

Fundamental problems in the calculation of interaction potentials

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Abstract - The energy of *interaction* of two general molecules is reduced directly to a sum of physically recognizable terms, for which explicit expressions are given. These expressions contain only quantities (e.g. electron densities and certain generalized dynamic polarizabilities) which may be calculated, once and for all time, for the isolated molecules and then used to obtain the interaction energy for any given conformation.

INTRODUCTION

Most of chemistry is concerned with the *interactions* between molecules, usually in the fluid phase and consequently, on average, at relatively large distances. Such interactions are generally regarded as 'weak' - much weaker than those involved in chemical bonds - and are often referred to as "non-bonded interactions" or "van der Waals interactions" (from the equation of state in which they were first invoked).

The interaction energy associated with two molecules (denoted in this paper by A and B) is so small compared with the total electronic energies of A and B separately that any attempt to calculate it non-empirically is bound to meet enormous problems. To see why this is so it is sufficient to consider the interaction between two nitrogen molecules: the form of the interaction potential (Fig.1) is typical, indicating weak attraction at long range, a shallow minimum in the 'van der Waals region', and strong repulsion at short range. The quantity of interest is the depth of the shallow minimum: for $N_2..N_2$ this is of the order -0.1 kJ mol^{-1} ($-6 \times 10^{-5} E_h$); but the energy of each molecule is about $-109 E_h$ and an *ab initio* calculation of this quantity at the Hartree-Fock limit would be in error by a little under 1%, this being the 'correlation error' whose removal requires a vast computational effort even for small molecules. In this example, then, the errors in calculating the energies of the separate molecules are likely to be at least 10 000 times the required interaction energy! The situation is of course much worse for larger molecules, whose total energies increase rapidly with the number of inner shells but whose interaction energies remain small.

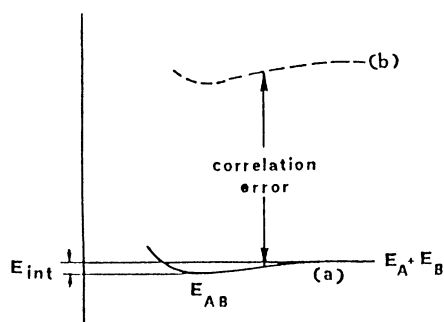


Fig.1 Typical potential curve
(a) exact (b) Hartree-Fock

No detailed discussion of previous efforts to calculate interaction energies will be attempted here. It is sufficient to distinguish two main types: both essentially work on the upper curve (broken line) in Fig.1, since removal of the correlation energy is not generally feasible, and assume that the depth and position of the actual minimum will be adequately accounted for (i.e. that the upper and lower curves will exhibit the same general features); but one family of methods starts from the *separate molecules*, introducing their interaction as a perturbation, while the other starts from the 'supermolecule' in which AB is treated by conventional methods as a single system whose geometry is varied.

The perturbation methods encounter certain difficulties (ref.1) in defining the Hamiltonian for the 'unperturbed' system, connected with the incorrect symmetry imposed by putting electrons $1, 2, \dots, N_A$ in molecule A and the remaining $N_B (= N - N_A)$ in molecule B. The supermolecule approach encounters problems connected with the *superposition* of the separate basis sets used in constructing wavefunctions for the individual molecules; for the supermolecule calculation uses a much larger basis than that used for either molecule separately, giving a spurious lowering of the supermolecule energy relative to that of the fragments and consequently an exaggerated depth of the minimum - an effect which has come to be known as a "basis

set superposition error". Ingenious 'counterpoise' methods of correcting for this error have been devised (e.g. ref.2) ; they depend basically on using the full orbital set (i.e. for *both* molecules) even for A and B separately, in the hope that the error in the upper curve (Fig.1) will then be more uniform over the whole range. Efforts to pass from the upper curve to the lower curve (by admitting correlation effects) are then usually made by perturbation theory; and often (e.g. ref.3) the intermolecular terms in the correlation energy are identified with the long-range interactions (the 'dispersion energy' of London (ref.4) while the large intermolecular terms from the supermolecule calculation are assumed to account for the short and medium range behaviour. Clearly such procedures are not completely satisfactory and it would be better to attempt a direct calculation of the interaction energy itself by separating it *theoretically* from the total energy and expressing it in terms of properties of the free molecules. There are problems in this approach too; but considerable progress has been made, and explicit expressions for the principal terms in the interaction energy will be given in later Sections. Although we normally consider the ground state, it will be evident that the formalism may be applied more generally.

