

Weak Interactions Between Molecules

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Explicit formulae are derived for the calculation of dispersion energies between large molecules, at various levels of approximation. The derivation introduces frequency-dependent polarizabilities (FDPs), which describe the propagation of electron density fluctuations within each of the separate molecules, but avoids the usual multipole expansion. The resultant dispersion energy formula reveals the presence of long-range (R^{-2}) energy terms between atoms of the different molecules and provides a basis for semi-empirical models based on pairwise atom-atom interactions.

A rapidly convergent SCF procedure for calculating the required FDPs is also described.

I. INTRODUCTION

One of the outstanding problems of quantum chemistry is the calculation of the long-range interactions between molecules (*inter*-molecular forces) or between distant parts of the same molecule (*intra*-molecular forces). Such interactions play a particularly important role in biology, where the molecules concerned (*e. g.* protein chains) may be so large that the prospects of making satisfactory *ab initio* calculations using conventional methods are still remote. Efforts to understand the origin of such interactions have consequently been dominated by the use of classical models and semiempirical theories (for a review, see Ref. 1). The problems involved, and some of the methods available for their solution, have been reviewed elsewhere (see, for example, Refs. 1—6).

For small molecules (*A* and *B*, say) it is possible to consider the two systems as weakly interacting parts of a »supermolecule« (*AB*) and to perform highly accurate *ab initio* calculations of total energy as a function of geometry; but for weak interactions very extensive configuration interaction (CI) is required, and calculations even on few-electron molecules are only just becoming feasible. For large molecules, this approach is excluded and it is usual to fall back on some kind of perturbation method which seeks to evaluate the interaction energy directly, making use of approximate wavefunctions for the separate molecules (see, for instance, Refs. 5, 6; this approach is in principle preferable since the required interaction energy is an exceedingly small fraction of the total electronic energy (whose variation with geometry must be calculated in the supermolecule approach). The difficulty with any kind of perturbation method arises principally from lack of knowledge of the wavefunctions (for all states) of the separate molecules. Formally, it is possible to

show (e. g. Ref. 7) that at large distances (where A and B have zero overlap and exchange effects are negligible) that

$$E = E_A + E_B + E_{\text{elec}} + E_{\text{pol}} + E_{\text{disp}} + \dots \quad (1.1)$$

where E_A and E_B are electronic energies of the separate molecules, E_{elec} is their classical electrostatic interaction, E_{pol} is the joint polarization energy of each molecule in the field of the other, and E_{disp} is the so-called »dispersion energy« first introduced by London⁸. In calculating E_{elec} , each molecule is regarded as a collection of nuclei embedded in a static distribution of negative charge of density $-eP(\mathbf{r})$ where $P(\mathbf{r})$ is the unperturbed ground state electron density. The calculation of E_{pol} is more difficult because it involves the *perturbation* of each molecule in the field produced by the other (computed as in the calculation of E_{elec}), and this perturbation is usually expressed formally as an expansion over the complete set of unperturbed functions — which, of course, is never available in practice. Fortunately, E_{pol} is often small enough to be neglected, because the field at large distance from a neutral molecule is too small to produce appreciable polarization unless the molecule is very strongly polar; and large organic molecules most frequently fall into this category. On the other hand, E_{disp} is generally regarded as the principal component of the van der Waals attraction; for non-polar neutral molecules it is the first significant term in the perturbation expansion, and it is difficult to calculate.

The dispersion energy may be expressed in the form⁷

$$E_{\text{disp}} = - \sum_{a', b'} \frac{|\langle Aa', Bb' | \hat{H} | Aa, Bb \rangle|^2}{\Delta E(Aa \rightarrow Aa', Bb \rightarrow Bb')} \quad (1.2)$$

where the matrix element in the numerator connects the ground state $|Aa, Bb\rangle$, in which molecule A is in (unperturbed) state a and molecule B in state b , with the state $|Aa', Bb'\rangle$, in which there is a *double* excitation $Aa \rightarrow Aa', Bb \rightarrow Bb'$. The denominator of (1.2) is the corresponding excitation energy, for the unperturbed molecules and may thus be written

$$\Delta E(Aa \rightarrow Aa', Bb \rightarrow Bb') = E_{a'}^A - E_a^A + E_{b'}^B - E_b^B \quad (1.3)$$

At distances where exchange is negligible the matrix element in (1.2) reduces to

$$\langle Aa', Bb' | \hat{H} | Aa, Bb \rangle = \frac{e^2}{(4\pi\epsilon_0)} \int \frac{P_A(aa' | \mathbf{r}_1) P_B(bb' | \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (1.4)$$

in which $P_A(aa' | \mathbf{r}_1)$ is the *transition density* associated with $a \rightarrow a'$ in molecule A and $P_B(bb' | \mathbf{r}_2)$ is a similar quantity for molecule B .

Since information on excited states is usually very limited, the summation in (1.2) must normally be confined to the first few strongly allowed transitions for each molecule; and with a multipole expansion of r_{12}^{-1} the integral (1.4) can be expressed in terms of multipole moments of transition densities. The latter are hard to calculate, but observed oscillator strengths allow empirical estimates of at least the dipole-dipole terms; these depend on the inverse cube of the intermolecular distance and thus account for the R^{-6} dependence of van der Waals interactions. For large molecules, data are more scarce and the multipole expansion is unreliable; it has therefore become the custom to

represent the interaction as a sum of atom-atom terms with an empirically determined dependence on interatomic distances. Although this practice seems to work fairly well, its status remains obscure and it evidently fails to take account of delocalization of the bonding — a defect which would be particularly serious in the case of organic molecules containing conjugated chains or rings.

