A REVIEW OF CURRENT METHODS OF EVALUATION OF INTERMOLECULAR INTERACTIONS BETWEEN LARGE MOLECULES*

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ABSTRACT

Ab initio *calculations on interaction between small molecules are within the reach of ' present-day ' computers, while for large molecules, the computational costs prohibit such studies. The various semi-empirical schemes, approximating the* ab initio *methods that are currently in use suitable for the evaluation of electrostatic, exchange, polarisation, delocalisation, and dispersion forces, between large molecules are presented. Certain ' unsolved ' problems arising due to advances in the SCF theory of molecules are also documented.*

Key words: Intermolecular forces, molecular interaction evaluation.

1. INTRODUCTION

Molecular interactions are responsible for a variety of biological[1, 2] and chemical phenomena.[3-5] An understanding of the theory and methods of evaluation of intermolecular interactions is therefore essential. The object of this work is to popularise among chemists and experimental physicists the language/methods of quantum mechanical treatment of intermolecular forces. We shall be restricting ourselves to those parts of literature (covered up to the end of 1976) concerning the evaluation of intermolecular interactions between large molecules. For general reviews see Refs. 6-9. *Ab initio* calculations are within the reach of ' present-day ' computers for small molecules,[10-14] while the computational costs prohibit such studies

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for large molecules. The various semi-empirical methods, approximating the *ab initio* methods, suitable for evaluating the various components of molecular interactions are presented here. The emphasis is more on methods/techniques and less on documentation of extensive applications (which are yet to come!). Certain 'unsolved' problems arising from the advances in self-consistent field (SCF) theory of molecules are also documented. Before we go into details it is perhaps worth spending some time on the path that has led to our present-day knowledge on the topic.

Broadly speaking, molecular interactions can be classified into two groups:

(*a*) Chemical and (*b*) Physical.

Chemical interactions involve very close approach of the interacting molecules and therefore they are of 'short range' and a theory of such interactions is essentially the theory of valence. Physical interactions, on the other hand, do not involve very close approach of the interacting systems, are of 'long range' and are easily reversible. They are better understood than chemical interactions because the perturbations responsible (for the interaction) are small. A typical spherically averaged intermolecular potential curve is shown in Fig. 1, together with the classification (which is rather arbitrary) with respect to 'range', overlap (of electronic clouds of the two systems) and energy variation (as a function of R, intermolecular distance).

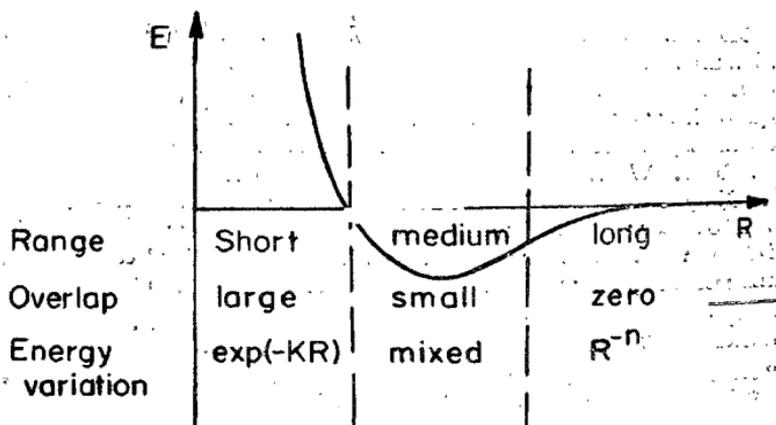| E			
Range	Short	medium	long R
Overlap	large	small	zero
Energy variation	exp(-KR)	mixed	R^{-n}

Fig. 1. A typical spherically averaged intermolecular potential energy curve.

Often, chemical interactions are referred to as strong interactions, while interaction in the medium ranges (where both short range and long range forces have appreciable effects) are termed as weak interactions. Essentially this work is concerned with methods suitable for studying weak interactions.

2. INTERACTION IN REGIONS OF ZERO ORBITAL OVERLAP

London[15] made the first attempt to investigate the nature of long range intermolecular forces, using quantum mechanical perturbation theory. Consider two molecules A and B, separated by a large distance so that the electronic clouds of the two *do not* overlap. Let $\phi_o{}^A, \phi_r{}^A$, etc., be the ground and excited state wave functions of molecule A and $\phi_o{}^B, \phi_s{}^B$ be those of B. The total Hamiltonian of the system is

$$H = H_A + H_B + V \tag{1}$$
$$= H_O + V$$

where the intermolecular perturbation operator, V, is given by

$$V = e^2 \Big[\sum_{\alpha\beta'} \frac{Z_\alpha\, Z_{\beta'}}{|\,r_\alpha - r_{\beta'}\,|} - \sum_{\nu\beta'} \frac{Z_{\beta'}}{|\,r_{\beta'} - r_\nu\,|} - \sum_{\alpha\nu'} \frac{Z_\alpha}{|\,r_\alpha - r_{\nu'}\,|} + \sum_{\nu} \sum_{\nu'} \frac{1}{|\,r_\nu - r_{\nu'}\,|} \Big] \tag{2}$$

where we denote by α and ν the nuclei and electrons of A and β' and ν' those of B. The first term is the nuclear-nuclear repulsion term, second and third terms being the electron-nuclear attractive terms while the last term is the electron-electron repulsion term. One may note the electrical nature of interaction operator. According to standard perturbation theory, the interaction energy, correct to second order in V, is given by

$$\Delta E = \Delta E^{(1)} + \Delta E^{(2)}$$

$$\Delta E^{(1)} = \langle \phi_o{}^A \phi_o{}^B \mid V \mid \phi_o{}^A \phi_o{}^B \rangle \tag{3 a}$$

$$\Delta E^{(2)} = \sum_r{}' \frac{\langle \phi_o{}^A \phi_o{}^B \mid V \mid \phi_r{}^A \phi_o{}^B \rangle}{E_o{}^A - E_r{}^A} + \sum_s{}' \frac{\langle \phi_o{}^A \phi_o{}^B \mid V \mid \phi_o{}^A \phi_s{}^B \rangle}{E_o{}^B - E_s{}^B}$$
$$+ \sum_r{}' \sum_s{}' \frac{\langle \phi_o{}^A \phi_o{}^B \mid V \mid \phi_r{}^A \phi_s{}^B \rangle}{E_o{}^A - E_o{}^B - E_r{}^A - E_s{}^B} \tag{3 b}$$

