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The Present State of Quantum-chemical Calculations of the Intermolecular Interaction of Polyatomic Molecules

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In the present review, the results of quantum-chemical calculations of the energy of the interaction of polyatomic molecules are discussed for the case of dimers. The main theoretical approaches used in the calculation of intermolecular interaction, the self-consistent field method (supermolecule approximation) and perturbation theory, are analysed briefly. The range of applicability and the advantages and disadvantages of these main approaches are evaluated. The results of non-empirical calculations of the interaction of molecules forming dimers of different kinds: with the participation of hydrogen bonds, donor-acceptor complexes, and others, are examined. The accuracy of non-empirical calculations and the influence of the basis set used are discussed, and recommendations for improving the non-empirical data are given. The possibility of constructing analytical potentials (including atom-atom potentials), which can be used to study many-particle systems, from the results of non-empirical calculations is analysed. In addition to non-empirical calculations, the possibilities provided by semi-empirical methods of calculating the intermolecular interaction of polyatomic molecules both in the self-consistent field approximation and using perturbation theory are also examined. The bibliography contains 202 references.

CONTENTS

I.	Introduction	595
II.	Non-empirical methods for calculating intermolecular interactions	596
III.	Non-empirical calculations for dimers of different chemical character	598
IV.	Non-empirical analytical potentials	603
V.	The accuracy of non-empirical calculations of intermolecular interaction	605
VI.	Semi-empirical calculations of intermolecular interaction	606

I. INTRODUCTION

Intermolecular interactions (IMI) play an important role in many physical and chemical phenomena. The existence of liquid and solid phases, the effects of the self-organisation of biological molecules and more complex structures, solution and adsorption processes, etc. are determined by IMI.

One of the main tasks in the theoretical study of IMI is the study of the potential energy surface for the interaction of two molecules—a dimer. The total intermolecular potential can be obtained from the experimental data only in rare cases, so that extensive use has been made of theoretical approaches to the estimation of IMI using the most varied approximations and methods, from empirical atom-atom potentials to non-empirical (*ab initio*) quantum-chemical calculations. The most reliable data are obtained from precision non-empirical calculations, in which the wavefunctions are constructed using a sufficiently broad set of basis functions (extended basis) and, in addition, account is taken of electron correlation. These calculations are extremely laborious, and up to the present it has been possible to use them to study only the interaction of atoms and various small molecules. To analyse

the IMI of polyatomic molecules, it is necessary to carry out less rigorous non-empirical calculations using restricted basis sets. For complex molecules, however, even these calculations are extremely laborious, and often present an insoluble computational problem, and it is then necessary to resort to the semi-empirical methods of quantum chemistry; the results of non-empirical calculations for model molecules with a small number of atoms can be used to estimate the reliability of semi-empirical methods.

Data on the potential energy surface of the dimer make it possible to proceed to the study of a system of many molecules and to study the structure and properties of liquids and solids. A natural step on going from the dimer to a system consisting of a large number of molecules is the construction of analytical pair potentials of the atom-atom type, carried out on the basis of information on the potential energy surface, obtained non-empirically. The analytical potentials found in this way are used to calculate various characteristics of polyatomic systems; in a number of cases, the Monte Carlo method is used.

Considerable experience of non-empirical calculations of IMI has now accumulated, calculations have been carried out for a large number of dimers with different types of bonding, and definite ideas exist on the most effective methods of calculation and their accuracy and ranges of application. In the present review, the results of non-empirical calculations of IMI, different methods of constructing analytical IMI potentials on the basis of *ab initio* calculations, and the results of IMI calculations obtained by various semi-empirical quantum-chemical methods are discussed. The review deals chiefly with the results of calculations on polyatomic molecules; the large number of papers dealing with the interaction of atoms and diatomic molecules of the type $H...H^+$, $H...H$, $H_2...H_2$, $He...He$ etc. are not examined in the present work.

II. NON-EMPIRICAL METHODS FOR CALCULATING INTERMOLECULAR INTERACTIONS

There are two main approaches to the calculation of the energy of IMI. One is based on the variation principle. This principle is applied in a system consisting of several molecules, which is regarded as a single quantum system—a supermolecule. The energy of the interaction is calculated as the difference between the energy of the ground state of the supermolecule and the total energy of the corresponding isolated molecules. Since the most widespread method for estimating the energy and constructing the wavefunctions of molecules is the method of molecular orbitals (MO), which are determined from the solution of the Hartree–Fock–Roothaan equations, often called self-consistent field (SCF) equations, this approach will subsequently be called the SCF approximation or the supermolecule approximation. In the second approach, the energy of the interaction of the molecules is determined using perturbation theory, whose application requires a knowledge of the wavefunctions and energies of not only the ground states but also the excited states of the isolated molecules.

1. The Method of Molecular Orbitals and the Basis Sets Used in Non-empirical Calculations

Molecular orbitals are usually constructed as linear combinations of atomic orbitals (LCAO) and are determined from the solution of the SCF equations. The principles of SCF theory have been described in detail in many monographs (see, for example, Refs.1–4), so that only those points necessary for the subsequent discussion will be considered here.

The wavefunction of the system is represented in the form of a Slater determinant, constructed from the MO with allowance for the spin properties of the system. This wavefunction with energy E^{SCF} is an approximate solution of the Schrödinger equation corresponding to the ground state. To obtain a better approximation to the solution of the Schrödinger equation, it is necessary to take account of electron correlation. Although the energy of electron correlation E^{cor} makes up only a small fraction of the total energy, allowance for this energy is nevertheless important in the examination of many properties of molecules, The value of E^{cor} is determined either by the method of configurational interaction (CI) or from perturbation theory.

The accuracy of non-empirical calculations of E^{SCF} and E^{cor} depends on the type and number of the basis AO used in the construction of the MO. If Slater orbitals (ϕ_{STO}) are used as AO, completely satisfactory results are obtained if each AO is represented by a linear combination of two ϕ_{STO} (double zeta basis, DZ). A basis set in which there is one ϕ_{STO} for each AO is called a minimum basis set.

In the Slater basis, however, it is difficult to calculate a number of integrals appearing in the SCF equations. In most cases, therefore, non-empirical calculations are carried out with Gaussian orbitals (ϕ_G). Since these functions decrease too rapidly with distance, to obtain results equivalent to those obtained with Slater orbitals, each of the functions ϕ_{STO} is represented in the form of a sum of several functions ϕ_G, leading to an increase in the number of SCF equations. Grouping of some of the functions ϕ_G (contraction) makes it possible to decrease the number of SCF equations. The most widely encountered basis sets, consisting of Gaussian functions, and the methods for contraction are described in Refs.5 and 6.

To find a wavefunction close to the Hartree–Fock limit, basis sets consisting of a large number of functions are required. At the present time, this procedure can be carried out only for small molecules. Calculations for polyatomic systems are usually carried out in restricted basis sets. In particular, extensive use is made of the minimum STO-3G basis set[7], in which there are three ϕ_G for one ϕ_{STO}. The basis set 4-31G,[8] in which the orbitals of the valence shells are divided into two groups, is close to the DZ Slater basis sets. There are also basis sets containing polarisation functions P, describing AO of the d and f type for atoms of the second period (for example, the basis sets 6-31G* and 6-31G**).[9] The selection of the optimum basis set represents one of the most important problems in non-empirical calculations.

2. The SCF Approximation

In SCF methods, the energy of intermolecular interaction is calculated using the equation

$$E_{int}^{SCF} = E_{AB}^{SCF} - E_{A}^{SCF} - E_{B}^{SCF} \quad (1)$$

where E_{AB}^{SCF}, E_{A}^{SCF}, and E_{B}^{SCF}, represent respectively the Hartree–Fock energies of the supermolecule AB and the isolated non-interacting molecules A and B. Eqn.(1) makes it possible to obtain only an approximate (Hartree–Fock) value of the energy of interaction, and for the further refinement of the energy of interaction it is necessary to take account of correlation corrections: $E_{int} = E_{int}^{SCF} + E_{cor}^{SCF}$. The correlation energy is made up of the intramolecular and intermolecular correlation energies. The most significant for

IMI is allowance for intermolecular correlation, which at large distances is equivalent to the dispersion energy E_{disp},[10] obtained in perturbation theory.

Calculations in the SCF approximation can be divided into three classes, depending on the nature of the basis set used.

1) Calculations in Hartree–Fock basis sets taking complete account of correlation. The accuracy of the results of these calculations is comparable with that of experiment, but the calculations can only be carried out for small systems. Calculations of this kind have been reviewed in Ref.11.

2) Calculations in DZ + P extended basis sets, and also in the basis sets DZ, 6-31G**, etc., are restricted to comparatively small systems, but their range of applicability is expanding rapidly.

3) The most widely encountered calculations are those in restricted basis sets (of the type 4-31 G) and particularly in minimum basis sets. As shown below, calculations in minimum basis sets can be applied to fairly complex systems.

In calculations in extended, restricted, and minimum basis sets, allowance for electron correlation usually reduces to the calculation of the dispersion energy.

The accuracy of calculations in restricted basis sets can be increased if the basis set superposition error (BSSE) is eliminated; this error arises because the basis set in the calculation of the supermolecule AB is broader than that in the calculation of the isolated molecules A and B. To eliminate this error, the calculation of E_A^{SCF} and E_B^{SCF} is carried out in the basis set used for the system AB (the counterpoise (CP) method[11,12].

For the analysis of the physical nature of IMI, it is of considerable interest to separate E_{int}^{SCF} into its components, although this separation is somewhat arbitrary. The principal components of E_{int}^{SCF} are the electrostatic energy ($E_{el\text{-}st}$), the exchange energy (E_{exch}), the induction (or polarisation) energy (E_{ind}), and the energy of delocalisation or charge transfer (E_{ct}), so that it is possible to write:

$$E_{int}^{SCF} = E_{el\text{-}st} + E_{exch} + E_{ind} + E_{ct} \qquad (2)$$

Effective methods exist[13–16] for separating E_{int}^{SCF} into its components. Usually, E_{ct} is determined as the difference $E_{int}^{SCF} - (E_{el\text{-}st} + E_{exch} + E_{ind})$. It is only in the improved scheme proposed in Ref.14 that E_{ct} is calculated directly, and an additional component is introduced, $E_{mix} = E_{int} - (E_{el\text{-}st} + E_{exch} + E_{ind} + E_{ct})$, in which account is taken of interactions of higher orders between different components.

The MO LCAO SCF approximation is now the principal method in non-empirical calculations of IMI for polyatomic molecules, since there exist well developed procedures for solving the Hartree–Fock–Roothaan equations. On the other hand, the procedure for calculating IMI using perturbation theory is still not fully developed (see below). Another advantage of the SCF method is the possibility of studying the interaction of molecules at short distances.

