THE QUANTUM MECHANICS OF COHESION

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Dedicated to the memory of Professor Jaroslav Koutecký.

We consider the fundamental problem of "what makes atoms stick together in molecules, crystals, or clusters?" The Heitler and London paper (1927) on the hydrogen molecule marked a first attempt to discuss, in terms of quantum mechanics, the interaction of two atoms with unpaired spins. The aim of this note is to show how the primitive concepts used eighty years ago still retain a certain validity even in a much more general context. We consider in fact the interaction of two arbitrary systems, each with a resultant spin angular momentum, and show how the interaction energy depends on the scalar product of the two resultants. The actual nature of the two systems is irrelevant: they may be atoms, molecules, or ionic species of any kind each described by a wave function which may be, in principle, exact. This provides a first step in the formulation of any general theory of cohesion.

Keywords: Cohesion; Intermolecular interaction; Electron density; Density matrix; Spin coupling; Hamiltonian; Quantum chemistry.

Jaroslav Koutecký will always be remembered as one of the founders of quantum chemistry in the Czech Republic. Throughout his life he grappled with the fundamental problem of "what makes atoms stick together in molecules or clusters?" and his many outstanding publications testify to the success of this enterprise. The present work, affectionately dedicated to his memory, treats one aspect of this very general problem.

The famous paper of Heitler and London[1] provided a first step towards answering the question in terms of quantum mechanics: if the electrons on two atoms have their spins coupled antiparallel (giving a singlet state) they can provide an "electron-pair" bond, while if they are parallel coupled (giving a triplet state) the interaction will be repulsive at all distances. An interpretation of the origin of the interaction, in terms of forces acting on the nuclei, had to await the formulation of the Hellmann–Feynman theorem, first demonstrated by Hellmann[2] and rediscovered by Feynman[3]. The theo-

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rem states that these forces are exactly what one would expect from classical physics, for nuclei embedded in a ‘charge cloud’ of density $-eP(\mathbf{r})$, where $P(\mathbf{r})$ is the probability density for finding an electron at point $\mathbf{r}$, just as if the electronic charge $(-e)$ was ‘smeared out’ into a continuous distribution of negative charge. This interpretation is nowadays universally accepted.

Figure 1 shows the power of the density concept, in the context of the hydrogen molecule calculation: the energy curves on the left provide no simple picture of the origin of H–H interactions. But the build-up of negative charge in the region between the nuclei gives a graphic interpretation of the singlet state bonding, while its depletion in the triplet state clearly corresponds to repulsion at all distances.

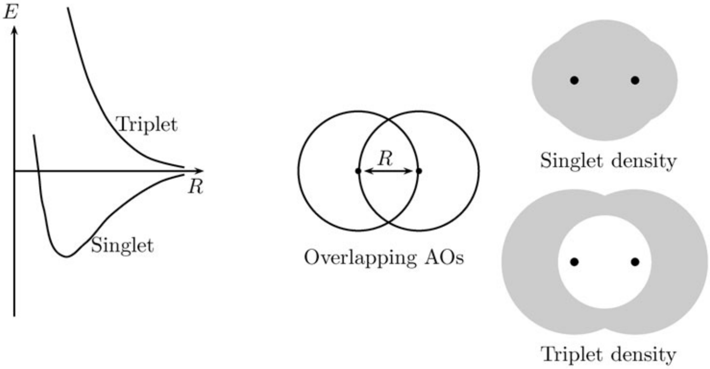

FIG. 1
Singlet and triplet states of H_2 (Heitler and London[1])

In this paper we explore, in a very general way, the link between the two points of view: interactions in terms of alternative spin couplings, or in terms of differences of electron density.