GENERAL APPROACH

In order to introduce properties of the free molecules, A and B, it is necessary to assume knowledge (in principle only) of the exact wavefunctions of both systems in isolation. Let us denote these functions by $\Phi_a^A, \Phi_{a'}^A, \dots$ for A in states a, a', \dots and likewise for B. An exact wavefunction for the two systems in their ground states (a, b - assumed for the moment non-degenerate), at infinite distance, would then be

$$\Phi_{ab}^{AB} = K \hat{A}[\Phi_a^A \Phi_b^B] \quad (1)$$

where Φ_a^A contains electronic variables $bfx_1, bfx_2, \dots, bfx_{N_A}$, Φ_b^B contains variables $bfx_1, bfx_2, \dots, bfx_{N_B}$ (using \bar{n} to denote $n + N_A$), and the operator \hat{A} correctly imposes antisymmetry with respect to all N variables. Explicitly,

$$\hat{A} = (N!)^{-1} \sum_P \epsilon_P \hat{P} = (N_A! N_B! / N!) \hat{A}' \hat{A}_A \hat{A}_B, \quad (2)$$

in which $\hat{A}' = \sum_T \epsilon_T \hat{T}$ is a sum over all transpositions *between* A and B, while \hat{A}_A and \hat{A}_B are antisymmetrizers for the separate systems. When the wavefunctions of A and B are already antisymmetric and normalized, the partial antisymmetrizers \hat{A}_A and \hat{A}_B are redundant (and will be discarded) and the normalizing factor in (1) becomes

$$K = \sqrt{(N! / N_A! N_B!)}. \quad (3)$$

We adopt this value in all that follows, even when the two factors of the product in (1) begin to overlap appreciably and give a function which is no longer normalized to unity.

When there is no interaction between A and B the Hamiltonian for the whole system AB is simply $H = \hat{H}_A + \hat{H}_B$ and (1) yields an energy

$$E = \langle \Phi_{ab}^{AB} | \hat{H} | \Phi_{ab}^{AB} \rangle = E_a^A + E_b^B, \quad (4)$$

the asymptotic value for the lowermost curve in Fig.1. At *finite* separations there will be additional terms on the right in (4) and these will represent the required interaction energy; the aim will be to extract and calculate these terms directly, without any differencing of enormous total energies, so that even an error of, say 1%, will only be 1% of the *interaction energy* - which would be entirely acceptable.

To obtain expressions for the interaction terms we make one fundamental assumption: that the wavefunction for the whole system AB may be expanded, with adequate precision, in the form

$$\Psi = \sum_{\kappa} C_{\kappa} \Phi_{\kappa} \quad (5)$$

where κ indicates a pair of states (e.g. $ab, a'b, ab', a'b', \dots$). This assumption has non-trivial implications, whenever A and B are not strictly separable (i.e. infinitely remote). Thus, the A- and B-factors in any function might be constructed from orbital sets $\{\phi_i^A\}$ and $\{\phi_j^B\}$, respectively, which would normally be assumed complete; but then, by definition, there is a redundancy; for *either set alone* would be sufficient for constructing the wavefunction for the *whole* N -electron system AB and the partitioning into two subsets is evidently artificial. Moreover, if the partitioning is made, then the N -electron wavefunction would have to be expanded in terms of products which did not contain always N_A factors from $\{\phi_i^A\}$ and N_B from $\{\phi_j^B\}$; there would have to be products with $N_A + 1$ A-factors and $N_B - 1$ B-factors, for example, associated formally with 'charge transfer' terms corresponding to $\Lambda^- B^+$ etc.. This suggests that the partitioning $N = N_A + N_B$ should be relaxed and that the expansion (5) should contain terms for all positive and negative ions of A and B; but, apart from purely technical difficulties, the results of partitioning the basis are inescapable - the full

orbital set will be *overcomplete*. In practice, of course, the sets actually used in molecular calculations are so far from completeness that such inconsistencies are unlikely to be serious as long as the molecules overlap only slightly. The individual wavefunctions for A and B would then be constructed by conventional methods (e.g. at a full-CI basis-set limit) from separate orbital sets and for fixed values of N_A and N_B , usually for neutral molecules but not excluding the possible admission of charged reference molecules in highly ionic situations. It is on this somewhat pragmatic level that we extend the use of the expansion (5) from the long-range region (where it is surely valid) to the shorter range, where it will become increasingly difficult (owing to charge-transfer and overcompleteness effects) to distinguish two separate molecules or ions.

