Chapter 6

Ab Initio Theoretical Methods for Studying Intermolecular Forces

Giuliano Alagona and Caterina Ghio*

CNR - Institute of Quantum Chemistry and Molecular Energetics, ICQEM,

Via Moruzzi 1, I-56124, Italy·

Introduction

Intermolecular forces (IF) such as responsible of the properties and phenomena, whether equilibrium or not, presented by the matter, have always received noticeable attention. Only after the development of quantum mechanics, however, and the advent of the computers era it was possible to determine them quantitatively at least between very simple molecules. Their presence is ubiquitous. The van der Waals' work (1873) demonstrated that the existence itself of the condensed phases of the matter (liquid and solid states) originates from the attractive forces among molecules and that at the same time their low compressibility takes origin from the repulsive forces acting at short separation (though at that moment the origin of these forces was not well understood). The physico-chemical (thermodynamic, static or dynamic) properties of gases, liquids, solids and intermediate phases are determined by the nature of the IF. Also the chemical reactions are modulated, and sometimes regulated, by IF.

A typical case is represented by the systems of biological interest, where IF not only rule the phenomena related to transport, dissolution and partition among the various phases, but also the tertiary structure (protein folding), the recognition (docking), the catalytic activity of enzymes and the interactions taking place between hor-

mones/drugs/ligands and receptors. In those systems mainly, it is evident that IF are local in character, because the molecular remainder constitutes only some kind of perturbation to the interaction involving two or more chemical centers. It should be noticed however that local interactions may have long range effects (consider, for instance, the triggering devices and the chain of molecular interactions in biological systems). Another important feature they have is to be non additive. Therefore it is necessary, when dealing with more than two interacting subsystems, resort to a many body treatment.

Definition, origin and classification of IF

We refer of course to the forces occurring in non-covalent molecular interactions [1-6], i.e. interactions usually named *weak*, because the energy produced during the formation of a mole of the adduct (also defined a "van der Waals molecule") ranges from few calories up to about 10 kcal. The separations among the interacting subsystems are within 2 and 5 Å. This is the reason why the geometry and the electronic structure of the subsystems do not affect appreciably each other. A peculiar feature of these interactions is related to the fact that no classical chemical bonds are formed or broken. In addition these associates are formed with a downhill reaction coordinate; that is, when the separation decreases there is an energy gain with respect to the energy of the partners at infinite separation. On the energy hypersurface there can be a large number of shallow minima, separated by low saddle points demanding a very low energy to be overcome. The condition for the existence of a van der Waals[1] molecule is that its ground vibrational state should lie below its dissociation limit. These systems however, though displaying a stability similar to the transient species one, can be often prepared even at the crystal state and be stable to the normal lab conditions.

In order to put forward and illustrate terms and concepts exploited in the forthcoming mathematical treatment and explain the physical origin of IF, we use the simplest model available, i.e. two interacting atoms, *a* and *b*, each composed of a nucleus and an electronic cloud with spherical symmetry. They do not interact when placed at infinite separation, and the total energy of the diatomic system is equal to the sum of the energies of the isolated atoms:

$$E_{tot}(\infty) = E_a + E_b. \tag{1}$$

When the two atoms come closer, their interaction supplies an additional contribution $U(r)$ to the total energy, which in this case (due to the spherical symmetry) depends only on the distance and not on the mutual orientation as well. This term, named "pair potential energy function", is a measure of the extent by which the total energy differs from the value for the two isolated atoms

$$U(r) = E_{tot}(r) - E_{tot}(\infty) \tag{2}$$

and it is equal to the work done to bring the two atoms from infinite separation to the distance *r*:

$$U(r) = \int_r^\infty F(r)dr \tag{3}$$

and thence

$$F(r) = - dU(r)/dr = - grad\ U(r) \tag{4}$$

is the force acting between the two atoms at distance *r*. As a conventional rule, the force

---

[1] In analogy with the "normal" systems, also vdW ions and radicals exist.

F is positive when repulsive and negative when attractive.

To derive this pair potential function, whose trend is displayed in Fig. 1 together with its gradient, we supposed the atoms in a steady state and placed at a distance r. This approximation, the well known Born-Oppenheimer one, is not dramatic because the mass of the nuclei, being much larger than that of the electrons, makes the nuclei motion to be much slower than the motion of the electrons, thus allowing the factorization of the wave function.
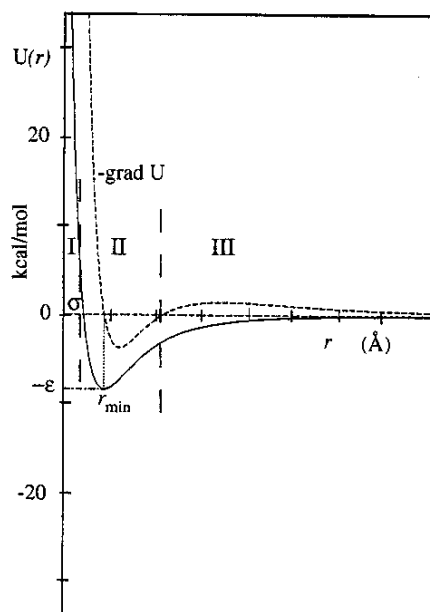

Fig. 1. Dependence on the distance of the total potential energy and of its gradient, which put forward some particular points and regions (see text).
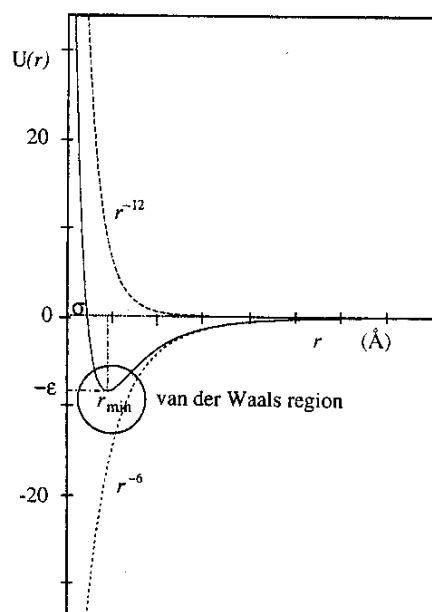
Fig. 2. Potential energy curve with the trend of its attractive and repulsive components in a popular analytical form (see text). The energy/distance values close to r_{min} define the van der Waals region.

The dependence on the distance of the total potential energy (Fig. 1) shows a typical form, in which we can distinguish three zones: a) region I, which is very repulsive, for $r < r_{min}$, b) region II, located in the vicinity of the minimum, r_{min}, and c) region III, which is attractive, for $r > r_{min}$. The parameters characterizing the potential energy, among which we already mentioned r_{min}, the distance where the energy has a minimum, are also indicated in the plot; $\Delta E(r_{min}) = -\varepsilon$, represents the *well depth*); another important parameter is σ, the distance for which the potential energy vanishes. Its form suggests that it can derive from the coupling of two different functions, one describing the attractive branch and one describing the repulsive branch:

$$U(r) = U^R(r) + U^A(r) \qquad (5)$$

The repulsive term (*short range*) is empirically represented by an exponential term or by an r^{-n} term, with $n \geq 10$, while the attractive term is proportional to r^{-6} and represents the effect of dispersion forces [7][2]. This latter term, for neutral, non polar systems,

---

[2] London derived his $1/r^6$ law [8] of dispersion forces at short distance with the harmonic oscillator model of a molecule, while for separations comparable to the wavelength of visible light Casimir and Polder [9] found $1/r^7$ instead. Using frequency-dependent electric polarizabilities at imaginary frequencies, McLachlan [10a] obtained a formula

with spherical symmetry, is rigorously derivable quantum-mechanically.