3. The Approximation of Perturbation Theory

In perturbation theory (PT), the Hamiltonian H_{AB} of the system AB is written as follows:

$$H_{AB} = H_A + H_B + V_{AB} = H_0 + V_{AB} \qquad (3)$$

where H_A and H_B are the energy operators of the isolated molecules A and B, V_{AB} the operator of the interaction, regarded as a perturbation, and $H_0 = H_A + H_B$. For large intermolecular distances (0.5–0.8 nm) it is possible to use as the basis functions of perturbation theory the products of the wavefunctions $A_i^0.B_j^0$ of the isolated molecules (i and j are the indices for the states). This method makes it possible to estimate the long-range components of E_{int} : $E_{el\text{-}st}$ in first-order perturbation theory, and E_{ind} and E_{disp} in second-order[11,17–19]. At distances close to the van der Waals minimum (0.3–0.4 nm), it is necessary to take account of exchange effects, and as functions of zeroth order it is necessary to take the antisymmetrised products $\mathscr{A}(A_i^0.B_j^0)$, which, however, unlike the products $A_i^0.B_j^0$ are not eigenfunctions of the Hamiltonian H_0. This leads to difficulties in the construction of the series of perturbation theory.

In the "symmetrical" approaches to this problem, the operator H_{AB} is divided more or less arbitrarily into $H^0 + V^{AB}$ [$H^0 \neq H_0$, $V^{AB} \neq V_{AB}$, compare with Eqn.(3)] in such a way that the antisymmetrised products $\mathscr{A}(A_i^0.B_j^0)$ are eigenfunctions of the operator H^0.[18,20,21] This makes it possible to take account of exchange effects using ordinary perturbation theory. The "non-symmetrical" formalism starts from the natural choice of H_0 and V_{AB} [Eqn.(3)], but in the expansion, forced antisymmetrisation of the wavefunction is carried out by means of the appropriate projection operators. Different "non-symmetrical" perturbation schemes differ from one another in the choice of projection operators and the method of applying them[22–27]. Although the two approaches in principle give equivalent results[18], the "non-symmetrical approaches" have been more widely used.

Different versions of perturbation theory have been used to carry out detailed studies of interaction in the simplest systems (H...H, He...He). The results obtained, in particular the ratio of the contributions of second and third orders, make it possible to state[18,26,28] that in the attraction region the interaction between molecules with closed shells can be explained by restricting the treatment to terms of second order, that is by representing approximately the IMI energy in the form:

$$E_{int}^{PT} = \Delta E^{(1)} + \Delta E^{(2)} \qquad (4)$$

where $\Delta E^{(1)} = E_{el\text{-}st} + E_{exch}$ is the first order contribution, $\Delta E^{(2)} = E_{ind} + E_{disp} + E_{exch}^{(2)}$ the second order contribution, and E_{exch} the second order exchange energy, taking account of the exchange corrections to E_{ind} and E_{disp}. This conclusion is confirmed by calculations for more complex systems[29,30].

The different versions of perturbation theory generally differ only in the expressions for $E_{exch}^{(2)}$.

Precise calculations of the interaction H...H and He...He have shown[18] that the contribution of $E_{exch}^{(2)}$ represents a few percent of E_{int}^{PT}. This contribution has not been estimated for more complex systems, but a precise calculation for the dimer $(H_2O)_2$ showed[30] that satisfactory values of E_{int}^{PT} are obtained without taking account of E_{exch}. It may be assumed that the part played by $E_{exch}^{(2)}$ is also small in the case of the interaction of polyatomic molecules. A rigorous analysis of E_{ind} [28] showed that in the range of non-negligible overlap, allowance for induction interaction requires the introduction of significant ionic terms into the wavefunction. This means that for the correct calculation of E_{ind}^{PT} it is necessary to use as basis functions the wavefunctions of excited states, which contain ionic terms, that is states with charge transfer.

Thus in the calculation of the interaction energy from perturbation theory in extended basis sets which make it possible to take account of ionic states, it is possible to restrict the treatment to the contributions $E_{el\text{-}st}$, E_{exch}, E_{ind}, and E_{disp}. If however the basis set of the excited states is restricted and does not contain ionic terms, it is necessary

to take direct account of the contribution of E_{ct}. This quantity is used in explicit form in the perturbation theory developed by Murrell and co-workers[31], and also in the "symmetrical" theory[20].

The possibilities provided by perturbation theory and the SCF method can now be compared. Unlike E_{int}^{SCF}, the quantity E_{int}^{PT} contains E_{disp} directly. For the other components, for exact (correlated) wavefunctions, the calculation of the electrostatic and exchange energies from perturbation theory and in the SCF approximation leads to identical results. The differences for the Hartree–Fock limit are also negligible. In the calculation in a basis set containing ionic terms, E_{ind}^{PT} corresponds to the sum of E_{ind}^{SCF} and E_{ct}^{SCF} from Eqn.(2) (it must be borne in mind that E_{ind}^{SCF} and E_{ct}^{SCF} also contain added terms from higher order contributions). In the calculation in restricted basis sets without ionic states, E_{ind}^{PT} is compared only with E_{ind}^{SCF},[29] but in this case it is necessary to estimate E_{ct}^{PT}, for example according to Ref.31. It is suggested[18] that $E_{exch}^{(2)}$ corresponds to a certain fraction of E_{ct}^{SCF}.

There are grounds for assuming that the SCF method and perturbation theory give equivalent results[29,30,32], particularly in calculations in extended basis sets[30]. The methods of perturbation theory have as yet been little tested for polyatomic molecules, and at present, the great majority of non-empirical calculations of IMI for complex molecules are carried out by the SCF method.

The questions dealt with in this section are examined in more detail in monographs[11,17]† and reviews[18,19]. The most complete analysis of "unsymmetrical" perturbation theory is given in Refs.19, 26, and 27.

III. NON-EMPIRICAL CALCULATIONS FOR DIMERS OF DIFFERENT CHEMICAL CHARACTER

The IMI calculations discussed in this section were carried out chiefly in restricted basis sets. As indicated above, this means that the data obtained in the calculations on the equilibrium geometry and energy of interaction may differ slightly from the experimental results.

1. Hydrogen Bonding

Systems with a hydrogen bond have been studied in detail, both theoretically and experimentally (see published monographs[33–35] and reviews[36,37]). The interest in these systems is due to the fact that they include such materials as water and biopolymers. From the theoretical viewpoint, it is of interest to determine why the hydrogen bond is generally stronger than other types of IMI, and has a definite direction in space.

The water dimer can be considered first. Non-empirical calculations have been carried out for this dimer, which have made it possible to determine the three-dimensional structure and bond energy of the dimer and to distinguish the most important factors determining the stability of the dimer. Calculations for the dimer $(H_2O)_2$ have been carried out in different approximations as far as the use of Hartree–Fock basis sets with allowance for correlation. All non-empirical calculations, irrespective of the choice of basis set, indicate that the most favourable of the three possible structures—linear, crossed, and cyclic (Fig.1)—is the linear structure with a distance between the oxygen atoms R_{O-O} close to 0.3 nm. This result agrees with the experimental data[38], according to which $R_{O-O} = 0.298$ nm and $\theta = 60°$. The magnitude of the energy of interaction depends on the method of calculation. The results of a detailed calculation for the dimer $(H_2O)_2$ by the SCF method and perturbation theory in a basis set close to the Hartree–Fock set are given in Ref.30. The calculation using perturbation theory gave the components E_{el-st}, E_{exch}, E_{ind}, and E_{disp}. Since the basis functions used to calculate E_{ind} contained functions of the charge transfer type, E_{ind} in Ref.30 in fact took account of the contribution of E_{ct}. It is natural to compare the sum $E'_{PT} = E_{el-st} + E_{exch} + E_{ind}$ with the quantity E_{int}^{SCF} calculated in the same basis set. It was found (Table 1) that for distances greater than 0.275 nm, E_{int}^{SCF} is reproduced with a good accuracy by the quantity E'_{PT}. The distance $R_{O-O} = 0.3$ nm corresponds to the minimum values of E_{int}^{SCF} and E'_{PT}: $E_{int}^{SCF} = -16.2$ kJ mole^{-1}, $E'_{PT} = -16.1$ kJ mole^{-1}. According to Ref.39, the Hartree–Fock limit for E_{int}^{SCF} is 16.3 ± 1.1 kJ mole^{-1}. The fact that the minimum values of E_{int}^{SCF} and E'_{PT} coincide provides evidence that the two approaches to the calculation of IMI, based on SCF theory and on perturbation theory, are equivalent. The discrepancies between E_{int}^{SCF} and E'_{PT} at short distances is attributed to the presence in E_{int}^{SCF} of corrections of higher orders, and various other characteristics of the SCF method[29]. When allowance is made for E_{disp} from perturbation theory (see Table 1), the value of R_{equil} is found to be 0.286 nm, and $E_{int} = E_{int}^{SCF} + E_{disp} = -24.3$ kJ mole^{-1}.[30] The data from Ref.40, obtained for the dimer $(H_2O)_2$ in an extended basis set with allowance for correlation by CI methods are: $E_{int}^{SCF} = -18.1$ kJ mole^{-1}, $E_{int}^{cor} = -3.6$ kJ mole^{-1}, and $E_{int} = -21.7$ kJ mole^{-1}.

From experimental data it is known that the bond energy in the water dimer lies in the range -16 kJ mole^{-1} to -28 kJ mole^{-1}[11,38,41]. The calculation gives satisfactory values for the bond energies, but the scatter in the experimental data makes it impossible to determine which is the best method for taking account of the correlation correction to E_{int}^{SCF}.

The results of calculations carried out for a linear dimer using perturbation theory in a basis set close to the Hartree–Fock set[30] and by the SCF method in different restricted basis sets with separation of E_{int}^{SCF} into its components[42] are compared in Table 2. The data in Table 2 make it possible to follow the influence of the basis set on the results and to analyse the nature of the bond in the dimer $(H_2O)_2$. It follows from Table 2 that the greatest contribution to the bond energy is made by the electrostatic interaction, and the contributions of E_{ct} and E_{ind} are less significant [$E_{disp} = -6.4$ kJ mole^{-1} (Table 1) is also not decisive]. In the STO-3G basis set, the contribution of E_{el-st} is lowered, and the role of E_{ct} is increased. The calculation in the basis set 4-31G leads to an increase in the bond energy in $(H_2O)_2$ as a result of an excessive value of the electrostatic attraction. More balanced data

† See also I.G.Kaplan, "Vvedenie v Teoriyu Mezhmolekulyarnykh Vzaimodeistvii" (Introduction to the Theory of Intermolecular Interactions), Izd.Nauka, Moscow, 1982.

are obtained in the basis set 6-31G**, which contains polarisation functions, but in this case also the role of E_{ct} is increased. It should be noted that the minimum basis set[43], optimised for calculating IMI, in the case of the linear dimer of water gives $E_{int}^{SCF} = -18.6$ kJ mole^{-1} for $R_{O-O} = 0.3$ nm, which is close to the results of the calculation in the Hartree–Fock basis set[39]. The influence of the basis set on the calculated values of E_{int}^{SCF} will be considered below.

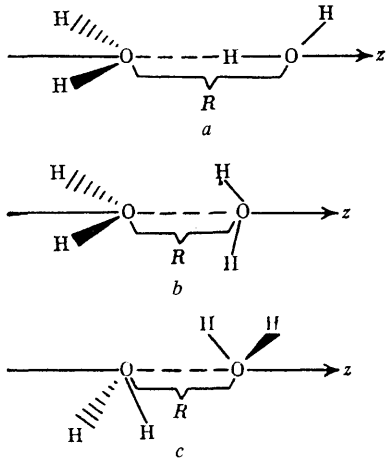


Figure 1. Linear (*a*), crossed (*b*), and cyclic (*c*) configurations of the water dimer[42].

