect equilibrium geometries for some molecules; for example it predicts H_2O to be linear, NH_3 planar and the C—O—H part in CH_3OH linear⁶.

Dispersion energy. Dispersion energies for various configurations of X_2 dimers (Table I) are minimal for configurations 2 and 3 (Fig. 1) and maximal (*i.e.* the opti-

TABLE I

Perturbation Results on the Interaction Energy Partitioning for Various Models of Approaching of Nonpolar or Weakly Polar Molecules^{a,b}

| Dimer of | Mode of approaching ^c | R^d | Energy, kcal/mol | | | | | total |
|----------|----------------------------------|--------|------------------|------------|-------------------|------------------------|---------------------|----------|
| | | | Coulomb | dispersion | polariza- tion | exchange- repulsion | charge- transfer | |
| H_2 | 4 ^e | 4.85 | 0.0 | -0.004 | 0.0 | 0.001 | 0.0 | -0.003 |
| N_2 | 1 | 3.50 | 0.005 | -0.202 | 0.0 | 0.047 | 0.0 | -0.150 |
| | | (3.30) | (0.014) | (-0.303) | (0.0) | (0.078) | (0.0) | (-0.211) |
| | 4 | 4.14 | 0.030 | -0.401 | 0.0 | 0.092 | -0.001 | -0.280 |
| | | (4.00) | (0.016) | (-0.402) | (0.0) | (0.106) | (-0.010) | (-0.290) |
| F_2 | 1 | 2.80 | 0.003 | -0.045 | 0.0 | 0.017 | 0.0 | -0.025 |
| | 4 | 3.72 | 0.006 | -0.055 | 0.0 | 0.026 | -0.001 | -0.024 |
| CH_4 | 1 ^c | 3.90 | 0.003 | -0.027 | 0.0 | 0.005 | -0.001 | -0.020 |
| | 2 ^e | 4.70 | 0.011 | -0.048 | 0.0 | 0.011 | -0.003 | -0.029 |
| | 3 ^e | 4.50 | 0.004 | -0.039 | 0.0 | 0.013 | -0.002 | -0.024 |
| | 4 ^e | 4.60 | 0.001 | -0.033 | 0.0 | 0.001 | 0.0 | -0.031 |

^a The entries are results of perturbation CNDO/2 calculations, the perturbation MINDO/2 results are given in parentheses. ^b Only those modes of approaching are included which lead to an energy minimum. ^c *cf.* Fig. 1. ^d Equilibrium intermolecular distance in Å. ^e MINDO/2 gives no minimum.

TABLE II
 Perturbation CNDO/2 Results on the Interaction Energy Partitioning for Various Modes of Approaching of Strongly Polar Systems^{a,b}

| Dimer of | Mode of approaching ^c | R^d | Energy, kcal/mol | | | | | |
|------------------|----------------------------------|--------|------------------|------------|--------------|--------------------|-----------------|----------|
| | | | Coulomb | dispersion | polarization | exchange-repulsion | charge-transfer | total |
| HF | 1 | 2.90 | -0.568 | -0.036 | -0.010 | 0.100 | -0.002 | -0.616 |
| | 4 | 2.70 | -0.646 | -0.045 | -0.066 | 0.066 | -0.002 | -0.693 |
| H ₂ O | 1 ^e | 2.80 | -0.225 | -0.063 | -0.045 | 0.065 | -0.004 | -0.272 |
| | 2 | 3.50 | -0.262 | -0.036 | -0.032 | 0.055 | -0.004 | -0.279 |
| | | (6.30) | (-0.227) | (-0.002) | (-0.008) | (0.0) | (0.0) | (-0.237) |
| NH ₃ | 1 | 2.80 | -0.055 | -0.083 | -0.026 | 0.051 | -0.008 | -0.121 |
| | | (5.60) | (-0.031) | (-0.003) | (-0.014) | (0.0) | (0.0) | (-0.048) |
| | 2 | 3.70 | -0.039 | -0.046 | -0.008 | 0.029 | -0.002 | -0.066 |
| | | (6.80) | (-0.057) | (-0.002) | (-0.007) | (0.0) | (0.0) | (-0.066) |

^a The entries are results of perturbation CNDO/2 calculations, the perturbation MINDO/2 results are given in parentheses. ^b Only those modes of approaching are included which lead to an energy minimum. ^c cf. Fig. 2. ^d Equilibrium intermolecular distance in Å. ^e MINDO/2 gives no minimum.