One of the most popular analytical functional forms (used in the vast majority of empirical force fields) is the Lennard-Jones potential. By substituting in the expression above (eqn. 5) we obtain:

$$U(r) = \frac{C_1}{r^{12}} - \frac{C_2}{r^6} \tag{6}$$

which, using the aforementioned parameters, becomes:

$$U(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right\}, \tag{7}$$

hence:
$$F(r) = 4\varepsilon \left\{ \frac{12}{r}\left(\frac{\sigma}{r}\right)^{12} - \frac{6}{r}\left(\frac{\sigma}{r}\right)^6 \right\} . \tag{8}$$

The potential energy curve is again reported in Fig. 2, now together with the trend of its attractive and repulsive components in the analytical form displayed above. In the general case of two molecules without spherical symmetry, however, the molecular interaction energy depends on the mutual orientation as well. In addition the roto-vibrational states may contribute to further complicate the problem.

What's the origin of IF? At present we know four categories of forces acting among particles: gravitational forces, electromagnetic forces, strong nuclear forces and weak nuclear forces. While gravitational forces are extremely long range and thus produce energies several order of magnitude below the aforementioned interval, both strong and weak nuclear forces are very short range. Therefore none of them contribute to IF, which should consequently be electromagnetic in nature. They are thus ascribable to the charged particles, electrons and protons, which constitute atoms and molecules. Since IF are repulsive at short range and attractive at long range we can infer they are made up at least by two different contributions.

The qualitative explanation of short range repulsive IF is very simple: when the electronic clouds of the two systems come close enough to overlap, some electrons cannot be found in this zone because of the Pauli exclusion principle, and thus the electron density decreases, reducing the mutual shielding among the nuclei of the two subsystems, which therefore exert a repulsive force on each other. These forces are called *overlap* forces. The attractive forces, which become significant when the overlap between the electronic clouds is negligible or small, have varied origins and depend on the nature of the interacting systems. They are usually divided into three classes: electrostatic forces, induction-polarization forces and dispersion forces, that we are going to examine in this order. Only London's dispersion forces are present in all kinds of molecular interactions.
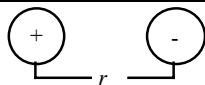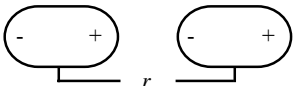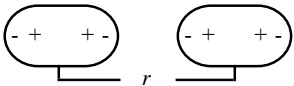
(a) *Electrostatic (or Coulombic) Term*: It concerns molecules with multipole moments.

---

for the mutual dispersion energy of two molecules which "reduces to Casimir and Polder's result at long distances and London's at close range" [10b].

When two molecules, bearing a permanent dipole moment (due to their peculiar charge distribution), come close to each other, the main contribution to their interaction energy is due to the electrostatic interaction between their dipole moments. This interaction does not request a previous distortion of the charge distribution (Table 1) on any molecule: thus it is a 1st order effect. The electrostatic energy between two dipoles (or higher multipoles) depends heavily on the mutual orientation and thus it is sometimes referred to as orientational energy. Molecules without a permanent dipole moment can have a quadrupole moment, which analogously contributes to the interaction energy, though it contributes less. The higher are the involved multipoles, in fact, the lower is the interaction energy:

$$E_{charge-charge} > E_{charge-dipole} > E_{dipole-dipole} > E_{dipole-quadrupole} \cdots \quad (9)$$

Table 1. Interaction energy between permanent multipoles[a]: Coulombic term.

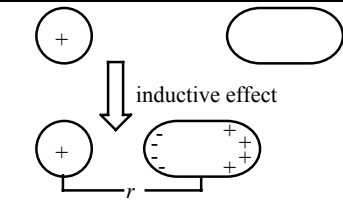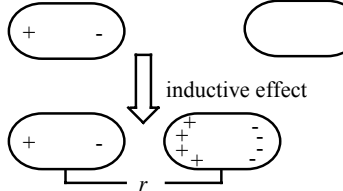| Subsystem		Interaction type	E_{Coul}
a	b		
		charge-charge	$-\dfrac{1}{4\pi\,\varepsilon_0}\dfrac{q_a q_b}{r}$
		dipole-dipole	$-\dfrac{K}{4\pi\,\varepsilon_0}\dfrac{\mu_a \mu_b}{r^3}$
		quadrupole-quadrupole	$-\dfrac{K}{4\pi\,\varepsilon_0}\dfrac{Q_a Q_b}{r^5}$

[a] q = charge; μ = dipole moment, Q = quadrupole moment.

(b) *Induction or Polarization Term.* This term refers to multipole-induced multipole interactions. Upon interaction with a molecule bearing a dipole moment, a non polar molecule is polarized inducing in itself a dipole moment, which interacts with the inducing dipole producing an attractive force. This interaction is similar to that discussed above, but it is necessary a previous distortion of the electronic clouds (see Table 2); therefore it is a second order effect. Dealing with two polar molecules this contribution is present together with the electrostatic one.

A satisfactory explanation also in terms of classical physics can be given to both the aforementioned contributions (E_{Coul} and E_{Ind}). On the contrary, the third contribution, the dispersion one, can be explained only resorting to quantum mechanics.
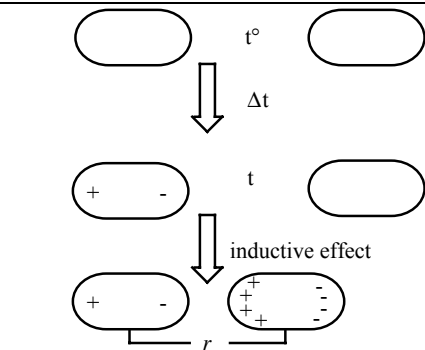
c) *Dispersion Term.* It concerns correlations between electron density fluctuations. Nuclei and electrons oscillations, even in spherical non-polar molecules, give origin to a temporary dipole moment. Its value, which varies in time but vanishes on an average, depends on the instantaneous positions of electrons and nuclei. When the temporary dipole moment differs from zero, it produces its instantaneous induction effect on the neighboring molecules (Table 3): the induced dipole interacts with the temporary dipole, with attractive interaction energy (named dispersion energy, in analogy

Table 2. Interaction energy between a permanent multipole and an induced multipole: Inductive term.

Subsystem		Interaction type	E_{Ind}
a	*b*		

charge-induced dipole

$$-\frac{1}{2r^4}q_a^2\,\alpha_b$$

α = polarizability

dipole-induced dipole

$$K\left(-\frac{1}{2r^6}\mu_a^2\,\alpha_b\right)$$

with the phenomenon of the dispersion of light in gases). It is a second order term as well, because it originates from electron density distortions and it is a purely quantum effect. As already recalled this is the only long range contribution to the interaction energy in neutral non-polar molecules.

Table 3. Interaction energy between a temporary dipole and an induced multipole: Dispersion term.

Subsystem		E_{Dis}
a	*b*	

$$-\frac{K\alpha_a\,\alpha_b}{r^6}$$

(d) *Charge Transfer Term.* This is a controversial term, because not all the authors agree to consider it a real effect. Some authors however include in the IF classification this contribution, which is rather significant dealing with systems composed of an electron donor (low ionization potential) and an electron acceptor (high electron affinity) with a relatively small energy gap ($\Delta\varepsilon < 2$ eV) between the donor's highest occupied molecular orbital (HOMO) and the acceptor's lowest unoccupied molecular orbital (LUMO). Moreover these two molecular orbitals should present a non negligible overlap (Table 4). The extent of this overlap is measured by the overlap integral, S_{hl}:

$$S_{hl} = \int \varphi_h\,\varphi_l\,\,d\tau. \tag{10}$$

This phenomenon could however be determined by the limitacy of the basis set used to describe the electron donor.