The leading term in (5) will be denoted by $\Phi_0 (= \Phi_{ab}^{AB})$ and we shall choose $C_0 = 1$, normalizing later. The corresponding secular equations are easily set up and solved by a partitioning method (ref.5) and give, up to second order in off-diagonal elements,

$$E = \frac{H_{00}}{M_{00}} + \sum_{\kappa} \frac{[H_{\kappa 0} - M_{\kappa 0}(H_{00}/M_{00})]^2}{[(H_{00}/M_{00}) - (H_{\kappa\kappa}/M_{\kappa\kappa})]} \quad (6)$$

where generally

$$H_{\kappa\lambda} = \langle \Phi_{\kappa} | \hat{H} | \Phi_{\lambda} \rangle, \quad M_{\kappa\lambda} = \langle \Phi_{\kappa} | \Phi_{\lambda} \rangle \quad (7)$$

and H is the full Hamiltonian for AB. At long range $M_{00} \rightarrow 1$ and the leading term in (6) becomes (ref.6)

$$E_0 = \langle \Phi_{ab}^{AB} | \hat{H} | \Phi_{ab}^{AB} \rangle = E_a^A + E_b^B + E_{ab}^{AB}(\text{elec}) \quad (8)$$

where E_a^A and E_b^B refer to the *isolated molecules* in their ground states, while

$$E_{ab}^{AB}(\text{elec}) = E_{nuc}^{AB} + \int V_B(\mathbf{r})P_A(aa|\mathbf{r})d\mathbf{r} + \int V_A(\mathbf{r})P_B(bb|\mathbf{r})d\mathbf{r} + \int g(1,2)P_A(aa|\mathbf{r}_1)P_B(bb|\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \quad (9)$$

Here, for example, $P_A(aa|\mathbf{r})$ is the electron density for A in state a , while $V_B(\mathbf{r})$ is the potential energy of an electron at point \mathbf{r} in the field of the *nuclei* of B. The notation "electrostatic" is clearly justified, (9) being the classical interaction energy of two continuous charge distributions, each with embedded nuclei.

Evidently, at long range, (6) and (8) lead directly to an expression for the interaction energy,

$$E_{int} = E - (E_a^A + E_b^B) = E_{ab}^{AB}(\text{elec}) + \Sigma_{AB} \quad (10)$$

where the last term stands for the sum in (6). To show how (10) is modified by overlap effects, we develop the matrix elements in (7) into terms which involve, successively, 0,1,2,... transpositions in the operator \hat{A} which appears in (2). Thus, with $\kappa = a'b', \lambda = ab$,

$$H_{\kappa\lambda} = K^2 \langle \hat{A}\Phi_{a'}^A\Phi_{b'}^B | \hat{H} | \hat{A}\Phi_a^A\Phi_b^B \rangle = \langle \Phi_{a'}^A\Phi_{b'}^B | \hat{H} \sum_T \epsilon_T \hat{T} | \Phi_a^A\Phi_b^B \rangle \quad (11)$$

where we use the property $\hat{A}^2 = \hat{A}$ and the antisymmetry of the separate molecular wavefunctions. Consequently (ref.7)

$$M_{\kappa\lambda} = M_{\kappa\lambda}^{(0)} - M_{\kappa\lambda}^{(1)} + \dots \quad (12)a$$

$$H_{\kappa\lambda} = H_{\kappa\lambda}^{(0)} - H_{\kappa\lambda}^{(1)} + \dots \quad (12)b$$

where, for not too large overlap, multiple-interchange terms rapidly become negligible (ref.8). Before substituting in (6) we note that all energies are conveniently referred to $E_a^A + E_b^B$ as a reference level by subtracting this quantity from both E and \hat{H} ; this changes nothing except the interpretation of the Π -terms in (6). Thus, including up to single-interchange terms and noting that (with the energy-shifted Hamiltonian) $H_{00}^{(0)}$ is given by (8) with $E_a^A + E_b^B$ removed, we obtain easily

$$E_{int} = E_{ab}^{AB}(\text{elec}) + \left[\frac{E_{ab}^{AB}(\text{elec})M_{00}^{(1)} - H_{00}^{(1)}}{1 - M_{00}^{(1)}} \right] + \Sigma_{AB} \quad (13)$$