Other approaches to the evaluation of (1.2) also use a multipole expansion but then employ a transformation⁹ which leads to an expression containing frequency-dependent multipole polarizabilities, of the separate molecules, evaluated at pure imaginary frequency ($i\omega$) and integrated over all values of ω . This type of method avoids the summation over excited states but is instead faced with the evaluation of the polarizabilities, and *ab initio* calculations (e. g. Ref. 10) have been confined mainly to the interaction of small atoms, though semi-empirical procedures have also been proposed.^{11,13} Again the multipole expansion would be an unsatisfactory feature in the case of large molecules.

In this paper we develop an approach which uses frequency-dependent polarizabilities but which does not contain a multipole expansion. In this way we obtain physical insight into the origin of the dispersion interactions and also find some justification for a model based on pairwise (atom-atom) interactions, supplemented by delocalization terms. We also use time-dependent self-consistent perturbation theory to obtain expressions for the required polarizabilities. Applications are possible at various levels of approximation; for small molecules completely *ab initio* calculations are feasible; but the theory also suggests a number of clearly defined theoretical models, with which calculations on large molecules are certainly possible.

II. FREQUENCY-DEPENDENT POLARIZABILITIES

The frequency-dependent polarizability (FDP) relates the *linear response* of a system, measured by the change in expectation value of some quantity with operator \hat{B} , to an oscillating perturbation (operator \hat{A}); it is essentially the propagator defined by Zubarev¹⁴ and permits a similar spectral resolution.

We consider in general an oscillating perturbation of the Hamiltonian of the form

$$\hat{H}'(\omega) = \frac{1}{2} f(\omega) [\hat{A}_\omega e^{-i\omega t} + \hat{A}_{-\omega} e^{i\omega t}] \quad (2.1)$$

which reduces to $f(\omega) \hat{A} \cos \omega t$ for a Hermitian operator, $\hat{A}_\omega = \hat{A}_{-\omega} = \hat{A}$. In general $f(\omega)$ is a real strength parameter and, in order for \hat{H}' to be Hermitian, $\hat{A}_{-\omega} = \hat{A}_\omega^\dagger$. We use $\hat{A}_\omega (= \hat{A})$ and $\hat{A}_{-\omega} (= \hat{A}^\dagger)$ for the operators attached to $e^{-i\omega t}$ and $e^{i\omega t}$, respectively, simply for notational convenience (both being frequency independent). An arbitrary time-dependent perturbation may then be expressed in terms of Fourier components as

$$\hat{H}' = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{1}{2} f(\omega) [\hat{A}_\omega e^{-i\omega t} + \hat{A}_{-\omega} e^{i\omega t}] d\omega \quad (2.2)$$

where the requirement $f(-\omega) = f(\omega)$ ensures that $f(\omega)$ is the Fourier transform of a *real* time factor $F(t)$. Thus (2.2) obviously yields

$$\hat{H}'(t) = \frac{1}{2} F(t) (\hat{A}_\omega + \hat{A}_{-\omega}), \quad F(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} f(\omega) e^{-i\omega t} d\omega \tag{2.3}$$

When the individual operators are Hermitian ($\hat{A}_\omega = \hat{A}_{-\omega} = \hat{A}$) this reduces to $F(t) \hat{A}$; more generally \hat{A} should be interpreted as $1/2 (\hat{A}_\omega + \hat{A}_{-\omega})$.

On considering the single Fourier component (2.1), it is easy to show that the first-order variation in the expectation value of some observable B , with (Hermitian) operator \hat{B} , is

$$\delta \langle B \rangle_\omega = \frac{1}{2} \sum_{n(\neq 0)} \frac{1}{\hbar} \left[\frac{\langle 0 | \hat{B} | n \rangle \langle n | \hat{A}_\omega | 0 \rangle}{(\omega^+ - \omega_{0n})} - \frac{\langle 0 | \hat{A}_\omega | n \rangle \langle n | \hat{B} | 0 \rangle}{(\omega^+ + \omega_{0n})} \right] e^{-i\omega t} + (\omega \rightarrow -\omega) \tag{2.4}$$

where we use ω_{0n} for the excitation frequency $(E_n - E_0)/\hbar$ and all matrix elements are between time-independent unperturbed states. The term $(\omega \rightarrow -\omega)$ is obtained from the one written explicitly by reversing the sign of ω ; and ω^+ is used to indicate that near a pole ω is replaced by $\omega + i\eta$ (η a positive infinitesimal) with $\eta \rightarrow 0$ when necessary. This result may be written

$$\delta \langle B \rangle_\omega = \frac{1}{2} [II(\hat{B}\hat{A}_\omega | \omega) f(\omega) e^{-i\omega t} + II(\hat{B}\hat{A}_{-\omega} | -\omega) f(\omega) e^{i\omega t}] \tag{2.4}$$

where

$$II(\hat{B}\hat{A}_\omega | \omega) = \sum_{n(\neq 0)} \frac{1}{\hbar} \left[\frac{\langle 0 | \hat{B} | n \rangle \langle n | \hat{A}_\omega | 0 \rangle}{(\omega^+ - \omega_{0n})} - \frac{\langle 0 | \hat{A}_\omega | n \rangle \langle n | \hat{B} | 0 \rangle}{(\omega^+ + \omega_{0n})} \right] \tag{2.5}$$

and is called the »frequency dependent polarizability (FDP) of B with respect to A «. $II(\hat{B}\hat{A}_{-\omega} | -\omega)$ is defined similarly but with $\omega \rightarrow -\omega$, and the fact that $\hat{A}_{-\omega} = \hat{A}_\omega^\dagger$ implies that the two FDPs in (2.4) are complex conjugate. The result is then real and the response to a general perturbation (2.3) is easily obtained, by Fourier transformation of (2.4), in the form

$$\delta \langle B \rangle_t = \int_{-\infty}^t K(\hat{B}\hat{A} | t-t') F(t') dt' \tag{2.6}$$

where $K(\hat{B}\hat{A} | t-t')$ is a real time-correlation function.