Table 4. Interaction energy between an electron donor (a) and an electron acceptor (b): Charge transfer term.

Subsystem		E_{CT}
a	*b*	

$$-\frac{\left|KS_{hl}\right|^2}{\Delta E}$$

Ab Initio Computational Methods

The interaction energy, ΔE, whose typical trend is displayed in Fig. 1, is not a physical observable, but it can be computed in two ways:

1) as a difference between the supersystem energy and the sum of the energies of the two isolated systems:

$$\Delta E(r) = E_{ab}(r) - (E_a + E_b) \tag{11}$$

These energies can be obtained using the variational method and contain the Hartree-Fock (HF) term and the electron correlation term. Of course this evaluation as a difference between large numbers can be affected by numerical errors.

2) via direct determination with a perturbation scheme,

$$\Delta E(r) = E_{Coul} + E_{pol} + E_{CT} + E_{exc} + E_{Dis} \tag{12}$$

The perturbation theory, which seems to be the most suitable method, suffers from intrinsic limitations and shows several problems: in practice the variational method is preferred for whatever value of r and ΔE.

Assuming in fact that the systems considered (*a*, *b* and *ab*) are described with sufficient accuracy with the variational method, this procedure can be used in a fairly general way for every value of system separation and interaction energy. On the contrary, though the interaction energy is a sufficiently small fraction of the supersystem energy thus justifying a perturbation treatment, however the gradual change from weak to strong interactions does not allow a univocal determination of its applicability limit.

The overlap between the orbitals of the two systems is used as a qualitative index to estimate the applicability limit: the higher the overlap, the lower is the reliability of the perturbation scheme.

In what follows it is shown that the HF energy includes all the aforementioned interaction terms but the dispersion contribution, which however at large separation can be

considered to be identical to the *a-b* intersystem correlation energy.

1. Long Range Rayleigh-Schrödinger (RS) Perturbation Theory.

The interaction energy between the systems *a* and *b* can be determined by solving the Schrödinger equation with parametric dependence on the mutual position and orientation of the two molecules:

$$H_{ab} (r_a, r_b; r) \psi = E_{ab} (r) \psi \tag{13}$$

where the total Hamiltonian operator is given by:

$$H_{ab} = H^0 + \lambda U_{ab}(r) \tag{14}$$

with $H^0 = H_a + H_b$. The wave function which solves the equation is

$$\psi = \psi^0 + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots . \tag{15}$$

For $r = \infty$, λ turns out to be equal to zero, and thus $H_{ab} = H^0$, the Hamiltonian of the two isolated systems; in the equation $H^0 \varphi^0 = E^0 \varphi^0$ one has $\varphi^0 = \psi^0_a \cdot \psi^0_b$ and $E^0 = E^0_a + E^0_b$. Other solutions of course exist ($\varphi^1, .., \varphi^k, ...$) besides the ground state one, φ^0.

When *a* and *b* come closer to each other, the supersystem wave function can be expanded into the series up to a rather large separation,

$$\varphi^0 = \psi^0_a \cdot \psi^0_b + c_1 \psi^1_a \cdot \psi^1_b + \ldots , \tag{16}$$

deriving the coefficients from the standard perturbation theory. A first order perturbation in the wave function corresponds to a second order perturbation in the energy.

There are a few problems connected to this formulation, such as a slow convergence at large separations and wrong values in region II. However, its main inconvenience is due to the fact that it cannot be used at short separations, because the wave function does not allow for the electron exchange between the two subsystems. Thus this theory is based on the assumption that the electron exchange and the overlap between the charge distributions of the two subsystems are vanishingly small.

The individual contributions to the interaction energy are

$$\Delta E = \langle \psi^0_a \psi^0_b | U | \psi^0_a \psi^0_b \rangle \qquad \text{Coulombic interaction I order} \tag{17}$$

$$- \sum_k \frac{|\langle \psi^0_a \psi^0_b | U | \psi^k_a \psi^0_b \rangle|^2}{E^k_a - E^0_a} \qquad \text{Polarization of } a \tag{18}$$

$$- \sum_l \frac{|\langle \psi^0_a \psi^0_b | U | \psi^0_a \psi^1_b \rangle|^2}{E^1_b - E^0_b} \qquad \text{Polarization of } b \qquad \text{II order} \tag{19}$$

$$- \sum_k \sum_l \frac{|\langle \psi^0_a \psi^0_b | U | \psi^k_a \psi^1_b \rangle|^2}{(E^k_a + E^1_b) - (E^0_a + E^0_b)} \qquad \text{Dispersion} \tag{20}$$

+ higher order terms

1.1. Contributions to ΔE in the RS Perturbation Theory.

It is convenient to briefly examine the meaning of the various terms up to the II order, because these definitions are going to be exploited in the forthcoming treatment.

$$\Delta E = E^1{}_{RS} + E^2{}_{RS} + \ldots , \qquad (21)$$

where the I order term, $E^1{}_{RS} = E_{el}$, is the electrostatic contribution previously defined, while the II order one is the sum of a number of contributions $E^2{}_{RS} = E^2{}_{Ind} + E^2{}_{Dis}$. The inductive term in turn groups the polarization energies of a and b, already defined

$$E^2{}_{Ind} = E^2{}_{Ind}(a) + E^2{}_{Ind}(b). \qquad (22)$$

The RS formalism however presents several defects, as previously stated, because it shows a slow convergence in region III (and sometimes even diverges), it can produce non satisfactory (when non completely wrong) values in region II. All these shortcomings derive from the bad description of the permutational symmetry, since the electron exchange between a and b is not taken into account. Therefore $\mathcal{A}\varphi^0$ should be used as an unperturbed wave function in place of φ^0. Unfortunately however $\mathcal{A}\varphi^0$ is not an eigen function of $H^0 = H_a + H_b$ (because H^0 and $\mathcal{A}$ do not commute) and cannot be used in the perturbation theory in connection with H^0 as unperturbed operator. In order to overcome this difficulty there are two choices available: 1) to use a "symmetric" perturbation scheme, i.e. one should abandon the natural partition of H^0 and find another perturbation, such as $\mathcal{A}\varphi^0$ is an eigenfunction of the new zeroth order operator and the new perturbation is small in any case, or 2) to change the perturbation scheme, forcing the correct symmetry on the wave function though retaining the non symmetric operator H^0. The first approach has not produced new satisfactory operators thus far, while the second one can be tackled resorting to "symmetry adapted" formulations.

1.2. Symmetry adapted (SA) Perturbation Theory.

The perturbation problem makes use of a resolvent R^0 [11], called "reduced resolvent of H^0 corresponding to the eigenvalue E^0":

$$R^0 = \sum_{k \neq 0} \frac{\left| \varphi^k \right\rangle \left\langle \varphi^k \right|}{E^k - E^0} \qquad (23)$$

where E^k and φ^k are eigenvalues and eigenfunctions for excited states of H^0.