The first two terms in (13) comprise the electrostatic energy and a non-orthogonality correction which goes to zero exponentially as the overlap diminishes; they are of first order in the usual sense, arising from an expectation value calculated using the 'unperturbed function' Φ_{ab}^{AB} .

The second-order sum Σ_{AB} contains the remaining long-range interactions, usually described as polarization (or induction) and dispersion energies. Since the second-order terms are small anyway, it is unnecessary to make overlap corrections to the terms under the summation in (6): the denominator is roughly an electronic excitation energy (typically several electron volts) and is not modified significantly by the presence of intermolecular terms (typically $10^{-2} - 10^{-4}$ eV) which may therefore be ignored; the numerator contains an overlap term multiplied by an interaction energy, which may also be neglected by comparison with the zero-interchange term in $H_{\kappa 0}$, as will become clear presently.

To summarize: the interaction energy calculated with a function of the type (5) may be expressed, through (13), as a sum of terms whose physical meaning is clear; and all terms may be calculated *directly*, without reference to the total electronic energy of the molecules, for all distances and geometries excluding those of closest approach - in which the two systems lose their individuality. We write (3) in the form

$$E_{int} = E_{ab}^{AB}(\epsilon lec) + E_{ab}^{AB}(pen) + E_{ab}^{AB}(\epsilon x) + E_{ab}^{AB}(pol) + E_{ab}^{AB}(disp) \quad (14)$$

where the second and third terms ('penetration' and 'exchange') arise from the square-bracket quantity in (13), the remaining two from Σ_{AB} , and now turn to methods of evaluation.

EVALUATION OF THE FIRST-ORDER TERMS

The expression for $E_{ab}^{AB}(\epsilon lec)$ has been given already in (9) and requires little discussion. Even when the wavefunctions Φ_a^A and Φ_b^B are elaborate multiconfiguration functions, at or near the full-CI limit, the density functions assume simple forms in terms of the orbitals employed. Thus,

$$P_A(aa|x) = \sum_{r,s} P_{rs}^A \phi_r^A(\mathbf{r}) \phi_s^A(\mathbf{r})^* \quad (15)$$

and similarly for molecule B. The integrals in (9) then reduce to sums of 1- and 2-electron terms, giving

$$\begin{aligned} E_{ab}^{AB}(\epsilon lec) &= E_{nuc}^{AB} + \sum_{r,s} P_{rs}^A \langle \phi_s^A | V_B | \phi_r^A \rangle + \sum_{t,u} P_{tu}^B \langle \phi_u^B | V_A | \phi_t^B \rangle \\ &+ \sum_{r,s,t,u} P_{rs}^A P_{tu}^B \langle \phi_s^A \phi_u^B | g | \phi_r^A \phi_t^B \rangle \end{aligned} \quad (16)$$

Here, for example, V_A is the potential energy of an electron in the field of the nuclei of molecule A and the integrals have their usual meanings; all may be evaluated in terms of standard integrals over basis functions, using appropriate 2- or 4-index transformations.

The next two terms in (9) are much more difficult: they have been considered in detail elsewhere (refs.7,8), even for molecules in spin-degenerate states where alternative spin couplings can lead to alternative interaction surfaces. The resultant expressions, although cumbersome, have the merit of complete generality, being expressed in terms of electron and (for non-singlet states) spin density functions *without reference to orbital approximations*; they could, in principle, be derived from "exact" molecular wavefunctions. For present purposes, however, we pass immediately to the orbital forms analogous to (16). We specialize also to molecules in closed-shell ground states of Hartree-Fock form, remembering that since we calculate the interaction energy *directly* (not as an energy difference) this should be a useful first approximation: in this case $P_{rs}^A = P_{rs}^B = 2\delta_{rs}$.