Table 1. Energy characteristics of the IMI, found by the SCF method and from perturbation theory (PT) for the dimer $(H_2O)_2$.

R_{O-O}, nm	E_{PT}	E_{int}^{SCF}	E_{disp}	$E_{int}^{SCF} + E_{disp}$
0.212	54.8	144.9	—60.5	84.4
0.233	13.6	44.9	—35.2	9.7
0.254	—5.3	3.8	—20.5	—16.7
0.275	—13.4	—11.6	—11.9	—23.5
0.300	—16.1	—16.2	—6.4	—22.6
0.370	—12.0	—12.4	—1.3	—13.7
0.476	—4.8	—4.8	—0.2	—5.0

Other examples of small molecules with a hydrogen bond have been examined in a large number of studies. Some of the results obtained in the SCF approximation for different basis sets are given in Table 3 (the data in Table 3 were taken from Ref.43, which gives references to the original papers). The values of E_{int}^{SCF} obtained for $(H_2O)_2$ and $(HF)_2$ in Hartree–Fock basis sets are the most reliable. The bond energies for the systems $HOH...NH_3$ and $H_2O...HNH_2$, calculated in extended basis sets, are slightly too high[43] (absolute values). It may also be noted that a number of calculations carried out without eliminating the superposition error in other basis sets (for example in the standard minimum STO-3G and (7*s*3*p*), denoted OLD in Ref.43, in the minimum basis set NEW, obtained in Ref.43 by optimising the basis set OLD for the calculation of IMI, in the basis set of intermediate type 4-31G, and in the basis set 6-31G*, containing polarisation functions) lead to values of E_{int}^{SCF} which are higher than those obtained using an extended basis set. Elimination of the superposition error by the counterpoise method in the case of calculations carried out in the basis sets OLD and NEW gives results close to those obtained with Hartree–Fock and extended basis sets. Unfortunately, a correct comparison of the values of E_{int}^{SCF} found from the calculation with the experimental data is difficult. Firstly, the experimental data are not always available, and their accuracy is low. Secondly, a meaningful comparison of E_{int}^{SCF} with experiment requires at least an approximate estimate of E_{disp}. Table 3 gives the values of E_{disp} calculated in Ref.43 using an equation of the London type in terms of bond polarisability. Although these values of E_{disp} are too low[44], they nevertheless make up an appreciable part of the total energy of interaction. Allowance for dispersion corrections improves the agreement between the experimental data and the calculated bond energies, obtained by the SCF method in extended Hartree–Fock basis sets and also in the basis sets OLD and NEW. It may be noted that different dimers with a hydrogen bond were also examined in Ref.42 in the basis set 4-31G and without additional allowance for dispersion corrections. The most characteristic properties of hydrogen bonds, which make them unique, were discussed in this paper. The authors[42] studied different dimers, in which the proton donors were HF, H_2O, NH_3, and CH_4, and the proton acceptors HF, H_2O, and NH_3. It was shown that the bond energy E_{int}^{SCF} varies over a fairly wide range from -68.2 kJ mole^{-1} for the complex $H_3N...HF$ to -42.0 kJ mole^{-1} for the complex $H_3N...HF$ to -4.6 kJ mole^{-1} for the $H_2O...H_4C$ system. An analysis of the components of the energy E_{int}^{SCF} found using the published scheme[14] led to the following conclusions about the nature of the hydrogen bond [for the dimer $(H_2O)_2$ see Table 2].

Table 2. Components of the energy of the IMI in the linear dimer $(H_2O)_2$ with $R_{O-O} = 0.3$ nm, obtained in different approximations[30,42].

Components of the energy, kJ mole^{-1}	Perturbation theory[a]	SCF method[b]		
		3-31G**	4-31G	STO-3 G
ΔE[c]	—16.1	—23.4	—32.2	—21.3
$E_{el\text{-}st}$	—29.8	—31.4	—37.2	—17.6
E_{exch}	20.5	18.0	17.6	6.7
E_{ind}	—6.8[d]	—2.1	—2.1	—0.4
E_{ct}	—	—7.2	—8.8	—20.1
E_{mix}^{e}	—	—0.4	—1.7	0.1

[a]Basis set close to the Hartree–Fock set[30]; $R_{O-O} = 0.3$ nm, $\theta = 0°$ (see Fig.1).

[b]$R_{O-O} = 0.298$ nm, $\theta = 60°$. According to Ref.42, the results change little with change in θ.

[c]$\Delta E = E''_{PT}$ in perturbation theory[30] and $\Delta E = E_{int}^{SCF}$ in the calculation by the SCF method.

[d]E_{ind} from perturbation theory contains E_{ct} (see text of the present review and Ref.30).

[e]See discussion of Eqn.(2).

1) All the hydrogen bonds are electrostatic in character, that is the stabilisation is determined chiefly by the electrostatic contribution.

2) The relative part played by E_{ct} is slight in strongly bonded dimers, but increases in weakly bonded dimers.

3) The length and degree of departure from linearity of a hydrogen bond Y–H...X are determined by the ratio of E_{exch} and E_{disp}.

Table 3. Energies E_{int}^{SCF}, kJ mole^{-1}, calculated in different basis sets for the equilibrium configurations of various dimers with a hydrogen bond[43].

Dimer	E_{int}^{SCF}									E_{disp}^{e}	E_{int} (expt)
	OLD[a]	NEW[b]	STO-3G	4-31G	6-31G	OLD (CP)[c]	NEW (CP)	extended basis	HF[d]		
$H_3N\cdots HF$	−59.5	−50.4	−34.7	−68.1	51.0	−49.7	−42.0	—	—	−8.1	—
$HOH\cdots H_3N$	−33.3	−27.8	−24.7	−37.6	−27.2	−25.2	−21.3	−26.3	—	−5.4	—
$H_2O\cdots H_2O$	−31.2	−25.3	−25.1	−33.9	−23.4	−20.4	−18.6	−18.2	−16.3	−3.1	−21.8±6.3
$HF\cdots HF$	−33.1	−22.2	−23.0	−32.2	−24.7	−15.9	−12.2	−19.4[f]	−13.4	−3.6	−25.1±6.3
$H_3N\cdots NH_3$	−15.9	−12.8	−15.9	−17.1	−12.1	−11.1	−9.6	—	—	−2.8	−18.8±1.7
$H_2O\cdots HNH_2$	−15.5	−11.3	−17.1	−17.1	−7.1	−9.2	−8.4	−9.6	—	−2.3	—

[a]Minimum basis set (7*s*3*p*) from Ref.43,

[b]Minimum basis set, obtained in Ref.43 by optimising the basis set OLD for the calculation of intermolecular interaction.

[c]Calculation with elimination of the superposition error by the counterpoise (CP) method.

[d]Hartree–Fock basis set.

[e]Values of E_{disp} calculated in terms of bond polarisability.

[f]See pp.63 and 175 of Ref.11.

Both the calculated and the experimental data indicate that the absolute magnitude of the energy of a normal hydrogen bond does not exceed 60–70 kJ mole^{-1} (ionic hydrogen bonds $NH_3...H^+$ or $FH...F^-$, where the bond energies reach hundreds of kJ mole^{-1}, are not considered here). Comparison of the hydrogen-bonded dimers with the lithium complexes $(LiF)_2$ and $(LiH)_2$ [42] and the strong electron donor–acceptor (EDA) complexes $H_3N...BH_3$ and $BH_3...OC$,[45] in which the bond energy reaches between −150 kJ mole^{-1} and −300 kJ mole^{-1}, makes it possible to estimate the position of dimers with a hydrogen bond in the general series of strongly bonded complexes. The authors[42] consider that the unique character of the hydrogen bond is determined by the fact that in it the proton donor has a short strong bond Y–H of medium polarity. Since the bond has medium polarity, the energy of electrostatic attraction is insufficiently large, and therefore does not compensate the contribution of E_{exch}, which increases rapidly as the atoms H and X approach one another. Since the atoms Y and X are insufficiently far apart, and the bond Y–H is short and its stretching is difficult, the interaction of the atoms Y and X also makes a significant contribution to the exchange energy. In the strong EDA complexes and in the lithium complexes, the strong electrostatic interaction compensates the exchange repulsion, and the atoms of different molecules approach one another to distances less that 0.2 nm [$R_{N...B} = 0.175$ nm in $H_3N...BH_3$, and $R_{Li...F} = 0.180$ nm in $(LiF)_2$]. In the lithium complexes, the bond in the monomer is easily stretched, and this leads to greater possibilities for bond formation in the complex. Thus in $(LiF)_2$ and $(LiH)_2$, the cyclic structure, and not the linear structure, is more favourable. The stretching of the strong bond Y–H, however, requires too great an expenditure of energy. Thus in accordance with published work[42,46], the normal hydrogen bond is characterised by a definite (linear) direction and intermediate energy values.

Various other polyatomic systems with a hydrogen bond can now be considered. A cycle of studies by Pullman and co-workers[47–61] (see also references therein) was devoted to a study of hydrogen bonding involving biological molecules, in particular their mono- and polyhydration. The calculations were carried out in the SCF approximation in restricted basis sets and without additional allowance for E_{disp}. The energy of interaction E_{int}^{SCF} was analysed by the scheme of Ref.15, which is simpler than the schemes of Refs.13 and 14. The contributions E_{el-st}, E_{exch}, and $E_{ind}+E_{ct}$ were separated. The electrostatic energy in some cases was approximated by the energy of interaction of the point multipole moments of the molecules, and this simplifies considerably the estimation of this contribution. Pullman and co-workers have studied in detail the hydration of amides[53,54,57], nucleotide bases[47], urea and thiourea[58,59], and the carboxylate anion[60]; they showed that the characteristic features of the hydration are determined by the magnitude of the contribution E_{el-st}, since E_{exch} and $E_{ind}+E_{ct}$ approximately compensate one another. A more detailed review of this work can be found in Ref.61.

Many authors have studied hydrogen bonding in formamide oligomers[62–66], which provides a model of the interaction in polypeptides and proteins. The most interesting results were obtained for the description of the interaction of amide groups in different configurations, which are characteristic of polypeptides; mention must also be made of the study of cooperative effects[65]. It was recently shown[66] that the attraction of amide groups is stronger in an α-spiral than in a 3_{10} spiral, and cooperative effects were detected on going from the dimer to the trimer.

Table 4. Components of the energy of IMI in the dimers $(HCONH_2)_2$ and $(HCOOH)_2$, calculated in different basis sets (from data in Refs.67 and 68).

Components of the energy, kJ mole^{-1}	$(HCONH_2)_2$	$(HCOOH)_2$		
	STO–3G[a]	STO-3G[a]	minimum basis set	DZ[b]
E_{el-st}	−45.7	−60.0	−94.4[c]	−103.6[c]
E_{exch}	46.5	96.0	89.7	142.9
E_{ind}	−3.2	−3.5	−16.7	−27.5
E_{ct}	−61.2	−97.9	−46.2	−43.1
E_{disp}	—	—	−31.8[d]	−28.0[d]
E_{int}	−63.6	−65.5	−99.6	−59.4

[a]From Ref.67, for $R_{O-O} = 2.73$ Å.

[b]From Ref.68, for $R_{O-O} = 2.7$ Å in minimum and DZ basis sets.

[c]Corrected with allowance for the ratio μ_{calc}/μ_{expt}, where μ is the dipole moment.

[d]Non-empirical calculation using perturbation theory.