THE INTERACTION OF TWO SYSTEMS

Suppose we have two systems, A and B, with given wave functions – possibly ‘exact’[+], $\Psi_{\mathrm{A}a}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_{N_\mathrm{A}})$ and $\Psi_{\mathrm{B}b}(\mathbf{x}_{\bar{1}},\mathbf{x}_{\bar{2}},\ldots,\mathbf{x}_{\bar{N}_\mathrm{B}})$. Here $\mathbf{x}_n$ stands for the space-spin variables of electron n and the numbering is such that $\bar{n} = n + N_\mathrm{A}$ will label the electrons of the second system (B); p will serve as a general label. The composite subscript Aa is read as “system A in state a” and simi-

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[+] The term is used with its usual meaning, implying ‘clamped nuclei’ and ‘non-relativistic’.

larly for system B; when the two systems are spin degenerate, the label *a*, for example, might stand for one of the $2S_A + 1$ values of M_A ($= S_A, S_A - 1, \ldots, -S_A$), the spin *z*-component.

For two infinitely remote systems, the product $\Psi_{Aa}\Psi_{Bb}$ will then be a virtually exact wave function, with energy eigenvalue $E = E^A + E^B$ a sum of the energies of the separate systems. When the systems are not remote, it is important to recognize the Pauli principle, making all permutations of the electronic variables and combining the results with ± signs to obtain a properly antisymmetric wave function.

The wave function for the composite system A + B may then be written

$$\Psi_\kappa(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = K\mathsf{A}[\Phi_{Aa}(\mathbf{x}_1, \ldots, \mathbf{x}_{N_A})\Phi_{Bb}(\mathbf{x}_{\bar{1}}, \ldots, \mathbf{x}_{\bar{N}_B})] \qquad (\bar{r} = r + N_A) \tag{1}$$

where the label κ indicates a particular choice of the individual group states, in this case A*a* and B*b*, *K* is simply a normalizing factor.

The antisymmetrizer, for all $N = N_A + N_B$ electrons, is usually written (normalized so the $\mathsf{A}^2 = \mathsf{A}$)

$$\mathsf{A} = (N!)^{-1} \sum_{\mathsf{P}} \epsilon_{\mathsf{P}} \mathsf{P} \tag{2}$$

where $\epsilon_{\mathsf{P}} = \pm 1$ according to the parity (even or odd) of P. This may be rewritten as

$$\mathsf{A} = \frac{N_A!N_B!}{(N_A + N_B)!} \mathsf{A}'\mathsf{A}_A\mathsf{A}_B \tag{3}$$

where A_A and A_B are antisymmetrizers for the separate systems, while A' is a sum of transpositions of variables between the A and B systems. The total transposition operator, for single exchanges,

$$\mathsf{T}_1 = \sum_i \sum_{\bar{j}} (i, \bar{j}) \tag{4}$$

is a sum of single transpositions $(i, \bar{j})$ for all choices of $\mathbf{x}_i$ in Φ_{Aa} and $\mathbf{x}_{\bar{j}}$ in Φ_{Bb}. Similar sums can be defined for multiple exchanges involving *n* pairs of variables.

When the system wave functions are individually antisymmetric, the operators A_A and A_B in (*3*) can each be replaced by unity and the all-electron antisymmetrizer becomes simply a sum over transpositions, one at a time, two at a time, etc., plus the unit operator (no transpositions). The factor K is then conveniently chosen so that the functions are normalized when A and B are remote. In that case

$$\langle \Psi_\kappa | \Psi_\kappa \rangle = K(N_A\,!N_B\,!/\,N\,!)\langle \Phi_{Aa}\Phi_{Bb} | \Phi_{Aa}\Phi_{Bb} \rangle$$

leads at once to

$$K = (N_A\,!N_B\,!/\,N\,!)^{-1/2}\,. \tag{5}$$

To allow for spin degeneracy, the wave function for the whole system will have to be written as a linear combination of terms like (*1*), with coefficients determined by solving secular equations, or from symmetry considerations. We therefore need to evaluate matrix elements of the Hamiltonian H between functions of type (*1*); and it is well known (see, for example, McWeeny[4]) that the results can be given in terms of a small number of density matrices.

