Theoret. chim. Acta (Berl.) 21, 267—279 (1971)

A Simple Model of Short-Range Interactions

I. Theory

VALERIO MAGNASCO

Istituto di Chimica Industriale dell'Università, 16132 Genova, Italy

Received October 5, 1970

The short-range interaction between any two molecular fragments can be split into coulombic and penetration components, the last part being dominant in neutral systems. A simple theoretical model is developed to describe the penetration part of the short-range interaction between two localized electron pairs. The main body of the interaction is seen to take place through the overlap arising between nonorthogonal electron groups. For closed-shell fragments the interaction can be visualized in terms of a distortion of the electron density resulting in a decrease of charge in the overlap region and in an increase of charge in the region of the component groups.

Die Wechselwirkung kurzer Reichweiten zwischen zwei Molekülteilen kann in Coulomb- und Durchdringungsanteile aufgeteilt werden, von denen der letztere in neutralen Systemen dominiert. Ein einfaches Modell wird entwickelt, das den gesamten Durchdringungsanteil der Wechselwirkung zweier lokalisierter Elektronenpaare kurzer Reichweite beschreibt. Der Hauptanteil der Wechselwirkung kommt durch die Überlappung zwischen nichtorthogonalen Elektronengruppen zustande. Für Bruchstücke mit abgeschlossenen Schalen kann man sich die Wechselwirkung mit Hilfe einer Verlagerung der Elektronendichte vorstellen, die zu einer Verminderung der Ladung in der Überlappungsregion und einer Vermehrung der Ladung im Gebiet der beiden Gruppen führt.

L'interaction à courte distance entre deux fragments moléculaires quelconques peut être decomposée dans une composante coulombienne et une composante pénétrative, cette dernière étant dominante dans le cas de systèmes neutres. Un modèle théorique simple a été developé pour décrire la composante pénétrative de l'interaction à courte distance entre deux paires localisées d'électrons. La partie la plus importante de l'interaction a lieu via le recouvrement entre groupes nonorthogonales d'électrons. Pour des fragments moléculaires correspondants à des couches complètes l'interaction peut être visualisée dans une distortion de la densité electronique aboutissante à une diminution de charge dans la région de recouvrement et à une augmentation de charge dans la région des groupes composants.

Introduction

The theory of separated electron pairs [1–3] and its generalisations [4] suggests itself as a powerful tool in describing the short-range forces existing between different molecules or different parts of the same polyatomic molecule. Indeed while it shares with perturbation theory the attractive feature of allowing a partition of the molecular energy into terms referring to individual parts and interactions between them, in its SCF formulation the theory has the further advantage that it is possible to account for polarization forces even without the explicit introduction of excited functions. The relaxation of the strong orthogonality constraint in the case of two general interacting electron groups although yielding a bit of tedious algebra [5] allows, at the same time, the separation of the interaction into terms with a direct physical interpretation [6].

In the paper just referred to [6] it has been shown that the short-range interaction between any two molecular fragments can be split into coulombic and penetration components, the last part being dominant in neutral systems.

Purpose of the present paper is to develop a semiempirical approach within the frame of the general theory in order to grasp the main features of the penetration part of the short-range interaction for the simple model of two separated electron pairs which are in weak interaction with each other. In view of the rather good results obtained in an accurate numerical calculation on the H_2–H_2 system [6], each electron pair will be approximately described in terms of one-electron functions (group orbitals) localized in given regions of space and not orthogonal to each other. The energy of the composite system is first analyzed by a perturbation method which allows to separate a zero-order term describing the energy of the individual components and a first-order term which describes the interaction between the two parts. The first approximation in which the zero-order orbitals resulting from the eigenvalue problem for separate groups are used to compute the cross terms representing the interaction between A and B is then improved by admitting the mutual polarization of the two groups in a self-consistent way. The actual eigenvectors which describe mutually polarized orbitals are found as approximate solutions to a system of two coupled eigenvalue equations each involving an effective one-electron Hamiltonian which depends explicity on the density of the other group.

The analysis of the resulting interaction energy shows that overlap forces play a dominant role in the short-range region, both attractive and repulsive contributions being strongly dependent on the relative orientation of the interacting partners.

1. Outline of the General Theory

Following Longuet-Higgins [7] let us denote by μ, i the nuclei and electrons belonging to system A, and by ν, j the nuclei and electrons belonging to system B. If $\hat{H}^{\mathrm{A}}, \hat{H}^{\mathrm{B}}$ are the many-electron Hamiltonians for the separate systems, the coulombic interaction between A and B will be

$$V = -\sum_{\mu,j} Z_\mu r_{\mu j}^{-1} - \sum_{\nu,i} Z_\nu r_{\nu i}^{-1} + \sum_{i,j} r_{ij}^{-1} + \sum_{\mu,\nu} Z_\mu Z_\nu r_{\mu\nu}^{-1}, \tag{1.1}$$

where atomic units have been used and Z_μ, Z_ν are the nuclear charges. The molecular Hamiltonian can be written as a sum of the unperturbed Hamiltonian $\hat{H}_0$, and the perturbation V

$$\hat{H} = \hat{H}_0 + V = \hat{H}^{\mathrm{A}} + \hat{H}^{\mathrm{B}} + V. \tag{1.2}$$