Similar results are obtained for a single-term perturbation of the form

$$\hat{H}'(\omega) = f(\omega) \hat{A} e^{i\omega t} \tag{2.7}$$

which increases exponentially from zero at $t = -\infty$ and corresponds to the $e^{-i\omega t}$ Fourier term in (2.1) with ω replaced by $i\omega$. Instead of (2.4) we obtain

$$\delta \langle B \rangle_\omega = II(\hat{B}\hat{A} | i\omega) f(\omega) e^{i\omega t} \tag{2.8}$$

in which the FDP at pure imaginary frequency ($i\omega$, ω real and positive) is

$$\Pi(\hat{B}\hat{A}|i\omega) = \sum_{n(\neq 0)} \frac{1}{\hbar} \left[\frac{\langle 0|\hat{B}|n\rangle\langle n|\hat{A}|0\rangle}{(i\omega - \omega_{0n})} - \frac{\langle 0|\hat{A}|n\rangle\langle n|\hat{B}|0\rangle}{(i\omega + \omega_{0n})} \right] \quad (2.9)$$

This is simply the analytic continuation of the quantity defined in (2.5), along the imaginary axis in the upper half of the complex ω -plane; there are no poles along this axis and it turns out that $\Pi(\hat{B}\hat{A}|i\omega)$ is usually easier to calculate than $\Pi(\hat{B}\hat{A}|\omega)$.

When both operators are Hermitian and all matrix elements are real (a case which arises very frequently) the expression (2.9) reduces to

$$\Pi(\hat{B}\hat{A}|i\omega) = -\frac{2}{\hbar} \sum_{n(\neq 0)} \frac{\omega_{0n} \langle 0|\hat{B}|n\rangle\langle n|\hat{A}|0\rangle}{(\omega_{0n}^2 + \omega^2)} \quad (2.10)$$

This is the form we shall use later.

III. THE DISPERSION ENERGY

To see how the FDPs arise in the calculation of E_{disp} we first express the transition density functions in (1.4) as matrix elements of appropriate density operators. Thus

$$P_A(aa'|\mathbf{r}) = \langle \Psi_{a'}|\hat{D}_r|\Psi_a\rangle = \langle \Psi_{a'}|\sum_{i=1}^N \hat{D}_r(i)|\Psi_a\rangle \quad (3.1)$$

In which $\hat{D}_r(i)$ is a one-electron integral operator with a delta-function kernel¹⁵:

$$\hat{D}_r(i) \rightarrow D_r(\mathbf{r}_i; \mathbf{r}'_i) = \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r} - \mathbf{r}'_i) \quad (3.2)$$

The effect of $\hat{D}_r(i)$ on any function containing \mathbf{r}_i is

$$\hat{D}_r(i)\Psi(\dots\mathbf{r}_i\dots) = \int D_r(\mathbf{r}_i; \mathbf{r}'_i)\Psi(\dots\mathbf{r}'_i\dots) d\mathbf{r}'_i = \delta(\mathbf{r}_i - \mathbf{r})\Psi(\dots\mathbf{r}\dots)$$

and hence (3.1) (which contains N identical contributions) yields

$$P_A(aa'|\mathbf{r}) = N \int \Psi_a(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots) \Psi_{a'}^*(\mathbf{r}, s_1, \mathbf{r}_2, s_2, \dots) ds_1 d\mathbf{r}_2, ds_2 \dots ds_N \quad (3.3)$$

which is the usual (Schrödinger) definition of a 1-electron transition density*.

It is worth noting that \hat{D}_r has a simple analogue in second quantization language, corresponding to the spin-traced product of two field operators:

$$\sum_i \hat{D}_r(i) \rightarrow \sum_{\sigma} \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma}(\mathbf{r}) \quad (\sigma = \alpha, \beta) \quad (3.4)$$

where, in terms of the creation and annihilation operators for any complete orbital set $\{\chi_{\mu}\}$,

* The transition density matrices $P_A(aa'|\mathbf{r}; \mathbf{r}')$ are obtained in a similar way, using an operator $D_{rr'}(i)$ whose kernel is like that in (3.2) except that \mathbf{r} in the first factor is replaced by \mathbf{r}' . Here we need only the »diagonal elements« with $\mathbf{r}' = \mathbf{r}$.

$$\psi_{\sigma}(\mathbf{r}) = \sum_{\mu} \chi_{\mu}(\mathbf{r}) a_{\mu\sigma}, \quad \psi_{\sigma}^{\dagger} = \sum_{\mu} \chi_{\mu}^*(\mathbf{r}) a_{\mu\sigma}^{\dagger} \quad (3.5)$$

If desired, the argument is easily recast with the field operators in place of \hat{D} , and $|\Psi_a\rangle$ regarded as a vector in Fock space.