The one-electron density matrix for Ψ_κ is

$$\rho_1(\kappa\kappa|\mathbf{x};\mathbf{x}') = N\int \Psi_\kappa(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)\,\Psi^*{}_\kappa(\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)\mathrm{d}\mathbf{x}_2\ldots\mathbf{x}_N \tag{6}$$

where the variables $\mathbf{x}$, $\mathbf{x}'$ (without the label ‘1’) refer to two generic space-spin points, not to a particular labelled ‘electron 1’, and the integrations are over the last $N - 1$ variables alone. There is a corresponding ‘transition’ density matrix, connecting Ψ_κ with $\Psi_{\kappa'}$, obtained on replacing $\Psi^*{}_\kappa$ in (*6*) by $\Psi^*{}_{\kappa'}$, denoted by $\rho_1(\kappa\kappa'|\mathbf{x};\mathbf{x}')$.

In dealing with operators which do not involve spin, it is useful to define a spinless analogue of (*6*), simply by putting $s' = s$ in the variable $\mathbf{x}'$ and integrating over s alone to obtain in general

$$P_1(\kappa\kappa'|\mathbf{r};\mathbf{r}') = \int_{s'=s} \rho_1(\kappa\kappa'|\mathbf{x};\mathbf{x}')\mathrm{d}s\,. \tag{7}$$

Corresponding two-electron quantities may be defined in a similar way.

Matrix elements of all the operators which appear in the Hamiltonian as symmetric sums, typically $\sum_{p=1}^{N} \mathsf{h}(p)$ and $\sum_{p \neq q=1}^{N} g(p,q)$, are readily obtained in terms of the density matrices. Thus, for example, the expectation value of the one-electron operator sum is[++]

$$\langle \Sigma \mathsf{h}(p) \rangle = \langle \Psi_\kappa | \Sigma \mathsf{h}(p) | \Psi_\kappa \rangle = \int_{\mathbf{x}' = \mathbf{x}} \mathsf{h} \rho_1 (\kappa\kappa | \mathbf{x}; \mathbf{x}') \mathrm{d}\mathbf{x} \qquad (8)$$

where the notation $\mathbf{x}' = \mathbf{x}$ means the integration is completed after the operator has worked on the function of $\mathbf{x}$; this defines the 'integral trace' operation. The off-diagonal matrix element $\langle \Psi_{\kappa'} | \Sigma \mathsf{h} | \Psi_\kappa \rangle$ follows in the same way from $\rho_1(\kappa\kappa'|\mathbf{x};\mathbf{x}')$. It should be noted that the order of the functions Ψ_κ and $\Psi_{\kappa'}$ is important: the primed function, on the left in the matrix element, appears on the right in the density matrix – being the complex conjugate function in each case. The operator h works always on the unprimed variable $\mathbf{x}$. It is important to remember the general form of $\rho_1(\kappa\kappa'|\mathbf{x};\mathbf{x}')$ when spin variables are explicitly included. For any given state $\kappa = \kappa'$, dropping the redundant state labels, expectation values of one-electron operators follow from

$$\rho_1(\mathbf{x};\mathbf{x}') = P_{\alpha,\alpha}(\mathbf{r};\mathbf{r}')\alpha(s)\alpha^*(s') + P_{\alpha,\beta}(\mathbf{r};\mathbf{r}')\alpha(s)\beta^*(s') + \\ + P_{\beta,\alpha}(\mathbf{r};\mathbf{r}')\beta(s)\alpha^*(s') + P_{\beta,\beta}(\mathbf{r};\mathbf{r}')\beta(s)\beta^*(s') \qquad (9)$$

this being the integral-operator form of the density operator ρ_1, whose effect on any space-spin function $\psi(\mathbf{x})$ is given by $\rho_1\psi(\mathbf{x}) = \int \rho_1(\mathbf{x};\mathbf{x}')\psi(\mathbf{x}')\mathrm{d}\mathbf{x}'$. For any state of definite spin, however, only the α,α and β,β components are non-zero. On using (*7*),

$$P_1(\mathbf{r};\mathbf{r}') = P_{\alpha,\alpha}(\mathbf{r};\mathbf{r}') + P_{\beta,\beta}(\mathbf{r};\mathbf{r}') \qquad (10)$$

and on using the analogue of (*8*), with spin included, to evaluate the expectation value of the total spin z-component, we obtain