$\Delta E^{(1)}$, called the first order energy, represents the electrostatic energy arising from the coulombic repulsion between the permanent electric moments of the two molecules. $\Delta E^{(2)}$, the second order energy, the first two terms define the induction/polarisation energy, while the last term defines the dispersion energy. Longuet-Higgins[16] has shown that it is possible to write an 'integral' form of the operator V as

$$V = \int \int \frac{\rho(r)\,\rho'(r')}{|r - r'|}\, dr\, dr' \tag{4}$$

where $\rho(r)$ and $\rho'(r')$ are the density operators defined as

$$\rho(r) = e\,[\sum_{\alpha} Z_\alpha\, \delta(r - r_\alpha) - \sum_{\nu} \delta(r - r_\nu)] \tag{5}$$

$$\rho'(r') = e\,[\sum_{\beta'} Z_{\beta'}\, \delta(r' - r_{\beta'}) - \sum_{\nu'} \delta(r' - r_{\nu'})]$$

where δ's are the famous Dirac delta functions. Further, Longuet-Higgins define two types of densities— real three-dimensional functions which represent the actual distribution of electricity in the system (molecule)— *viz.*,

(i) Static density $= \left\langle \begin{matrix} \text{ground state} \\ \text{wave function} \end{matrix} \right|$ density operator $\left| \begin{matrix} \text{ground state} \\ \text{wave function} \end{matrix} \right\rangle$

$e.g.,\ \langle \phi_0^A \,|\, \rho(r)\,|\, \phi_0^A \rangle$ for molecule A. (6 a)

(ii) Transition density (for the system undergoing transition from ground state ϕ_0, to excited state ϕ_r)

$= \left\langle \begin{matrix} \text{ground state} \\ \text{wave function} \end{matrix} \right|$ density operator $\left| \begin{matrix} \text{excited state} \\ \text{wave function} \end{matrix} \right\rangle$

$e.g.,\ \langle \phi_0^A \,|\, \rho(r)\,|\, \phi_r^A \rangle$ for molecule A^* (6 b)

and similar definitions are applied to the other molecule B. Further, the matrix elements, that appear in equations 3, are interpreted in terms

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* The appropriateness of these terminologies can be understood in the following way. The electric moment for this transition $o \rightarrow r$ state is

$$\langle \phi_0^A \,|\, M \,|\, \phi_r^A \rangle = \langle \phi_0^A \,|\, \int r\rho(r)\, dr \,|\, \phi_r^A \rangle = \int r\, \langle \phi_0^A \,|\, \rho(r) \,|\, \phi_r^A \rangle\, dr.$$

therefore $\langle \phi_0^A \,|\, \rho(r) \,|\, \phi_r^A \rangle$ is an electrical distribution whose dipole moment is equal to the transition moment between the two states. Further $\langle \phi_0^A \,|\, \rho(r)\, \phi_r^A \rangle$ is just the amplitude with which the electrical density at r oscillates when the system (molecule) is passing from ground state to an excited state. Hence it is appropriate to term $\langle \phi_0^A \,|\, \rho(r) \,|\, \phi_r^A \rangle$ as the 'transition density' between O & r states.

of interaction between these densities. A typical matrix element is interpreted as

$$\langle \phi_o{}^A \phi_o{}^B \mid V \mid \phi_r{}^A \phi_o{}^B \rangle$$

$$= \int \int \frac{\langle \phi_o{}^A \mid \rho(r) \mid \phi_r{}^A \rangle \langle \phi_o{}^B \mid \rho'(r') \mid \phi_o{}^B \rangle}{\mid r - r' \mid} \; dr dr' \qquad (7)$$

the interaction between transition density of A with the static density of B. The matrix elements are expressed in different ways by London and Longuet-Higgins. London expands them in powers of R (the intermolecular distance). The successive terms are identified as the interaction between multiple moments (of the two subsystems) of increasing order, while in $L - H$ approach they are accurately expressed as the electrostatic repulsion between three-dimensional charge distributions localised on the two systems. The interpretation of the various terms in the two approaches can be summarised as follows:

Interpretation of interaction

Term	London's approach	Longuet-Higgins treatment
Electrostatic	Permanent electric moment (of A) $\leftrightarrow$ permanent electric moments (of B)	Static density (of A) $\leftrightarrow$ static density (of B)
Induction polarisation	Permanent electric moment (A) $\leftrightarrow$ induced moment in the non-polar molecule (B)	Static density (A) $\leftrightarrow$ transition density (B)
Dispersion	Instantaneous dipole moment (A) $\leftrightarrow$ instantaneous dipole moment (B) brought about by fluctuations of their own charge distributions	Transition density (A) $\leftrightarrow$ transition density (B)
How matrix elements are evaluated	By expansion in terms of R^{-n}	Accurately, the three-dimensional electronic charge distribution

The celebrated London's formula for dispersion energy for a pair of atoms or spherical molecules is

$$E_{dis} = -\frac{3}{2} \alpha_A \alpha_B \frac{I_A \cdot I_B}{I_A + I_B} \cdot \frac{1}{R^6_{AB}} \tag{8}$$

α's are the polarisabilities and I's the ionisation potentials and R the distance of separation. The important feature of London's formula is inverse sixth power variation (of the dispersion energy) with distance. Equation (8) is valid for large separation ($R \gg l$; l, the molecular diameter).

3. Interactions in Regions of Small Orbital Overlap

3.1. *The Exchange Problem*

When two molecules/atoms approach closely then their electronic clouds begin to overlap and one has to take into account the possibility of electron exchange between the systems. It is common/natural to choose the unperturbed Hamiltonian H_0, to be the sum of the Hamiltonian of the non-interacting molecules, i.e., $H_0 = H_A + H_B$. This choice implies that we are associating particular electrons to each molecule and thus the symmetry of H (Hamiltonian of the complex $A \cdots B$) with respect to permutation of electrons is greater than H_0. This leads to certain mathematical complications/difficulties referred to as the ' exchange problem ', to develop a perturbation expansion for intermolecular forces which take full account of symmetry. Some of the difficulties are[8]:

(i) the order of perturbation term is not uniquely defined: Suppose A is an operator which projects the component with the symmetry of desired total wave function, then A commutes with H, but does not commute separately with either H_0 or V rather,

$$[A, H_0] = [V, A]. \tag{9}$$

In any conventional perturbation scheme, left-hand side of eqn. (9) is zeroth order (in V) while on the right-hand side one is first order. This means the orders in ' V ' is ambiguous.