Each density function in (1.4) may now be expressed as a matrix element and on inserting the results in (1.2) we obtain*, with an obvious notation

$$E_{\text{disp}} = - \left(\frac{e^2 \hbar}{4 \pi \epsilon_0} \right)^2 \int \frac{d\mathbf{r}_1, d\mathbf{r}_2, d\mathbf{r}'_1, d\mathbf{r}'_2}{r_{12} r'_{12}}$$

$$\sum_{a', b'} \frac{\langle Aa | \hat{D}_{r'_1} | Aa' \rangle \langle Bb | \hat{D}_{r'_2} | Bb' \rangle \langle Aa' | \hat{D}_{r_1} | Aa \rangle \langle Bb' | \hat{D}_{r_2} | Bb \rangle}{(\omega_{aa'} + \omega_{bb'})} \quad (3.6)$$

where $\omega_{aa'}$, $\omega_{bb'}$ are transition frequencies for the two molecules (e.g. $\hbar\omega_{aa'} = E_{A_{a'}} - E_{A_a}$). It is now possible to rewrite the summand as a product of two factors by making use of the integral identity⁹

$$\frac{1}{\omega_{aa'} + \omega_{bb'}} = \frac{2}{\pi} \int_0^{\infty} \frac{\omega_{aa'}}{(\omega_{aa'}^2 + \omega^2)} \frac{\omega_{bb'}}{(\omega_{bb'}^2 + \omega^2)} d\omega \quad (3.7)$$

On assuming real wavefunctions and noting that the \hat{D} -operators are real Hermitian, it is evident that each factor may then be identified as an FDP. Thus by comparison with (2.10)

$$\sum_{a'} \frac{\langle Aa | \hat{D}_{r'_1} | Aa' \rangle \langle Aa' | \hat{D}_{r_1} | Aa \rangle \omega_{aa'}}{(\omega_{aa'}^2 + \omega^2)} = - \frac{\hbar}{2} \Pi_A(\hat{D}_{r'_1}, \hat{D}_{r_1} | i\omega) \quad (3.8)$$

and in terms of the FDPs (3.6) then becomes

$$E_{\text{disp}} = - \frac{2}{\pi} \left(\frac{e^2 \hbar^2}{16 \pi \epsilon_0} \right)^2 \int \frac{d\mathbf{r}_1, d\mathbf{r}_2, d\mathbf{r}'_1, d\mathbf{r}'_2}{r_{12} r'_{12}} \int_0^{\infty} \Pi_A(\hat{D}_{r'_1}, \hat{D}_{r_1} | i\omega) \Pi_B(\hat{D}_{r'_2}, \hat{D}_{r_2} | i\omega) d\omega \quad (3.9)$$

This expression for the dispersion energy has an interesting physical interpretation (Figure 1): the energy is a sum (integral) of contributions which involve two points in each molecular charge cloud; every contribution contains the *inverse first powers* of two intermolecular distances (r_{12} , r'_{12}) with a strength factor which depends on how readily density fluctuations are propagated between points 1 and 1', in A, and 2, 2' in B. The factor $\Pi_A(\hat{D}_{r'_1}, \hat{D}_{r_1} | i\omega)$ for example determines the density changes at point 1' in molecule A due to a unit perturbation (building up exponentially) localized at point 1. The direct evaluation of (3.9) naturally presents formidable problems, including the evaluation of the FDP's and a numerical integration over the positions of four points in space; but it is a formally exact result which may be used at various levels of approximation.

* Note that \mathbf{r}_1 , \mathbf{r}_2 are now dummy variables, representing points in space rather than electron coordinates.

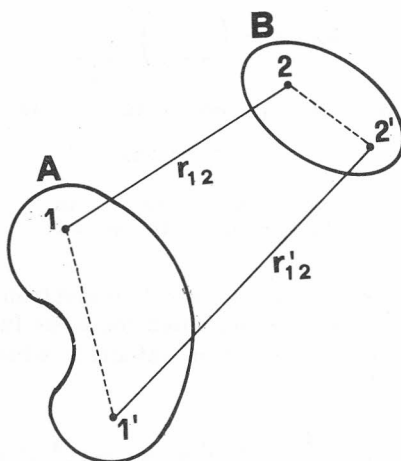


Figure 1. Origin of the dispersion energy. Distances r_{12} , r'_{12} occur in formula (3.6) along with FDPs (broken lines) connecting points 1,1' in molecule A and 2,2' in molecule B.

Let us now turn to orbital approximations, in which the wavefunctions of molecules A and B are constructed, respectively, from orthonormal bases $\{\chi_r^A\}$ and $\{\chi_s^B\}$ of localized orbitals; these may be, for example, Löwdin¹⁶ orthonormalized atomic orbitals, an important requirement being their strong localization around the various atomic centres in the molecules. We assume the sets to be disjoint and each to be »effectively complete« for the molecule to which it refers. Of course a truly complete set (which would contain continuum functions) would be complete for all states of both molecules; but the approximation implied is the one normally made, namely that wavefunctions for molecule A can be built from the finite basis $\{\chi_r^A\}$ (and likewise for molecule B) and that for well separated molecules the two bases are mutually orthogonal.

The density functions in (1.4) then assume finite basis forms,

$$P_A(aa' | \mathbf{r}) = \sum_{r,s} P_{aa',rs}^A \chi_r^A(\mathbf{r}) \chi_s^{A*}(\mathbf{r}) \quad (3.10)$$

with a similar expression for $P_B(bb' | \mathbf{r})$, and the whole derivation is easily repeated. Thus $P_{aa',rs}^A$ can be written as the matrix element

$$P_{aa',rs}^A = \langle Aa' | \hat{d}_{rs}^A | Aa \rangle = \langle Aa' | \sum_{i=1}^{N_A} \hat{d}_{rs}^A(i) | Aa \rangle$$

where in general $\hat{d}_{rs}(i)$ denotes an integral operator with kernel $\chi_s(\mathbf{r}_i) \chi_r^*(\mathbf{r}'_i)$:

$$\hat{d}_{rs}(i) \rightarrow \hat{d}_{rs}(\mathbf{r}_i; \mathbf{r}'_i) = \chi_s(\mathbf{r}_i) \chi_r^*(\mathbf{r}'_i) \quad (3.11)$$