If $\Phi^{\mathrm{A}a}$, $\Phi^{\mathrm{B}b}$ are suitable many-electron approximations to the wave functions describing the A-electron group in state a and the B-group in state b, the electronic states of the non-interacting composite system will be given in the product form [7]

$$\Phi_\kappa = \Phi^{\mathrm{A}a} \Phi^{\mathrm{B}b}. \tag{1.3}$$

Denoting the ground state with the subscript 0, we get that $\Phi_0 = \Phi^{A_0}\Phi^{B_0}$ is an approximate eigenvector and $E_0 = E^A + E^B$ an upper bound in the usual sense of variation theory to the lowest energy eigenvalue appearing in the unperturbed Schroedinger equation

$$\hat{H}_0 \Phi_0 = E_0 \Phi_0 . \tag{1.4}$$

When the two electron groups begin to interpenetrate exchange must be allowed for, and Eq. (1.3) must be replaced by the antisymmetrized product

$$\Psi_\kappa = M_\kappa \mathscr{A} \Phi_\kappa , \tag{1.5}$$

M_κ being a normalization factor for configuration $\kappa = (\mathrm{A}a, \mathrm{B}b)$, and $\mathscr{A}$ the antisymmetrizer which exchange electrons between *different* groups. We then seek for an *approximate* solution to the complete Schroedinger equation

$$\hat{H} \Psi = E \Psi \tag{1.6}$$

in the form of the interconfigurational wave function

$$\Psi = \Psi_0 + \sum_{\kappa(\neq 0)} \Psi_\kappa C_\kappa . \tag{1.7}$$

By exploiting a density matrix formalism it can be shown [8] that, up to second-order in the interaction Hamiltonian, the energy is given by the perturbation series

$$E = \frac{\langle \Psi | \hat{H} \Psi \rangle}{\langle \Psi | \Psi \rangle} = E^{(0)} + E^{(2)} + \cdots \tag{1.8}$$

where

$$E^{(0)} = H_{00} = \langle \Psi_0 | \hat{H} \Psi_0 \rangle \tag{1.9}$$

is the energy in the one-configuration approximation, and

$$E^{(2)} = - \sum_{\kappa(\neq 0)} \frac{|H_{\kappa 0} - H_{00} S_{\kappa 0}|^2}{H_{\kappa\kappa} - H_{00}} \tag{1.10}$$

is a second-order correction [9] arising from the interconfigurational mixing of Eq. (1.7). In the last equation,

$$H_{\kappa\kappa'} = \langle \Psi_\kappa | \hat{H} \Psi_{\kappa'} \rangle \tag{1.11}$$

is the matrix element of the Hamiltonian between states Ψ_κ and $\Psi_{\kappa'}$, and

$$S_{\kappa\kappa'} = \langle \Psi_\kappa | \Psi_{\kappa'} \rangle \tag{1.12}$$

the nonorthogonality integral between the two states. The problem of evaluating the general matrix elements has been solved by McWeeny [5, 10] in the general case of two nonorthogonal electron groups through an expansion of the one- and two-electron density matrices for the composite system in terms of those of its constituent parts.

In the short-range region of intermolecular forces the dominant contribution arises from the one-configuration approximation[1], $E^{(0)}$, which embodies the first-order interaction energy:

$$\Delta E = E - E_0 \approx \Delta E^{(1)} . \tag{1.13}$$

It has been shown by us elsewhere [6] that the one-configuration interaction energy can be split into coulombic and penetration components as follows

$$\Delta E^{(1)} = \Delta E^{(1)}_{\mathrm{cb}} + \Delta E^{(1)}_{\mathrm{pn}} . \tag{1.14}$$

Here $\Delta E^{(1)}_{\mathrm{cb}}$ describes the coulombic interaction between the nuclei and the static electron densities on both A and B; $\Delta E^{(1)}_{\mathrm{pn}}$ describes the additional interaction which arises from the perturbation of the charge clouds when they begin to interpenetrate. The largest terms in $\Delta E^{(1)}_{\mathrm{pn}}$ arise from the distortion of the electron density primarily due to *penetration effects*[2].

For neutral systems (e.g. saturated hydrocarbons) the contribution arising from $\Delta E^{(1)}_{\mathrm{cb}}$ is expected to be smaller than $\Delta E^{(1)}_{\mathrm{pn}}$ although not negligible[3]. In the remaining Sections we shall endeavour of finding a first approximation to the penetration energy in terms of a semi-empirical one-electron model which will prove useful for practical applications.

2. Electron Density of the Composite System

Localized electron pairs A and B will be approximately described in terms of one-electron orbitals

$$\Phi^{\mathrm{A}}(1) = \sum_{\mu}^{(\mathrm{A})} \phi^{\mathrm{A}}_{\mu}(1)\, C^{\mathrm{A}}_{\mu} , \qquad \Phi^{\mathrm{B}}(1) = \sum_{\nu}^{(\mathrm{B})} \phi^{\mathrm{B}}_{\nu}(1)\, C^{\mathrm{B}}_{\nu} , \tag{2.1}$$

where the summations are over all atomic hybrids ϕ^{A}_{μ} belonging to A in Φ^{A}, and over all hybrids ϕ^{B}_{ν} belonging to B in Φ^{B}. In order to simplify our notation henceforth we shall consistently assume μ, μ' as running indices of atomic orbitals (AO's) belonging to A, and ν, ν' as running indices of AO's belonging to B. Φ^{A}