(ii) The choice of an antisymmetrised basis set, for expansion of total wave function, is not uniquely determined. For instance, the set of function $A\phi_i^A\phi_j^B$, $i = 0, \ldots, n$; $j = 0, \ldots, n$ is linearly dependent and is not an eigenfunction of H_0, the unperturbed Hamiltonian.

(iii) Many other complications can be mentioned. (For a fuller account see the article by Certain and Bruch.[8])

The above mentioned difficulties do not mean that it is impossible to develop a perturbation scheme which takes full account of symmetry, but many different approaches are possible. There are a number of exchange perturbation theories[17-29] for regions of small orbital overlap, ($S \sim 10^{-2}$) but we shall be discussing the only theory, that has been proposed by Murrell, Randic and Williams[29] and by Salem,[30] for their method has been widely applied in studies on interactions between large molecules.[31-34] We shall also mention (in sec. 5) a recently proposed energy decomposition scheme within the Hartree-Fock procedure (as compared to perturbation approaches) which has the advantage of treating rather strong interactions (*i.e.*, rather large overlap cases).

3.2. *Theory of Murrell, Randic and Williams and of Salem*

Their theory is essentially an extension of Longuet-Higgins treatment of long range intermolecular forces where the intermolecular orbital overlap is neglected, rather than an extension of the short range or valence theories. This uses a basis set of functions which are antisymmetrised product of the eigenfunctions of the separate systems, *viz.*,

$$\hat{A}\phi_o{}^A \phi_o{}^B; \quad \hat{A}\phi_r{}^A \phi_o{}^B; \quad \hat{A}\phi_o{}^A \phi_s{}^B; \quad \hat{A}\phi_r{}^A \phi_s{}^B; \quad \hat{A}\phi^{A+} \phi^{B-};$$

$$\hat{A}\phi^{A-} \phi^{B+}, \text{ etc.} \tag{10}$$

where the functions $\phi^{A+} \phi^{B-}$ represent a charge transfer state in which an electron from an occupied orbital of A is transferred to an unoccupied orbital of B. Here $\hat{A}$ is the antisymmetriser[+]. The theory is essentially configuration interaction treatment in which locally excited, doubly excited and charge transfer states are allowed to mix with the ground state configuration. The interaction energy is then obtained as a double perturbation expansion in ' U ' the intermolecular perturbation operator and ' S ' the

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[+] The antisymmetrisation operator is hermitian;

$$\hat{A} = \frac{1}{\sqrt{N}} \sum_{P_{\nu\nu'}} (-1)^{P_{\nu\nu'}} P_{\nu\nu'} = \frac{1}{\sqrt{N}} \left[1 + \sum_{P_{\nu\nu'} \neq I} (-1)^{P_{\nu\nu'}} P_{\nu\nu'} \right]$$

where $P_{\nu\nu'}$ is the permutation operator and I the identity operator, N is the total number of permutation of electrons between A and B, Further $\hat{A} \cdot \hat{A} = \sqrt{N}\hat{A}$.

intermolecular overlap, up to order $V^2 S^2$. The various terms are as follows:

1. Terms of order $V^1 S^0$: This is identical with the classical electrostatic energy.

2. Terms of order $V^2 S^0$: These are the energies of induction and dispersion (of long range theory).

3. Terms of order $V^1 S^2$: Called the first order exchange energy. This defines the exchange repulsion energy which is the origin of overlap repulsion and non-bonded repulsions in intermolecular interactions.

4. Terms of the order $V^2 S^2$: This term is called by Murrell, Randic and Williams as the exchange polarisation energy or charge-transfer energy, depending on the choice of the basis set. The exchange polarisation energy term is shown[30] to be an order of magnitude smaller than the dispersion forces and is therefore generally less important than the other energies[21] we have so far discussed. So we shall neglect this term in our further discussion on evaluation of different interaction terms, in regions of small orbital overlap, *i.e.*, studies on weak intermolecular interactions. Perhaps it is worth recapitulating the significant interaction terms that arise in regions of weak (medium range) intermolecular interactions. In Fig. 2 is shown these terms together with their characteristic properties.

4. METHODS OF EVALUATION OF DIFFERENT INTERACTION TERMS

4.1. *Choice of Monomer Wavefunctions*

Like the developments in the molecular orbital theories of molecules which started from ϕ-electron methods, to all valence electron methods, to the present-day *ab initio* techniques, the studies on intermolecular interactions between large molecules appear to have followed a similar path. For aromatic hydrocarbons and other conjugated systems the $\sigma-\pi$ electron separation appears to be valid[36, 37] and the interactions can be split into two parts, one due to $\pi-\pi$ interactions only and the other due to $\sigma-\sigma$ electrons interactions (with no significant $\sigma-\pi$ mixing). Such an approach has been applied to studies on the formation of aromatic hydrocarbon dimer,[32] and thymine photodimer.[38] Recently Fueno *et al.*[34] and Nataga *et al.*[33] have applied the all valence electron CNDO/2 method to studies on interaction between large molecules. We shall present the formulae, in both the approaches, for different interaction terms in the following sections,

(i)
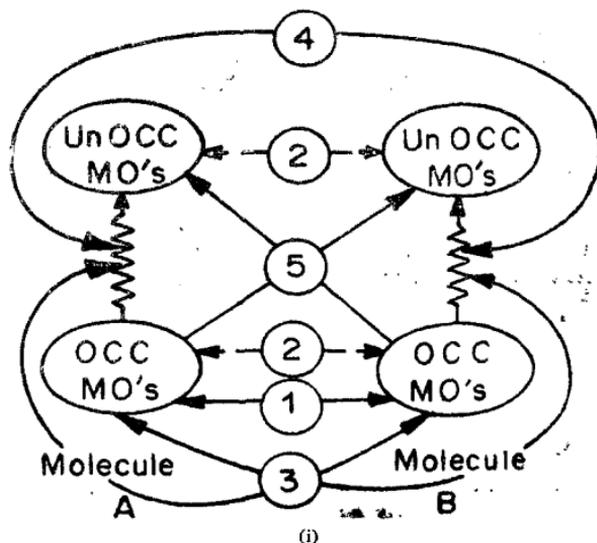
Type	Range	Attractive or Repulsive	Pairwise additive
Electrostatic	Long+	either	yes
Exchange	Short	repulsive††	nearly
Polarisation	Long	attractive	no
Dispersion	Long	attractive	yes
Charge-transfer or exchange polarisation	Short	attractive	nearly

+ Except for neutral spherical systems.
†† Except possibly for the interaction of two anions.