Substitution in (1.4) *etc.* then yields, instead of (3.6),

$$E_{\text{disp}} = - \left(\frac{e^2 \hbar}{4 \pi \epsilon_0} \right)^2 \sum_{\substack{p,q,r,s \\ t,u,v,w}} \sum_{a,a'} \frac{\langle Aa | d_{tu} | Aa' \rangle \langle Bb | d_{vw} | Bb' \rangle \langle Aa' | d_{pq} | Aa \rangle \langle Bb' | d_{rs} | Bb \rangle}{(\omega_{aa'} + \omega_{bb'})} \times \langle \overset{BA}{rp} | g | \overset{BA}{sq} \rangle \langle \overset{AB}{tv} | g | \overset{AB}{uw} \rangle \quad (3.12)$$

where, for example, $\langle \overset{BA}{rp} | g | \overset{BA}{sq} \rangle$ is a two-electron integral in the usual Dirac notation. A simplification occurs when the basis functions are real, owing to the high symmetry of the 2-electron integrals which is evident on using the »charge cloud« notation

$$(\overset{A}{pq}, \overset{B}{rs}) = \langle \overset{BA}{rp} | g | \overset{BA}{sq} \rangle = \int \chi_p^A(\mathbf{r}_1) \chi_q^A(\mathbf{r}_1) \frac{1}{r_{12}} \chi_r^B(\mathbf{r}_2) \chi_s^B(\mathbf{r}_2) d\mathbf{r}_1, d\mathbf{r}_2 \quad (3.13)$$

In this case, which may be assumed without loss of generality, the summations may be restricted to $p \geq q$, $r \geq s$, etc. a typical operator \hat{d}_{rs} in (3.12) being replaced by

$$\hat{D}_{rs} = \frac{1}{2} (\hat{d}_{rs} + \hat{d}_{sr}) (2 - \delta_{rs}) \quad (3.14)$$

which is Hermitian and may therefore be used in the simple expression (2.14) for the FDPs without need of generalization. On using the integral transform (3.7) we thus obtain finally

$$E_{\text{disp}} = - \frac{2}{\pi} \left(\frac{e^2 \hbar^2}{4 \pi \epsilon_0} \right)^2 \sum_{\substack{p,q,r,s \\ t,u,v,w}} \left[\int_0^\infty \hat{I}_A (\hat{D}_{tu}^A \hat{D}_{pq}^A | i\omega) \hat{I}_B (\hat{D}_{vw}^B \hat{D}_{rs}^B | i\omega) d\omega \right] \times (\overset{A}{pq}, \overset{B}{rs}) (tu, vw) \quad (3.15)$$

The only approximation made in deriving this expression is the use of a finite basis, in constructing the wavefunctions for each molecule, instead of a complete set: in principle, therefore, (3.15) provides a sound basis for completely *ab initio* multiconfiguration calculation of dispersion energies.

For all practical purposes, further approximations must be made. These are of two types (i) those involved in the calculation of FDPs for the separate molecules, and (ii) those which refer to simplification of (3.15). For the moment we consider only the latter, discussing the calculation of FDPs in the next section.

A moment's consideration shows that for two well-separated molecules the eightfold summation in (3.15) contains relatively few large terms; this is because we have assumed localized and orthogonal orbitals as basis functions.

Thus $(\overset{A}{pq}, \overset{B}{rs})$ represents the coulomb interaction between two fragments of charge density

$$\Omega_{pq}^A(\mathbf{r}) = \chi_p^A(\mathbf{r}) \chi_q^A(\mathbf{r}), \quad \Omega_{rs}^B(\mathbf{r}) = \chi_r^B(\mathbf{r}) \chi_s^B(\mathbf{r}) \quad (3.16)$$

When $p = q$ we may say Ω_{pp}^A »contains unit charge« (i. e. regarded as an electron density it integrates to unity); but when $p \neq q$ Ω_{pq}^A represents, for example, an electric dipole (or higher multipole) whose total charge is zero (overlap integral zero). The most extreme approximation is thus to consider only terms corresponding to $p = q, r = s, t = u, v = w$, thereby reducing (3.14) to a fourfold summation. This »zero differential overlap« (ZDO) approximation differs from that normally made in semi-empirical molecular orbital theory (e. g. in the CNDO approximation¹⁷) in that it is applied only to intermolecular integrals where the distances between charge fragments are large; and it is applied only at the level of the interaction energy (i. e. the quantity of interest) which is an almost infinitesimal part of the total electronic energy. An even better approximation, which we consider presently, would retain intra-atomic charge densities (as in the NDDO approximation¹⁷) these being the next most important terms — though much smaller than the Ω_{pp}^A -type, which give »charge-charge« interactions and fall off only as the inverse first power of an intermolecular distance.

With the above ZDO approximation of the intermolecular integrals, (3.15) reduces to

$$E_{\text{disp}} = -\frac{2}{\pi} \left(\frac{e^2 \hbar^2}{4 \pi \epsilon_0} \right)^2 \sum_{p,r,t,v} \gamma_{pr}^{AB} \gamma_{tv}^{AB} \int_0^\infty \Pi_{tt,pp}^A(i\omega) \Pi_{vv,rr}^B(i\omega) d\omega \quad (3.17)$$

where the γ s are coulomb integrals for the various charge fragments and an abbreviated notation has been used for the FDPs. The interpretation of (3.17) is obvious from Figure 2; each γ provides an approximately inverse-distance interaction between one atom in molecule A and one atom in molecule B, while each FDP measures the intensity with which a density fluctuation is propagated from one atom to another in the same molecule. The FDPs are characteristic of the separate molecules and can be calculated once and for all; the strength and geometry dependence of the intermolecular forces then follows from the other factors in the simple expression (3.17).