---

[1] An estimate of $\Delta E^{(2)}$ in the case of nonorthogonal group functions can be made for the short-range interaction between two H_2 molecules from the data quoted in Refs. [6] and [11]. The simple one-determinant wave function of nonorthogonal localized bond-orbitals for $D/R_0 = 2.0$ and $\theta = 0°$ gives $\Delta E^{(1)} = 0.0703$ a.u. When intramolecular correlation is admitted by mixing each bonding orbital with its corresponding antibonding partner a lowering of -0.0028 a.u. is obtained for the interaction energy. A further lowering of -0.0014 a.u. results if intermolecular correlation and delocalization are allowed for through the full interconfigurational wave function [11]. The total lowering of the short-range interaction due to interconfigurational mixing amounts to -0.0042 a.u. which gives for $|\Delta E^{(2)}|/|\Delta E^{(1)}|$ an estimate of about 6%.

[2] We would like to stress that we use the term *penetration* energy for describing the interaction energy associated with electron exchange between different electron groups (see Eqs. (3–18) and (3–30) in Ref. [6]). Confusion with the penetration part of the Coulombic energy as defined by Van Duijneveldt and Murrell [15] and with the penetration integral entering the Goeppert-Mayer-Sklar approximation should be carefully avoided.

[3] An estimate of the relative importance of the *coulombic* with respect to the *penetration* interaction for a neutral system can be gained from Ref. [6] (Table IV) for the H_2–H_2 system. At $D/R_0 = 2.0$ the ratio $|\Delta E_{\mathrm{cb}}|/|\Delta E_{\mathrm{pn}}|$ is about 21% irrespective of the relative orientation of the two molecules.

and Φ^{B} are normalized to unity but not orthogonal to each other:

$$\langle \Phi^{\mathrm{A}} | \Phi^{\mathrm{A}} \rangle = \sum_{\mu,\mu'} C^*_{\mu'} S_{\mu'\mu} C_\mu = 1 \,, \tag{2.2}$$

$$\langle \Phi^{\mathrm{A}} | \Phi^{\mathrm{B}} \rangle = \sum_{\mu,\nu} C^*_{\mu} S_{\mu\nu} C_\nu = S \,, \tag{2.3}$$

$S_{\mu'\mu}$ and $S_{\mu\nu}$ being elements of the overlap matrix over the hybrid basis

$$S_{\mu'\mu} = \langle \phi_{\mu'} | \phi_\mu \rangle \,, \tag{2.4}$$

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_\nu \rangle \,. \tag{2.5}$$

The simplest pair functions describing the singlet ground state for each electron pair are:

$$\Phi^{\mathrm{A}}(1,2) = 2^{-\frac{1}{2}} \det[\Phi^{\mathrm{A}}(1)\,\alpha(1)\,\Phi^{\mathrm{A}}(2)\,\beta(2)] \,, \tag{2.6}$$

$$\Phi^{\mathrm{B}}(3,4) = 2^{-\frac{1}{2}} \det[\Phi^{\mathrm{B}}(3)\,\alpha(3)\,\Phi^{\mathrm{B}}(4)\,\beta(4)] \,. \tag{2.7}$$

When electron exchange is allowed for, the correct wave function for the singlet ($S=0, M_S=0$) ground state of the composite system A + B has to be written as the antisymmetrized product

$$\Psi = M \mathscr{A} [\Phi^{\mathrm{A}}(1,2)\,\Phi^{\mathrm{B}}(3,4)] \,. \tag{2.8}$$

Ψ may be alternatively written as a single determinant of nonorthogonal localized orbitals which, when properly normalized, is

$$\Psi = (4!)^{-\frac{1}{2}} (1-S^2)^{-1} \det[\Phi^{\mathrm{A}}(1)\,\alpha(1)\,\Phi^{\mathrm{A}}(2)\,\beta(2)\,\Phi^{\mathrm{B}}(3)\,\alpha(3)\,\Phi^{\mathrm{B}}(4)\,\beta(4)] \,. \tag{2.9}$$

These Ψ expressions are, of course, entirely equivalent, Eq. (2.8) emphasizing the localization of the two electron pairs, and Eq. (2.9) the independent particle model of our approximation. Although exceedingly simple, such a one-determinant wave function constructed from SCF bond orbitals was found in the H_2–H_2 problem to give numerical results within 5 to 10% of the reference value [11] for the interaction, and within 3 to 5% for the energy difference between different relative orientations of the two molecules [6].

The one-electron density matrix [9b] for the composits system[4]

$$P(1;1') = 4 \int \Psi(1s_1, x_2, x_3, x_4)\, \Psi^*(1's_1, x_2, x_3, x_4)\, \mathrm{d}s_1 \mathrm{d}x_2 \mathrm{d}x_3 \mathrm{d}x_4 \,, \tag{2.10}$$

simply reduces to

$$\begin{aligned} P(1;1') = 2(1-S^2)^{-1} [&\Phi^{\mathrm{A}}(1)\,\Phi^{\mathrm{A}*}(1') + \Phi^{\mathrm{B}}(1)\,\Phi^{\mathrm{B}*}(1') \\ &- S(\Phi^{\mathrm{A}}(1)\,\Phi^{\mathrm{B}*}(1') + \Phi^{\mathrm{B}}(1)\,\Phi^{\mathrm{A}*}(1'))] \,. \end{aligned} \tag{2.11}$$

