WEAK INTERMOLECULAR INTERACTIONS: INTRODUCTORY REMARKS AND METHODS USED

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This paper gives a critical summary of nonempirical, semiempirical and empirical methods applicable to studies of weak interactions. The aim is to provide a clear picture of this field in its present state of rapid development. The methods described represent a methodical basis for the subsequent papers in this series.

To define weak and strong intermolecular interactions is rather difficult. It is possible to roughly characterize the region of strong interactions as that where a covalent bond is formed or broken and to attribute weak interactions to that region of complex formation of closed shell molecules. There is still a third region which lies between the two extremes and represents a gradual passage from one to the other. It is just this region which is extraordinarily interesting and important, but unfortunately it is theoretically less accessible than the two extreme cases. In the past strong and weak interactions have received differing degrees of attention. While the former have been intensively studied for almost half a century, less effort has been devoted to the latter. The methods applicable to computations of weak interactions range from simple empirical methods to those of rigorous calculations (up to now feasible only for interactions such as He + He or $H_2 + H_2$). That is to say, one can make use of the variation or perturbation method at the empirical, semiempirical, or nonempirical levels.

The aim of this introductory paper is to survey the significant methods. For most of them the description to be given here is rather detailed, since we wish to avoid it in the subsequent papers dealing with applications. For the procedures reported in the literature we will limit ourselves to reproducing expressions that, in our opinion, are necessary for clearness. The range of applicability of the methods just mentioned is large and covers several fields of extraordinary importance in chemistry, physics, and biology, for example:

1. Pair interactions: *a)* association of identical closed-shell molecules, *b)* charge-transfer complexes, *c)* collision complexes. *2.* Bulk interactions: *a)* phase changes (melting, evaporation, sublimation), *b)* Henry and Nernst laws. *3.* Conformation problems and steric hindrance. *4.* Solvation energy.

Although it was the tremendous importance of solvation in chemistry which prompted

our endeavours in this field, we believe it is desirable to begin with more tractable problems such as those noted in items 1 and 2; the subsequent papers of this series will therefore deal predominantly with these topics.

Variation Methods

Nonempirical method. We define the interaction energy as the difference between the total energy of a supersystem and the sum of total energies of isolated systems R and T:

$$E^{INT} = E^{R,T} - (E^R + E^T). \qquad (1)$$

By the total energy we imply the sum of the Hartree-Fock energy and the correlation energy. A rigorous computation of the interaction energy requires the inclusion of inter- as well as intrasystem correlation energy in the total energy of the supersystem. In practice mostly, however, one neglects the intrasystem correlation energy by assuming it to be equal to the correlation energy of the two isolated systems. The correlation energy can be determined either by the SCF calculation followed by the complete configuration interaction treatment (CCI) or by the multiconfiguration (MCI) self-consistent field technique.* Consequently it might appear that the computation of interaction energy should be straightforward, at least with simple systems. In fact satisfactory results were not obtained until the early seventies. The first studies of this type dealt with He—He, Li—He, and H—He interactions[2−4]. The interaction energy of two He atoms was determined by both the SCF-CCI (ref.[2]) and MCI-SCF (ref.[3]) calculations and the results of the two procedures are in very good agreement. McLaughlin and Schaefer[5] studied the interaction of two He atoms in more detail and demonstrated the effect of individual atomic orbitals on the depth of the energy minimum. They arrived at the value of $3·606 . 10^{-5}$ a.u. which is in very good agreement with the current experimental value of $3·15 . 10^{-5}$ a.u. (ref.[5] and papers cited therein). The interaction of two H_2 molecules was studied by Tapia and Bessis[6]. They showed a linear approach to be the most likely on energy grounds. The most accurate results available for this orientation were reported by Bender and Schaefer[7]; the SCF-CCI calculation in the contracted $[2s1p]$ basis set yielded the energy minimum of $6·6 . 10^{-5}$ a.u. which is comparable to the recent value of $10·44 . 10^{-5}$ a.u. given by molecular beams experiments[8].

Semiempirical methods. Again, the interaction energy is given by Eq. (*1*). However with semiempirical methods the problem of which geometry to use for isolated systems R and T arises. Should one prefer the experimental, optimized, or some assumed

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*   We would like to note here the computations of the interaction energy for two hydrogen atoms, reported as early as in 1965 by Kołos and Wolniewicz[1] who introduced the correlation effect by including the interelectronic coordinate.

standard geometry?* In our opinion, the only justifiable procedure is that in which the interaction energy is treated as a difference between the energy of the optimized supersystem and the sum of energies of optimized isolated systems. That is to say, that not only the intermolecular but also the intramolecular distances should be optimized in the supersystem. The second question which can be asked is whether or not the CI should be included. Here the situation is also clear-cut, as there are strong arguments[9] against the use of CI except for special cases for example the homolytic fission of a covalent bond[10]. Applications of semiempirical methods to systems with hydrogen bonds have been critically reviewed by Kollman and Allen[11]. A more general account of these method is however still lacking, in particular the interactions of nonpolar systems.