At large distances an even simpler approximation may be sufficient to give a useful semi-quantitative account of the geometry dependence of the interactions. In this approximation we perform the summations in (3.17) atom-by-atom, so that p and t run over atoms A_i, A_j of molecule A while r and v run over atoms B_k, B_l of molecule B, giving each γ -factor a mean value

$$\gamma_{pr}^{AB} \approx R(A_i, B_j)^{-1} \quad (p \text{ on atom } A_i, r \text{ on atom } B_j) \quad (3.18)$$

corresponding to charge densities centred on the atoms. The final summation is then over all pairs of atoms:

$$E_{\text{disp}} = -\frac{2}{\pi} \left(\frac{e^2 \hbar^2}{4 \pi \epsilon_0} \right)^2 \sum_{\substack{A_i, A_j \\ B_k, B_l}} \frac{F(A_i, A_j, B_k, B_l)}{R(A_i, B_k) R(A_j, B_l)} \quad (3.19)$$

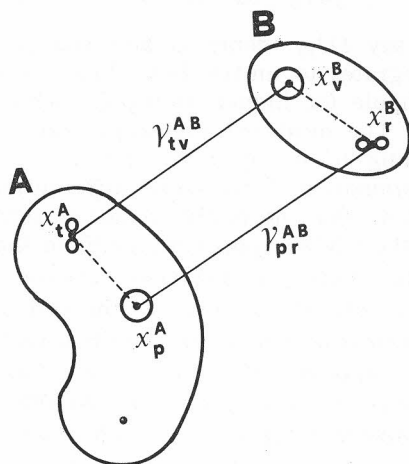


Figure 2. Origin of the dispersion energy in LCAO approximation. Electron repulsion integrals γ_{tv}^{AB} , γ_{pr}^{AB} occur in formula (3.17), along with FDPs (broken lines) connecting AOs χ_v^A , χ_p^A in molecule A, χ_v^B , χ_r^B in molecule B.

where the strength factor is

$$F(A_i, A_j, B_k, B_l) = \int_0^{\infty} \Pi(A_i A_j | i\omega) \Pi(B_k B_l | i\omega) d\omega \quad (3.20)$$

The factors in the integral (3.20) are »atom-atom FDPs at pure imaginary frequency«; they relate, essentially, the response of the charge density at one atom to a change of density at another atom. We note that the possibility of summation in (3.17) arises because we are dealing with the *linear* response, the effect of component perturbations being additive. It is also interesting to note that (3.19) has the an »atom-atom« form, as commonly assumed in semi-empirical discussions of the dispersion energy, *except* that the denominator has dimensions (distance)² instead of (distance)⁶. The inverse square dependence arises because density fluctuations *in a molecule* involve flow of charge from one atom to another and hence lead to charge-charge interactions between atoms of the two different molecules.

IV. CALCULATION OF THE FDPs

Ideally, the FDPs would be calculated with high precision from multiconfiguration molecular wavefunctions; this is no mean task, although it is known that high accuracy is attainable (*e. g.* Ref. 18) even with rather limited CI. For large molecules such calculations are not at present feasible and we shall be content with more modest approximations obtained using time-dependent Hartree-Fock (TDHF) theory. Since, however, even the TDHF equations in their usual form¹⁹ are too unwieldy for use with large basis sets, we shall use

a variant which is more closely related to the so called coupled Hartree-Fock (CHF) perturbation theory, in which self-consistency in the presence of the time-dependent perturbation is introduced by an iterative method. In this approach, first developed for time-independent perturbations²⁰, the dimension of the matrix equations is equal to that of the basis set and solution is thus feasible even for quite large molecules. As the method has been discussed elsewhere²¹ we give only a brief summary of the main equations.

The closed-shell Hartree-Fock equations in finite basis form are equivalent to a commutation condition for the Fock matrix \mathbf{h}^F and the (spinless) density matrix \mathbf{P} ($= 2\mathbf{R}$). When \mathbf{h}^F contains a time-dependent perturbation, the commutator no longer vanishes and the TDHF equations may be stated in the form

$$\mathbf{h}^F \mathbf{R} - \mathbf{R} \mathbf{h}^F = i\hbar (\partial \mathbf{R} / \partial t) \quad (4.1)$$

As usual, \mathbf{R} is constrained to be idempotent ($\mathbf{R}^2 = \mathbf{R}$) and

$$\mathbf{h}^F = \mathbf{h} + \mathbf{G}(\mathbf{R}) = \mathbf{h} + 2\mathbf{J}(\mathbf{R}) - \mathbf{K}(\mathbf{R}) \quad (4.2)$$

where \mathbf{J} and \mathbf{K} are the Coulomb and exchange terms in the Roothan \mathbf{G} -matrix (see, for example, Ref. 22).