The diagonal element of $P(1;1')$ is the electron density function

$$P(1;1) = 2(1-S^2)^{-1} [|\Phi^{\mathrm{A}}(1)|^2 + |\Phi^{\mathrm{B}}(1)|^2 - S(\Phi^{\mathrm{A}}(1)\,\Phi^{\mathrm{B}*}(1) + \Phi^{\mathrm{B}}(1)\,\Phi^{\mathrm{A}*}(1))] \,, \tag{2.12}$$

which by integration over the whole electron space yields the total electronic charge carried by the composite system A + B

$$\int P(1;1)\,\mathrm{d}v_1 = 4 \,. \tag{2.13}$$

---

[4] The integration is over the spin-space coordinates of all electrons but one, for which the integration is carried out only over the spin coordinate s_1.

The coefficients of each individual density in (2.12) are the elements of a *charge and bond-order matrix* over the localized orbitals:

$$\tilde{q}^{\mathrm{A}} = 2(1-S^2)^{-1} \tag{2.14}$$

the charge on Φ^{A};

$$\tilde{p}^{\mathrm{AB}} = -2S(1-S^2)^{-1} \tag{2.15}$$

the bond-order between Φ^{A} and Φ^{B}. According to (2.1) we may as well express the density in the hybrid basis as

$$\begin{aligned} P(1;1) = & \sum_{\mu,\mu'} \tilde{P}_{\mu\mu'} \phi_\mu(1)\, \phi^*_{\mu'}(1) + \sum_{\nu,\nu'} \tilde{P}_{\nu\nu'} \phi_\nu(1)\, \phi^*_{\nu'}(1) \\ & + \sum_{\mu,\nu} \left(\tilde{P}_{\mu\nu} \phi_\mu(1)\, \phi^*_\nu(1) + \tilde{P}_{\nu\mu} \phi_\nu(1)\, \phi^*_\mu(1)\right), \end{aligned} \tag{2.16}$$

where the coefficients are now elements of the charge and bond-order matrix over the hybrids:

$$\tilde{P}_{\mu\mu} = \tilde{q}^{\mathrm{A}} C_\mu C^*_\mu \tag{2.17}$$

the charge on orbital ϕ_μ;

$$\tilde{P}_{\mu\mu'} = \tilde{q}^{\mathrm{A}} C_\mu C^*_{\mu'} \tag{2.18}$$

the bond-order between ϕ_μ and $\phi_{\mu'}$ in A;

$$\tilde{P}_{\mu\nu} = \tilde{p}^{\mathrm{AB}} C_\mu C^*_\nu \tag{2.19}$$

the bond-order between orbital ϕ_μ belonging to A and orbital ϕ_ν belonging to B. When expressed in terms of ordinary atomic orbitals $\{\chi\}$, to which the hybrids are related through

$$\phi_\mu = \sum_\lambda \chi_\lambda A_{\lambda\mu}, \tag{2.20}$$

$A_{\lambda\mu}$ being the elements of a block-diagonal matrix, the density becomes

$$P(1;1) = \sum_{\lambda,\sigma} \chi_\lambda(1)\, \bar{P}_{\lambda\sigma} \chi^*_\sigma(1), \tag{2.21}$$

$$\bar{P}_{\lambda\sigma} = \sum_{\mu,\nu} A_{\lambda\mu} \tilde{P}_{\mu\nu} A^*_{\nu\sigma}. \tag{2.22}$$

3. One-Electron Hamiltonian and Zero-Order Approximation to the Energy

Let us introduce at this point an unspecified one-electron Hamiltonian $H(1)$, which will be assumed Hermitean but not dependent in an explicit way on the molecular environment (e.g. a Hückel-type Hamiltonian, although reference to Hückel theory is unnecessary here).

The diagonal and off-diagonal elements of $H(1)$, namely

$$H^{\mathrm{A}} = \langle \Phi^{\mathrm{A}} | H \Phi^{\mathrm{A}} \rangle, \qquad H^{\mathrm{B}} = \langle \Phi^{\mathrm{B}} | H \Phi^{\mathrm{B}} \rangle, \tag{3.1}$$

$$H^{\mathrm{AB}} = \langle \Phi^{\mathrm{A}} | H \Phi^{\mathrm{B}} \rangle, \qquad H^{\mathrm{BA}} = \langle \Phi^{\mathrm{B}} | H \Phi^{\mathrm{A}} \rangle = H^{\mathrm{AB}\dagger}, \tag{3.2}$$

may be expressed in terms of elementary integrals over the hybrids

$$H_{\mu\mu'} = \langle \phi_\mu | H \phi_{\mu'} \rangle , \qquad H_{\nu\nu'} = \langle \phi_\nu | H \phi_{\nu'} \rangle , \tag{3.3}$$

$$H_{\mu\nu} = \langle \phi_\mu | H \phi_\nu \rangle = H^\dagger_{\nu\mu} . \tag{3.4}$$

The energy of the composite system A + B, which within our approximation must be understood to embody both electronic and nuclear contributions, is written as the integral

$$E = \int H(1)\, P(1;1)\, \mathrm{d}v_1 , \tag{3.5}$$

and ultimately breaks into

$$E = \tilde{E}^{\mathrm{A}} + \tilde{E}^{\mathrm{B}} + \tilde{E}^{\mathrm{AB}} + \tilde{E}^{\mathrm{BA}} . \tag{3.6}$$