(ii)

FIG. 2. Feature of various components of molecular interaction, (i) In terms of inter-on and mixing of MO's (ii) Characteristic properties.

2. *Electrostatic Energy*

4.2.1. *Multipole expansion method*: If the two molecules are separated a large distance, the electrostatic energy is given by a few terms of the eractions of two multipole expansion[39]

$$E_{el} = E_{q_A q_B} + E_{q_A \mu_B} + \cdots + E_{\theta_A \theta_B} + \cdots \tag{11}$$

where q's are charges, μ's the dipoles and the θ's the quadrupole moments of molecules A and B. When the dimensions of the molecules are of the same order as the intermolecular separation, R, the expansion (12) converges slowly.[40, 65] In order to circumvent this 'convergence problem' the molecule is divided into segments, and then a multipole expansion is made on each segment. It has been recently shown[41] that this segmental multipole expansion is convergent in regions of our interest namely regions of small orbital overlap/intermediate ranges ($R < 5$ Å). Further, for systems with permanent moments, an expansion up to octupole terms is necessary. So that electrostatic energy is now given by the formula

$$E_{el} = \sum_{\alpha}^{A} \sum_{\beta}^{B} \sum_{i=0}^{3_\alpha} \sum_{j=0}^{3_\beta} \epsilon_{ij}^{\alpha\beta} \tag{12}$$

$$\text{(Atoms)} \qquad \text{(moments)}$$

where $\epsilon_{ij}^{\alpha\beta}$ denotes/represents the interaction between i-th moment of α-th atom in A with j-th moment of β-th atom in the other molecule B. The relevant formulae being [42,43]

$$m - m \qquad \epsilon_{00}^{\alpha\beta} = q_\alpha q_\beta / R$$

$$m - d \qquad \epsilon_{01}^{\alpha\beta} = -(q_\alpha \mu_\beta \cdot \boldsymbol{R}) / R^3$$

$$d - m \qquad \epsilon_{10}^{\alpha\beta} = (q_\beta \mu_\alpha \cdot \boldsymbol{R}) / R^3$$

$$d - d \qquad \epsilon_{11}^{\alpha\beta} = (\mu_\alpha \cdot \mu_\beta) / R^3$$
$$- 3(\mu_\alpha \cdot \boldsymbol{R})(\mu_\beta \cdot \boldsymbol{R}) / R^5$$

$$m - q \qquad \epsilon_{02}^{\alpha\beta} = (q_\alpha \boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\beta \cdot \boldsymbol{R}) / R^5$$

$$q - m \qquad \epsilon_{20}^{\alpha\beta} = (q_\beta \boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R}) / R^5$$

$$d - q \qquad \epsilon_{12}^{\alpha\beta} = -2(\mu_\alpha \cdot \overset{\leftrightarrow}{Q}_\beta \cdot \boldsymbol{R}) / R^5$$
$$+ 5(\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\beta \cdot \boldsymbol{R})(\mu_\alpha \cdot \boldsymbol{R}) / R^7$$

$$q - d \qquad \epsilon_{21}^{\alpha\beta} = 2(\mu_\beta \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R}) / R^5$$
$$- 5(\mu_\beta \cdot \boldsymbol{R})(\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R}) / R^7$$

$$q - q \qquad \epsilon_{22}^{\alpha\beta} = \frac{2}{3} \frac{1}{6} (\overset{\leftrightarrow}{Q}_\alpha : \overset{\leftrightarrow}{Q}_\beta)/R^5$$

$$-\frac{20}{3} (\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\beta \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R})/R^7$$

$$+\frac{35}{5} (\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R})(\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\beta \cdot \boldsymbol{R})/R^7$$

$$m - o \qquad \epsilon_{03}^{\alpha\beta} = q_\alpha \boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R}/R^7$$

$$o - m \qquad \epsilon_{30}^{\alpha\beta} = - q_\beta \boldsymbol{R} \cdot (\Omega_\alpha \cdot \boldsymbol{R}) \cdot \boldsymbol{R}/R^7$$

$$d - o \qquad \epsilon_{13}^{\alpha\beta} = 3\mu_\alpha \cdot (\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R}/R^7$$

$$-7 (\mu_\alpha \cdot \boldsymbol{R})(\boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R})/R^9$$

$$o - d \qquad \epsilon_{31}^{\alpha\beta} = 3\mu_\beta \cdot (\Omega_\alpha \cdot \boldsymbol{R}) \cdot \ \cdot \boldsymbol{R}/R^7$$

$$-7 (\mu_\beta \cdot \boldsymbol{R})(\boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\alpha \cdot \boldsymbol{R}) \cdot \boldsymbol{R})/R^9$$

$$q - o \qquad \epsilon_{23}^{\alpha\beta} = (\overset{\leftrightarrow}{Q}_\alpha : \overset{\overleftrightarrow}{\Omega}_\beta) \ \boldsymbol{R}/R^7$$

$$-7 (\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha)((\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R})/R^9$$

$$+10.5 (\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R})(\boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R})/R^{11}$$

$$o - q \qquad \epsilon_{32}^{\alpha\beta} = - \boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\alpha : \overset{\leftrightarrow}{Q}_\beta)/R^7$$

$$+7 (\boldsymbol{R} \cdot (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\alpha)) \cdot (\overset{\leftrightarrow}{Q}_\beta \cdot \boldsymbol{R})/R^9$$

$$-10.5 (\boldsymbol{R} \cdot (\overset{\overleftrightarrow}{\Omega}_\alpha \cdot \boldsymbol{R}) \cdot \boldsymbol{R})(\boldsymbol{R} \cdot \overset{\leftrightarrow}{Q}_\alpha \cdot \boldsymbol{R})/R^{11}$$

$$o - o \qquad \epsilon_{33}^{\alpha\beta} = 0.4 \, \text{Tr} \, [(\Omega_\beta)(\Omega_\alpha)]/R^7$$

$$-8.4 (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\alpha) : (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\beta)/R^9$$

$$+37.8 (\boldsymbol{R} \cdot (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\alpha)) \cdot ((\overset{\overleftrightarrow}{\Omega}_\beta \cdot \boldsymbol{R}) \cdot \boldsymbol{R})/R^{11}$$

$$-46.2 (\boldsymbol{R} \cdot (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\alpha) \cdot \boldsymbol{R})(\boldsymbol{R} \cdot (\boldsymbol{R} \cdot \overset{\overleftrightarrow}{\Omega}_\beta) \cdot \boldsymbol{R})/R^{13}$$