The SCF method has been used[67] to study hydrogen bonding in the dimers $(HCOOH)_2$, $(HCONH_2)_2$, and $[B(OH)_3]_2$ in an STO-3G basis set without additional allowance for E_{disp}

(Table 4). The value found for E_{int}^{SCF} (STO-3G) for $(HCOOH)_2$ is close to the experimental value, and amounts to between -60.8 kJ mole^{-1} and -73.3 kJ mole^{-1}.[67,68]. It follows from Table 4 that in the basis set STO-3G, the bond energy in the dimers $(HCONH_2)_2$ and $(HCOOH)_2$ is determined chiefly by the contributions E_{el-st} and E_{ct}. In the STO-3G basis set, however, the contribution E_{ct} is too large. This follows from a comparison of the components of E_{int}^{SCF} in the dimer $(HCOOH)_2$, obtained in the basis set STO-3G [67] and in the DZ basis set[68] (see Table 4). According to Ref.68, the greatest contribution to the bond energy in $(HCOOH)_2$ is made by E_{el-st}. In the case of the DZ basis set, to obtain results close to the experimental data, it is necessary to take additional account of the dispersion contributions E_{disp}. It may also be noted that the data obtained in Ref.68 were used in Ref.69 to construct model potentials (see R.p. 1073). Calculations carried out in an STO-3G basis set gave satisfactory values for the enthalpies of formation of the dimers of a number of alcohols [70], and were also found to be suitable for the study of the intramolecular hydrogen bond in 7-norbornenol[71]. Mention must also be made of the extensive series of studies by Del Bene (see Refs.72 and 73 and references therein), devoted to the examination of hydrogen bonds in various systems. Lack of space makes it impossible to give a detailed description of the results of recent calculations[74–77] for systems containing a hydrogen bond, such as nitric acid and ammonia, pyrrole and acetonitrile, formaldehyde and hydrogen sulphide, and the sulphide anion and water.

In Ref.78, the $HO^-...H_2O$ system was studied, and data were obtained on the influence of the solvent on the relative acidity of water and methanol.

In most of the work discussed, the MO LCAO SCF approximation was used. Perturbation theory was used in Refs.30, 79, and 80. The last two papers also discuss calculations carried out by the self-consistent field method for the systems $(H_2CO)_2$, $(H_2O)_2$, and $(HF)_2$ in different approximations. Symmetrical perturbation theory[20] has been used successfully [32] to calculate the bond energy in the systems $H_2CO...OH^-$ and $H_2CO...NH_3$.

2. Electronic Donor–Acceptor Complexes

From Mulliken's model for EDA complexes[81] it followed that in these systems an important part is played by charge transfer; in particular, it was suggested that the structure of a complex is determined by the interaction between the occupied MO of the donor and the unoccupied MO of the acceptor. Semi-empirical calculations for EDA complexes[82,83] showed, however, that E_{ct} does not make the decisive contribution to the interaction energy, and the electrostatic interaction is generally more significant. Non-empirical calculations for EDA complexes have begun to appear only comparatively recently. It has been shown[84,85] that in a minimum basis set and the DZ basis, the equilibrium geometries in the complexes formed by H_3N and $(CH_3)_3N$ with F_2, Cl_2, FCl, ClF, SO_2, and O_3 are approximately the same, but higher values are obtained for the bond energy in the DZ basis set. These calculations showed that the bond energy of the complexes of H_3N with F_2, Cl_2, FCl, and SO_2 is greater than the bond energy of the corresponding complexes of trimethylamine. In contrast to the complexes $H_3N...F_2$ and $H_3N...Cl_2$, in the case of the complexes $H_3N...FCl$ and $H_3N...ClF$ the results depend markedly on the choice of basis set. From qualitative considerations, a high bond energy is expected for the complex $H_3N...ClF$, since in the ClF molecule the Cl atom is positively charged, and the N atom in the NH_3 molecule is negatively charged. According to the results of the calculation carried out in the DZ basis set, the bond energy in the complex $H_3N...ClF$ is -32.2 kJ mole^{-1}, and the complex $H_3N...FCl$ is unstable, whereas according to the calculation in the minimum basis set, the complex $H_3N...FCl$ is more favourable. The reason for this lack of agreement between the results of the calculation in different basis sets is apparently that in the minimum basis set it is not possible to estimate correctly the direction of the dipole moment in the ClF molecule.

A systematic study of EDA complexes has been carried out [45,46,86,87]. The calculations were carried out chiefly in the basis set 4-31G. For some of the complexes examined, perturbation theory was used to estimate the value of E_{disp}.

Table 5. Energy characteristics of IMI, kJ mole^{-1}, for the optimised intermolecular distances (R_{equil}), and the classification of the EDA complexes (calculation in the basis set 4-31G).

	Type of complex	R_{equil}	E_{el-st}	E_{exch}	E_{ind}	E_{ct}	E_{mix}	E_{int}^{SCF}	E_{disp}	$E_{int}^{SCF}+E_{disp}$	Classification	Refs.
$H_3N...BH_3$	$n\sigma^*$	0.160	−595.4	570.3	−178.7	−220.5	125.1	−299.2	—	—	s., el-st	[45, 46]
$OC...BH_3$	$\sigma\sigma^*$	0.163	−254.8	413.8	−258.6	−285.8	266.1	−119.6	—	—	s., ct-ind-el-st	[45, 46]
$(CN_2)CO...H_2O$	$n\pi^*$	0.270	−40.6	18.4	−4.2	−7.5[d]		−33.9	−5.0[a]	−38.9	int., el-st	[87]
$(CN)_2CO...H_2O$	$n\pi^*$	0.270[b]	−17.6	8.4	−0.8	−4.6[d]		−14.6[c]	−1.8[a]	−16.2	ditto	[86]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.360	−11.7	7.5	−7.1	−6.7	0.4	−17.6	−10.9	−28.5	int., disp-el-st	[46]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.360[b]	−4.0	2.1	−0.2	−0.6[d]		−2.7[b]	−3.7[a]	−6.4	ditto	[87]
$(CN)_2CO...C_6H_6$	$\pi\pi^*$	0.320[b]	−6.1	12.5	−0.4	−3.1[d]		2.9[b]	−23.3[c]	−20.4		[89]
$Cl_2...C_6H_6$	$\pi\sigma^*$	0.360	−2.1	2.9	−0.4	−3.3	0	−2.9	−2.9[a]	−5.8	w., disp-ct-el-st	[46]

[a] The value of E_{disp} was calculated non-empirically using perturbation theory.

[b] STO-3G basis set.

[c] The value of E_{disp} was calculated in terms of bond polarisability.

[d] $E_{ct}+E_{mix}$.

Breakdown of the energy E_{int}^{SCF} into its components made it possible to determine the interactions responsible for bond formation in the complexes. All the complexes examined were classified according to the values of the bond energy as strong (s.) with E_{int} in hundreds of kJ mole^{-1}, intermediate (int.) with E_{int} in tens of kJ mole^{-1}, or weak (w.) with E_{int} in units of kJ mole^{-1}, and according to the nature of the bond as electrostatic (el-st), induction (ind), and charge-transfer (ct).

The calculated characteristics of some of the complexes examined in these studies are given in Table 5. The data in Table 5 show that the EDA complexes are not charge-transfer complexes. The influence of charge-transfer is different for different EDA complexes and does not correlate with the strength of the complexes. Thus the suggestion[81] that EDA complexes are always charge-transfer complexes was not confirmed in the non-empirical calculations. Significant contributions from E_{ct} were found for the $n\sigma^*$– and $\sigma\sigma^{**}$–complexes formed by polar molecules (H_3N, BF_3, OC, BH_3). These complexes are characterised by strong electrostatic interaction and short equilibrium distances. With decrease in the polarity of the molecules, the complexes become weaker ($H_2CO...F_2$). It may be noted that the values of the energy E_{int}^{SCF} calculated in the 4-31G basis set are found to be too high, since, for example, in the strong complexes $R_3N...BF_3$ and $R_3N...BH_3$ ($R = CH_3$, C_2H_5), which have similar bond character, the experimentally determined values of the bond energy lie in the range from −110 kJ mole^{-1} to −150 kJ mole^{-1}.[88]

Complexes involving molecules containing π-electrons are of considerable interest. For a complex of the type $n\pi^*$ [for example $(CN)_2CO...H_2O$], the most favourable configuration was found to be that in which the water molecule is situated above the plane of the $(CN)_2CO$ molecule[86] (Fig.2). Calculations were carried out in this configuration for the water...tetracyanoethylene (TCE) $n\pi^*$-complex. In these configurations, the stabilisation of the complexes is determined by $E_{el\text{-}st}$.

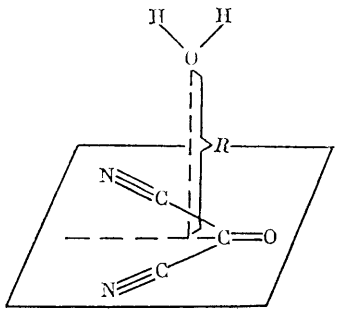


Figure 2. Configuration of the dimer $H_2O...(CN)_2CO$.[86]

The equilibrium distances (0.27–0.30 nm) are greater in the $n\pi^*$-complexes than in the strong $n\sigma^*$-complexes, so that the contributions of E_{ct} and E_{ind} are small. The role of dispersion energy in these systems is slight. It may be noted that the choice of the basis set has a significant influence on the calculated values of the bond energy. For example, in the STO-3G basis set the energy E_{int}^{SCF} of the complex $(CN)_2CO...H_2O$ is −16.3 kJ mole^{-1},[86,87] whereas in the 4-31G basis set it is −38.8 kJ mole^{-1}.[87] The value $E_{int}^{SCF} = -38.9$ kJ mole^{-1} is too high, as is typical of calculations in the 4-31G basis set. The experimental value of the bond energy in the similar system $(CN)_2CO...$diethyl ether is −18.4 kJ mole^{-1}.[86]

For the $\pi\pi^*$-complex $(CN)_2COC_6H_6$ in Ref.87 a "stacking" configuration was chosen, in which the distance between the planes of the molecules and the position of the centre of the benzene ring relative to the C=O axis were optimised (in an STO-3G basis set). A calculation in the 4-31G basis set was carried out for the equilibrium configuration obtained, with $R_{equil} = 0.36$ nm.

The differences in the values of E_{int}^{SCF} for the two basis sets (see Table 5) are due to the characteristic features of the electron distributions obtained in the different basis sets, since these influence the values of $E_{el\text{-}st}$ and E_{ind}. The experimental bond energies for these systems are between −20 kJ mole^{-1} and −25 kJ mole^{-1},[87] which appear to agree only with the results of the calculation in the 4-31G basis set: $E_{int}(4\text{-}31G) = E_{int}^{SCF}(4\text{-}31G) + E_{disp}(4\text{-}31G) = -28.5$ kJ mole^{-1}. It should be noted, however, that the value $E_{disp}(STO\text{-}3G) = -3.7$ kJ mole^{-1}, calculated in the STO-3G basis set using perturbation theory, is clearly too low. The calculation of E_{disp} in terms of the bond polarisability for the dimer $(CN)_2CO...C_6H_6$ being discussed gives the value −13.1 kJ mole^{-1} for $R = 0.36$ nm.[89] Kolos[89] points out that if the more realistic values of E_{disp} calculated in terms of the bond polarisability are added to the values of $E_{int}^{SCF}(STO\text{-}3G)$ from Ref.87, then R_{equil} becomes 0.31 nm, and the bond energy −20.4 kJ mole^{-1} (see Table 5). It may therefore be assumed that the bonding in the dimer involves both dispersion interactions and electrostatic interactions, and the estimate of their contributions to the bond energy depends on the basis set (the value of $E_{el\text{-}st}$ is smaller for the STO-3G basis set, and larger for the 4-31G basis set).