In this expression

$$\tilde{E}^{\mathrm{A}} = \tilde{q}^{\mathrm{A}} H^{\mathrm{A}} , \qquad \tilde{E}^{\mathrm{B}} = \tilde{q}^{\mathrm{B}} H^{\mathrm{B}} \tag{3.7}$$

are the energies of *distorted* nonorthogonal groups, and

$$\tilde{E}^{\mathrm{AB}} = \tilde{p}^{\mathrm{AB}} H^{\mathrm{BA}} , \qquad \tilde{E}^{\mathrm{BA}} = \tilde{p}^{\mathrm{BA}} H^{\mathrm{AB}} \tag{3.8}$$

are those parts of the interaction which arise from the cross-terms in the Hamiltonian. Using the identity

$$(1 - S^2)^{-1} = 1 + S^2 (1 - S^2)^{-1} , \tag{3.9}$$

we are allowed to write

$$\tilde{q}^{\mathrm{A}} = q^{\mathrm{A}}_0 + q^{\mathrm{A}}_{\mathrm{ex}} , \tag{3.10}$$

$$q^{\mathrm{A}}_0 = 2 , \qquad q^{\mathrm{A}}_{\mathrm{ex}} = 2S^2 (1 - S^2)^{-1} = -\tilde{p}^{\mathrm{AB}} S^{\mathrm{BA}} , \tag{3.11}$$

q^{A}_0 being the charge in the *undistorted* A-group, and $q^{\mathrm{A}}_{\mathrm{ex}}$ the *extra-charge* on A due to the distortion of the density arising from nonorthogonality. The interaction terms embodied in $\tilde{E}^{\mathrm{A}}$ and $\tilde{E}^{\mathrm{B}}$ because diagonal elements of the Hamiltonian are weighted with charges which include overlap cross-terms between the two groups, are then readily separated as

$$\tilde{E}^{\mathrm{A}} = E^{\mathrm{A}}_0 + E^{\mathrm{AB}}_{\mathrm{ex}} , \qquad \tilde{E}^{\mathrm{B}} = E^{\mathrm{B}}_0 + E^{\mathrm{BA}}_{\mathrm{ex}} , \tag{3.12}$$

$$E^{\mathrm{A}}_0 = q^{\mathrm{A}}_0 H^{\mathrm{A}} , \tag{3.13}$$

$$E^{\mathrm{AB}}_{\mathrm{ex}} = -\tilde{p}^{\mathrm{AB}} S^{\mathrm{BA}} H^{\mathrm{A}} . \tag{3.14}$$

When Eq. (3.12) is introduced into Eq. (3.6), the energy may be written as

$$E = E_0 + \Delta E^{(1)} , \tag{3.15}$$

where E_0 is a zero-order term giving the energy of separate groups

$$E_0 = E^{\mathrm{A}}_0 + E^{\mathrm{B}}_0 , \tag{3.16}$$

and the perturbation energy, $\Delta E^{(1)}$,

$$\Delta E^{(1)} = E^{\mathrm{AB}} + E^{\mathrm{BA}} , \tag{3.17}$$

$$E^{\mathrm{AB}} = E^{\mathrm{AB}}_{\mathrm{ex}} + \tilde{E}^{\mathrm{AB}} . \tag{3.18}$$

Within our assumptions (cf. Section 2) $\Delta E^{(1)}$ is to be understood as a first approximation to the *penetration* part of the interaction. The distortion of the electron density is here visualized in terms of a shift of charge from the *interbond* region towards the space occupied by each individual fragment. If $(1-S^2)^{-1}$ is expanded in powers of S^2 it is easily seen that the leading term in $\Delta E^{(1)}$ is of the order of S^2. Taking $S \sim 0.1$, $H^{\mathrm{A}} \sim 10$ eV, $H^{\mathrm{AB}} \sim 1$ eV, both components of E^{AB} will be of the order of a tenth of eV.

If the zero-order problem for separate groups has been solved through eigenvalue equations of the type

$$\sum_{\mu'} (H_{\mu\mu'} - \lambda^0 S_{\mu\mu'})\, C_{\mu'} = 0 \qquad \mu, \mu' = 1, 2, \ldots \tag{3.19}$$

yielding zero-order orbitals $\Phi^{\mathrm{A}(0)}$, $\Phi^{\mathrm{B}(0)}$, the first approximation to the interaction energy in the usual sense of perturbation theory will be obtained when each individual component in Eq. (3.15) is understood to be computed over the zero-order orbitals. This first approximation to the perturbation energy will now be improved by allowing the mutual "polarization" of the two groups in a self-consistent way.

4. SCF-Polarization of the Component Groups

The polarization of the component groups occurring under the interaction will change the eigenvectors resulting from Eq. (3.19) into functions which describe *polarized orbitals* Φ^{A}, Φ^{B} which will differ from the *unpolarized orbitals* $\Phi^{\mathrm{A}(0)}$, $\Phi^{\mathrm{B}(0)}$ used as a first approximation in our perturbation approach. The actual eigenvectors describing mutually polarized orbitals will be found as approximate solutions to a system of two coupled pseudo-eigenvalue equations, each involving an effective Hamiltonian which depends explicity on the density of the other group.