Definition of moments

Monopole (m) (charge)

$$q_\alpha = \rho\,(\bar{r}_a)$$

Dipole (d)

$$\mu = \int \rho\,(r)\,\boldsymbol{r}\,dr$$

Quadrupole (q) (tensor element)

$$Q_{ij} = \tfrac{1}{2}\,\int \rho\,(r)\,(3x_i\,x_j - r^2\,\delta_{ij})\,dr$$

Octupole (o) (tensor element)

$$\Omega_{ijk} = -\,\int \rho\,(r)\,[5x_i\,x_j\,x_k - r^2\,(x_i\,\delta_{jk} + x_j\,\delta_{ik} + x_k\,\delta_{ij})]\,.\,d\tau$$
$$i = 1, 2, 3$$

x_i are defined w.r.t. centre of mass as origin of coordinate system

$\boldsymbol{R}$ vector from α-th atom in A to the β-th atom in B, $R = R$

μ dipole vector

$\overset{\leftrightarrow}{Q}$ quadrupole tensor of rank 2

$\overset{\leftrightarrow}{\Omega}$ octupole tensor of rank 3

$\cdot$ designates dot product

$:$ designates a trace between two second order tensors

$$\overset{\leftrightarrow}{Q}_\alpha : \overset{\leftrightarrow}{Q}_\beta = \sum_{ij} Q^\alpha{}_{ij}\,Q^\beta{}_{ij}$$

$$= \text{Trace of } \overset{\leftrightarrow}{Q}_\alpha \,.\, \overset{\leftrightarrow}{Q}_\beta$$

$$\boldsymbol{A}\,.\,(\overset{\leftrightarrow}{\Omega}\,.\,\boldsymbol{B})\,.\,\boldsymbol{C} = \Omega_{ijk}\,A_i\,B_j\,C_k$$

$$A\,.\,(\overset{\leftrightarrow}{\Omega} : \overset{\leftrightarrow}{Q}) = \Omega_{ijk}\,A_i\,Q_{jk}$$

$$(\overset{\leftrightarrow}{Q}\,.\,A)_i = Q_{ik}\,A_j$$

$$\big((\overset{\leftrightarrow}{\Omega}\,.\,\boldsymbol{B})\,.\,\boldsymbol{C}\big)_i = \Omega_{ijk}\,B_j\,C_k$$

Repeated subscript implies summation over that index.

Note:

$$\sum_{i,j,k}^{3} \Omega_{ijk}\,\delta_{jk} = 0$$

The monomer wavefunctions used being IEHT (superior to CNDO/2). For further details on evaluation of segmental moments, see the original references or a recent review by Rein.[44] It may be appropriate to mention here that other more refined all valence electron methods[45-48] have not been so far tried (see Sec. 6 below).

4.2.2. *Fueno's formula*: Uses CNDO/2 monomer wavefunctions and explicit form of perturbation operator.

The expression for the case of interaction between a singlet molecule and a radical is

$$E = 2 \sum_{i}^{A} \langle \rho_{ii} \mid V(B) \rangle + \sum_{j^\alpha}^{B} \langle \rho_{j^\alpha j^\alpha} \mid V(A) \rangle + \sum_{j^\beta}^{B} \langle \rho_{j^\beta j^\beta} \mid V(A) \rangle$$
$$- 2 \sum_{i}^{A} \left[\sum_{j^\alpha}^{B} \langle \rho_{ii} \mid \rho_{j^\alpha j^\alpha} \rangle + \sum_{j^\beta}^{B} \langle \rho_{ii} \mid \rho_{j^\beta j^\beta} \rangle \right]$$
$$+ \sum_{\mu}^{A} \sum_{\nu}^{B} \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \tag{13}$$

where transition density

$$\rho_{mn} = \begin{cases} mm & \text{when } m = n \\ mn - \sum_{p} S_{mp}\ mp & \text{when } m \neq n \end{cases} \tag{14 a}$$

the interaction potential field

$$V(A) = \int 2 \sum_{i}^{\text{occ}} i\,(2)\,i\,(2)\frac{1}{r_{12}}\,d\tau_2 - \sum_{\mu}^{A} \frac{Z_\mu}{r_{1\mu}} \tag{14 b}$$

$$V(B) = \int \left[\sum_{j^\alpha}^{B} j^\alpha(2)\,j^\alpha(2) + \sum_{j^\beta}^{B} j^\beta(2)\,j^\beta(2) \right]$$
$$\times \left(\frac{1}{r_{12}} \right) d\tau_2 - \sum_{\nu}^{B} \frac{Z_\nu}{r_{1\nu}}$$

$$\langle \rho_{mn} \mid V \rangle = \int \rho_{mm}(1)\,V(1)\,d\tau_1$$

$$\langle \rho_{mn} \mid \rho_{mn} \rangle = \int \rho_{mn}(1) \left(\frac{1}{r_{12}} \right) \rho_{mn}(2)\,d\tau_1 d\tau_2$$

i and k (j and l) refer to occupied and vacant MO's of A (B) Z_μ (Z_ν) nuclear charge on μ-th (ν-th) atom in A (B) S overlap integral (over MO's) and R the distance. While intramolecular differential overlap is neglected, inter-molecular overlap is retained (intentionally). Mulliken approximation is employed for the evaluation of intermolecular multicentre integrals. The overlap integrals are computed by the Mulliken *et al.*[49] method, while other integrals by Roothaan procedure[50] (for closed shell molecules $j^\alpha = j^\beta$).