In conclusion, mention may be made of a paper[90] describing a study of charge transfer in the glyoxal-water, $(H_2O)_2$, and $H_2O...Li^+$ systems by different methods (supermolecule, perturbation theory, etc.).

3. Dimers With Other Types of Bond

There have been comparatively few studies of weakly polar or non-polar van der Waals systems, whose stabilisation is determined chiefly by dispersion interactions. Here, mention must be made of detailed studies[91–94] of the potential energy surface for the dimers $(N_2)_2$ and $(C_2H_4)_2$. A significant feature of these studies is that they examined a large number of possible configurations of the dimers and obtained fairly complete information on the potential energy surface.

The authors[91–94] used perturbation theory, and represented the bond energy E_{int} as the sum of $E_{el\text{-}st}$, E_{exch}, E_{ind}, and E_{disp}. The calculations were carried out in DZ and DZ+P basis sets. It was found that in the systems studied, the attraction involves chiefly dispersion interaction; the absolute magnitude of the electrostatic components is several times smaller than that of E_{disp}. The conclusion that E_{disp} plays a decisive role in the stabilisation of dimers containing non-polar systems was also reached by other workers, who calculated the energies of IMI in the dimers $Ar...H_2O$, $Ar...HCl$, $Ar...HF$,[95] and $CH_4...CH_4$.[44] In Ref.44, the results of calculations of E_{int}^{SCF} carried out in different basis sets were given (E_{disp} was estimated in terms of the bond

polarisability), and it was concluded that it is appropriate to use the previously mentioned minimum basis set[43] for IMI calculations. At the same time, as shown by other authors[91,94], although the attraction is determined by E_{disp}, the structure of the equilibrium van der Waals dimers depends to a significant extent on the energy of exchange repulsion E_{exch}. The configurations of the most stable dimers correspond to the lowest exchange repulsion, and in these configurations the attraction (E_{disp}) may not be a maximum. For example, for the dimer $(N_2)_2$ the most stable structure corresponds to the crossed (cross-shaped) arrangement of the molecules[93,94], although the dispersion energy is a maximum in the energetically less favourable linear configuration, in which the exchange repulsion is large. For a distance R between the centres in $(N_2)_2$ equal to 0.4 nm, for the crossed configuration, $E_{exch} = 0.25$ kJ mole^{-1} and $E_{disp} = -1.35$ kJ mole^{-1}, and for the linear configuration $E_{exch} > 3$ kJ mole^{-1} and $E_{disp} = -2.7$ kJ mole^{-1}. The absolute minimum on the potential energy surface corresponds to the crossed structure with values $E_{int} = -1.5$ kJ mole^{-1} and $R = 0.35$ nm.

For the dimer $(C_2H_4)_2$, two structures with low values of E_{exch} were found to be most favourable[92,94]: the staggered parallel configuration and the screw configuration (bond energies -5.01 kJ mole^{-1} and -5.05 kJ mole^{-1} respectively), although the value of E_{disp} is a maximum for the linear arrangement of the molecules, and the value of $E_{el\text{-}st}$ is a maximum for the T-shaped structure. Thus in each case the equilibrium structure of the van der Waals dimer is determined by a fine balance between the forces of repulsion and dispersion attraction, and its determination requires a detailed non-empirical calculation.

These results cast doubt on the reliability of the prediction of the structure of van der Waals dimers on the basis of simple considerations[96,97]. The use of such characteristics of the individual molecules as the dipole and quadrupole moments and polarisability tensors makes it possible to characterise only the long-range contributions of E_{disp} and $E_{el\text{-}st}$, which have been shown to be non-decisive. It has also been suggested that information on the structure of the free dimer can be obtained from the packing of the molecules in the crystal, since the relative arrangement of the nearest neighbours in the crystal should correspond to structures with a low value of the energy of exchange repulsion. The most stable structure of the free dimer, however, may differ from the relative orientation of the nearest neighbours in the crystal. Of the two most favourable structures of the dimer $(C_2H_4)_2$, only one (the screw structure) resembles the packing of the C_2H_4 molecules in the crystal; the staggered parallel structure of $(C_2H_4)_2$, like the crossed configuration of the dimer $(N_2)_2$, differs considerably from the packing of the molecules in the crystal.

Another important result from these studies[92-94] is the conclusion that for the dimers being discussed, there are a large number of structures in which the bond energy amounts to more than 80% of the maximum value. This distinguishes van der Waals dimers from systems with a hydrogen bond and from donor-acceptor complexes, for which there are only a few energetically favourable configurations of the dimers.

Model calculations of the energy of interaction in biological systems are of considerable interest. The study of the interaction of hydroxytryptamines (HT) with the imidazole (IMD) cation has been described in a series of papers[98-100]. The calculation for a system consisting of these fairly large molecules was carried out in a minimum basis set in the "stacking" configuration. Analysis of the components of E_{int}^{SCF} showed that the principal contribution to the stabilisation of the complex is made by electrostatic interaction. The same conclusion was reached in a calculation in a 4-31G basis set with partial allowance for correlation in the interaction of fragments providing models of HT and IMD.[99]

The interactions in the imidazole–methanethiol system, the imidazole–methanethiol–formaldehyde system, and the imidazole–methanethiol–formaldehyde system in the electric field created by the charges on the atoms of an α-spiral which provided a model of the active centre of the enzyme papaine have been studied[101] in minimum and extended basis sets. It was shown that the electrostatic field created by the spiral is responsible for the formation of an ion pair $RS^-...ImH^+$ from the basic residues Cys 25 and His 159. The anomalous values of pK for these residues were also explained[101]. The authors[101] concluded that the α-spirals are important parts of enzymes and play an important role in the catalytic process. An analogous problem and similar substances were studied in Ref.102, where STO-3G and 4-31G basis sets were used to study the interaction in systems containing imidazole, methanol, formic acid, and methanethiol, which provided models of the active centres of serine and cysteine proteases. The number of papers devoted to the non-empirical calculation of the interaction of large molecules is still small, however; the calculation of the interaction of such large molecules as tetracyanoquinodimethane $(CN)_2CC_6H_4C(CN)_2$ and tetrathiofulvene $H_2C_2S_2C_2S_2C_2H_2$ [103] as yet represents the exception.

The thermodynamic stability of dimers at finite temperatures is determined not only by the enthalpy of the system, but also by its entropy. Particular attention was paid to the calculation of the entropy in Refs.104–107. In particular, mention must be made of results[104] which showed that even in polar systems, the role of the entropy term is significant, and in non-polar systems the entropy determines the behaviour of the dimer (see Ref.105). The role of entropy was discussed in Ref.106, devoted to a study of the nature of the stationary points of the potential energy surface for the dimer $(HCl)_2$, and in Ref.107 in a study of the interaction of water with chloroform, fluoroform, and cyclopropane.

IV. NON-EMPIRICAL ANALYTICAL POTENTIALS

The theoretical analysis of IMI for complex many-particle systems is carried out chiefly using simple potentials. The results of non-empirical IMI calculations have recently begun to be used to obtain analytical potentials. An extensive cycle of studies has been carried out by Clementi and co-workers[108-132]. The structure and thermodynamic properties of solutions of ions and biological molecules have been studied. The overall calculation procedure was broken down into three stages.

1. Non-empirical calculations were first carried out for a large number (up to several hundred) different configurations of the corresponding dimer, to obtain sufficiently complete information on the potential energy surface for the system.

2. A set of pair potentials was then chosen in the form of functions of a definite type, depending on the parameters. The parameters were selected to give the best reproduction of the potential surface obtained in the non-empirical calculation.

3. Finally, the analytical potentials obtained in the previous stage were used to calculate the thermodynamic and structural characteristics of the system being studied. Usually, at this stage, the Monte Carlo method was used for the calculation.

The procedure described above was used to study the structure and properties of liquid water[108]. An extended basis set was chosen for the calculation on the $(H_2O)_2$ dimer, and 216 different configurations were calculated in the SCF

approximation. The results of the calculation were approximated by a fairly complex analytical expression consisting of the sum of pair contributions[108].

A calculation by the Monte Carlo method of the radial distribution functions in water and their characteristics gave results close to the experimental data. Particularly good agreement with experiment was obtained using analytical potentials[108] approximating the potential surface of the $(H_2O)_2$ system found with allowance for correlation by the CI method. This result clearly demonstrates the possibilities provided by quantum-chemical methods for estimating various characteristics of many-particle systems.

To investigate the relative role of regular structures in the overall structure of water, the analytical potentials obtained were used to study small regular and non-regular clusters of the form $(H_2O)_n$ ($n = 3$–8). It was found that for the trimer, the most favourable structure is a cyclic structure with symmetry close to C_{3v}; for $n = 4$ and 5, the cyclic structures are energetically most favourable, and for $n = 6$, 7, or 8 there are a large number of non-regular configurations with similar energies. These results, and the fact that the bond energy corresponding to one molecule increases with increase in the number of molecules in the cluster, led the authors[108] to the conclusion that the energy properties of water apparently cannot be described by modelling the liquid phase as an ideal mixture of small regular clusters.

By studying dimers of the type formed by water with the ions Li^+, K^+, F^-, Cl^-, Na^+, etc.[109–112], and also the interaction of water molecules or ions with fragments of proteins and nucleic acids (aminoacids in different forms[113–115], the polypeptide core[116], nucleotide bases[114,117], and phosphate groups[118,119]), Clementi and co-workers created a library of model potentials based chiefly on the results of non-empirical calculations in a minimum basis set. These potentials, and the Monte Carlo method, were used to study a large number of systems. In particular, solutions of ions[120,121] and ion pairs[122,123] in water were examined. Particular attention was paid to the investigation of the structure of water close to nucleotide bases[124], DNA fragments[125,126], aminoacids[127,128], and various enzymes[129–131]. A detailed analysis of the results of this important cycle of studies is beyond the scope of the present review; they can be found in a recently published monograph by Clementi[132]. It is appropriate, however, to deal with various methodological features of these calculations[108,115].

In the construction of the analytical potentials, Clementi and co-workers took account of the fact that the same atoms in molecules may be present in different valence states (for example, the states of the oxygen atom are different in the OH group, in the C=O bond of the COOH group, and in the C=O group, where the C atom is in an aromatic ring). For most systems (except water), the potentials were chosen in the form of a Lennard-Jones potential with allowance for electrostatic corrections. The reliability of the analytical potentials was estimated from the accuracy of the non-empirical calculations.

In the opinion of the authors of Ref.44, however, the values of the energy E_{int}^{SCF} are determined more accurately in minimum basis sets optimised for the calculation of intermolecular interaction (see for example Ref.43), with elimination of the superposition error by the counterpoise method, than in standard basis sets of the DZ+P type. It is recommended[44,89] that allowance for correlation be made using perturbation theory, by expressing E_{disp} in terms of bond polarisability, and this has been confirmed by recent results[44].