A key quantity in the short-range region is the "generalized overlap" defined by

$$m_{ab}^{AB} = \int P_A(aa|\mathbf{r}_2; \mathbf{r}_1) P_B(bb|\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (17)$$

in which off-diagonal elements of the density matrices appear. The orbital approximation thus becomes

$$m_{ab}^{AB} = \sum_{r,s,t,u} P_{rs}^A S_{st}^{AB} P_{tu}^B S_{ur}^{BA} = 4 \sum_{r,s} S_{rs}^{AB} S_{sr}^{BA} \quad (18)$$

in which the elements of the intermolecular overlap matrix are $S_{rt}^{AB} = \langle \phi_r^A | \phi_t^B \rangle$, quantities which all fall off exponentially with intermolecular distance.

The exchange term in (9) goes over, in the long-range limit, to the well known form for strong-orthogonal systems (ref.6): it contains an integrand like that in (17) but with an extra factor r_{12}^{-1} and the corresponding orbital form is found to be

$$E_{ab}^{AB}(\epsilon x) = -2(1 - m_{ab}^{AB}/2)^{-1} \sum_{r,s} \langle \phi_r^A \phi_t^B | g | \phi_t^B \phi_r^A \rangle \quad (19)$$

This quantity is essentially negative and consequently there is an exchange *attraction* between nonbonded systems in singlet states, not the "exchange repulsion" commonly referred to in textbooks.

The 'penetration energy' depends on *one*-electron integrals and for molecules in singlet states invariably becomes large and positive as soon as overlap becomes appreciable. Again, for closed-shell Hartree-Fock functions, the general expression reduces to simple form. After considerable cancellation of terms in the numerator of the square-bracket term in (13) we find

$$E_{ab}^{AB}(pen) = -2(1 - m_{ab}^{AB}/2)^{-1} F_{ab}^{AB} \quad (20)$$

where, momentarily using the convention that a repeated index (e.g. a, a', \dots or b, b', \dots) means summation over the doubly occupied orbitals (of A or B),

$$\begin{aligned} F_{ab}^{AB}(pen) = & \langle a|\hat{h}|b \rangle \langle b|a \rangle - \langle a|\hat{h}|a' \rangle \langle a'|b \rangle \langle b|a \rangle \\ & + 2 \langle b|a \rangle \langle aa'|ba' \rangle + 2 \langle b|a \rangle \langle ab'|bb' \rangle \\ & + 2 \langle b|a \rangle \langle ab'|g|a'b \rangle \langle a'|b' \rangle - 2 \langle b|a \rangle \langle a|b' \rangle \langle b'a'|g|ba' \rangle \\ & + (A \rightarrow B) \end{aligned} \quad (21)$$

and as usual $(A \rightarrow B)$ indicates a similar term with the roles of A and B reversed*.

The expressions given above are easy to evaluate and are capable in principle of giving a good account of intermolecular repulsions. They are, however, sensitive to the quality of the orbitals used (especially in the 'tail' regions) and must therefore be used with care.

POLARIZATION AND DISPERSION TERMS

The last two terms in (14) cannot be evaluated from a knowledge of groundstate wavefunctions; they involve the *response* of each system to the perturbation caused by the other and, being of second order already, will be evaluated *without* overlap corrections. Here we indicate how both terms may be expressed in terms of response functions, without making any of the usual restrictive approximations such as the multipolar expansion of interaction terms in the Hamiltonian.

First we note the long-range forms of $E_{ab}^{AB}(pol)$ and $E_{ab}^{AB}(disp)$: they derive, respectively, from the summation in (6) over $\kappa = a'b, ab'$ and over $\kappa = a'b'$ (i.e. over single and double excitations) and become (ref.6)

$$E_{ab}^{AB}(pol) = - \sum_{a'} \frac{|\langle \Phi_a^A | \hat{H}_{eff}^A | \Phi_{a'}^A \rangle|^2}{\Delta E(Aa \rightarrow Aa')} - (A \rightarrow B) \quad (22)$$

where $(A \rightarrow B)$ means a similar sum for B instead of A, and

$$E_{ab}^{AB}(disp) = - \sum_{a'b'} \frac{|\langle \Phi_{a'b'}^{AB} | \hat{H} | \Phi_{ab}^{AB} \rangle|^2}{\Delta E(Aa \rightarrow Aa'; Bb \rightarrow Bb')} \quad (23)$$

Here H is the full Hamiltonian (for AB) while \hat{H}_{eff}^A is an N_A -electron Hamiltonian for the electrons of A in the 'effective field' due to B (in its ground state); and the denominators are transition energies, computed as differences of expectation values of H for the ground and excited state functions.