TABLE III
 Coulomb Energies for the Predicted Most Stable Configurations of CH₄, NH₃, and H₂O Dimers^a

| Mode of approaching ^b | Energy, kcal/mol | |
|----------------------------------|----------------------------------|-------------------------------|
| | net charges considered | net charges set equal to zero |
| 4 ^c | CH ₄ dimer 0.001 | 0.001 |
| | NH ₃ dimer -0.055 | 0.041 |
| 2 | (-0.057) | (0.030) |
| 2 | H ₂ O dimer -0.262 | 0.024 |
| 2 | (-0.227) | (0.112) |

^a The entries are results of perturbation CNDO/2 calculations, the perturbation MINDO/2 results are given in parentheses. ^b cf. Figs 1 and 2. ^c MINDO/2 gives no minimum.

mum) for the linear configuration 4 by both CNDO/2 and MINDO/2. The different behaviour of the F_2 dimer is easily explained by examination of the expression for the dispersion energy²

$$E_D = -4 \sum_i^{\overbrace{R}} \sum_j^{\overbrace{unocc}} \sum_k^{\overbrace{R}} \sum_l^{\overbrace{T}} \left[\sum_r^R \sum_s^T c_{ir} c_{jr} c_{ks} c_{ls} \gamma_{rs} \right]^2 / (\Delta E_{i \rightarrow j} + \Delta E_{k \rightarrow l}). \quad (6)$$

Here the first and third summation are over occupied MOs of isolated systems, the second and fourth over unoccupied MOs, and the fifth and sixth over all AOs; γ_{rs} denotes repulsion integrals and $\Delta E_{i \rightarrow j}$ the SCF excitation energy. Obviously, the most significant contribution to the dispersion energy is due to the frontier orbitals

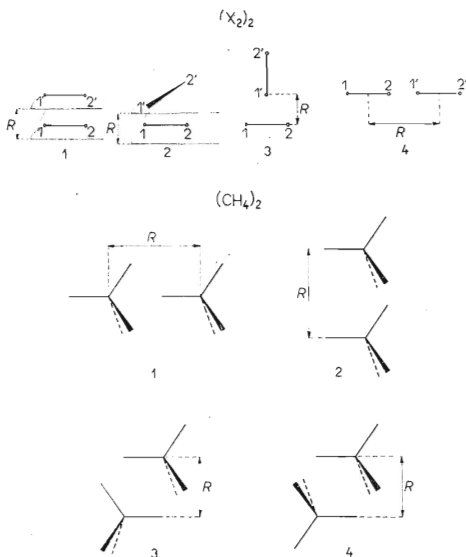


FIG. 1
Configurations of X_2 ($X = H, N, F$) and CH_4 Dimers

(in which case $\Delta E_{i \rightarrow j}$ is the lowest), provided they have the same symmetry. The only unoccupied MO available in F_2 is that of the σ^* type, whereas the highest occupied MO is of the π^* type. The dispersion energy computed for $(F_2)_2$ is therefore very small; this fact is due to the AO basis set used (*vide infra*). A preferred linear orientation in the approaches of other systems studied may seem somewhat surprising at first sight; it can however be explained simply. The HOMO and LFMO of H_2 and N_2 are of the same type (either σ or π) and differ only by the signs of the expansion coefficients. Hence, the pertinent contribution to the dispersion energy is merely proportional to the difference between $\gamma_{11'}$ and $\gamma_{21'}$ integrals (Fig. 1), which is vanishing for configurations 2 and 3 but maximum for the linear configuration 4. Similar conclusions can be drawn for more complex molecules whose frontier molecular orbitals