An analogous series of studies was carried out by Jorgensen and co-workers[133–138]. The calculation procedure was identical to that described above. Systems with hydrogen bonds $(HF)_2$, $(H_2O)_2$, $(CH_3OH)_2$, etc. were studied, and the potentials were taken in the form (12-6-3-1) or (12-6-1). The calculation for the dimer $(HF)_2$ [133,134] was carried out in the 6-31G basis set for 250 points on the potential surface. The model potentials obtained were used to calculate the properties of liquid hydrogen fluoride. The calculations carried out in the 6-31G basis set, however, give a value for the energy of attraction which is too large, so that the calculated heat of volatilisation obtained was too high. Better agreement with experiment was obtained in a calculation for the dimer $(HF)_2$ in the minimum basis set STO-3G. Similarly, in the case of water[136], the results of calculations in the STO-3G basis set also show fairly good agreement with the experimental data. Jorgensen, like Clementi, recommends the use of a minimum basis set in calculations for polar systems, and also that allowance be made for dispersion interactions when non-polar groups are present.

The pair potentials (in the Lennard-Jones form) used in these studies should not be confused with the generally adopted atom–atom potentials, which are capable of reflecting more or less realistically the interaction of individual atoms. Fig.3 gives curves[132] describing the interaction of the oxygen of a water molecule with a nitrogen atom in different fragments of biological molecules. It can be seen that for a nitrogen atom in glycine or asparagine, there is no region of attraction at all. For nitrogen in guanine or 4-hydroxypyridine, however, the potential curves show minima corresponding to equilibrium distances of ~0.30–0.31 nm. The potentials obtained by Clementi and co-workers (Fig.3) and by Jorgensen and co-workers apparently must be regarded only as an analytical approximation to the results of the calculations, making it possible to go from quantities characterising individual molecules to macroscopic quantities, and the physical significance of individual curves cannot be discussed.

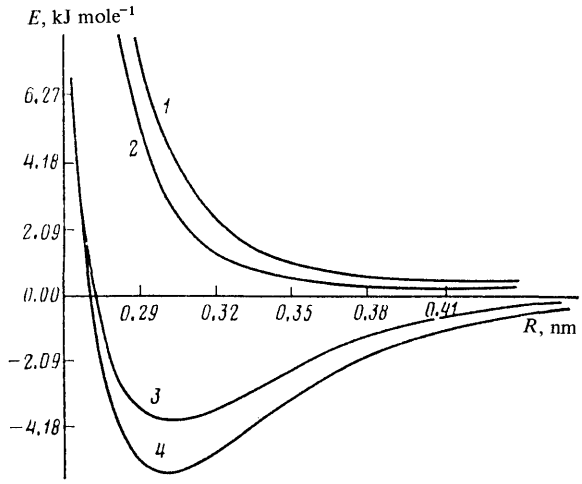


Figure 3. Potentials of the interaction between the oxygen atom of water and a nitrogen atom in different fragments of biological molecules (*1*—glycine, *2*—asparagine, *3*—guanine, *4*—hydroxypyridine).[132]

In another approach, the breakdown of the energy E_{int}^{SCF} into its components is used to construct analytical potentials on the basis of non-empirical calculations. In this case, the

individual components of E_{int}^{SCF} are approximated, and this method makes it possible to reduce the number of configurations whose energy must be calculated non-empirically. Moreover, the pair potentials found in this way acquire a definite physical significance (they can be regarded as non-empirical atom–atom potentials). This method has been used to carry out calculations for crystals of carboxylic acids[68,69]. In Ref.69, the model potentials for the atoms i and j were sought in the form

$$\varphi_{ij} = q_i q_j r_{ij}^{-1} + B^{XY} \exp(-C^{XY} r_{ij}) + A_{XY} r_{ij}^{-6} - D^{XY} \exp(-F r_{ij}) \quad (5)$$

where r_{ij} is the distance between the atoms i and j; q_i and q_j the effective charges on the atoms i and j; and X and Y denote the chemical elements corresponding to the atoms i and j (X, Y = C, O, H).

The individual terms in the right-hand side of Eqn.(5) were compared[69] with the corresponding components of the energy E_{int}^{SCF}, determined in Ref.13, and also with E_{disp} calculated using perturbation theory. The first term in Eqn. (5) was used to approximate the contribution of E_{mult}, where E_{mult} is the part of E_{el-st} which is independent of penetration effects[69]; the second term was used to approximate $E_{ex} + E_{el-st} - E_{mult}$; the third term is compared with the part of $E_{ind} + E_{disp}$ proportional to R^{-6}; and the last term takes account of E_{ct} and the corrections to $E_{ind} + E_{disp}$. The constants A, B, C, D, and F were determined from the results of non-empirical calculations for 12 configurations of $(HCOOH)_2$ and 16 configurations of the dimer $H_2CO...CH_3OP$, which is only one tenth of the number of dimer configurations studied by Clementi and Jorgensen.

The analytical potentials obtained in this way were used[69] to carry out calculations for the dimers of formic and acetic acids and crystals of formic acid and α- and β-acetic acids. The structures found for the dimers and crystals of the carboxylic acids are close to the experimental structures. Unfortunately, the calculation of the energies gives an error of 20–30 kJ mole^{-1} (~30%).

As noted in Ref.69, the errors arising in a calculation of this kind are of different character: for example, they may be associated with the use of restricted basis sets and non-correlated wavefunctions. In addition, errors arise when the analytical potential is fitted to the energy values obtained non-empirically. In Refs.139 and 140, the values of the dispersion energy found in Refs.141 and 142 by a non-empirical method in a DZ basis set for dimers consisting of azabenzenes were approximated as $E_{disp} = \sum_{i \in A} \sum_{j \in B} A_{ij}^{XY} r_{ij}^{-6}$, where r_{ij} is the distance between the atom i of the molecule A and the atom j of the molecule B, and A_{ij}^{XY} represents the parameters of the atom–atom interactions (X, Y = C, N, H). An interesting feature is that the values of these parameters were found to be very close to the empirical atom–atom parameters given by Williams[143]. An attempt to reproduce the non-empirical values of the electrostatic interaction between the azabenzenes in the form of the sum of atom–atom interactions was less successful.

Non-empirical atom–atom potentials have been constructed [92,93] for the dimers $(N_2)_2$ and $(C_2H_4)_2$. Atom–atom potentials have been used[93] to calculate the potential energy surface of the dimer $(N_2)_2$ and various characteristics of the α and β crystalline forms of molecular nitrogen. Analytical atom–atom potentials have been used to carry out a calculation for the ethylene crystal[92].

Non-empirical pair potentials have also been constructed for the complexes formed by water with ammonia[144] and ethanol[145].

V. ACCURACY OF NON-EMPIRICAL CALCULATIONS OF INTERMOLECULAR INTERACTION

Analysis of the above results makes it possible to reach various conclusions about the accuracy of non-empirical calculations. The best agreement with experiment is given by calculations with Hartree–Fock basis sets with complete allowance for correlation (see the calculations of the structural characteristics of water[108]). These calculations, which are close to the exact solution of the Schrödinger equation, can be regarded as standard. These calculations are not readily accessible, however, and it is necessary to know what can be expected from less precise calculations. Here it must be borne in mind that the value of non-empirical IMI calculations lies in their giving not only the quantitative characteristics of IMI but also data on the nature of the bonding in dimers. In addition, the relative values of IMI characteristics may often be useful. The calculation of the correlation energy can be considered first. In the many-configuration approximation, account is taken of both intermolecular and intramolecular correlation. These calculations are much more complex than the calculation of E_{int}^{SCF}, from both the computational and theoretical viewpoints. This is related to the fact that there are serious difficulties in the optimum choice of the excited configurations included in the CI. The treatment is therefore usually restricted to taking account of intermolecular correlation, and E_{disp} is calculated from perturbation theory. To obtain satisfactory values of E_{disp}, it is necessary to use DZ + P basis sets with diffuse polarisation functions P (Ref. 142 and p.60 of Ref.11). DZ basis sets apparently underestimate the value of E_{disp} only slightly, since published data[142] indicate that the DZ and DZ + P basis sets give similar values for E_{disp}.

Calculations carried out in intermediate basis sets, for example in the basis set with split valence 4-31G give values of E_{disp} which are 1.5–2 times smaller than the actual values[87], and minimum basis sets are not suitable for calculating E_{disp}. Kolos and Clementi[44,89] recommend that in these cases E_{disp} should be estimated in terms of the bond polarisability, although the values of E_{disp} obtained are slightly too low[44]. The dispersion energy makes up an appreciable proportion of the bond energy (in the case of van der Waals dimers its role is decisive), but intramolecular correlation may decrease this contribution slightly. For example, the correlation corrections for $(H_2O)_2$ for $R_{O-O} = 0.3$ nm in extended basis sets are −6.4 kJ mole^{-1} (perturbation theory[30]) and −3.6 kJ mole^{-1} (CI [40]). As yet, however, little is known about the influence of intramolecular correlation on E_{int}, [146, 18], and this question will not be discussed further in the present review. The correct calculation of the energies E_{el-st} and E_{exch} requires wavefunctions which provide a sufficiently good description of the multipole moments of the molecules. These requirements are satisfied by the wavefunctions found in DZ + P basis sets with polarisation functions P localised close to the nuclei. The correct calculation of E_{ind} requires a DZ + P basis set with diffuse P functions, in which the polarisabilities of the molecules are effectively reproduced. From what has been said above about the basis sets required for the correct calculation of E_{disp}, it is to be expected that non-empirical IMI calculations in DZ + P basis sets with two types of polarisation function should give reliable results. Calculations of this kind are not very practicable for complex systems.

Calculations with DZ basis sets without polarisation functions or with polarisation functions of one type (basis sets 6-31G and 6-31G**, and also the basis sets DZ and DZ + P, described in Refs.92–94) are more readily accessible. The use of these basis sets for the small systems $(H_2O)_2$, [42]

$(HF)_2$,[147] $(N_2)_2$,[93] and $(C_2H_4)_2$ [92,142] has been fairly effective (see Tables 2 and 3). The calculations already mentioned for the crystal of ethylene[92] and molecular nitrogen[93] also indicate that the calculation of E_{int}^{SCF} and E_{disp} in DZ basis sets is reliable from the quantitative viewpoint.

Of the intermediate basis sets, the basis set 4-31G is used most frequently. The energies E_{int}^{SCF} calculated in the 4-31G basis set are apparently more than double the exact values (see the data for $(H_2O)_2$ in Table 2 and the results of the calculation for the dimer $H_3N...BH_3$ in Table 3). The error of the calculation of IMI in the 4-31G basis set is to a large extent related to the overestimation of the electrostatic interaction. Calculations in the 4-31G basis set, however, apparently give sufficiently reliable information on the nature of the bonding in dimers (Tables 2 and 5).