With neglect of overlap the matrix elements reduce at once; in (23) for example,

$$\langle \Phi_{a'b'}^{AB} | \hat{H} | \Phi_{ab}^{AB} \rangle = \frac{\epsilon^2}{(4\pi\epsilon_0)} \int r_{12}^{-1} P_A(aa'|\mathbf{r}_1) P_B(bb'|\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (24)$$

where $P_A(aa'|\mathbf{r}_1)$, for example, is a *transition density* (for $Aa \rightarrow Aa'$) for molecule A, evaluated at point \mathbf{r}_1 . For transitions which are strongly 'dipole-allowed' the integral represents roughly the interaction energy of two extended dipoles in close proximity; such terms are large, justifying the neglect of overlap corrections as indicated in (13) et seq.

* With the abbreviated integral notation, $\langle \phi_r^A \phi_t^B | g | \phi_s^A \phi_u^B \rangle$ is of the type $\langle ab|g|a'b' \rangle$ and, for example, $\langle ab||a'b' \rangle$ would stand for $\langle ab|g|a'b' \rangle - (1/2) \langle ab|g|b'a' \rangle$

The terms in (22) reduce on noting that, for example,

$$\hat{H}_{eff}^A = \hat{H}^A + \sum_{i=1}^{N_A} [V_B(\mathbf{r}_i) + eJ_B(\mathbf{r}_i)] = \hat{H}^A + \sum_{i=1}^{N_A} \delta V_A^{(B)}(\mathbf{r}_i) \quad (25)$$

where \hat{H}^A is the free-molecule Hamiltonian for A, while the sum gives the change due to the electron distribution of B and the nuclei it contains (i.e. the usual coulomb interactions). The off-diagonal elements of \hat{H}^A vanish and hence

$$\langle \Phi_{a'}^A | \hat{H}_{eff}^A | \Phi_a^A \rangle = \int \delta V_A^{(B)}(\mathbf{r}) P_A(aa'|\mathbf{r}) d\mathbf{r} \quad (26)$$

which again has a classical interpretation.

The main difficulty in calculating the interaction energy from (22) and (23) is the summation (in principle infinite) over the excited states of one or both molecules; but this difficulty can be circumvented by an integral transform which introduces instead certain linear response properties of the *ground* states, properties which may be calculated for the individual molecules by standard variational methods. It will be sufficient to consider (23), introducing the dynamic or 'frequency-dependent' polarizabilities (FDPs) which serve in both cases.

First we write the transition densities in (24) as matrix elements of density operators by introducing an integral operator with the Schrödinger representation *

$$\hat{E}_{r,s}(i) \rightarrow E_{r,s}(\mathbf{r}_i; \mathbf{r}'_i) = \phi_r(\mathbf{r}_i) \phi_s^*(\mathbf{r}'_i). \quad (27)$$

The effect of $\hat{E}_{r,s}(i)$ on any function $\psi(\mathbf{r}_i)$ is to replace the variable \mathbf{r}_i by \mathbf{r}'_i , multiply by the kernel $E_{r,s}(\mathbf{r}_i; \mathbf{r}'_i)$, and integrate over \mathbf{r}'_i to obtain a new function $\psi'(\mathbf{r}_i)$. If we use $\hat{E}_{r,s}$ to denote the sum over all N electrons, the effect of the operator on any Slater determinant is to replace ϕ_s (with either spin factor) by ϕ_r (with the same spin factor) or, if no such spin-orbital is present, to produce zero. In terms of these 'substitution' operators, the transition densities in (24) become

$$P_A(aa'|\mathbf{r}) = \langle \Phi_{a'}^A | \hat{d}_{r'}^A | \Phi_a^A \rangle, \quad \hat{d}_{r'}^A = \sum_{r,s} \hat{E}_{r,s}^A \phi_s^A(\mathbf{r}) \phi_r^A(\mathbf{r})^*, \quad (28)$$

with a similar result for molecule B. We note in passing that any one-electron operator F can be written in terms of the E - operators in the form

$$\hat{F} = \sum_{r,s} \langle \phi_r | \hat{F} | \phi_s \rangle E_{r,s} \quad (29)$$

where $\langle \phi_r | \hat{F} | \phi_s \rangle$ is the usual matrix element.