The energy, Eq. (3.6), for the composite system A + B is readily written in the two equivalent forms[5]

$$E = E^{\mathrm{A}} + \tilde{E}^{\mathrm{B}}_{\mathrm{eff}} = E^{\mathrm{B}} + \tilde{E}^{\mathrm{A}}_{\mathrm{eff}} \tag{4.1}$$

where

$$\tilde{E}^{\mathrm{A}}_{\mathrm{eff}} = \tilde{E}^{\mathrm{A}} + E^{\mathrm{BA}}_{\mathrm{ex}} + \tilde{E}^{\mathrm{AB}} + \tilde{E}^{\mathrm{BA}} = 2\,\frac{\langle \Phi^{\mathrm{A}} | \tilde{H}^{\mathrm{A}} \Phi^{\mathrm{A}} \rangle}{\langle \Phi^{\mathrm{A}} | \tilde{S}^{\mathrm{A}} \Phi^{\mathrm{A}} \rangle} \tag{4.2}$$

is the approximate expectation value in the actual A-space of an *effective* one-electron Hamiltonian for group A

$$\tilde{H}^{\mathrm{A}} = H + \langle \Phi^{\mathrm{B}} | H \Phi^{\mathrm{B}} \rangle\, |\Phi^{\mathrm{B}}\rangle \langle \Phi^{\mathrm{B}}| - H |\Phi^{\mathrm{B}}\rangle \langle \Phi^{\mathrm{B}}| - |\Phi^{\mathrm{B}}\rangle \langle \Phi^{\mathrm{B}}|\, H \tag{4.3}$$

which involves the density of the B-group. The integral at denominator in Eq. (4.2) describes the distortion of the A-space in the presence of B through the distortion operator

$$\tilde{S}^{\mathrm{A}} = 1 - |\Phi^{\mathrm{B}}\rangle \langle \Phi^{\mathrm{B}}| \,. \tag{4.4}$$

---

[5] $E^{\mathrm{A}} = 2\langle \Phi^{\mathrm{A}} \mid H \Phi^{\mathrm{A}} \rangle$, where Φ^{A} is the actual polarized orbital.

When Eq. (2.1) is taken into account, we may rewrite Eq. (4.1) in matrix form

$$E = E^{\mathrm{A}} + \frac{\mathscr{C}^{\mathrm{B}\dagger}\tilde{\mathscr{H}}^{\mathrm{B}}\mathscr{C}^{\mathrm{B}}}{\mathscr{C}^{\mathrm{B}\dagger}\tilde{\mathscr{S}}^{\mathrm{B}}\mathscr{C}^{\mathrm{B}}} = E^{\mathrm{B}} + \frac{\mathscr{C}^{\mathrm{A}\dagger}\tilde{\mathscr{H}}^{\mathrm{A}}\mathscr{C}^{\mathrm{A}}}{\mathscr{C}^{\mathrm{A}\dagger}\tilde{\mathscr{S}}^{\mathrm{A}}\mathscr{C}^{\mathrm{A}}}, \tag{4.5}$$

where $\tilde{\mathscr{H}}^{\mathrm{A}}$ and $\tilde{\mathscr{S}}^{\mathrm{A}}$ are the matrix representatives of operators (4.3) and (4.4) in the hybrids basis which belongs to A, with elements

$$\tilde{H}_{\mu\mu'} = H_{\mu\mu'} + \sum_{\nu,\nu'} C_\nu C^*_{\nu'}(S_{\mu\nu}S_{\nu'\mu'}H^{\mathrm{B}} - S_{\mu\nu}H_{\nu'\mu'} - H_{\mu\nu}S_{\nu'\mu'}), \tag{4.6}$$

$$\tilde{S}_{\mu\mu'} = S_{\mu\mu'} - \sum_{\nu,\nu'} C_\nu C^*_{\nu'} S_{\mu\nu}S_{\nu'\mu'}. \tag{4.7}$$

We now look for a small change in the coefficients $\mathscr{C}^{\mathrm{A}}$ and $\mathscr{C}^{\mathrm{B}}$ such that the two equations appearing in (4.5) be simultaneously satisfied. This is tantamount to requiring that E be stationary against arbitrarily small *independent* changes in the two sets of coefficients, and we are thus faced with a variational problem for the composite system which may be formulated in terms of its constituent parts A and B. Straightforward application of the variation theorem yields now two simultaneous pseudo-eigenvalue equations of the type

$$\sum_{\mu'} (\tilde{H}_{\mu\mu'} - \lambda\tilde{S}_{\mu\mu'})\, C_{\mu'} = 0 \qquad \mu, \mu' = 1, 2, \ldots \tag{4.8}$$

from which eigenvalues λ and eigenvectors $\mathscr{C}^{\mathrm{A}}$ are obtained through the solution of the secular equation

$$\det(\tilde{H}_{\mu\mu'} - \lambda\tilde{S}_{\mu\mu'}) = 0. \tag{4.9}$$

As usual in self-consistent field (SCF) theories the pair of coupled equations (4.5) are conveniently solved in an iterative way, starting from the zero-order values for the coefficients corresponding to unperturbed separate groups, computing $\tilde{\mathscr{S}}^{\mathrm{R}}$ and $\tilde{\mathscr{H}}^{\mathrm{R}}$(R = A, B) for each group in turn and solving the eigenvalue problem (4.8). The resulting coefficients are then used to compute revised $\tilde{\mathscr{S}}^{\mathrm{R}}$, $\tilde{\mathscr{H}}^{\mathrm{R}}$, and the process is repeated until self-consistency is achieved.