The most widely encountered calculations in minimum basis sets are those for the dimers of polar molecules, particularly dimers with a hydrogen bond. It has been found that in many cases[135-138], E_{int}^{SCF} shows good agreement with the experimental value of the bond energy. This is explained, firstly, by the relatively small contribution of E_{disp} to the energy of the interaction, and, secondly, to the mutual compensation of errors: the energy of repulsion E_{exch} and the electrostatic attraction are underestimated, and the contribution of E_{ct} is overestimated[42]. If however the dimers contain polar and non-polar molecules (for example $(CN)_2CO...C_6H_6$), E_{disp} must be taken into account to obtain the experimental values of the bond energies (see Ref.87 and also Table 5 and R.p.1069). No Hartree-Fock calculations have been carried out for systems of this kind, so that an exact estimate of the accuracy of the calculations in the minimum basis sets is impossible. The STO-3G basis set is apparently unsuitable for calculations for the dimers of non-polar molecules (for example the calculation for $(C_2H_4)_2$ in Ref.91).

The quantitative results obtained in calculations with minimum basis sets must be approached with care, but many other conclusions reached in these calculations (the nature of the stabilising forces, the most favourable structure of the dimer) for the case of polar molecules are also obtained in calculations in broader basis sets.

Kolos, Clementi, and co-workers[43,44] have now pointed out methods for improving considerably calculations in minimum basis sets, based firstly on the elimination of the superposition error and secondly on the use of minimum basis sets specially optimised for the calculation of IMI. This makes it possible to obtain in minimum basis sets results close to those obtained by calculations in extended basis sets not only for polar molecules (Table 3) but also for non-polar systems $[(CH_4)_2]$,[44] if E_{disp} is estimated in terms of bond polarisability.

Thus comparatively reliable results are obtained in calculations in DZ basis sets. It is difficult to reach a final conclusion about the accuracy of calculations in restricted basis sets, but several conclusions can be reached, for example that E_{int}^{SCF} is overestimated in the basis set 4-31G and that satisfactory results are obtained by calculating the interaction of small polar molecules in the basis set STO-3G. It should be noted that authors[86,87,98-100] who have used these basis sets in calculations for large molecules paid particular attention to the qualitative conclusions. The available data indicate that different restricted basis sets give values of the energies E_{int}^{SCF} and their components which differ from one another by a factor of more than two, and it is to be expected that these discrepancies increase with increase in the size of the systems. Thus the absolute and relative differences in the values of the components of E_{int}^{SCF}, calculated in the basis sets STO-3G and 4-31G for the dimers $(CN)_2CO...H_2O$ and $(CN)_2CO...C_6H_6$, increase with increase in the size of the molecules (Table 5), but at the same time the conclusions about the nature of the bond are independent of the basis set.

VI. SEMI-EMPIRICAL IMI CALCULATIONS

Semi-empirical IMI calculations retain their importance in those cases where non-empirical calculations cannot be carried out, for example for a system containing a large number of atoms. Like *ab initio* calculations, semi-empirical calculations are carried out in the supermolecule approximation and using perturbation theory. Supermolecule calculations are most frequently carried out using CNDO, INDO, etc. methods, which are based on neglect of differential overlap (NDO) and use SCF equations. In these calculations, no account is taken of dispersion energy. Unfortunately, the results of most supermolecule calculations carried out in the NDO approximation have proved to be unsatisfactory, and the observed discrepancies when compared with experimental data are not systematic.

Some typical results of IMI calculations in the NDO approximation can be considered. The CNDO/2 method gives a value of the energy of attraction for π-conjugated systems which is much too high. Thus for the $\pi\pi$-complex $C_6H_6...TCE$ in the "stacking" configuration this method gives the values $E_{int} \approx -520$ kJ mole^{-1} and $R_{equil} = 0.175$ nm,[148] whereas experiment gives E_{int} from -7.9 kJ mole^{-1} to -18.1 kJ mole^{-1} and $R_{equil} = 0.33-0.35$ nm.[149] On the other hand, for the dimer $(C_2H_4)_2$ the CNDO/2 calculation gives practically no minimum[150]. For dimers with a hydrogen bond this method often gives satisfactory values of E_{int} and R_{equil}.[151] A calculation by the MINDO/2 method showed that the $\pi\pi$-complex $C_6H_6...TCE$ should not be stable; satisfactory results were obtained for the $n\pi$-complex $NH_3...I_2$, but for the $\pi\sigma$-complex $C_6H_6...I_2$ the energy of attraction was too large[152]. The MINDO/2 and MINDO/3 methods are not suitable for the description of the hydrogen bond[153].

One of the main reasons for the inadequate results of supermolecule calculations in the NDO approximation is the unsatisfactory estimation of exchange terms. In the supermolecule calculation by the CNDO/2 method, account is taken of only the repulsion arising as a result of electrostatic interaction, parameterised in such a way that it leads to repulsion at short distances[154]. Thus for the complex $H_2CO...H_2O$, according to CNDO/2 estimates[13], the energy $E_{int} = -26.3$ kJ mole^{-1}, and from the breakdown of E_{int} into its components according to the scheme in Ref.13 it was found that $E_{el-st} = 20.1$ kJ mole^{-1}, $E_{ind} + E_{ct} = -46.4$ kJ mole^{-1}, and $E_{exch} = 0$. A non-empirical calculation[13] for the same system in the same configuration gives $E_{int} = -14.2$ kJ mole^{-1}, and the contribution of the electrostatic interaction is $E_{el-st} = -19.2$ kJ mole^{-1}; the other values are $E_{ct} + E_{ind} = -23$ kJ mole^{-1} and $E_{exch} = 28$ kJ mole^{-1}. These data show that the values of the individual contributions for E_{int}, obtained from non-empirical calculations, do not agree at all with one another; in particular, the values of E_{el-st} have opposite signs, and E_{exch} in the semi-empirical calculation is equal to zero. The breakdown of the balance between the components of E_{int} in the NDO approximation also leads to the random discrepancies in the results mentioned above. To improve the results, the CNDO/2 parametrisation is modified by changing the values of the intermolecular resonance integrals β. Decrease in β (absolute magnitude) makes it possible to obtain more realistic values of E_{int} for $\pi\pi$-complexes by the CNDO/2 method[155]; at the same time, increase in the value of β led to satisfactory results in a calculation for crystals of small molecules (C_2H_4, N_2, C_2H_2, etc.) by CNDO/2 and INDO methods[150].

In view of these fundamentally unsatisfactory features of the calculations in the NDO approximation, it must be concluded that the use of NDO methods to calculate the quantitative characteristics of supermolecules is not effective. Calculations of this kind may be useful, however, when dimers of similar chemical structure are being compared, and it is sufficient to know only the relative characteristics of the IMI in these dimers. For example, they have been used to determine the preferred configuration of approaching molecules in replacement or addition reactions[156,157] and to compare the qualitative characteristics of complexes with similar structures[158].

Calculation by the extended Hückel method (EHM) usually gives unsatisfactory results. This is related to the fact that in the EHM, account is taken of only the IMI components that depend on the overlap integrals, which at distances equal to or shorter than the van der Waals radius lead to repulsion. In Ref.159, the results of a calculation for the complex $(N_2)_2$ by the EHM were supplemented by calculating the dispersion energy, and in this approximation, good agreement with experiment was obtained for various characteristics of a molecular crystal of N_2. This approach has not been extended further, however. It may also be noted for excimers and exciplexes[160,161].

It is possible to avoid the extensive breakdown of the balance between the components of E_{int}, characteristic of semi-empirical IMI calculations in the supermolecule approximation, if the semi-empirical IMI calculation is carried out using perturbation theory. In the first semi-empirical calculations by purturbation theory, devoted to EDA complexes[82,83,162,163,164], it was assumed that the IMI energy can be represented in the form $E_{int} = E_{exch} + E_{ct} + E_{el\text{-}st} + E_{ind} + E_{disp}$ (that is the results of the theory of Murrell and coworkers[31] were used). Murrell's theory forms the basis of the semi-empirical calculations of IMI using perturbation theory, carried out at the present time. It is possible to distinguish two approaches to the estimation of the components of E_{int}. Studies in which the various components of E_{int} are calculated using the wavefunctions of the isolated molecules, obtained by some single method (usually the CNDO/2 method), can be considered first. In Ref. 154, all the integrals appearing in the expression of the theory[31] were calculated approximately. The differential overlap between AO relating to the same molecule was neglected, and account was taken of the overlap between the AO of different molecules. In Ref.165, to estimate the intermolecular integrals containing differential overlap, the Mulliken approximation was used at the AO level, but in Ref.166 this approximation was applied to the MO. This technique reduces considerably the number of two-electron and one-electron integrals, and simplifies the structure of the expressions under the integral sign. The other integrals are estimated using the approximations characteristic of the CNDO/1 and CNDO/2 methods.

A detailed analysis of possible versions of the approximations was carried out in Ref.154, where it was shown that the application of the Mulliken approximation to the MO gives better results than its application to the AO. In the latter case, the calculated energy E_{exch} is too large. (In Ref.154 it is pointed out that to obtain correct results for the $CH_2...CH_2$ system and for various other systems, the value of E_{exch} must be decreased by a factor of 10 relative to the data in Ref.165!) Ref.154 gives an optimum set of approximations, denoted PE-1 by the present authors. The application of PE-1 to the dimers $(H_2O)_2$ and $C_6H_6...(CN)_2CO$ gives results close to those of non-empirical calculations carried out in an STO-3G basis set (Table 6).

An approximate calculation of all the integrals required for the application of Murrell's theory was also carried out in Ref. 167, where complexes of nucleotide bases with hydrogen bonds were examined. In Refs. 168–170, devoted to an analysis of the interaction of molecules containing silicon, the wavefunctions of the isolated molecules, obtained by the CNDO/2 method, were used for the semi-empirical calculation of all the integrals appearing in "symmetrical" perturbation theory[20]. In the works cited above[154,165–170], the wavefunctions of the isolated molecules were calculated by the CNDO/2 method, after which perturbation theory was used. Perturbation theory is used in a slightly different form in the PCILO method[171,172]. Analysis of IMI by the PCILO method in the CNDO/2 parametrisation gives much better results[173,174] than supermolecule calculations by the CNDO/2 method.

Table 6. Energy characteristics of the IMI, kJ mole^{-1}, for the dimer $C_6H_6...(CN)_2CO$, obtained by different methods.

Method	E_{exch}	E_{ct}	$E_{exch} + E_{ct}$	$E_{el\text{-}st}$	E_{ind}	$E_{int} - E_{disp}$	E_{disp}	E_{int}	Refs.
				$R = 0.30$ nm					
STO-3G	28.7	−6.5	22.2	−8.7	−0.5	13.0	−9.0[a]	4.0	[87]
PE-1	18.5	−7.8	10.7	−4.2	−0.3	6.2	−10.5[b]	−4.19	[154]
PE-2	34.4	−12.0	22.4	−6.3	−1.7	14.4	−27.3[b]	−12.9	[188]
				$R = 0.32$ nm					
STO-3G	12.5	−3.1	9.4	−6.1	−0.4	2.9	−6.6	−3.7	[87]
PE-1	8.7	−3.5	5.2	−2.3	−0.2	2.7	−8.2	−5.5	[154]
PE-2	16.1	−5.7	10.4	−5.5	−1.3	3.6	−20.0	−16.4	[188]
				$R = 0.36$ nm					
STO-3G	2.1	−0.6	1.5	−4.0	−0.2	−2.7	−8.7	−6.4	[87]
PE-1	1.8	−0.7	1.1	−1.1	−0.1	−0.1	−5.3	−5.3	[154]
PE-2	3.3	−1.2	2.1	−5.2	−0.7	−2.8	−11.3	−14.1	[188]

[a] E_{disp} calculated using perturbation theory in a basis set of wavefunctions.