Perturbation Methods

By exploiting the first and second order perturbation theories and by making use of the experimental quantities such as dipole moment, polarizability, diamagnetic susceptibility, or ionization potential, the formulae have been derived for the Coulomb, induction, and dispersion energies[12]. The derivation was based on the assumption of large separation. In such a case the total wave function can be written as a simple product of wave functions of the two isolated systems. The problem of the exchange energy remained unresolved and one was forced to estimate it in an empirical way. The difficulty is that a nonantisymmetrized zero-order wave function does not give exchange, while a symmetrized one, is no longer an eigenfunction of the total hamiltonian $H_0 = H_R + H_T$: therefore, new versions of perturbation theories had to be developed. Recently several theories have been suggested[13-16] which solve the problem in different ways by considering the total energy as a sum of Coulomb, dispersion, induction, exchange-repulsion, and charge-transfer (delocalization) energies. Their application is still limited to interactions of the simplest systems[17]. In order to make it possible to treat systems of chemical interest, it was necessary to simplify the original expressions. A considerable simplification was brought about by making use of semiempirical wave functions instead of accurate wave functions by adopting approximations which involve semiempirical methods. Fujita and Imamura[18] used the perturbation theory of Murrell and coworkers[13,14]. They simplified the general expressions by means of the approximations and wave functions of the PPP type. Fueno and coworkers[19] used the same perturbation theory but based it on the CNDO/2 wave functions and approximations; the formula for the exchange-repulsion energy has already been derived earlier by Cook and Schug[20] within the framework of the same approach. A common feature in all methods noted is a

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*   Actually the same problem is met with *ab initio* calculations. Here, however, the difference between the optimized and experimental geometries is considerably smaller.

certain inconsistency in the use of the ZDO approximation. Whereas the intermolecular overlap is considered, the intramolecular overlap is neglected. If one neglected the intermolecular overlap too, the exchange-repulsion energy would not be accounted for. In such a case a repulsive nature of the mutual penetration of closed shells would be disregarded and the intersystem repulsion would be given merely by electron-electron and core-core repulsions. As the latter are significant only at small intersystem separations, it is most likely that the overall repulsion would be underestimated in the range of intermediate distances. It is thus desirable to allow for the above-mentioned inconsistency: to treat the isolated systems according to the ZDO approximation, which is a fundamental feature of semiempirical methods, and to maintain the intermolecular overlap, which is inevitable for accounting for the exchange repulsion energy (*vide infra*, however).

Next we mention other perturbation methods employed currently. In a series of papers[21-24] an SCF perturbation method was developed on the basis of MINDO/1, MINDO/2, and CNDO/2 formalisms. In contrast to methods noted above it makes a consistent use of the ZDO approximation, which leads to the consequence just described (we present some numerical results in Part II of this series). The total energy in this perturbation theory is given by the sum of the first and second order energies. The first order energy can be identified with the Coulomb energy derived by Fueno and coworkers[19], the second order energy comprises the induction energy as defined in ref.[19] and the charge-transfer energy.

Salem[25] expanded the interaction energy in the powers of the overlap and in addition Devaquet[26] expanded it in the powers of the total charge. In the former treatment based on the HMO quantities the total energy is given by the sum of the repulsion and charge-transfer (delocalization) energies. The latter makes use of the PPP method and the total energy also involves the Coulomb energy.

In our opinion, the methods noted in the last two paragraphs are not well suited for the study of intermolecular forces. Firstly, they neglect some energy terms and, secondly, the use of the HMO and PPP models represents a rather serious shortcoming. For the purposes of our study we adopted the expressions derived by Fueno and coworkers[19] and adopted them to the MINDO/2 approximation. The pertinent expressions, at both MINDO/2 and CNDO/2 levels, are discussed in Appendix.

Empirical Methods

The need to estimate interaction energy in studies of various physical and chemical problems stimulated the effort to formulate simple empirical relationships. Mostly they were based[12] on the combination of the attractive ($E \sim -(r^{-6} + r^{-8})$) and repulsive ($E \sim r^{-12}$ or $\exp(-r)$) terms and on subsequent attempts to determine the parameters involved from suitable experiments. For our purposes we have selected

a simplified Buckingham potential assuming the overall interaction energy as the sum of pair interaction energies over all atoms of the isolated systems R and T[27,28]

$$E^{INT} = -C_1 \sum_i^R \sum_j^T \left(\frac{r_{ij}}{R_i + R_j}\right)^{-6} + C_2 \sum_i^R \sum_j^T \exp\left(-C_3 \frac{r_{ij}}{R_i + R_j}\right). \qquad (2)$$

Here C_1, C_2, and C_3 are constants, R_i and R_j are experimentally determined van der Waals radii, and r_{ij} is the interatomic distance for atoms i and j. The parameters for H, C, N, F, S, Cl, Br, and I atoms were suggested by Eliel and coworkers[28]. We would like to emphasize that it is not our aim to find the optimal potential and the optimal parameter set but rather to show a large range of applicability of this simple method by making use of the single set of parameters.