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[++] Summation ranges are usually obvious and will not be indicated.

$$\langle \mathrm{S}_z \rangle = \int_{\mathbf{x}'=\mathbf{x}} \mathrm{S}_z \rho_1(\mathbf{x};\mathbf{x}')\mathrm{d}\mathbf{x} = \int Q_z(\mathbf{r};\mathbf{r})\mathrm{d}\mathbf{r} \qquad (11)$$

where, generally,

$$Q_z(\mathbf{r};\mathbf{r}') = \frac{1}{2}[P_{\alpha,\alpha}(\mathbf{r};\mathbf{r}') - P_{\beta,\beta}(\mathbf{r};\mathbf{r}')] \qquad (12)$$

and has a diagonal element^{+++} which is the density of spin angular momentum around the z-axis. Thus

$$P_1(\mathbf{r}) = P_\alpha(\mathbf{r}) + P_\beta(\mathbf{r}) \qquad (13)$$

$$Q_S(\mathbf{r}) = \frac{1}{2}[P_\alpha(\mathbf{r}) + P_\beta(\mathbf{r})] \qquad (14)$$

are, respectively, the electron density and the spin density.

It is convenient in what follows to express the density matrices themselves as expectation values, by defining an operator $\mathrm{O}_1(p)$ which (when it appears in a matrix element) replaces $\mathbf{x}_p$ in the Ψ-factor by $\mathbf{x}$; and in the Ψ^*-factor by $\mathbf{x}'$. Thus

$$\begin{aligned}\langle \Sigma \mathrm{O}_1(p)\rangle &= N\langle \Psi_\kappa | \Sigma \mathrm{O}_1(1) | \Psi_\kappa \rangle = \\ &= N\int \Psi_\kappa(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N)\Psi^*_\kappa(\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)\mathrm{d}\mathbf{x}_2\ldots\mathbf{x}_N \qquad (15)\end{aligned}$$

in agreement with (*6*). (The factor N results from the fact that (owing to antisymmetry in the variables $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N$) every term in $\Sigma\mathrm{O}_1(p)$ will give an identical contribution to the matrix element.)

Since the wave functions for systems A and B will in general have a non-zero overlap, the composite functions defined in (*1*) will usually be neither normalized nor orthogonal. Let us distinguish the corresponding density functions by adding a tilde. To get the electron density for two general systems, when they begin to interpenetrate, we shall have to evaluate the

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+++ In referring to diagonal elements we drop both the second variable and the corresponding spin index.

overlap integrals $\langle\Psi_{\kappa'}|\Psi_{\kappa}\rangle$ and corresponding one-electron density contributions. To obtain the energy we also need the two-electron or 'pair' density ρ_2. This will not be required explicitly in the present analysis, where attention is focussed on the electron density alone, but will be indicated for completeness.