Using the spectral representation of H^0, it can be verified that

$$R^0 (H^0 - E^0) = 1 - |\varphi^0\rangle\langle\varphi^0|, \qquad (24)$$

with $R^0|\varphi^0\rangle\langle\varphi^0| = 0$. R^0 can be considered the inverse matrix of $H^0 - E^0$ in the space of the functions orthogonal to φ^0. Starting from

$$(H^0 + U)\,\psi = (E^0 + \Delta E)\psi \qquad (25)$$

which can be also written as

$$(H^0 - E^0)\,\psi = (\Delta E - U)\psi \qquad (26)$$

and imposing the intermediate normalization $\langle\varphi^0| \psi\rangle = 1$, we obtain:

$$\psi = \varphi^0 + R^0 (\Delta E - U) \psi \qquad (27)$$

and analogously

$$\Delta E = \langle \varphi^0 | U \psi \rangle. \qquad (28)$$

An iterative solution of the equations above is obtained, by using the recursive formulas:

$$\psi^n = \varphi^0 + R^0 (\Delta E^n - U) \psi^{n-1} \qquad (29)$$

$$\Delta E^n = \langle \varphi^0 | U \psi^{n-1} \rangle \qquad (30)$$

Assuming that $\psi^0 = \varphi^0$ and iterating once, we obtain

$$\psi^1 = \varphi^0 - R^0 U \varphi^0 \qquad (31)$$

and

$$\Delta E^2 = \langle \varphi^0 | U \varphi^0 \rangle - \langle \varphi^0 | U R^0 U \varphi^0 \rangle \qquad (32)$$

namely the I order wave function and the II order energy of the RS "long range" perturbation theory. On the contrary, using $\psi^0 = N^0 \mathcal{A} \varphi^0$, we obtain an SA theory, proposed independently by Carr [12], Murrell and Show [13], Musher and Amos [14] and usually called Murrell & Show - Musher & Amos (MS-MA), which however introduces the antisymmetry only at the very beginning of the iterative process. The expressions obtained are:

$$\Delta E^1 = N^0 \langle \varphi^0 | U \mathcal{A} \varphi^0 \rangle \qquad (33)$$

and

$$\psi^1 = \varphi^0 + N^0 R^0 (\Delta E^{(1)} - U) \mathcal{A} \varphi^0. \qquad (34)$$

In contrast to the "polarization" approximation, the second term in the ψ^1 expression does not vanish for large values of r and supplies all the main exchange components of the wave functions.

There are several symmetry adapted theories. We are going to quote only the most important, illustrating very briefly their advantages and disadvantages:

1) The MS-MA theory was just considered, because it is the simplest one. It can introduce the correct antisymmetry, but only at the zeroth order. It has a very slow convergence and neglects a fraction of ΔE which cannot be recuperated.

2) The EL-HAV (Eisenschitz & London [15] - Hirschfelder [16] - van der AVoird [17]) theory is very complex and forces the antisymmetry at all the orders employing additional conditions. It produces rapidly converging perturbation expansions, but it is difficult to use already for n=2. However it describes sufficiently well strong valence interactions, where its incorrect distance dependence of the II order energy is irrelevant.

3) The ISF (*intermediate symmetry forcing* by Jeziorski & Kołos [18]) is the simplest of the absolutely converging expansions, even though the antisymmetry is forced at all the orders, with no additional constraints. It converges rapidly, assuring the correct asymptotic behavior of the interaction energy up to the second order. It is difficult to use as well, but for ≥ 3. It represents a compromise between the other two formulations.

4) The HS (Hirschfelder & Silbey [19]) theory is even more complex of the EL-HAV theory and was employed to study the interaction between the ground state of an H atom and a proton up to the 38th. order.

In order to put forward differences and analogies among the various theories the generalized recursive formula is shown, together with the values assumed by the parameters in the different theories (Table 5):

$$\psi^n = \phi^0 + R^0 (\Delta E^n - U) \mathbf{F} \psi^{n-1} \tag{35}$$

$$\Delta E^n = <\phi^0|U \mathbf{G} \psi^{n-1}> \tag{36}$$

Table 5. Values assumed by the parameters in the various theories.

Method	$\mathbf{F}$	$\mathbf{G}$	ψ^0
RS	1	1	ϕ^0
MS-MA	1	1	$\mathcal{A}'\phi^0$
EL-HAV	$\mathcal{A}$	$\mathcal{A}'$	$\mathcal{A}'\phi^0$
ISF	$\mathcal{A}$	1	$\mathcal{A}'\phi^0$

1.3. Decomposition of the ΔE contributions in the SA perturbation theories.

Reference is made to the RS theory terms, which however are not fully satisfactory, as already recollected, because the exchange contribution is missing:

$$\Delta E^n_{exc} = \Delta E^n - \Delta E^n_{RS}, \tag{37}$$

from which the general formula is obtained:

$$\Delta E = \Delta E^1_{RS} + \Delta E^1_{exc} + \Delta E^2_{RS} + \Delta E^2_{exc} + \ldots \tag{38}$$

What is the meaning of these terms? Let's analyze them:

$$\Delta E^1_{RS} = <\psi^0|U|\psi^0> = E_{el} = E_{Coul} \qquad \text{Electrostatic Contribution} \tag{39}$$

$$\Delta E^1_{exc} = \frac{\left\langle \Psi^0 \mid U\mathcal{A}\Psi^0 \right\rangle}{\left\langle \Psi^0 \mid \mathcal{A}\Psi^0 \right\rangle} - E_{el} \qquad \text{Exchange Contribution} \tag{40}$$

This latter contribution is common to all the SA theories. However this expression is very difficult to compute. In order to simplify it, a technique was proposed which consists in the substitution of $\mathcal{A}$ with $\mathcal{P}$, representing the exchange between a and b. $\mathcal{P}$ is expanded into the number of the permutations:

$$\mathcal{P} = -\mathcal{P}_1 + \mathcal{P}_2 - \mathcal{P}_3 + \ldots \tag{41}$$

Usually the expansion is truncated to the first term (or to the second at most); by using only $\mathcal{P}_1$, the following expression is obtained:

$$\Delta E^1_{exc} = \frac{\left\langle \Psi^0 \mid U \mathcal{P}_1 \Psi^0 \right\rangle - E_{el} \left\langle \Psi^0 \mid \mathcal{P}_1 \Psi^0 \right\rangle}{1 + \left\langle \Psi^0 \mid \mathcal{P}_1 \Psi^0 \right\rangle} \tag{42}$$
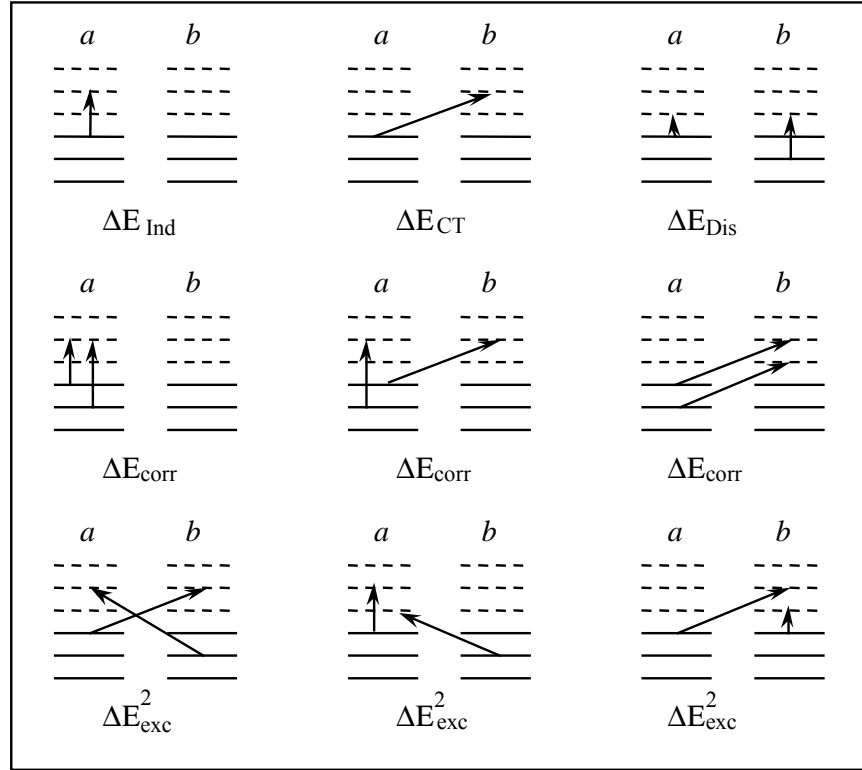
Fig. 3. Schematic origin [20] of the various second order contributions.