4.3. *Exchange Interaction Energy*

4.3.1. The first order exchange energy is the origin of non-bonded repulsion and π-overlap repulsion. The importance of non-bonded repulsions between intermolecular hydrogen atoms and CH, CH repulsion have been shown by Craig *et al.*[51], who have concluded that molecular orientation in aromatic hydrocarbon crystals is primarily fixed by minimisation of these energies. The non-bonded H $\cdots$ H interaction originates entirely from electron exchange between filled orbitals of the hydrogen atoms of the two molecules. Banerjee and Salem[52] have estimated this energy by the expression

$$E_{H \cdots H} = \beta \frac{S^2_{H \cdots H}}{R_{H \cdots H}} \tag{15}$$

where for β is chosen the value $21 \cdot 3$ Kcal/mole/Å. S_{HH} is the overlap integral between two 1s orbitals on hydrogen atoms and R the distance (in Å). Further they have shown that CH $\cdots$ CH repulsion is about $2 \cdot 3$ times the H–H repulsion energy. So that the total non-bonded repulsion is

$$E_{\text{non-bonded}} = 3 \cdot 3\, E_{H \cdots H} = 3 \cdot 3 \times 31 \cdot 3 \times \sum_{H_A} \sum_{H_B} \frac{S^2_{H_A H_B}}{R_{H_A H_B}} \tag{16}$$

while the π-overlap repulsion (between the overlapping π-electronic clouds of the large conjugated systems) is given by the formula[53]

$$E_{ov}(\pi\text{--}\pi) = -4 \sum_i^{\substack{A \\ \text{occ}}} \sum_{j'}^{\substack{B \\ \text{occ}}} \eta_{ij'}\, S_{ij'} \tag{17}$$

$$(\eta_{ij'} = -10 \cdot 0\, S_{ij'}).$$

4.3.2. In the all valence electron approach, the relevant formula is[34]

$$E_k = - \sum_i^A \sum_{j^\alpha}^B \{ \langle \rho_{ij\alpha} \mid \rho_{j\alpha_i} \rangle + S_{ij\alpha} [\langle \rho_{ij\alpha} \mid V(B) \rangle$$
$$+ \langle \rho_{j\alpha_i} \mid V(A) \rangle] \}$$
$$- \sum_i^A \sum_{j\beta}^B \{ \langle \rho_{ij\beta} \mid \rho_{j\beta_i} \rangle + S_{ij\beta} [\langle \rho_{ij\beta} \mid V(B) \rangle + \langle \rho_{j\beta_i} \mid V(A) \rangle] \} \quad (18)$$

where the notation is the same as that discussed in section 4.2.2.

4.3.3. *Atom–atom potentials*: Empirical potential functions of the type $B \exp(-KR)$, are also in wide use[54-57] for the estimation of exchange repulsion energy. There is considerable evidence[60] that this type of exponential expression is a reasonable approximation to the full (quantum mechanical) potential. Williams *et al.*[59] have claimed that their potential function is more accurate than the formula of Banerjee and Salem, while Mason,[61] on the other hand, has pointed out that this approach and the one used by Banerjee and Salem leads to near identical results for displacements along common axis of the molecules. However different sets of parameters have been suggested (for B, K) by different groups. The repulsion energy is given by the relation

$$E_{ex} = \sum_\alpha^A \sum_\beta^B \epsilon_{\alpha\beta}$$
$$(\text{atoms})$$

where $\epsilon_{\alpha\beta}$ is atom-atom repulsion energy between α-th atom in A with β-th atom in B.

4.3.3.1. Caillet and Claverie method[62]

$$\epsilon_{\alpha\beta} = K_\alpha K_\beta C_1 \exp(-C_2 Z)$$

where

$$Z = R_{\alpha\beta}/R^0{}_{\alpha\beta}; \qquad R^0{}_{\alpha\beta} = \sqrt{(2R_\alpha{}^0)(2R_\beta{}^0)}$$

$R_i{}^0$'s are the van der Waals' radii

$$C_1 = 4.7 \times 10^4 \text{ Kcal/mole}, \qquad C_2 = 12.35 \text{ Å}^{-1}$$

Atom	K	R° (Å)
H	1·0	1·20
C (aliphatic)	1·0	1·70
C (aromatic)	1·0	1·77
N (aromatic)	1·18	1·60
O (aromatic)	1·36	1·50

4.3.3.2. William's method[56]

$$\epsilon_{\alpha\beta} = B_{\alpha\beta} \exp\left(-D_{\alpha\beta} R_{\alpha\beta}\right)$$

$B_{\alpha\beta}$ and $D_{\alpha\beta}$ are parameters dependent on the nature of atom pairs $\alpha\beta$

Atom pair	B (kcal/mole)	D (Å^{-1})
H — H	2171	3·74
C — H	8503	3·67
C — C	71782	3·60
+N — H	4833	3·67
+N — C	11480	3·60
+N — N	105400	3·60

+ Ref. 63

The data are not available for many other interesting atom pairs. Clearly much more work is still needed. Perhaps it will be worthwhile to carry out a very careful and thorough investigation of these repulsive forces.

4.4. *Induction/Polarisation Energy*

There are two methods available for calculating this interaction energy. One approach due to Rein *et al.*[64] uses monopole (on one molecule)-bond polarisability (on the second molecule) approximation and the expression is

$$E_{\text{pol}} = E_{\text{pol}}^{A \to B} + E_{\text{pol}}^{B \to A} \tag{19}$$

with

$$E_{\text{pol}}^{A \to B} = -\tfrac{1}{2} \sum_{k=1}^{\text{Bonds}} [a_k^T \ (E_k \ \cdot \ E_k) + \delta_k \ (E_k \cdot a_k^L)^2]$$

where

$$E_k = \sum_{\alpha}^{\text{Atoms}} \frac{q_\alpha}{r^3{}_{\alpha k}} \ r_{k\alpha}$$

represents the electrostatic field at the midpoint of k-th bond (in molecule B). $r_{\alpha k}$ is the distance between α-th atom in A, and midpoint of k-th bond in B q_α is the net charge ($\sigma + \pi$) on the α-th atom.

$$\delta_k = a_k^T - a_k^L.$$

Recently a multipole expansion for electrostatic field E has been derived.[43] However for weak interaction studies, monopole approximation appears to be satisfactory.[43] The second approach, is that due to Fueno *et al.* The relevant expression is[34]

$$E_I = 2 \sum_i^A \sum_k^A \langle \rho_{ik} \mid V(B) \rangle^2 (E_0 - E_{i \to k})$$

$$+ 2 \sum_{j^\alpha}^B \sum_{l^\alpha}^B \quad \langle \rho_{j^\alpha l^\alpha} \mid V(A) \rangle^2 / (E_0 - E_{j^\alpha \to l^\alpha})$$

$$+ 2 \sum_{j^\beta}^B \sum_{l^\beta}^B \langle \rho_{j^\beta l^\beta} \mid V(A) \rangle^2 / (E_0 - E_{j^\beta \to l^\beta}) \tag{20}$$

where the notation is the same as that followed in section 4.2.2 (for closed shell ↔ closed shell interactions, $j^\alpha = j^\beta$). For non-polar molecules induction energy is very small in magnitude compared to the dispersion term (eq. 8).