With the antisymmetrized, but un-normalized, functions of type (*1*) we must therefore evaluate

$$\tilde{\rho}_0(\kappa\kappa') = \langle\Psi_{\kappa'}|\Psi_{\kappa}\rangle \qquad (16)$$

$$\tilde{\rho}_1|\kappa\kappa'|\,\mathbf{x}_1\,;\mathbf{x}'_1) = \langle\Psi_{\kappa'}|\sum_{p}\mathrm{O}_1(p)|\Psi_{\kappa}\rangle \qquad (17)$$

$$\tilde{\rho}_2\,|\kappa\kappa'|\,\mathbf{x}_1\,,\mathbf{x}_2\,;\mathbf{x}'_1\,,\mathbf{x}'_2\,) = \langle\Psi_{\kappa'}|\sum_{p\neq q}\mathrm{O}_1(p)\mathrm{O}_2(q)|\Psi_{\kappa}\rangle\,. \qquad (18)$$

These density functions will completely determine all matrix elements of one- and two-electron operator sums between functions of type (*1*). Corresponding spinless quantities follow at once on identifying spin variables s, s' and integrating over s, as in (*7*).

It will be noticed at this point that subscripts have been added to the variables in the density matrices simply to distinguish first and second variables – not indicating 'electron 1' and 'electron 2'. The Pauli principle has been respected from the start by insisting on the use of fully antisymmetric wave functions.

REDUCTION OF THE MATRIX ELEMENTS

Explicit and general results for all three densities have been given elsewhere[5] and will not be repeated here: one example will be sufficient. To reduce (*16*) we introduce the antisymmetrizer in the form (*4*) and take only up to single-interchange terms in $\mathrm{A}' = \mathrm{I} - \mathrm{T}_1 + \mathrm{T}_2 + \ldots$. Thus, with $\Psi_\kappa = K\mathrm{A}[\Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b}]$ it follows easily that

$$\tilde{\rho}_0(\kappa\kappa') = \langle\Psi_{\kappa'}|\Psi_{\kappa}\rangle = \langle\Phi_{\mathrm{A}a'}\Phi_{\mathrm{B}b'}|\mathrm{A}'|\Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b}\rangle \qquad (19)$$

using the 'normalization' given in (*5*).

On putting $\mathrm{A}' \approx \mathrm{I} - \mathrm{T}_1$, the term $\mathrm{T}_1 = \sum_{i,\bar{j}}(i,\bar{j})$ gives a contribution

$$\langle \Phi_{\mathrm{A}a'}\Phi_{\mathrm{B}b'} | \sum_{i,\bar{j}} (i,\bar{j}) | \Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b} \rangle = N_{\mathrm{A}} N_{\mathrm{B}} \langle \Phi_{\mathrm{A}a'}\Phi_{\mathrm{B}b'} | (1,\bar{1}) | \Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b} \rangle$$

where 1, $\bar{1}$ refer to the first variables in $\Phi_{\mathrm{A}a}$ and $\Phi_{\mathrm{B}b}$, respectively, the factor $N_{\mathrm{A}}N_{\mathrm{B}}$ resulting from the N_{A} choices of i and the N_{B} choices of $\bar{j}$. From the definition of the one-electron density matrix in (*6*) et seq., this last result may be written alternatively as

$$\langle \Phi_{\mathrm{A}a'}\Phi_{\mathrm{B}b'} | \sum_{i,\bar{j}} (i,\bar{j}) | \Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b} \rangle = \int \rho_1^{\mathrm{A}}(aa' | \mathbf{x}_{\bar{1}} ; \mathbf{x}_1) \rho_1^{\mathrm{B}}(bb' | \mathbf{x}_1 ; \mathbf{x}_{\bar{1}}) \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_{\bar{1}} \ .$$

Equation (*19*) now yields

$$\tilde{\rho}_0(\kappa\kappa') = \delta_{aa'}\delta_{bb'} - \int \rho_1^{\mathrm{A}}(aa' | \mathbf{x}'_1 ; \mathbf{x}_1) \rho_1^{\mathrm{B}}(bb' | \mathbf{x}_1 ; \mathbf{x}'_1) \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}'_1 \qquad (20)$$

where the name of the dummy variable $\mathbf{x}_{\bar{1}}$ has been changed to $\mathbf{x}'_1$ for typographical convenience.

The one- and two-electron densities in (*17*) and (*18*) may be reduced in a similar way, the full expansions being given elsewhere[5].