The second order terms consist in the summation of two contributions:

$$\Delta E^2_{RS} = \Delta E^2_{Ind} + \Delta E^2_{Dis} \tag{43}$$

and

$$\Delta E^2_{exc} = \Delta E^2_{exc\text{-}Ind} + \Delta E^2_{exc\text{-}Dis} \tag{44}$$

The first and second order RS contributions have been already examined and discussed. It is sufficient here to recall that the inductive term accounts for the excitation of b on a and of a on b, separately, whereas the dispersion considers the excitation of a and b, at the same time. As far as the second order exchange terms are concerned, they depend on the SA theories and represent, together with the first order one, the SA corrections to the RS theory. The origin of the various second order contributions is reported in Fig. 3, following the scheme proposed by Daudey et al. [20]. Some correlation contribution corresponds to terms beyond the second order in the overlap expansion. Some of the terms reported in Fig. 3 are estimated with common approximations.

1.4. Approximations used to estimate the various contributions.

The electrostatic term is usually evaluated with expansion of multipole moments (μ, θ, Ω, ...); the first order exchange term through the expansion of $\mathcal{P}$, multipole moments and overlaps; the inductive term (a second order term) is expanded in terms of static multipolar polarizabilities (α, β, γ, ...) [21a], while for the dispersion term either the dynamic multipolar polarizabilities [21b] or the static multipolar polarizabilities with the

addition of the average energies of electron excitation are used. A very simple formula to estimate this term was proposed by Slater-Kirkwood [22]:

$$E_{Dis} \approx -\frac{3}{2}\frac{1}{r^6}\frac{\alpha_a\,\alpha_b}{(\alpha_a/n_a)^{1/2}+(\alpha_b/n_b)^{1/2}} \qquad (45)$$

where α is the polarizability and n the number of valence electrons.

An interesting approach for predicting intermolecular forces between closed-shell atoms, ions and molecules, due to Gordon and Kim [23], exploits the electron densities of the separate partners evaluated from Hartree-Fock wavefunctions. A nice feature of this approach is that the total Coulombic interaction is obtained directly after the integration, not as a difference between large, separately integrated terms. At large distances, however, the model fails to account for the induction and the dispersion contributions.

2. HF Approximation

In general the exact solutions of the Hamiltonian are unknown
$$H^0 = H_a + H_b . \qquad (46)$$

The HF solutions of the isolated molecules *a* and *b* are on the contrary well known:
$$|\Phi^0_a> \dots |\Phi^r_a> \dots \qquad (47)$$
and
$$|\Phi^0_b> \dots |\Phi^r_b> \dots \qquad (48)$$

The problem of determining ΔE must therefore be re-examined as a triple perturbation. The perturbations to be considered are:

1) the *interaction potential* between *a* and *b*, which we are going to indicate with the parameter s and index n;
2) the *fluctuation potential* of *a* (parameter t and index i) and
3) the *fluctuation potential* of *b* (parameter v and index j).

The general expression turns out to be:

$$\Delta E = \sum_{n=1}^{\infty}\sum_{i=0}^{\infty}\sum_{j=0}^{\infty} s^n t^i v^j E^{n,i,j} \qquad (49)$$

The HF part is given by:

$$\Delta E^{HF} = \sum_{n=1}^{\infty} s^n E^{n,0,0} \qquad (50)$$

2.1. Analysis of correlation corrections

Let us briefly examine in sequence the aforementioned terms of the perturbation theory and explicitly display the relevant contributions:

$$\Delta E^1_{RS} = \Delta E^{100}_{RS} + \Delta E^{120}_{RS} + \Delta E^{102}_{RS} + \dots \qquad (51)$$

All these corrections are important and rather easy to compute. Notice that on the contrary all the terms $\Delta E^{110}_{RS} = \Delta E^{101}_{RS} = \Delta E^{121}_{RS} = \Delta E^{112}_{RS}$ vanish because of the Brillouin theorem.

$$\Delta E^1_{exc} = \Delta E^{100}_{exc} + \sum_i \sum_j E^{1ij}_{exc} \tag{52}$$

These corrections in contrast are little known and the terms containing them show a slow convergence.

$$\Delta E^2_{Ind} = \Delta E^{200}_{Ind} + \sum_i \sum_j E^{2ij}_{Ind} \tag{53}$$

These terms are also important, but they are difficult to compute ought to the resolvent R^0. In addition, part of the energy contributions due to the $\Phi^0_a \longrightarrow \Phi^k_a$ excitation are not ascribable to correlation.

A proposal to solve these problems was put forward by the Pisa group [24]. They suggested to exploit a different basis consisting of molecular orbitals (MO) polarized by the presence of the other molecule.

$$| \Phi'^0_a > \ldots | \Phi'^r_a > \ldots \tag{54}$$

and
$$| \Phi'^0_b > \ldots | \Phi'^r_b > \ldots \tag{55}$$

With this basis $\Delta E'^{200}_{Ind}$ does contain all the non-correlation contributions, while the corrections $\sum_i \sum_j E'^{2ij}_{Ind}$ are due to pure correlation contributions.

$$\Delta E^2_{Dis} = \Delta E^{200}_{Dis} + \sum_i \sum_j E^{2ij}_{Dis} \tag{56}$$

The separation between the HF terms and the correlation corrections is questionable, because also ΔE^{200}_{Dis} originates from correlation. That separation can be done for large separations only, but there is a slow convergence in the corrections. We avoid to undertake the analysis of the coupling terms

$$\Delta E^2_{exc\text{-}Ind} = \Delta E^{200}_{exc\text{-}Ind} + \sum_i \sum_j E^{2ij}_{exc\text{-}Ind} \tag{57}$$

$$\Delta E^2_{exc\text{-}Dis} = \Delta E^{200}_{exc\text{-}Dis} + \sum_i \sum_j E^{2ij}_{exc\text{-}Dis} \tag{58}$$

because these corrections are not known as the 200 terms. $\Delta E^{200}_{exc\text{-}Ind}$ is often told to be opposite to ΔE^{200}_{Ind}.

2.2. Variational approach to bimolecular interactions

As already mentioned in the introduction, in the variational approach the interaction energy, ΔE, is not computed directly, but is obtained as a difference between the super-system energy and that of the isolated partners:

$$\Delta E(r) = E_{ab}(r) - (E_a + E_b) \tag{59}$$

The interaction energy analysis (via its decomposition in various contributions) allows to compute much more easily than with perturbation methods the different components of ΔE for whatever separation and orientation of the subsystems involved in the interaction. This method however fails for very short separations, such as those encountered in the sharply repulsive branch of the plot of ΔE versus r. The evaluation of the various components at the equilibrium distance (r_{min} or R_{eq}) only, in fact, though important, is not the best way to use this analytic tool: it is advisable to examine how the interaction strengthens when a and b come closer. In addition it is possible that corrections to ΔE produce a non negligible shift in the equilibrium distance of the adduct.