Hybrid Methods

These methods involve some inconsistency *viz.* that the individual energy terms which appear in the summation are evaluated by different methods at different theoretical levels. We note only the most important procedures, in particular those that will be used in our calculations. The interaction energy determined by the variation method is given by subtracting the sum of energies of two isolated systems from the total energy of a supersystem. If one makes use of the nonempirical SCF method, the total energy is equal to the sum of the Hartree–Fock energy and correlation energy. It has been shown[29-31] that the Hartree-Fock energy comprises Coulomb, exchange-repulsion, induction, and charge-transfer energy. The only component lacking here is the dispersion energy which constitutes the main part of the correlation energy. Hence, if one adds the dispersion energy computed by the perturbation theory to the Hartree–Fock energy, one should arrive at reasonable estimates of the total energy. The dispersion energy can be evaluated by means of the second-order perturbation theory[32] through the following equation.

$$E^D = -4 \sum_r^{\overbrace{occ}^{R}} \sum_s^{\overbrace{unocc}} \sum_t^{\overbrace{occ}^{T}} \sum_u^{\overbrace{unocc}} \langle rs|tu\rangle^2 / (\Delta E_{r\to s}^R + \Delta E_{t\to u}^T), \qquad (3)$$

where the first and second (the third and forth) summations extend over all occupied and virtual orbitals of the system R (of the system T). The term in the denominator expresses the energy difference between excited and ground states in systems R and T. The computation of the dispersion energy is carried out with the wave function given by the SCF calculation. The effect of the size of the basis set used and the effect of the values of exponents in AOs on the computed interaction energy were investigated by Kochanski[33-35] for the case of two H_2 molecules. The total energy was treated as a sum of the dispersion energy (given by the perturbation calculation) and the

Coulomb and exchange-repulsion energy (given by the variation calculation). The last two terms were equated to the difference between the energy of the supersystem in the first iteration and the sum of energies of isolated systems[32]; this is done computationally by starting the SCF procedure for the supersystem with the eigenvectors of the two isolated systems. The total energy computed in this way is thus lacking the induction and charge-transfer energies. The author considered them insignificant for all orientations of isolated systems.

As stated in the section about the perturbation method, the perturbational expression for Coulomb, induction, and dispersion energies is straightforward. On equating some terms in these expressions to experimental quantities, one arrives at considerably simpler formulas without loss in accuracy. An analogous treatment for the repulsion energy has not yet been formulated. Here it is necessary to evaluate the expression obtained perturbationaly by means of wave functions given by MO methods. The use of such a procedure was reported by Cook and Schug[20] in a study of charge-transfer complexes. The total energy was treated as a sum of Coulomb, induction, dispersion, repulsion, and charge-transfer energies; the repulsion energy was computed perturbatively by making use of CNDO/2 approximations and wave functions and the charge-transfer energy was estimated empirically following Mulliken[36]. Mostly[37,38], however, the repulsion energy is estimated empirically either by exploiting the repulsion term of some empirical potential or by making it proportional to different powers of the overlap. It is just this circumstance which causes difficulty because it leads to correct estimates of attraction on the one hand but to rather rough estimates of repulsion on the other hand. Hanna and Williams[37] made use of this type of procedure in the study of charge-transfer complexes; the repulsion energy was approximated by the powers of the overlap and the charge-transfer energy was determined, once again, according to Mulliken[36]. With larger systems the use of empirical potentials represents mostly the only feasible treatment. The difficulty encountered here is that the potentials currently used were adjusted to interaction energies between uncharged nonpolar systems. In the case of charged or polar systems the lacking terms for the Coulomb and induction energies may be of crucial significance. Ordinarily, one adds them simply *a posteriori* by use of the expressions[39,40] (4), (5) following from the perturbation theory

$$E^Q = \sum_i^R \sum_j^T \frac{q_i q_j}{r_{ij}}, \qquad (4)$$

$$E^I = -\tfrac{1}{2}\{\sum_p^R \left[\alpha_p^R(\xi_p \xi_p) + \delta_p(\xi_p \alpha_p^L)^2\right] + \sum_q^T \left[\alpha_q^T(\xi_q \xi_q) + \delta_q(\xi_q \alpha_q^L)^2\right]\}, \qquad (5)$$

where $\xi_p = \sum_j^T q_j/r_{jp}^3 \, \mathbf{R}_{jp}$, $\delta_p = (\alpha_p^L - \alpha_p^T)$, q denotes the net charges, ξ_p, α_p^L, $\mathbf{R}_{jp}$ unit

vectors, $\alpha_p^{T,L}$ transversal and longitudinal polarizability of the bond p, and r distance. It is evident that the subsequent adding of these terms destroys the balance between attraction and repulsion terms of an empirical potential because of the simultaneous adjusting of parameters in the latter.