On using (29) and (24) in (23), the dispersion energy is represented as the integral (over four volume elements) of a product of two A-factors and two B-factors, divided by an excitation energy of the form

$$E_{a'}^A - E_a^A + E_{b'}^B - E_b^B = \hbar(\omega_{aa'}^A + \omega_{bb'}^B) \quad (30)$$

where the ω s are excitation frequencies, in good approximation (see (13) et seq.) for the free molecules. It would clearly be an advantage if the *whole integrand* were a product of two factors, one for A and one for B; and such a form may be achieved by using the integral transform

$$\frac{1}{(x+y)} = \frac{2}{\pi} \int_0^\infty \frac{x}{(x^2 + \omega^2)} \frac{y}{(y^2 + \omega^2)} d\omega \quad (31)$$

- at the expense of one further integration, over ω . The summations over excited states in (24) may then be taken inside the integral and performed separately to give a final result (ref.9)

$$E_{ab}^{AB}(\text{disp}) = - \left(\frac{\hbar}{2\pi} \right) \left(\frac{\epsilon^2}{4\pi\epsilon_0} \right)^2 \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}'_1 d\mathbf{r}'_2 (r_{12} r'_{12})^{-1} \int_0^\infty \Pi_A(\hat{d}_{r'_1}^A \hat{d}_{r_1}^A | i\omega) \Pi_B(\hat{d}_{r'_2}^B \hat{d}_{r_2}^B | i\omega) d\omega \quad (32)$$

where the Π -factors, which are sums over excited states of the separate molecules, are FDPs at pure

* In Fock space the operator is $(\hat{a}_{r\alpha}^\dagger \hat{a}_{s\alpha} + \hat{a}_{r\beta}^\dagger \hat{a}_{s\beta})$ where, for example, $\hat{a}_{r\alpha}^\dagger$ and $\hat{a}_{r\alpha}$ create or destroy an electron in spin-orbital $\phi_{r\alpha}$. The use of a complete set of spin-orbitals is convenient but not essential to the argument, which may be formulated also using field operators.

imaginary frequency'. In general the FDP $\Pi(\hat{G}\hat{F}|i\omega)$ determines the first-order change in $\langle G \rangle$ caused by an exponentially growing perturbation $\hat{F}e^{\omega t}$, in the form

$$\delta \langle \hat{G} \rangle = \Pi(\hat{G}\hat{F}|i\omega)e^{\omega t} \quad (33)$$

and may be calculated by any convenient method.

Formula (32) is an exact expression for the dispersion energy and has an interesting physical interpretation. There are two electrostatic interactions, that for electronic charges in $d\mathbf{r}'_1$ (in A) and $d\mathbf{r}'_2$ (in B), bringing in the factor r_{12}^{-1} , and that for charges in $d\mathbf{r}'_1$ and $d\mathbf{r}'_2$, supplying the further factor r'_{12} : these interactions are multiplied by FDPs (properties of the *individual molecules*) which determine how density fluctuations propagate from point \mathbf{r}_1 to point \mathbf{r}'_1 (in A) or from \mathbf{r}_2 to \mathbf{r}'_2 (in B); and, after a frequency integration, the results are summed over all positions of the four volume elements. The FDPs are in fact *propagators*.

To introduce orbital approximations it is only necessary to write the operators in each FDP explicitly as in (29): the integrations then lead to sums of ordinary 2-electron integrals multiplied by FDPs for pairs of the E-operators. In the most commonly occurring case, where the orbitals are real, the permutation symmetry of the integrals may be exploited by introducing the Hermitian combinations

$$\hat{D}_{rs} = (1/2)(2 - \delta_{rs})(\hat{E}_{rs} + \hat{E}_{sr}) \quad (r \geq s) \quad (34)$$

and restricting the summations accordingly. The final expression (with "charge cloud" notation for the integrals) is then