The most commonly used ΔE decomposition [6], due to Kitaura and Morokuma (KM) [25], can be written:

$$\Delta E(r) = E_{ES} + E_{PL} + E_{CT} + E_{EX} + E_{MIX} + E_{Dis} \qquad (60)$$

First of all it should be noticed that this decomposition is defined at the SCF level and therefore the dispersion contribution must be computed apart. On the contrary, if one is not interested in the ΔE decomposition, but wishes E_{Dis} to be included, ΔE can be computed with correlation corrections. As far as the various terms are concerned, the electrostatic, polarization and exchange terms have the meaning already explained in the previous discussion. The charge transfer term is missing in the rigorous perturbation theories, but it plays an important role in semiquantitative theories of chemical reactivity (Fukui, Klopman, etc.).

2.3. KM decomposition of the interaction energy.

From the computational point of view, the technique used to perform the ΔE decomposition exploits the calculations performed on the supermolecule *ab*: the additional Fock matrix diagonalizations needed are carried out with the appropriate matrix elements set equal to zero. In order to explain in a more comprehensible way the computational method is better to use a schematic representation of the orbital space (Scheme 1).

The electrostatic term is due to the interaction between the rigid charge distributions of the isolated partners and exactly corresponds to the ΔE^1_{RS} term; the polarization term consists of the interaction between the charge distributions of the two partners, each polarized because of the presence of the other system, and is more complete than the E^2_{Ind} term; the exchange term accounts for electron exchange between the occupied orbitals of one partner with those of the other and is equal to ΔE^1_{exc}; the charge transfer term accounts for the electron transfer from the occupied orbitals of one partner to the virtual orbitals of the other and is only partially evaluated in some formulation of SA perturbation theory. The coupling term among the aforementioned contributions, E_{MIX}, is the contribution with the less intuitive physical meaning; in general it is computed as a difference between the total interaction energy and its various contributions.
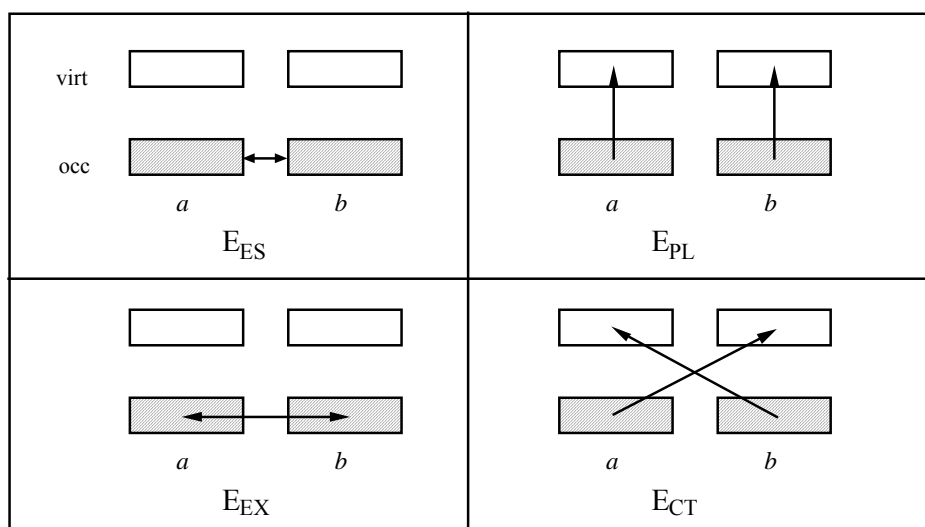

Scheme 1. Individual interaction energy terms.

This term can however be furtherly analysed following the Nagase-Fueno-Yamabe-Kitaura (NFYK) scheme [26], which is anyway scarcely employed, though it can be fairly interesting:

$$E_{MIX} = E_I + E_{II} + E_{III} + E_{IV} + E_{RES} \qquad (61)$$

E_{RES}, the residual term, is again determined as a difference. The meaning of the other terms, rather cryptic from the abbreviations (I, II, III and IV) is on the contrary fairly evident if we resort to their graphical representation, using the conventions previously employed to explain on which kind of interactions the different principal components of the interaction energy depend (Scheme 2).

We already stressed the importance to examine the trend of the various components of the interaction energy along the approaching path beside that of the interaction energy itself. This allows to verify that at large separations the interaction is mainly electrostatic, while at the equilibrium distance the sum of the polarization and charge transfer terms ($E_{POL} + E_{CT}$) is close in absolute value to the repulsive exchange term (E_{EX}): therefore E_{ES} is a good approximation to ΔE (the E_{MIX} value is negligible). The equilibrium distance however is not due to E_{ES} alone, but it depends on the balance among all the energetic components. This feature which is so important in non covalent binding in fact cannot be reduced to a classical electrostatic effect only. The mutual orientation of the two subsystems is, on the contrary, determined by the electrostatic term, in that a rotation of the molecule mainly affects the electrostatic term, because of its angular dependency much larger than E_{PL} and E_{EX}, which are short range terms.
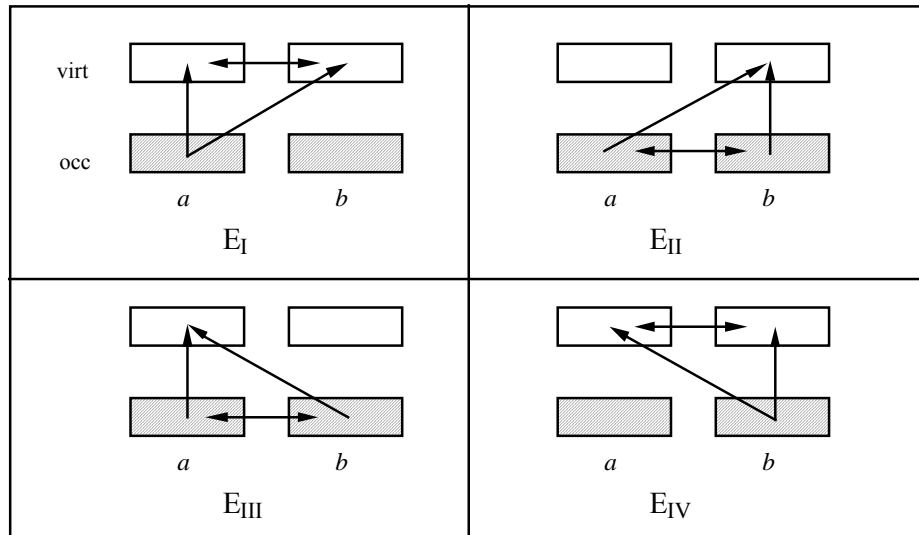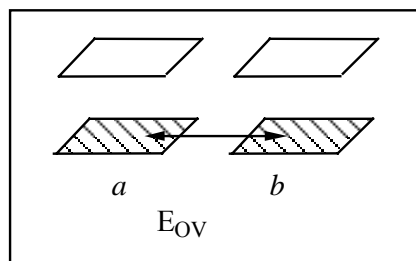

Scheme 2. E_{MIX} Decomposition

2.4. BCPT Decomposition [27]

This scheme is partially different from the KM one because a basis of polarized molecular orbitals is employed in the calculations. The interaction energy therefore consists of the following contributions:

$$\Delta E(r) = E_{ES} + E_{PL} + E_{ET} + E_{OV} + E_{COUP} + E_{Dis} \qquad (62)$$

with a perfect consistency of the electrostatic and polarization terms with the KM ones, while E_{OV} (Scheme 3) and E_{ET} are more complete than the corresponding terms in the

other formulation (E_{EX} and E_{CT}). This thus produces a minor incidence of the E_{COUP} term with respect to E_{MIX}. Continuing the decomposition of the coupling term E_{COUP} in the NFYK scheme, a residual term $E_{RES'}$ which is much smaller than E_{RES} is obtained.
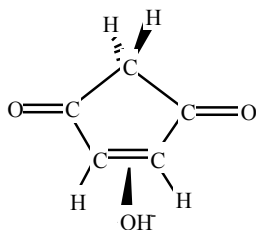

Scheme 3.