APPENDIX

Details on actual calculations. In this series of papers the interaction energy is determined as a sum of Coulomb (E^Q), exchange-repulsion (E^K), induction (E^I), dispersion (E^D), and charge-transfer (E^{CT}) energies.

Within the CNDO/2 approach we make use of the expressions derived by Fueno and coworkers[19]. We note in detail only two terms: the excitation energy, $\Delta E_{j \to l}$, and the electron-core attraction integrals,* $V_{a,rs}$. The denominators in the terms for the induction and dispersion energies express the intramolecular excitation energy, $\Delta E_{j \to l}$, which we evaluate by means of the single determinant transition energy

$$\Delta E_{j \to l} = E_l - E_j + 2K_{jl} - J_{jl}, \tag{6}$$

where all symbols have their usual meaning. The denominator in the term for the charge-transfer energy expresses the intermolecular excitation energy, $\Delta E_{i \to l}$. We proceeded here analogously as in the preceeding case; the intermolecular $\langle ii \mid ll \rangle$ and $\langle il \mid il \rangle$ integrals were evaluated by means of the Mulliken's formula[41]. We think that this approximation is better substantiated than that used by Fujita and Imamura[18], who set the intermolecular excitation energy equal to the energy difference between the pertinent molecular orbitals. To illustrate the importance of the intermolecular excitation, we calculated it within the CNDO/2 approach for several distances between two approaching N_2 molecules in an rectangular configuration. For the excitation energy from the lowest-energy occupied orbital of one molecule to the lowest-energy virtual orbital of the other molecule we obtained the following results (in eV, intersystem separations in A are given in parentheses): 30·969 (3·1); 31·187 (3·3); 31·386 (3·5); 31·652 (3·8); 31·885 (4·1). This implies that the change in excitation energy which is due to a change in the intersystem separation is by no means to be neglected.

The terms for the exchange-repulsion and charge-transfer energies contain intermolecular electron-core attraction integrals that, once again, are evaluated by the Mulliken's approximation[41]

$$V_{a,rt} = (V_{a,rr} + V_{a,tt}) \, S_{rt}/2, \tag{7}$$

where S_{rt} denotes the intermolecular overlap integral, atomic orbitals r and t refer to isolated systems R and T respectively, and a is an atom of the system R. It has not yet been established how to evaluate the intramolecular integral $V_{a,rr}$ if the orbital r is located on the atom a. Should this integral have differing values according to the types of AOs or should it have a single value (appropriate to the s orbital) regardless of the nature of the AO? We favour the former view and assume different values of integrals for s and p-type orbitals, in accordance with the approximation involved in the CNDO/2 method.

The application of the MINDO/2 method is straightforward. In terms for the Coulomb, induction, and dispersion energies, it is only necessary to substitute wave functions, energies, γ integrals, and core-core repulsions by characteristics appropriate for the MINDO/2 method.

* We follow the notation of ref.[19].

The situation with the exchange-repulsion and charge-transfer terms is slightly more complicated because MINDO/2 retains different types of one-centre repulsion integrals. The general expressions, containing two, three and four-centre integrals, are simplified by the Mulliken[41] formula

$$(rt \mid uv) = \left\{ (rr \mid uu) + (rr \mid vv) + (tt \mid uu) + (tt \mid vv) \right\} S_{rt} S_{uv}/4 \qquad (8)$$

where atomic orbitals r and u refer to the system R, and t and v to T. Note that Eq. (8) alone implies the assumption of vanishing one-centre integrals unless they are of the $(ss \mid ss)$, $(ss \mid pp)$, $(pp \mid pp)$, or $(pp \mid p'p')$ type. Intra- and intermolecular excitation energies and electron-core attraction integrals are computed analogously as in CNDO/2, by making use of the appropriate MINDO/2 characteristics.

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Note added in proof: Recently a few important papers appeared on SCF-CI studies of weak inter-
system interactions: He—H_2(a); Li^+—H_2(b); He—HF, He—H_2O, H_2—HF, H_2—H_2O(c);
H_2—H_2(d) and LiH—LiH(e).

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