5. The Short-Range Interaction Energy

When that part of the interaction embodied in $E^{(0)}$ through the SCF-eigenvectors is separated from the energy E_0 describing unperturbed and unpolarized groups, according to the equation

$$E^{(0)} = E_0 + E'_0 + \Delta E^{(1)} \tag{5.1}$$

with

$$E_0 = E_0^{\mathrm{A}} + E_0^{\mathrm{B}} \tag{5.2}$$

$$E'_0 = E_0^{\mathrm{A}\prime} + E_0^{\mathrm{B}\prime}, [6] \tag{5.3}$$

---

[6] $E_0^{\mathrm{A}\prime}$ is the difference between the self-energy of the *polarized* A-group and the self-energy of A when B is at infinity (E_0^{A}).

the penetration component of the short-range interaction between A and B may be written as

$$\Delta E \approx E_0' + \Delta E^{(1)}. \tag{5.4}$$

Each of the terms appearing in Eq. (5.4) will now be discussed in some detail.

We first notice that since E_0 is the minimum energy for noninteracting groups in the usual sense of variation theory, any change in the coefficients from the "best" value $\mathscr{C}_0$ must *raise* the energy of the *separate* groups. Hence E_0', which is the difference between the self-energies of polarized groups and the corresponding self-energies of *unpolarized* groups (E_0), will be positive

$$E_0' > 0, \tag{5.5}$$

representing a *repulsive* contribution to the interaction energy.

The total polarization energy[7], of course, is in itself negative, because the component charge clouds do rearrange themselves so as to lower the total energy giving some additional stabilization to the composite system, but the largest negative contribution arising from the actual interaction between the polarized groups is still embodied in $\Delta E^{(1)}$, in which the whole Hamiltonian is weighted with the *perturbed* density involving SCF-coefficients. The situation is much the same as that encountered in the interaction of two H atoms in their ground state, a small polarization of their charge clouds [12] yielding a lower energy for the whole system and a better bond energy. On the other hand, if we could keep the interaction frozen while mixing to a small extent orbitals having *p*-character with the 1*s* orbital in order to obtain a quantum-mechanical description of the polarization, the energy would increase because the *lowest* electronic energy for the free atoms occurs for the pure 1*s* atomic orbital. Actual calculations on saturated hydrocarbons [13] show that for vicinal interactions E_0' is at least two orders of magnitude smaller than $\Delta E^{(1)}$ and has a rather peculiar dependence on the relative orientation of the two groups.

According to Eq. (3.18) the second term in Eq. (5.4) may be written as the sum of two parts. In the first part,

$$2S^2(1-S^2)^{-1}(H^{\mathrm{A}}+H^{\mathrm{B}}), \tag{5.6}$$

the diagonal elements of the Hamiltonian are weighted with the extra-charge $2S^2(1-S^2)^{-1}$ present in each polarized group. Because

$$H^{\mathrm{A}} = \sum_{\mu,\mu'} C_\mu^* H_{\mu\mu'} C_{\mu'}, \qquad H^{\mathrm{B}} = \sum_{\nu,\nu'} C_\nu^* H_{\nu\nu'} C_{\nu'} \tag{5.7}$$

are expected to be negative and $S<1$, this term turns out to be negative, representing a *lowering* of the energy of the composite system A + B. Hence the extra-charge pushed onto each group acts so as to screen the interaction, smoothing repulsion wherever stronger. In the second part,

$$-2S(1-S^2)^{-1}(H^{\mathrm{AB}}+H^{\mathrm{BA}}), \tag{5.8}$$

---

[7] The total polarization energy may be defined as the energy lowering in going from zero-order group functions over to SCF-group functions.

where

$$H^{AB} = \sum_{\mu,\nu} C_\mu^* H_{\mu\nu} C_\nu , \qquad H^{BA} = H^{AB\dagger} \tag{5.9}$$

are the off-diagonal terms of H representing the interaction between the *polarized* groups A and B. Arising from typical cross-terms in the Hamiltonian this contribution depends strongly on the overlap between the charge clouds belonging to different groups. Insofar as its sign is concerned we see that it will describe repulsion or attraction depending on the sign of the intergroup overlap S and the cross-terms of H. When spherical orbitals are used to construct localized electron groups, $(H^{AB}+H^{BA})$ will be negative, S will be positive, and this term will be positive, describing repulsion between the two groups (e.g. two He atoms interacting in their ground state). But if strongly directed AO's (e.g. p-functions in the atomic hybrids) are embodied into the localized orbitals, $(H^{AB}+H^{BA})$ and S may be of both signs as well, and this term will describe repulsion or attraction depending on the relative orientation of the two groups.

According to Eq. (3.18) we obtain a partition of $\Delta E^{(1)}$ into interatomic components

$$\Delta E^{(1)} = \sum_{\mu,\nu} E_{\mu\nu} , \tag{5.10}$$

where

$$E_{\mu\nu} = \tilde{P}_{\mu\nu}(H_{\nu\mu} - H^A S_{\nu\mu}) + \tilde{P}_{\nu\mu}(H_{\mu\nu} - H^B S_{\mu\nu}) \tag{5.11}$$

represents the contribution to $\Delta E^{(1)}$ arising from ϕ_μ (an hybrid atomic orbital belonging to A) and ϕ_ν (an hybrid atomic orbital belonging to B).