[b] E_{disp} calculated in terms of bond polarisability.

In many calculations, the components of E_{int} are estimated using different approximations, corresponding to the physical nature of the individual contributions. In these calculations, the representation of the components of E_{int} as the sum of terms characterising the interactions between the separate fragments of the molecules (atoms or groups of atoms) is widely used. This approach is based on the possibility of representing the density matrix of the molecule as the sum of local charge densities. In the case of the long-range components $E_{el\text{-}st}$, E_{disp}, and E_{ind}, the potential for the interaction between the local charge distributions can be represented as a multipole series, and it is possible to obtain, for these components, multipole many-centre expansions, which reduce to simplified equations. In particular, the value of $E_{el\text{-}st}$ is usually estimated in terms of the energy of the interaction of atomic multipoles (up to quadrupoles), and in the calculation of E_{disp}, the treatment is restricted to dipole-dipole terms, and E_{disp} is expressed in terms of the bond polarisability tensor and the effective ionisation potentials. The energy E_{ind} is expressed in terms of the bond polarisability and the atomic multipole moments. In the calculation of $E_{el\text{-}st}$ and E_{ind}, the atomic moments are calculated by a semi-empirical method, suitable for these purposes (CNDO/2 or EHM),[175] and the bond polarisability values for the calculation of E_{ind} and E_{disp} are taken from experiment.

An analysis of various simplified expressions for the long-range components is given in various reviews[18,176,177] and other works[178,179].

Simplified equations are also used to calculate E_{exch}. Murrell and co-workers[31] showed that the energy E_{exch} of two one-electron atoms can be approximated successfully by the expression CS^2/R, where S is the overlap integral of the corresponding atomic orbitals. For a polyatomic system, an expression of more general form is used: $\sum_a \sum_b C_{ab} S_{ab}^2 / R_{ab}$, where a and b are the atomic orbtials of the interacting molecules. The constants C_{ab} are chosen from a comparison with non-empirical calculations[18,180,181]. Different versions of simplified equations for E_{exch} were discussed in Ref.18.

There are no equations expressing the contribution of E_{ct} to the energy E_{int} as the sum of the interactions between local electron density distributions. This term, therefore, is often not included in calculations using simplified equations [181]; alternatively, it is estimated as $|kS_{mn}*|^2/h\nu_{mn}*$,[83] where $h\nu_{mn}*$ is the energy of the charge-transfer transition, $S_{mn}*$ is the overlap integral of the corresponding MO, and the coefficient k depends on the chemical structure of the interacting molecules[83].

Calculations using simplified equations (or hybrid calculations, as they are sometimes called) have been carried out for different systems. In particular, it has been shown[83,162] that the stability of the EDA complexes C_6H_6...TCE, p-xylene...TCE, and C_6H_6...Hal is determined chiefly by the magnitude of the contributions $E_{el\text{-}st}$ and E_{disp}. These conclusions about the forces bonding the complexes agree with the results of non-empirical calculations (Ref.46, see Tables 5 and 6).

Mention must also be made of a study[162] in which good agreement was obtained between experimental data and the calculated bond energies in complexes of tetracyanoethylene with substituted benzenes. Many studies have been made of the influence of the long-range interactions $E_{el\text{-}st}$, E_{ind}, and E_{disp} between nucleotide bases on the stability of the secondary structure of nucleic acids[179,182]. The long-range components were calculated for two cases, for a hydrogen bond between the nucleotide bases and for their "stacking" configuration. In Ref.183, bond energies for the van der Waals dimers $(N_2)_2$, $(C_2H_4)_2$, and $(C_6H_6)_2$, showing good agreement with the experimental values, were obtained, but the conclusions reached by the authors[183] about the structure of the equilibrium dimers $(N_2)_2$ and $(C_2H_4)_2$ differed from the results of non-empirical calculations[92-94]. This is quite natural, since the non-empirical calculation revealed a large number of structures with energies close to that of the energetically most favourable structure, and the semi-empirical calculation cannot take account of all the fine differences between dimers with similar energies.

In Ref.180 it was shown that the crystal lattice energy of benzene is determined chiefly by two contributions: E_{disp} and E_{exch}. Calibration of the parameters in simplified equations for E_{exch}, E_{disp}, and E_{ind} made it possible[181] to obtain for the dimers of the cations Na^+, K^+, and NH_4^+ with H_2O results equivalent to the results of non-empirical calculations. The use of these parameters made possible a successful description of the interaction of ions with more complex molecules. Various other applications of calculations using simplified schemes have been described[18].

In addition to semi-empirical calculations in which account is taken of all the integrals appearing in the expression for the energy E_{int}, and calculations using simplified equations, there are calculations combining these two approaches. The complex $C_6H_6Cl_2$ has been studied[184]. The contributions E_{ind} and E_{disp} were calculated using simplified equations, and in the estimation of the values of E_{exch} and $E_{el\text{-}st}$, account was taken of all the integrals appearing in the corresponding equations from Ref.31, as was done in Ref.165. As in Ref.165, the value of E_{exch} was found to be much too large. In calculations for the systems $(C_6H_6)_2$, C_6H_6...TCE, naphthalene-TCE,[185] and $(\text{pyromellitimide})_2$,[186] the contributions $E_{el\text{-}st}$, E_{ind}, and E_{disp} were calculated using the simplified equations proposed in Refs.176 and 179, and E_{exch} and E_{ct} were calculated using the MO found by the EHM. These MO in the one-electron approximation were used to calculate the values of the contributions E_{exch} and E_{ct} in accordance with Murrell's theory[31] (this calculation scheme is denoted PE-2). The approach used in Ref.187 to analyse EDA complexes of the $\pi\pi$ type has been justified. The interaction of the π-electrons was taken into account in explicit form, and the interaction of the σ-electron cores was estimated in terms of the atom–atom potentials; the agreement with experiment was satisfactory.

In the analysis of the results of semi-empirical IMI calculations using perturbation theory, it should be noted that a successful choice of approximations makes it possible to obtain useful information on the nature of IMI; the calculated bond enegies and equilibrium distances are often close to the experimental values, and the conclusions about the nature of the forces stabilising the dimers agree with the results of non-empirical calculations.

Table 7. Dependence of E_{int} on the distance R_{O-O} for the dimer $(H_2CO)_2$ in kJ mole^{-1} (data from Ref.189).

R_{O-O}, nm	S configuration[a]		P configuration[a]	
	non-empirical method	PE-2	non-empirical method	PE-2
0.28	—	—	4.1	4.3
0.29	9.5	8.7	1.4	2.0
0.31	1.9	1.6	—0.1	—0.1
0.33	—1.6	—1.5	—1.1	—0.8
0.35	—3.0	—2.7	—1.3	—1.0
0.37	—3.4	—3.0	—	—

[a]For configuration notation see Fig.4.

Table 6 compares the results of calculations for the dimer C_6H_6...$(CN)_2CO$ with allowance for all the integrals (PE-1 approximation[154]) and calculations using the PE-2 hybrid scheme with the results of non-empirical calculations. Although the semi-empirical methods used differ considerably from one another, they give results close to those obtained non-empirically (an exception is the dispersion energy, for which the value obtained in the calculation in a minimum basis set is much too low, irrespective of whether the calculation is non-empirical or semi-empirical).

Calibration of the parameters in semi-empirical schemes to bring their results closer to the results of non-empirical calculations or to experimental data can make it possible to obtain values which are satisfactory from the quantitative viewpoint, and in this case, semi-empirical schemes can be used in the same way as non-empirical pair potentials. Calculations using simplified equations are more suitable for these purposes, since unlike calculations with allowance for all the integrals, these calculations contain parameters convenient for calibration. An example of this approach is provided by the above-mentioned work[181] in which semi-empirical

methods were used to examine the interaction of cations with water molecules and various other molecules. Table 7 gives the results of a calculation[189] for the dimer $(H_2CO)_2$ for the case of antiparallel and perpendicular configurations (Fig.4) in a non-empirical version in Kolos' basis set and by a semi-empirical method using the PE-2 scheme, in which some of the parameters were calibrated from the results of non-empirical calculations. The semi-empirical scheme not only reproduces the difference in the IMI energies in different configurations but also gives results showing quantitative agreement with the results of a non-empirical calculation.

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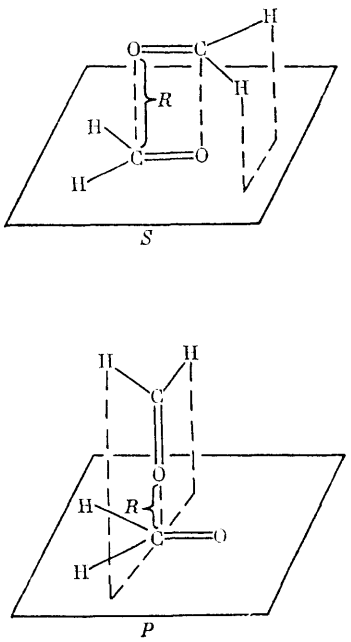


Figure 4. Parallel (*S*) and perpendicular (*P*) configurations of the formaldehyde dimer[189].

Thus the information that can be obtained from IMI calculations depends to a marked extent on the size of the system. If the interacting molecules are small (water, ethylene, etc.) and it is practicable to carry out non-empirical calculations in basis sets of the DZ type, it is possible to obtain satisfactory quantitative results both for a dimer and for many-particle systems.

Non-empirical calculations in restricted and minimum basis sets, which can be carried out for more complex systems, give valuable qualitative results, but their quantitative reliability is low, and appreciable departures from the Hartree–Fock or experimental bond energies (several tens percent) are possible.

Semi-empirical calculations undoubtedly retain their importance in those cases where non-empirical calculations are impossible even in minimum basis sets. Semi-empirical calculations often give results close to the experimental data; with appropriate parameterisation they can be used to obtain results equivalent to *ab initio* data.

The present state of quantum-chemical IMI calculations gives grounds for assuming that IMI calculations will develop in two directions: increase in the accuracy of non-empirical calculations, associated with the development of computational technique, and the creation of flexible semi-empirical schemes making it possible to reproduce experimental and non-empirical data.

While the present review was being prepared for publication, two monographs[190,191] devoted to the analysis of IMI were published. It also seems useful to mention some other recent studies. The influence of the basis set error (BSSE) on the properties of interacting molecules has been examined [192], the breakdown of E_{int}^{SCF} into its components has been analysed[193], and it has been shown[194] for the case of $(HF)_2$ that exchange interactions of second order decrease E_{disp} by 10%. Exchange repulsion has been analysed[195,196]; in particular, SCF calculations of the interaction between valence-non-bonded atoms have been used to obtain simple atom-atom potentials for E_{exch}.[195]

It has been shown non-empirically in a 4-31G basis set[197] that chloroform can bring about the rupture of peptide bonds, and this possibly explains its anaesthetising action. An additive semi-empirical scheme[181] has been used[198,199] to analyse the interaction of biologically active molecules with ions. A semi-empirical IMI calculation scheme which uses an expansion with respect to inverse powers of the intermolecular distance has been proposed[200]. Super-molecule *ab initio* calculations and semi-empirical calculations using perturbation theory have been compared for the case of the hydrogen bond and ion pairs[201]. Various present-day theoretical and experimental problems relating to IMI have been examined in a collection of IMI papers[202].

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