Fig. 4. Test case. The hydroxy ion approaches the midpoint of the double bond along a perpendicular to the ring plane

We report in Table 6 a comparison between the values obtained using the two decomposition schemes for the interaction between an anion and a neutral molecule (displayed in Fig. 4). The results refer to the equilibrium distance ($r = 2.10$ Å) between the hydroxy anion and the ethylene double bond.

Table 6. *Comparison between the KM and BCPT decompositions for the system of Fig. 4 at the equilibrium distance (kcal/mol).*

KM		BCPT	
$\Delta E(r)$	-28.68	-28.68	$\Delta E(r)$
E_{ES}	-20.22	-20.22	E_{ES}
E_{PL}	-5.60	-5.60	E_{PL}
E_{EX}	29.70	28.87	E_{OV}
E_{CT}	-28.65	-31.34	E_{ET}
E_{MIX}	-3.90	-0.38	E_{COUP}

3. Correlation Effects. Corrections to the Basis Set Superposition Error (BSSE).

The electron correlation can be divided into two parts: a) the correlation internal to each subsystem (intramonomer) and b) the correlation between the two subsystems (intermonomer). The intramolecular or intramonomer correlation, which considerably contributes to the internal energy of the two subsystems, is not only a shift in the energy of the whole system, but produces also changes in the energy components, because modifies the first order density matrices (diagonal and off-diagonal terms) of the subsystem determining the components values. This problem has not been studied thoroughly, but these changes are in general smaller than those produced by the use of a different basis set in the SCF calculation. The most important contribution remains the dispersion term, which can be computed with approximate methods [28]. This is the most convenient way to proceed for bulky dimers. For model systems the correlation effect can be evaluated with perturbation approximations, such as the Møller-Plesset one. Latajka and

Morokuma presented in 1985 a contribution to a conference an interaction energy decomposition scheme including correlation effects, thus far not published to the best of our knowledge.

The BSSE is a non-physical error due to limitacy of the basis set employed to perform the SCF calculation. This artifact produces an overestimate of the interaction energy measured with respect to the energies of the isolated subsystems, which constitute the most natural reference, as we have seen. The overestimate is due to the fact that when the two subsystems approach each other, the functional space made available to electrons is much wider than at large separation, because of the vicinity of the partner orbitals. This fact produces an additional spurious stabilization in the supersystem. In fact:

$$\Delta E_{ab}(r_{ab}) = E_{ab}(\chi_{ab}; r_{ab}) - E^0_a(\chi_a) - E^0_b(\chi_b) \tag{63}$$

where $\chi_{ab} = \chi_a \oplus \chi_b$ is the supersystem orbital space.

Satisfactory, though often questioned, results have been obtained with the procedure proposed several years ago by Boys and Bernardi [29], named counterpoise correction (CP). This correction consists in performing the SCF calculation on the monomers using the dimer basis set and evaluating the interaction energy ΔE with respect to the values of the isolated monomers determined in this way as a reference energy:

$$\Delta E^{CP}_{ab} = E_{ab}(\chi_{ab}; r_{ab}) - E^{CP}_a(\chi_{ab}; r_{ab}) - E^{CP}_b(\chi_{ab}; r_{ab}) \tag{64}$$

Our group in Pisa proposed a CP correction scheme to be applied to the interaction energy decomposition [6], where the CP corrected components of ΔE_{ab} can be written as:

$$E^{CP}_X = E_X + \Delta^X, \tag{65}$$

with $\Delta^X = \Delta^X_a + \Delta^X_b$ and $\Delta^X_M = E^0_M - E^X_M$ (new reference energies) and M=a,b.

For every X there is a different modification in the reference energy, which corresponds to different enlargements of the monomer basis set intermediate between the single monomer basis and the complete dimer basis, as can be derived by examining Scheme 4, where χ_M is the complete monomer subspace, while φ^o_M and φ^v_M are the occupied and virtual orbital subspaces of the monomer, respectively. E_{ES} and E_{PL} don't have any basis set enlargement in the calculations, thus they don't need corrections.

CP Component	Functional Space of Each Subsystem	
	a	B
Δ^{TOT}_M	$\chi_a \oplus \chi_b$	$\chi_b \oplus \chi_a$
Δ^{EX}_M	$\varphi^o_a \oplus \varphi^o_b$	$\varphi^o_b \oplus \varphi^o_a$
Δ^{CT}_M	$\varphi^o_a \oplus \varphi^v_b$	$\varphi^o_b \oplus \varphi^v_a$

Scheme 4

The extension of this computational scheme to the use of polarized orbitals is straightforward: it is sufficient to adopt the polarized orbital set φ'^o_M and φ'^v_b, already

present in the code, to compute Δ^{OV}_M and Δ^{ET}_M.

Many-Body Interactions

Thus far we considered interacting systems made up of only two molecules *a* and *b*. This constitutes a noticeable simplification because it is evident that phenomena in the real world are governed by a number of concomitant interactions. Chemical interactions in the condensed phases are affected by interactions with the nearby components of the system, such as in the case of solutions, but also in crystals and glasses. It is therefore advisable to include into the microscopic model a limited number of additional molecules, which are supposed to be able to describe these further features. The "supermolecule" approach, in this way it is usually defined, can present some advantage, but in general the additional number of components which turns out to be necessary is so huge to prevent a quantum-mechanical treatment. On the other hand the structure corresponding to the energy minimum often is void of interest. Imagine for instance dilute solutions, where it is more sensible to talk about probability distributions of various configurations, rather than about a single configuration corresponding to the energy minimum.

An extremely interesting concept concerns non additive effects. If we consider a system made up of N molecules in a given spatial arrangement, its energy will be:

$$E(1,2,...,N) = \sum_i^N E_i(i) + \frac{1}{2}\sum_i\sum_j' E_i(i,j) +$$
$$\frac{1}{3!}\sum_i\sum_j'\sum_k' E_i(i,j,k) + \frac{1}{4!}\sum_i\sum_j'\sum_k'\sum_l' E_i(i,j,k,l) + ... \tag{66}$$

the system has been decomposed in all the possible pairs (i,j), triples (i,j,k), and so on ($\sum'$ indicates that the summation is extended to all the values of the indices different from the previous ones). Non additive terms are those related to three or more bodies. The interaction energy is then given by:

$$\Delta E(1,2,...N) = E(1,2,...N) - \sum_i^N E_i(i) \tag{67}$$

which can be decomposed in analogy to what examined before into:

$$E_{ES}(1,2,...N) + E_{PL}(1,2,...N) + E_{CT}(1,2,...N) + E_{EX}(1,2,...N) +$$
$$E_{MIX}(1,2,...N) + E_{Dis}(1,2,...N) \tag{68}$$

The electrostatic interaction is pairwise by definition and thus is a purely additive contribution, while E_{PL} shows a non additive component which becomes important at large separations.

$$E_{ES}(1,2,...N) = \frac{1}{2}\sum_i\sum_j E_{ES}(i,j) \tag{69}$$

$$E_{PL}(1,2,...N) = \frac{1}{2}\sum_i\sum_j E_{PL}(i,j) + \frac{1}{6}\sum_i\sum_j\sum_k E_{PL}(i,j,k) + ... \tag{70}$$

$$E_{CT}(1,2,...N) = \frac{1}{2}\sum_i\sum_j E_{CT}(i,j) + \frac{1}{6}\sum_i\sum_j\sum_k E_{CT}(i,j,k) + \cdots \qquad (71)$$

$$E_{EX}(1,2,...N) = \frac{1}{2}\sum_i\sum_j E_{EX}(i,j) + \frac{1}{6}\sum_i\sum_j\sum_k E_{EX}(i,j,k) + \cdots \qquad (72)$$

$$E_{Dis}(1,2,...N) = \frac{1}{2}\sum_i\sum_j E_{Dis}(i,j) + \frac{1}{6}\sum_i\sum_j\sum_k E_{Dis}(i,j,k) + \cdots \qquad (73)$$

On the contrary the exchange component shows non additive three-body contributions which are considerable already at short separation. In perturbation theories E^2_{exc} is additive in the current version of the theory as well as E^2_{Dis}. In contrast E^3_{Dis}, called also the dipole-dipole-dipole term, which is important for the closed shell spherical clusters such as He_3, is non-additive. McLachlan applied his already quoted approach to determine three- and N-body dispersion forces [10]

Importance of non-additive terms.