The interaction between pairs of atomic orbitals belonging to different electron groups is thus seen to depend on the whole system through the bond-orders $\tilde{P}_{\mu\nu}$.

6. Concluding Remarks

The simple theory outlined in the preceding Sections shows that for neutral systems the main body of the short-range interaction takes place through the overlap arising between nonorthogonal electron groups. For closed-shell fragments the consequent distortion of the electron density generally results in a decrease of charge in the overlap region and in an increase of charge in the region of the component groups. These conclusions are similar to those obtained by Salem [14], who investigated short-range forces on the basis of the Hellmann-Feynman theorem.

It is of interest to notice that the density of the composite system A + B, Eq. (2.12), may be also written in the alternative way

$$P(1;1) = P_0(1;1) + \Delta P(1;1) , \tag{6.1}$$

where

$$P_0(1;1) = 2(|\Phi^A|^2 + |\Phi^B|^2) \tag{6.2}$$

is the density of *undistorted* groups (except for the small second-order polarization), and

$$\Delta P(1;1) = 2(1-S^2)^{-1} \left[S^2(|\Phi^A|^2 + |\Phi^B|^2) - S(\Phi^A\Phi^{B*} + \Phi^B\Phi^{A*})\right] \tag{6.3}$$

is that part of the actual density which describes the distortion in the electron distribution. Since the integral of the *distortion density* $\Delta P(1;1)$ over the whole electron space vanishes,

$$\int \Delta P(1;1)\,dv_1 = 0\,, \tag{6.4}$$

we see that the largest contribution to the penetration energy, $\Delta E^{(1)}$, originates from a density which, although giving point-by-point contributions to the electron population, does not give contribution to the overall negative charge. This is because the same amount of normalized charge weights different parts of the Hamiltonian, diagonal ("unperturbed") terms occurring in Eq. (5.6) and off-diagonal ("perturbations") terms in Eq. (5.8). The polarization of the localized orbitals introduced in a self-consistent way in Section 4 does improve the first approximation to the interaction energy by allowing the component charge clouds to rearrange themselves so as to minimize the total energy and reduce the effective interaction.

Since no expansion whatsoever has been involved in our previous discussion, the theory is not strictly limited to regions of small orbital overlap, being appropriate in all cases where it is meaningful to distinguish between separate electron pairs. It is suitable, for instance, to study geminal as well as vicinal interactions in polyatomic molecules. Interactions between *geminal* pairs, namely those electron pairs which are directly connected, are of interest in understanding molecular vibrations, while the interactions between electron pairs not directly connected (*vicinal* pairs) should be responsible for most of the conformational properties of polyatomic molecules. In this last case the orientation dependence of the short-range interaction through the overlap between different vicinal groups is expected to play a fundamental role.

Within the given assumptions, the theory developed here does not depend on the explicit form of the matrix elements of the Hamiltonian, so that different levels of approximation are possible as well, which should allow a certain degree of flexibility in dealing with the applications.

Acknowledgements. The research described in this paper has been partly supported by the Italian National Research Council (C. N. R.) through the Center of Theoretical Chemistry. The author gratefully acknowledges the award of a C. N. R. fellowship during 1969, and is deeply indebted with Prof. Roy McWeeny for the warm hospitality and the useful discussions at the University of Sheffield.

References

1. Hurley, A. C., Lennard-Jones, J. E., Pople, J. A.: Proc. Roy. Soc. (London) A **220**, 446 (1953).
2. Parr, R. G., Ellison, F. O., Lykos, P. G.: J. chem. Physics **24**, 1106 (1956).
3. Parks, J. M., Parr, R. G.: J. chem. Physics **28**, 335 (1958).
4. McWeeny, R.: Proc. Roy. Soc. (London) A **253**, 242 (1959).
5. — Sutcliffe, B. T.: Proc. Roy. Soc. (London) A **275**, 103 (1963).
6. Magnasco, V., Musso, G. F., McWeeny, R.: J. chem. Physics **47**, 4617 (1967).
7. Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) A **235**, 537 (1956).
8. Magnasco, V.: Unpublished results (1967).
9. Compare the corresponding formulae, given in the orthogonal case, by (a) Löwdin, P. O.: J. chem. Physics **19**, 1396 (1951); and (b) McWeeny, R.: Rev. mod. Physics **32**, 335 (1960).

10. McWeeny, R.: Uppsala Univ. Quantum Chem. Group, Tech. Note n. 50, January 15, 1959 (unpublished). See also the Appendix in Ref. [5].
11. The value obtained when a full configurational interaction among the many-electron basis functions was allowed for. See Magnasco, V., Musso, G. F.: J. chem. Physics **47**, 1723 (1967).
12. Rosen, N.: Physic. Rev. **38**, 2099 (1931).
13. Magnasco, V., Musso, G. F.: J. chem. Physics, in press. Part III.
14. Salem, L.: Proc. Roy. Soc. (London) A **264**, 379 (1961).
15. Van Duijneveldt, F. B., Murrell, J. N.: J. chem. Physics **46**, 1759 (1967).

Prof. Dr. V. Magnasco
Istituto di Chimica Industriale
Università di Genova
Via Pastore, 3
I-16132 Genova, Italy