The perturbation (2.9) corresponds to a change $\mathbf{h} \rightarrow \mathbf{h} + \delta \mathbf{h}$ where

$$\delta \mathbf{h} = \mathbf{A} f e^{i\omega t} \quad (4.3)$$

\mathbf{A} being the Hermitian matrix (referred to an orbital basis χ) of a one-electron perturbation operator. The corresponding first-order perturbation of the density matrix will be

$$\delta \mathbf{R} = \mathbf{d} f e^{i\omega t} \quad (4.4)$$

and on separating the orders in (4.1) and using the projection operator properties of \mathbf{R}_0 (the unperturbed density matrix, which commutes with \mathbf{h}_0^F) we obtain a first-order equation

$$(\mathbf{h}_0^F - i\hbar\omega) \mathbf{x} - \mathbf{x} \mathbf{h}_0^F + (\mathbf{1} - \mathbf{R}_0) [\mathbf{A} + \mathbf{G}(\mathbf{d})] \mathbf{R}_0 = \mathbf{0} \quad (4.5)$$

where

$$\mathbf{d} = \mathbf{x} + \mathbf{x}^\dagger, \quad \mathbf{x} = (\mathbf{1} - \mathbf{R}_0) \mathbf{d} \mathbf{R}_0 \quad (4.6)$$

The matrices \mathbf{R}_a and $(\mathbf{1} - \mathbf{R}_0)$ represent projection operators onto the subspaces of the occupied and virtual orbitals, respectively, and other projections of \mathbf{d} must vanish in order to preserve idempotency ($\mathbf{R}^2 = \mathbf{R}$) to first order.

The equation (4.5) may be solved formally by putting $\mathbf{x} = \sum_{K,J} X_{KJ} \mathbf{c}_K \mathbf{c}_J^\dagger$, in which \mathbf{c}_K and \mathbf{c}_J represent occupied and virtual eigenvectors of the unperturbed Fock matrix h_0^F , and identifying the coefficients X_{KJ} . As the \mathbf{G} -term depends on the solution (\mathbf{d}), it is of course necessary to satisfy the resultant equations by iteration.

Since, however, (4.5) contains an imaginary term, we write

$$\mathbf{x} = \mathbf{p} + i\mathbf{q} \quad (4.7)$$

where \mathbf{p} and \mathbf{q} are real, thus avoiding complex arithmetic. Equation (4.5) then separates and the solution is obtained when

$$\left. \begin{aligned} \mathbf{p} &= - \sum_{\substack{J \text{ (occ.)} \\ K \text{ (unocc.)}}} \frac{\varepsilon_{JK} P_{JK} + \hbar\omega Q_{JK}}{(\varepsilon_{JK}^2 + \hbar^2 \omega^2)} \mathbf{c}_J \mathbf{c}_K^\dagger \\ \mathbf{q} &= - \sum_{\substack{J \text{ (occ.)} \\ K \text{ (unocc.)}}} \frac{\varepsilon_{JK} Q_{JK} - \hbar\omega P_{JK}}{(\varepsilon_{JK}^2 + \hbar^2 \omega^2)} \mathbf{c}_J \mathbf{c}_K^\dagger \end{aligned} \right\} \quad (4.8)$$

where P_{JK} , Q_{JK} are »matrix elements« $\mathbf{c}_j^\dagger \mathbf{P} \mathbf{c}_k$ and $\mathbf{c}_j^\dagger \mathbf{Q} \mathbf{c}_k$ of

$$\mathbf{P} = \mathbf{A} + \mathbf{G} (\mathbf{p} + \mathbf{p}^\dagger), \quad \mathbf{Q} = \mathbf{G} (\mathbf{q} - \mathbf{q}^\dagger) \quad (4.49)$$

The »excitation energy« $\varepsilon_{JK} = \varepsilon_K - \varepsilon_J$ refers to the unperturbed eigenvalues and equations (4.8) (4.9) are solved by iteration, starting from $\mathbf{p} = \mathbf{q} = \mathbf{0}$ in (4.9) and calculating new approximations from (4.8). The denominators in (4.8) never vanish (*i. e.* the solutions do not exhibit poles, as they would for a real frequency) and convergence of the iteration is usually rapid.

To obtain an approximation to the FDP defined in (2.10) we note that from (4.4) and (4.6)

$$\delta \mathbf{R} = \mathbf{d} f e^{\omega t} = (\mathbf{x} + \mathbf{x}^\dagger) f e^{\omega t}$$

and that the first-order change in an expectation value $\langle B \rangle$, where the (one-electron) Hermitian operator \hat{B} has an associated matrix \mathbf{B} , is given by

$$\delta \langle B \rangle = 2 \operatorname{tr} (\mathbf{B} \delta \mathbf{R}) = 4 \operatorname{Re} \cdot [\operatorname{tr} (\mathbf{B} \mathbf{x}_A)] f e^{\omega t} \quad (4.10)$$

where a subscript A has been added to remind us that \mathbf{x} depends on the perturbation operator \hat{A} . Comparison with (2.10) then shows that

$$\Pi (\hat{B} \hat{A} | i\omega) = 4 \operatorname{Re} \cdot [\operatorname{tr} (\mathbf{B} \mathbf{x}_A)] \quad (4.11)$$

When \mathbf{B} is a real symmetric matrix (the most common case) the trace reduces according to (4.7), to $\operatorname{tr} (\mathbf{B} \mathbf{p}_A)$.

In evaluating an FDP such as $\Pi_{it, pp}^A(i\omega)$, for use in (3.17), \mathbf{A} is chosen as the matrix with $A_{pp} = 1$ and all other elements zero, and \mathbf{B} similarly with $B_{tt} = 1$; the FDP's for all values of t are thus obtained in a single calculation, from the diagonal elements of \mathbf{p}_A (as follows from (4.11) et seq.).

V. CONCLUSION

An explicit procedure for the calculation of dispersion interactions between large molecules has been described in some detail. An exact expression for E_{disp} (3.9) contains FDPs which are essentially »density correlation functions« for the separate molecules; these describe how a perturbation at one point in the charge cloud affects the density at a second point and may be calculated using response theory. On using a finite-basis orbital approximation, a similar expression (3.15) applies at a level corresponding to a complete configuration interaction calculation for each molecule.