Since non-additive terms depend on the basis set used, there is no universal agreement about their importance among the various authors. There are however a few pivotal points in the field: non additive terms are thought to stabilize equilibrium conformations (this phenomenon is also referred to as H-bond enhancement) and to further contribute to repulsive geometrical structures. In general thus they seem to have a tendency to stabilize clusters, even though the exceedingly large estimate furnished (10% in water trimers and tetramers) represents an upper bound. The success however of transferable potentials (for this very reason based on pairwise interactions) parametrized on experimental measurements, such as Jorgensen's OPLS (Optimized Potentials for Liquid Simulations) [30], depends actually on their inherent inclusion of many-body effects.

For a broad overview of many-body effects the readers are referred to an article [31] contained in a thematic issue of Chemical Reviews, the second devoted to van der Waals molecules (the first appeared in 1988). Several other interesting contributions can be found concerning weak intermolecular interactions [32], the perturbation theory approach [33] to their evaluation, a thorough discussion of the counterpoise procedure [34], in condensed phases represented as supermolecules or with a continuum description [35].

REFERENCES

1. (a) P. Hobza, R. Zahradnik, *Weak Intermolecular Interactions in Chemistry and Biology*, Elsevier, 1980; (b) R. McWeeny, *Methods of Molecular Quantum Mechanics*, Second Edition, Chapter 14, Academic Press, 1989.

2. G.C. Maitland, M. Rigby, E.B. Smith, W.A. Eakeham, *Intermolecular Forces: their Origin and Determination*, OUP, 1987.

3. (a) B. Jeziorski, W. Kołos, *Perturbation Approach to the Study of Weak Intermolecular Interactions*, in "Molecular Interactions Vol. 3", H. Ratajczak, W.J. Orville-

Thomas, Eds., Wiley, 1982; (b) J. Tomasi, *Electrostatic Molecular Potential Model and its Application to the Study of Molecular Aggregations*, ibidem.

4   (a) A.D. Buckingham, *Basic Theory of Intermolecular Forces: Applications to Small Molecules*, in: Intermolecular Interactions: From Diatomics to Biopolymers, B. Pullman, Ed., Wiley, 1978; (b) P. Claverie, *Elaboration of Approximate Formulas for the Interactions between Large Molecules: Applications in Organic Chemistry*, ibidem.

5.   V. Magnasco, R. McWeeny, *Weak Interactions between Molecules and their Physical Interpretation*, in "Theoretical Models of Chemical Bonding", Z.B. Maksic, Ed., Part 4, Springer-Verlag, 1991.

6.   G. Alagona, C. Ghio, R. Cammi, J. Tomasi, *A Reappraisal of the H-bonding Interaction Obtained by Combining Energy Decomposition Analyses and Counterpoise Corrections*, in "Molecules in Physics, Chemistry, and Biology, J. Maruani, Ed., Vol. II, p. 507-559, Kluwer, 1988.

7.   J. Mahanty, B.W. Ninham, *Dispersion Forces*, Academic Press, 1976, p. 1-9.

8.   F. London, *Z. f. Phys. Chem. B* **11** (1930) 222.

9.   H.B.G. Casimir, D. Polder, *Phys. Rev.* **73** (1948) 360.

10.   (a) A.D. McLachlan, *Proc. Roy. Soc. A* **271** (1963) 381; (b) A.D. McLachlan, *Mol. Phys.* **6** (1963) 423.

11.   P.-O. Löwdin, *J. Math. Phys.* **3** (1962) 969.

12.   W.J. Carr, *Phys. Rev.* **131** (1963) 1947.

13.   J.N. Murrell, G. Show, *J. Chem. Phys.* **46** (1967) 1768.

14.   I.J. Musher, A.T. Amos, *Phys. Rev.* **164** (1967) 31.

15.   R. Eisenschitz, F. London, *Z. Physik.* **60** (1930) 491.

16.   J.O. Hirschfelder, *Chem. Phys. Lett.* **1** (1967) 325, 363.

17.   A. van der Avoird, *J. Chem. Phys.* **47** (1967) 3649.

18.   (a) B. Jeziorski, W. Kołos, *Int. J. Quantum Chem.* **12** Suppl. 1 (1977) 91; (b) B. Jeziorski, K. Szalewicz, G. Chałasinski, *Int. J. Quantum Chem.* **14** (1978) 271.

19.   J.O. Hirschfelder, R.S. Silbey, *J. Chem. Phys.* **45** (1966) 2188.

20.   J.P. Daudey, P. Claverie, J.P. Malrieu, *Int. J. Quantum Chem.* **8** (1974) 1.

21.   (a) A.J. Stone, *Classical Electrostatics in Molecular Interactions*, in "Theoretical Models of Chemical Bonding", Z.B. Maksic, Ed., Part 4, Springer-Verlag, 1991, p. 122-126; (b) *ibidem*, p. 126-129.

22.   J.C. Slater, J. Kirkwood, *Phys. Rev.* **37** (1931) 632.

23. (a) R.G. Gordon, Y.S. Kim, *J. Chem. Phys.* **56** (1972) 3122; (b) Y.S. Kim, R.G. Gordon, *J. Chem. Phys.* **60** (1974) 4323.

24. R. Bonaccorsi, C. Petrongolo, E. Scrocco, J. Tomasi, *Chem. Phys. Letters* **3** (1969) 473.

25. K. Kitaura, K. Morokuma, *Int. J. Quantum Chem.* **10** (1976) 325.

26. S. Nagase, T. Fueno, S. Yamabe, K. Kitaura, *Theor. Chim. Acta* **49** (1978) 309.

27. R. Bonaccorsi, R. Cimiraglia, P. Palla, J. Tomasi, *Int. J. Quantum Chem.* **26** (1983) 307.

28. W.A. Lathan, G.R. Pack, K. Morokuma, *J. Amer. Chem. Soc.* **97** (1975) 6624; W. Kołos, *Theor. Chim. Acta*, **51** (1979) 219.

29. S.F. Boys, F. Bernardi, *Mol. Phys.* **19** (1970) 553.

30. J. Tirado-Rives, W.L. Jorgensen, *J. Amer. Chem. Soc.* **110** (1988) 1657.

31. M.J. Elrod, R.J. Saykally, *Chem. Rev.* **94** (1994) 1975.

32. G. Chałasinski, M.M. Szczesniak, *Chem. Rev.* **94** (1994) 1723.

33. B. Jeziorski, R. Moszynski, K. Szalewicz, *Chem. Rev.* **94** (1994) 1887.

34. F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, *Chem. Rev.* **94** (1994) 1873.

35. J. Tomasi, M. Persico, *Chem. Rev.* **94** (1994) 2027.