$$\begin{aligned} E_{ab}^{AB}(\text{disp}) = & -\frac{\hbar}{2\pi} \sum_{\substack{r \geq s \\ t \geq u}} \sum_{\substack{v \geq w}} (\phi_r^A \phi_s^A, \phi_t^B \phi_u^B) (\phi_r^A \phi_s^A, \phi_v^B \phi_w^B) \\ & \times \int_0^\infty \Pi_A(\hat{D}_{rs} \hat{D}_{pq}^A | i\omega) \Pi_B(D_{vw}^B D_{tu}^B | i\omega) d\omega \end{aligned} \quad (35)$$

where the FDPs have the form

$$\Pi(\hat{G}\hat{F}|i\omega) = -\frac{1}{\hbar} \sum_{n>0} \frac{2\omega_{0n} \langle 0 | \hat{G} | n \rangle \langle n | \hat{F} | 0 \rangle}{(\omega_{0n}^2 + \omega^2)} \quad (36)$$

in which \hat{F} and \hat{G} are arbitrary Hermitian operators, and $0, n$ denote ground and excited states.

The practical implementation of (35) has been discussed elsewhere (refs.9,10) along with methods of calculating the FDPs (refs.11,12). Reductions are possible at various levels of approximation, depending on choice of orbitals and method of calculation of the FDPs. If the orbitals are strongly localized and orthogonal (ref.9) terms for $p \neq q$, etc. become very small and (35) reduces effectively to a fourfold summation; while if the orbitals are SCF MOs, and the FDPs are calculated using time-dependent Hartree-Fock (TDHF) theory (also known as the random phase approximation (RPA)), then the summations again reduce significantly in terms of the RPA eigenvectors (ref.10).

Finally, the polarization energy (22) is expressible in terms of FDPs evaluated at the static limit $\omega \rightarrow 0$. To see this we write the first term in the form

$$\sum_a^i \frac{\langle \Phi_a^A | \delta V_A^{(B)} | \Phi_a^A \rangle \langle \Phi_a^A | \delta V_A^{(B)} | \Phi_a^A \rangle}{(E_a^A - E_a^A)} = (1/2) \int \delta V_A^{(B)}(\mathbf{r}) \delta P_A(\mathbf{r}) d\mathbf{r} \quad (37)$$

Here we have noted that the second-order sum may be written alternatively as either $\langle \Phi_a^A | \delta V_A^{(B)} | \delta \Phi_a^A \rangle$ or $\langle \delta \Phi_a^A | \delta V_A^{(B)} | \Phi_a^A \rangle$ where $\delta \Phi_a^A$ is the first-order change of Φ_a^A due to the perturbation $\delta V_A^{(B)}$; and half the sum of the two forms gives half the *change* in the expectation value of $\delta V_A^{(B)}$ arising from the density *change* δP_A . But $\delta V_A^{(B)}$ may be written, according to (29), as a weighted sum of E-operators in which E_{pq} (switched on exponentially) makes a change $\delta P_{sr} = \Pi(\hat{E}_{rs}^A \hat{E}_{pq}^A | i\omega) e^{\omega t}$ in P_{sr}^A ; and (37) then easily reduces to give (for $\omega \rightarrow 0$)

$$(1/2) \int \delta V_A^{(B)}(\mathbf{r}) \delta P_A(\mathbf{r}) d\mathbf{r} = (1/2) \sum_{r,s,p,q} \langle \phi_r^A | \delta V_A^{(B)} | \phi_s^A \rangle \Pi_A(\hat{E}_{rs}^A \hat{E}_{pq}^A | 0) \langle \phi_p^A | \delta V_A^{(B)} | \phi_q^A \rangle \quad (38)$$

On introducing the Hermitian combinations (34), the polarization energy (22) becomes

$$E_{ab}^{AB}(\text{pol}) = (1/2) \sum_{\substack{r \geq s \\ t \geq u}} \langle \phi_r^A | \delta V_A^{(B)} | \phi_s^A \rangle \Pi_A(\hat{D}_{rs}^A \hat{D}_{pq}^A | 0) \langle \phi_p^A | \delta V_A^{(B)} | \phi_q^A \rangle + (A \leftrightarrow B) \quad (39)$$

where ($A \rightarrow B$) denotes a similar term with A,B interchanged. The polarization energy is thus determined by the same FDPs as the dispersion energy.

Numerical tests (refs.13,14) on small molecular dimers confirm that calculations along the lines of this section and the last can give a good account of the structures of weakly bound species.

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