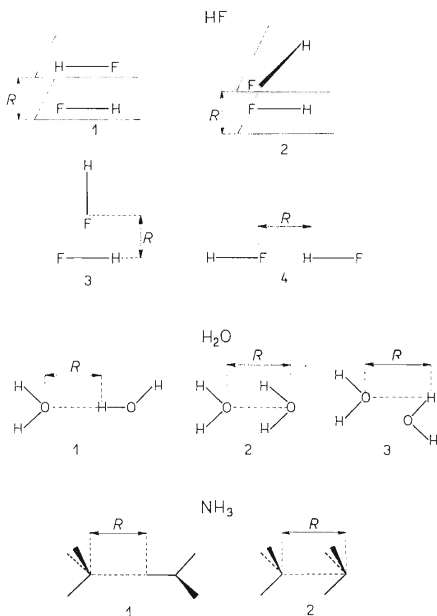


FIG. 2
Configurations of HF, H_2O , and NH_3 Dimers

TABLE IV
Dispersion Energies Given by Perturbation MINDO/2 Calculations for Various Configurations of Ethylene Dimer

| Mode of approaching ^a | R ^b | -E, kcal/mol | Mode of approaching ^a | R ^b | -E, kcal/mol |
|----------------------------------|----------------|--------------|----------------------------------|----------------|--------------|
| 1 | 2.5 | 2.480 | 3 | 3.0 | 17.524 |
| | 3.0 | 1.171 | | 3.5 | 10.389 |
| | 3.5 | 0.592 | | 4.0 | 5.331 |
| | 4.0 | 0.318 | | 4.5 | 2.747 |
| | 4.5 | 0.179 | | 4 | 3.0 |
| 2 | 2.5 | 1.945 | 3.5 | | 2.598 |
| | 3.0 | 0.958 | 4.0 | | 1.240 |
| | 3.5 | 0.498 | 4.5 | | 0.625 |
| | 4.0 | 0.263 | 5 | | 3.0 |
| | | 3.5 | | 3.822 | |
| | | 4.0 | | 1.803 | |
| | | 4.5 | | 0.882 | |

^a cf. Fig. 4. ^b Intermolecular distance in Å.

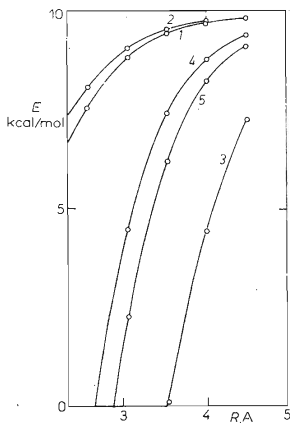


FIG. 3
MINDO/2 Dispersion Energy for the Ethylene Dimers
Configurations 1-5 are indicated in Fig. 4.

also exhibit some sort of this behaviour, *i.e.* at least for some atomic orbitals the respective expansion coefficients are close in absolute value, $|c_{ir}| \doteq |c_{jr}|$ (Eq. (6)). Table IV and Fig. 3 present the data for ethylene for various modes of approach (Fig. 4). Once again, a linear approach (type 3) is favoured; the approach 2 appears to be the least likely. In general, a significant dispersion energy can be expected with nonpolar, uncharged systems, in particular with conjugated systems where it may be a prevailing attraction term. The results obtained suggest that the semiempirical methods fail to give a good account of the dispersion energy for systems with an insufficient number of virtual MOs (HF, F_2); this problem is of course due to the AO basis set used. With regard to the absolute values of dispersion energies, MINDO/2 gives mostly higher values than CNDO/2 which is due to lower SCF excitation energies predicted by MINDO/2.