The last step in the reduction is the separation of space and spin variables. In general, for two systems with total-spin quantum numbers S_{A}, S_{B}, the wave functions $\Psi_\kappa = K\mathsf{A}[\Phi_{\mathrm{A}a}\Phi_{\mathrm{B}b}]$ will have degeneracy $(2S_{\mathrm{A}} + 1)(2S_{\mathrm{B}} + 1)$, corresponding to the quantum numbers M_{A}, M_{B}. These will serve to label different multiplet components in place of the indices a, b. The degeneracy is resolved on mixing the composite functions to get a resultant spin state with quantum numbers S, M, with S going from $S_{\mathrm{A}} + S_{\mathrm{B}}$ to $|S_{\mathrm{A}} - S_{\mathrm{B}}|$ in integer steps. A general spin-coupled product function will then be

$$\Phi_{S,M} = (-1)^{(S_{\mathrm{B}} - S_{\mathrm{A}} - M)} (2S+1)^{1/2} \sum_{M_{\mathrm{A}},M_{\mathrm{B}}} \Phi_{\mathrm{A},M_{\mathrm{A}}} \Phi_{\mathrm{B},M_{\mathrm{B}}} \times \begin{pmatrix} S_{\mathrm{A}} & S_{\mathrm{B}} & S \\ M_{\mathrm{A}} & M_{\mathrm{B}} & M \end{pmatrix}$$

where the round-bracket quantity is the coupling coefficient, expressed as a Wigner 3j-symbol (see, for example, Edmonds[6] for the usual phase conventions). A satisfactory wave function follows on normalizing and antisymmetrizing

$$\Psi_{S,M} = K\mathsf{A}\Phi_{S,M} \qquad (21)$$

where K will again be chosen so that $\Psi_{S,M}$ is normalized for infinite separation of A and B and takes the value $K = (N!/N_{\rm A}!N_{\rm B}!)^{1/2}$.

Again we choose only one example, that corresponding to (*16*), passing directly to the spinless quantity $\tilde{P}_0$ which follows after a final spin integration. This becomes

$$\tilde{P}_0 = \langle \Psi_{S,M} | (\mathsf{I} - \mathsf{T}_1 + \ldots) | \Psi_{S,M} \rangle \qquad (22)$$

and will give a zero-interchange term unity, followed by the single-interchange term

$$\langle \Psi_{S,M} | \mathsf{T}_1 | \Psi_{S,M} \rangle = \langle \Psi_{S,M} | \sum_{i,\bar{j}} (i,\bar{j})_{\rm space} (i,\bar{j})_{\rm spin} | \Phi_{S,M} \rangle \,. \qquad (23)$$

On using the Dirac identity

$$(i,\bar{j})_{\rm spin} \equiv \frac{1}{2}[1 + 4\mathbf{S}(i)\cdot\mathbf{S}(\bar{j})]$$

and noting there are $N_{\rm A}N_{\rm B}$ equivalent choices of the two summation indices, the single-interchange term (*23*) becomes

$$\frac{1}{2} N_{\rm A} N_{\rm B} \langle \Psi_{S,M} | (1,\bar{1})_{\rm space} | \Phi_{S,M} \rangle + 2 N_{\rm A} N_{\rm B} \langle \Phi_{S,M} | (1,\bar{1})_{\rm space} \mathbf{S}(1)\cdot\mathbf{S}(\bar{1}) | \Psi_{S,M} \rangle \,. \qquad (24)$$

The two matrix elements in this result may be dealt with separately: the first leads to a product $N_{\rm A}^{-1}\rho_1^{\rm A}(\mathbf{x}_1;\mathbf{x}_1)N_{\rm B}^{-1}\rho_1^{\rm B}(\mathbf{x}_{\bar{1}};\mathbf{x}_{\bar{1}})$, followed by one interchange of space variables and a final spin integration. This becomes

$$\text{Term 1} = \frac{1}{2}\int P_1^{\rm A}(\mathbf{r}_{\bar{1}};\mathbf{r}_1) P_1^{\rm B}(\mathbf{r}_1;\mathbf{r}_{\bar{1}}) {\rm d}\mathbf{r}_1 {\rm d}\mathbf{r}_{\bar{1}} \,. \qquad (25)$$