4.5. *Dispersion Energy*

Dispersion forces, which are of general occurrence, are always attractive for atoms/molecules in their ground state and are usually much larger in magnitude than polarisation forces. London was the first to demonstrate the R^{-6} dependence of this energy (eq. 8).

4.5.1. In $\sigma - \pi$ separation approach, this term is given by the following formulae

$\pi - \pi$ contribution[65]

$$E\text{dis} \ (\pi - \pi) = -4 \sum_{i j'}^{\text{occ}} \sum_{k l'}^{\text{unocc}} \frac{\langle ik \mid j'l' \rangle^2}{\mid \triangle E_{i \to k} \mid + \mid \triangle E_{j' \to l'} \mid} \tag{21}$$

where prime notation refers to the second molecule.

$$\langle ik \mid j' l' \rangle = \int \int i(\nu) \, k(\nu) \left(\frac{1}{r_{\nu \nu'}} \right) j'(\nu') \, l'(\nu') \, d\nu \, d\nu' \tag{22}$$

$\triangle E_{i \to k}$ is the intramolecular excitation energy.

It may be noted here that (i) there are $N_o^A N_v^A N_o^B N_v^B$ integrals of the type $\langle ik \mid j' l' \rangle$ to be evaluated where N_o^A and N_v^A (N_o^B and N_v^B) refer to the number of occupied and vacant molecular orbitals in A (B) respectively

(ii) low-lying excited states (of each molecule) make a major contribution to the total interaction energy (because of small $\triangle E$ values).

The σ–σ dispersion energy can be calculated according to the method of Rein *et al.*[64] based on the bond polarisability approximation

$$E\text{dis} (\sigma - \sigma) = - \frac{1}{4} \frac{I_A I_B}{I_A + I_B} \sum_{i}^{A} \sum_{j}^{(bonds)B} \frac{1}{r_{ij}{}^6} [6\alpha_i{}^T \alpha_j{}^T$$
$$+ \alpha_i{}^T \delta_j \{3 (\alpha_j{}^L \cdot r_{ij})^2 + 1\} + \alpha_j{}^T \delta_j \{3 (\alpha_i{}^L \cdot r_{ij})^2 + 1\}$$
$$+ \delta_i \delta_j \{3 (\alpha_i{}^L \cdot r_{ij}) (\alpha_j{}^L \cdot r_{ij}) - (\alpha_i{}^L \cdot \alpha_j{}^L)^2\}] \qquad (23)$$

where I's are the ionisation potentials

   $\alpha_i{}^L$ and $\alpha_i{}^T$ are the longitudinal and transverse polarisabilities of i-th bond

   $\alpha_i{}^L$ unit vector along the i-th bond

   r_{ij} unit vector in the direction of line joining the midpoints of the two bonds

   r_{ij} is the distance between midpoint of i-th bond in A and midpoint of j-th bond in B

$\delta_k = \alpha_k{}^L - \alpha_k{}^T$.

As dispersion energy term does not depend on orbital overlap, a $\sigma - \pi$ dispersion energy term can be included. The expression again is due to Rein *et al.*[64]

$$E\text{dis} (\sigma - \pi) = E_{\sigma_A \pi_B} + E_{\sigma_B \pi_A} \qquad (24)$$

with

$$E_{\sigma_B \pi_A} = - \frac{1}{2} \sum_{i}^{A \atop occ} \sum_{j}^{unocc} \sum_{k}^{B \atop Bonds} \frac{[\alpha_k{}^T (E_k{}^{ij} \cdot E_k{}^{ij}) + \delta_k (E_k{}^{ij} \cdot \alpha_k{}^L)]}{1 + \frac{|\triangle E_{i \leftrightarrow j}^A|}{I}}$$

where

$$E_k{}^{ij} = \sum_{a}^{A \atop Atoms} \frac{\rho_{ij} (a)}{r^3{}_{ak}} r_{ak}$$

is the electrostatic field at the midpoint of k-th bond created by a set of transition monopole $\rho_{ij}^a (\rho_{ij}^a = C_{ia} C_{ja})$. Other terms have the usual meaning.

4.5.2. The expression in the all valence electron model of Fueno *et al.*[34] is

$$E_{dis}(CNDO) = 2 \sum_{i}^{A} \sum_{k}^{A} \Big[\sum_{j^\alpha}^{B} \sum_{l^\alpha}^{B} \frac{\langle \rho_{ik} \mid \rho j^\alpha{}_l{}^\alpha \rangle^2}{E_0 - E_{i \to k, \, j^\alpha \to l^\alpha}}$$

$$+ \sum_{j^\beta}^{B} \sum_{l^\beta}^{B} \frac{\langle \rho_{ik} \mid \rho j^\beta{}_l{}^\beta \rangle^2}{E_0 - E_{i \to k, \, j^\beta \to l^\beta}} \Big] \tag{25}$$

Note here

$$E_{i \to k} = E_i - E_k + 2K_{ik} - J_{ik} \tag{26}$$

are intramolecular excitation energy term. All the symbols have the same meaning as in section 4.2.2.

4.6. *Charge-Transfer Interaction Energy*

This term may also be called the delocalisation energy of the composite system.

4.6.1. For a highly conjugated system, the π-electron contribution is more significant (than that due to σ electrons). This contribution is given by[32,53]

$$E_{CT} = -4 \sum_{i}^{occ} \sum_{j'}^{U_{nocc}} \frac{\eta_{ij'}{}^2}{|\triangle E_{i \to j'}|} \tag{27}$$

where

$$\eta_{ij'} = \langle i \mid V \mid j' \rangle = KS_{ij'} \tag{28}$$

with $K = -10 \cdot 0$ eV.

$E_{i \to j'}$ is the intermolecular excitation energy which in π-electron MO's case, is set equal to corresponding intramolecular excitation energy.