Polarization energy. On introducing atomic net charges q the expression for the polarization energy (Eq. (6) in ref.²) becomes

$$E^P = -2 \sum_i^{\overbrace{R}^{\text{occ unocc}}} \sum_j^R [\sum_r^R \sum_b^T c_{ir} c_{jr} q_b \gamma_{rb}]^2 / \Delta E_{i \rightarrow j} - 2 \sum_k^{\overbrace{T}^{\text{occ unocc}}} \sum_l^T [\sum_s^T \sum_a^R c_{ks} c_{ls} q_a \gamma_{sa}]^2 / \Delta E_{k \rightarrow l} \quad (7)$$

Here the indices a and b are over all atoms of individual systems. The meaning of the other symbols is the same as in Eq. (6). Eq. (7) gives us an obvious result. The polarization energy is negligibly small with nonpolar or weakly polar systems (Table I) and it becomes significant only with strongly polar systems (Table II). Compared with CNDO/2, MINDO/2 gives considerably higher polarization energies in absolute value as it gives higher atomic net charges and lower SCF excitation energies.

Exchange-repulsion energy. The manner of treating the exchange-repulsion energy in perturbation semiempirical approaches based on the ZDO approximation is still controversial. In the one extreme this term is completely neglected and in the other it is adequately accounted for. There is an intermediate treatment⁹ which only considers that part of the exchange-repulsion term lacking any explicit intermolecular overlap. In this case the expression for the exchange-repulsion energy reduces to the first term in Eq. (5) of ref.². The latter is in fact a negative value of the intermolecular exchange integral K_{ij} and therefore is attractive rather than repulsive, which contradicts the purpose of the approximation adopted.

We next present our arguments as to why we think that it is correct to maintain the exchange-repulsion energy. If this energy is neglected, the only intersystem repulsion accounted for are electron-electron and core-core repulsions given by the

expression for the Coulomb energy (in Eq. (1) of ref.²). MINDO/2 gives a sufficiently repulsive Coulomb energy (Tables I and II), but it is evident that this is due to the manner of expressing the core-core repulsion. This energy is even repulsive for a linear approach of two systems as polar as H₂O. With the CNDO/2 approximations the Coulomb energy for polar systems is attractive at large distances and only becomes repulsive in the range of short distances (where core-core interactions become significant). Obviously, a repulsion term is missing which corresponds to the exclusion principle of closed shell MOs. A logical consequence of such a neglect is the underestimation of equilibrium intermolecular distances. Furthermore, repulsion energy accounted for only by means of the Coulomb energy is merely the repulsion between point charges and is therefore not dependent on the mutual orientation but only on the interatomic distance. This is no longer the case if the exchange-repulsion energy is maintained because of the intermolecular overlap involved in the latter. Let us add that the complications discussed just are specific only for semiempirical methods; the situation concerning the exchange-repulsion energy is completely clear on the non-empirical level, however.

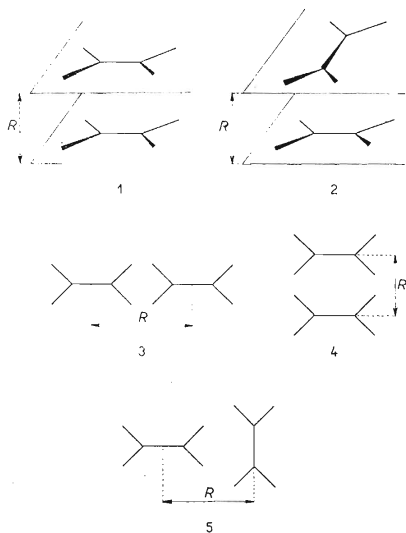


FIG. 4
Configurations of the C₂H₄ Dimer

A single value for $V_{a,rr}$ integrals both for s - and p -type AOs (Appendix in Part I) leads to the enhancement of the repulsion energy.