In order to make further progress feasible, particularly in the case of large molecules, it is necessary to introduce simplified »models«. Such models invariably presuppose that most of the two-electron integrals involved (*i. e.* matrix elements, within a finite basis, of two-electron terms in the Hamiltonian) can be neglected; and their validity, as a representation of the »real«

system, depends critically on the choice of basis functions. The most severe approximation consistent with a reasonable description of electron interaction effects is that of zero differential overlap, which is known to be acceptable provided the basis functions are strongly localized (*i.e.* »atomic«) and orthogonal. The model used in the present development differs, however, from the majority of those in current use (CNDO, NDDO, *etc.*) in so far as such approximations are made only in *intermolecular* matrix elements; all single-molecule quantities could in principle be calculated by conventional multiconfiguration *ab initio* methods. Consequently, the approximations apply directly to the quantity of interest (E_{disp}) and not to the total electronic energy. Use of a ZDO model for the interaction effects leads to a simple formula (3.17) for E_{disp} involving only »orbital-orbital« polarizabilities within the separate molecules; this may be further reduced, without great loss of accuracy, by an averaging procedure which introduces »atom-atom« polarizabilities and leads to an energy formula (3.19) not unlike those commonly employed in the empirical representation of intermolecular interaction energies. This formula exposes, however, the existence of strong, long-range (R^{-2}) interactions between the atoms of two different molecules, an interaction which is completely obscured whenever multipole expansions are employed. The description of the interactions in terms of atom-atom polarizabilities should therefore be of particular value for large molecules at distances where multipole expansions converge slowly (or not at all).

In the practical implementation of the present approach, the simplest method of calculating the required FDPs is provided by TDHF theory; the iterative procedure described in Section 4 has proved itself highly effective for this purpose, usually converging within a few cycles. Calculations at various levels of approximation are now in progress and will be fully reported elsewhere.

REFERENCES

1. A. T. Amos and R. J. Crispin, in: *Theoretical Chemistry: Advances and Perspectives* Vol. 2 H. Eyring and D. Henderson (Eds.), Academic Press, New York, 1976.
2. *Theory of Intermolecular Forces*, H. Margenau and N. R. Kestner, Pergamon Press, Oxford, 1969.
3. *Weak Intermolecular Interactions in Chemistry and Biology*, P. Hobza and R. Zahradnik, Elsevier, Amsterdam, 1980.
4. *Molecular Interactions* Vol. 1—3, H. Ratajczak and W. J. Orville-Thomas (Eds.), Wiley, Chichester, 1980—1982.
5. B. Jeziorski and W. Koloss in: *Molecular Interactions* Vol. 3, H. Ratajczak and W. J. Orville-Thomas (Eds.) Wiley, Chichester, 1982.
6. W. Kolos, in: *New Horizons of Quantum Chemistry* P.-O. Löwdin and B. Pulman (Eds.), Riedel, 1983.
7. R. McWeeny, *Proc. R. Soc. London Ser. A* **253** (1959) 242; see also *Rev. Mod. Phys.* **32** (1960) 335.
8. F. London, *Z. Phys.* **63** (1930) 245.
9. H. B. G. Casimir and D. Polder, *Phys. Rev.* **73** (1948) 360.
10. G. P. Arrighini, F. Biondi, and C. Guidotti, *J. Chem. Phys.* **55** (1971) 4090.
11. G. A. Victor and A. Dalgarno, *J. Chem. Phys.* **53** (1970) 1316.
12. P. W. Langhoff, R. A. Gordon, and M. Karplus, *J. Chem. Phys.* **55** (1971) 2126.
13. R. T. Pack, *J. Chem. Phys.* **61** (1974) 2091.
14. D. N. Zubarev, *Usp. Fiz. Nauk.* **71** 71 (*Sov. Phys.-Usp.* **3** (1960) 320).
15. R. McWeeny, *Proc. R. Soc. London Ser. A* **232** (1955) 114.

16. P. O. Löwdin, *J. Chem. Phys.* **18** (1950) 365.
17. *Approximate Molecular Orbital Theory*, J. A. Pople and D. L. Beveridge, McGraw Hill, New York, 1970.
18. R. McWeeny and M. Jaszunski, *Mol. Phys.* **46** (1982) 863.
19. *Quantum Mechanics of Many-Body Systems*, D. J. Thouless, Academic Press, New York, 1972, 2nd ed.
20. G. Dierksen and R. McWeeny, *J. Chem. Phys.* **44** (1967) 3554.
21. R. McWeeny, *J. Mol. Struct. Theochem* **93** (1983) 1.
22. *Methods of Molecular Quantum Mechanics*, R. McWeeny and B. T. Sutcliffe, Academic Press, London, 1969.

SAŽETAK

Slabe interakcije između molekula

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Izvedene su eksplicitne formule za računanje disperzijskih energija interakcije velikih molekula. Kao osnovna veličina u izvodu pojavljuju se polarizabilnost koja ovisi o frekvenciji (FDP), a izbjegnuta je upotreba multipolnog razvoja. FDP opisuje fluktuacije elektronske gustoće unutar svake od molekula. U konačnoj formuli prisutan je član R^{-2} koji opisuje međuatomske interakcije dugog doseg. Prikazani formalizam daje vrlo dobru osnovicu za razvoj semiempirijskog modela koji interakciju dviju molekula svodi na međudjelovanja parova atoma.

Opisan je SCF-postupak za računanje FDP koji vrlo brzo konvergira.