4.6.2. Fueno *et al.*'s formula is

$$E_{CT} = \sum_{i}^{A} \Big[\sum_{l^\alpha}^{B} \langle \rho_{il}{}^\alpha \mid V(B) \rangle^2 / (E_0 - E_{i \to l^\alpha})$$

$$+ \sum_{l^\beta}^{B} \langle \rho_{il}{}^\beta \mid V(B) \rangle^2 / (E_0 - E_{i \to l^\beta}) \Big]$$

$$+ \sum_{k}^{A} \left[\sum_{j^{\alpha}}^{B} \langle \rho_{j}{}^{\alpha}k \mid V(A) \rangle^{2}/(E_0 - Ej^{\alpha}{}_{\rightarrow k}) \right.$$

$$\left. + \sum_{j^{\beta}}^{B} \langle \rho_{j}\beta_{k} \mid V(A) \rangle^{2}/(E_0 - Ej^{\beta}{}_{\rightarrow k}) \right]. \tag{29}$$

It is interesting to note that this interaction term does not make significant contribution to the total interaction energy, even in so-called charge-transfer complexes.[31,66]

5. MOLECULAR INTERACTIONS WITHIN THE HARTREE-FOCK APPROXIMATION

There are several[35,67-73] energy decomposition procedures within the Hartree-Fock approximation. The one due to Kitaura and Morokuma[35] appears to be the most suitable for interactions which are rather strong (where the perturbational approaches discussed above cannot be applied), and hence has a promising future. Kitaura and Morokuma approach has the following features:

1. Any desired interaction energy term can be separately calculated, by setting certain blocks in the Fock matrix of the supermolecule (complex) to zero and diagonalising the resultant simplified matrix iteratively.

2. Can deal even cases which are rather strong interactions—large overlap.

3. Gives equal footing to the charge-transfer term with other terms.

   A more clear definition of charge-transfer interaction is given.

As the method has just been applied to very simple systems such as hydrogen bonded water dimer, we will not present the details of their technique. A basic drawback of any Hartree-Fock procedure is that the dispersion energy term cannot be calculated. This is because London forces arise from the correlation of electron motion in the combined system whereas the HF framework neglects electron correlation.[89] Hence it has to be calculated separately.

APPLICATIONS AND 'UNSOLVED' PROBLEMS

A few typical examples of energy decomposition in several interaction pairs are given in Table I. Many more interesting systems, such as the formation of porphyrin dimers and oligomers,[74] dimers of transition metal

TABLE I

Energy decomposition in several interaction pairs (Kcal/mole)

Pairs	E_{rep}				E_{ct}	E_{pol}	E_{dis}			E_{total}	Ref
	E_{el}	π-π	non-bonded	Total			π-π	σ-σ	Total		
G–C[a]	−22·843			52·8		−3·841			−2·49	−23·534	e
A–T[a]	−8·993			3·81		−1·090			−1·77	−8·04	e
A–T[b]	1·408			4·08		−3·033			−11·822	−9·367	e
G–C[b]	3·460			3·74		−5·029			−8·998	−6·827	e
Benzene[e]	1·322	5·282	0·015		0·0	0·0	−1·469	−3·023		2·174	f
Naphthalene[c]	1·466	9·216	0·007		−0·020	0·0	−3·318	−6·126		1·251	g
Anthracene[c]	1·812	13·14	0·044		−0·016	0·0	−5·608	−9·067		0·305	g
Azulene[e]	4·892	8·187	0·020		−0·248	..	−6·410	−5·724		0·717	f
Azulene[d]	−1·622	6·699	0·018		−2·057		−5·981	−5·724		−8·667	f

(a) Hydrogen-bonded   (b) averaged over all stacking forms   (e) sandwich form   (R = 3·5 Å)
(d) Head-tail form   (e) Ref. 44   (f) B. S. Sudhindra unpublished results   (g) Ref. 32.

complexes[75], etc., can be studied according to the methods discussed in earlier sections. There are several other problems which are yet to be resolved/understood in detail. Some of them arise from the advances in the SCF theory of molecules and their implications on intermolecular affairs. We shall mention them in the following:

1.   The all valence electron method so far tested[33,44] has only been the IEHT and CNDO/2. However, there are many other more refined all valence electron methods which take almost same comparable computational time such as CNDO/S,[45] INDO,[46] PRDDO,[47] CNDO/H,[48(a)] and INDO/S,[48 (b)] which can be tested for suitability/reliability in studies on intermolecular interactions. For instance, they can be applied to test (better) convergence of segmental multiple expansion series for calculation of electrostatic interaction energy.

2.   Much progress has been made in calculating more accurate excited state wavefunctions and energies,[76–80] especially in getting a set of virtual orbitals which are (what may be termed as) ' stable ' to excitations of electrons from occupied orbitals (in the ground state).[76,77] The methods have been applied only to studies on hydrogen bonded systems[81 (a)] and electron donor-electron acceptor complexes involving small molecules.[81 (b)] Of course, the methods described are very recent and how far/best these techniques will be useful in studies involving large molecules is to be seen in future. Their effects on induction and dispersion terms (for it is these terms which involve/contain excited states) is not known.

3.   The wavefunction in an excited singlet is more diffuse than the wavefunction for the corresponding triplet state,[82] which is rather contracted towards the nuclei. This result together with increasing feeling that one must use different sets of parameters for singlet and triplet states,[83] may be the source for seeking an explanation for the observed differences in the stability (and possibly structure) of singlet and triplet state excimer.[5] Earlier works in the area[84] have not taken these aspects into account and hence their failure to account for possible difference in geometries[85] of singlet and triplet state excimers. A more careful study is required.

4.   The choice of orbital exponents, suitable for studies in intermolecular affairs, is perhaps another area where much fruitful work can be done. The present studies have employed only the exponents used for monomer calculations, i.e., the Slater's values, and the question arises whether they are good even for intermolecular studies, where the distances

(between atoms) are much larger than one encountered in monomer calculations.

The PCILO method, which is known[86] to give satisfactory results for conformational analysis of large molecules, has just recently been applied[87] to studies on interaction between small molecules. So also the force field techniques.[88] Very recently Kjellander[90] has proposed a method of treating molecular interactions in the SCF–X_α–SW model and has applied to the water trimer system. It is to be seen, in future, how best these techniques as well as the diagrammatic perturbation theory[91] and the force approach,[92] will be suitable for studies involving large molecules. We have not discussed the role of solvent or environment on the interaction between pairs of molecules. The topic deserves a lengthy discussion and a recent account may be found elsewhere.[1 (b), 93–96]

7. CONCLUSIONS

I have presented the methods currently employed in calculation of interaction energies between large molecules. We have also documented many areas where something more can be done. Obviously the field of molecular interactions has a bright future.

Note added at proof stage : Appropriate changes have been made so as o cover the literature up to August 1977, in the revised manuscript.

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