Charge-transfer energy. The charge-transfer energy is seen, from Eq. (8) in ref.², to be proportional to the overlap of occupied MOs of one system with the unoccupied MOs of the other system and *vice versa*, and inversely proportional to intermolecular SCF excitation energies. Since none of the systems studied in this paper is neither a good donor or a good acceptor, the predicted charge-transfer energies are negligibly small in all cases (Tables I and II). Nevertheless, the values obtained allow one to draw some simple conclusions with regard to various configurations. As in the case with the dispersion energy, the most significant contribution is due to the frontier orbitals. In interactions of X_2 systems that have the frontier orbitals of the same type, the charge transfer energy is the highest for configuration 4 with the most powerful overlap of HOMO of one system with LFMO of the other system, and the lowest for configurations 1, 2, and 3 (Fig. 1) with the least effective overlap. A more detailed analysis and critical examination of CNDO/2 and MINDO/2 approximations is only possible with strong donors and acceptors. Making use of a single value of $V_{a,rr}$ integrals both for s - and p -type AOs (Appendix in Part I) leads to the enhancement of the charge-transfer energy. Of course, the greater the difference in ionization potentials of the s - and p -type AOs, the greater the increase in the charge-transfer energy. The effect however is only significant if the charge-transfer energy contributes predominantly to the total interaction energy.

CONCLUSIONS

The goal of this paper was to examine the utility of semiempirical methods in perturbation treatments. The results discussed in the preceding paragraphs indicate that the use of the standard versions of semiempirical methods does not appear to be promising.

A) CNDO/2 does not give a good account of interactions of nonpolar or weakly polar molecules owing to a poorly predicted balance between the dispersion and exchange-repulsion energies. With the nitrogen molecule this balance was correctly accounted for and therefore the calculated interaction energy reproduces well the experimental value. For a more specific comment *vide infra* (paragraph B). With strongly polar systems the results obtained are meaningful. This is partly due to relatively high negative values of the Coulomb energy which correctly compensates the exchange-repulsion energy. We now comment in detail on the calculated total interaction energies of polar systems. As suitable experimental data are not available, we attempt to judge our results against the results of other authors obtained by variation (nonempirical, semiempirical) and perturbation methods. In a comprehensive study Kollman and Allen¹⁰ examined critically the applicability of nonempirical and semiempirical methods to the computation of hydrogen bond energies. They

found that CNDO/2 gives good values for dimerization energies but values for the intermolecular distance, compared to *ab initio* results, are too short. Furthermore, CNDO/2 gives an incorrect order of the strengths of hydrogen bonds, $\text{H}_2\text{O} > \text{HF} > \text{NH}_3$; experiment suggests the order $\text{HF} > \text{H}_2\text{O} > \text{NH}_3$. Our results show that if CNDO/2 is used in a perturbation treatment, the predicted intermolecular distances are too large and interaction energies too low (Table II); both these defects are due to the overestimated exchange-repulsion energy.* With H_2O and NH_3 CNDO/2 favours configuration 1 (Fig. 2) whereas the perturbation treatment favours slightly configuration 2. Our perturbation treatment favours a linear approach of two HF molecules which is in agreement with *ab initio* and CNDO/2 variational calculations. In contrast to variation procedures, our perturbation method also gives a correct order of interaction energies (Table II).

B) MINDO/2 fails with all systems containing hydrogen because it overestimates the core-core repulsion; the computed Coulomb energy is so high that either the total interaction energy is repulsive at all distances or a predicted energy well is drastically underestimated. A different situation is met with the N_2 dimer. Here the attraction component of the total energy (Table I) is due to the dispersion energy (in all four considered modes of approaching): the highest value was found for a linear approach in which case also the highest total interaction energy was computed. The repulsion is mainly due to the exchange-repulsion energy. A weak Coulomb repulsion is roughly compensated for by the charge-transfer attraction. The ratio of the calculated magnitudes of individual energy contributions conforms to what is assumed about the nature of interaction forces of nonpolar systems which are not powerful donors or powerful acceptors.

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* Sustmann and Vahrenholt¹¹ studied the H_2O dimer by means of a perturbation method disregarding the exchange-repulsion energy; their results are close to those obtained variationally.