In the second matrix element, the scalar product may be written in spherical tensor form as

$$\mathbf{S}(1)\cdot\mathbf{S}(\bar{1}) = \sum_q (-1)^q \mathsf{S}_q(1)\mathsf{S}_{-q}(\bar{1})$$

where the tensor index takes the values $q = 0, \pm 1$ ($\mathbf{S}$ being of rank 1). We must then evaluate

$$\langle \Psi_{S,M} | (1,\bar{1})_{\text{space}} \sum_q (-1)^q \mathrm{S}_q(1)\mathrm{S}_{-q}(\bar{1}) | \Psi_{S,M} \rangle \tag{26}$$

in which $\mathrm{S}_q(1)$ works only on the A-factor $\Phi_{\mathrm{A},M_\mathrm{A}}$ and S_{-q} only on the B-factor $\Phi_{\mathrm{B},M_\mathrm{B}}$. That being so, the matrix element between spin-coupled functions can be expressed as one between single products (see, for instance, Edmonds^6) evaluated for a particular choice of the quantum numbers M_A, M_B. Thus we find

$$\langle \Psi_{S,M} | (1,\bar{1})_{\text{space}} \sum_q (-1)^q \mathrm{S}_q(1)\mathrm{S}_{-q}(\bar{1}) | \Psi_{S,M} \rangle =$$

$$= (-1)^{(S_\mathrm{B}-S_\mathrm{A}+S)} \begin{Bmatrix} S_\mathrm{A} & S_\mathrm{B} & S \\ S_\mathrm{B} & S_\mathrm{A} & 1 \end{Bmatrix} \begin{pmatrix} S_\mathrm{A} & 1 & S_\mathrm{A} \\ -S_\mathrm{A} & 0 & S_\mathrm{A} \end{pmatrix}^{-1} \begin{pmatrix} S_\mathrm{B} & 1 & S_\mathrm{B} \\ -S_\mathrm{B} & 0 & S_\mathrm{B} \end{pmatrix}^{-1} \times$$

$$\times \langle \Phi_{\mathrm{A},S_\mathrm{A}} \Phi_{\mathrm{B},S_\mathrm{B}} | (1,\bar{1})_{\text{space}} \mathrm{S}_z(1)\mathrm{S}_z(\bar{1}) | \Phi_{\mathrm{A},S_\mathrm{A}} \Phi_{\mathrm{B},S_\mathrm{B}} \rangle \tag{27}$$

where we have chosen $M_\mathrm{A} = S_\mathrm{A}$, $M_\mathrm{B} = S_\mathrm{B}$, in the product functions and $q = 0$ (spin z-component). The factor in curly brackets is a Wigner 6j-symbol.

On multiplying by $2N_\mathrm{A}N_\mathrm{B}$ and performing the space and spin integrations (*27*) takes the form

$$\text{Term 2} = 2f_1(S_\mathrm{A}, S_\mathrm{B}, S) \int Q_S^\mathrm{A}(\mathbf{r}';\mathbf{r}) Q_S^\mathrm{B}(\mathbf{r};\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{28}$$

where $Q_S^\mathrm{A}(\mathbf{r}';\mathbf{r})$ and $Q_S^\mathrm{B}(\mathbf{r};\mathbf{r}')$ are spin density matrices, which arise when the spin operator S_z works on the one-electron density ρ_1. Thus, in general,

$$Q_S(\mathbf{r};\mathbf{r}') = \int_{s'=s} \mathrm{S}_z \rho_1(\mathbf{x};\mathbf{x}')\mathrm{d}s\mathrm{d}s' \tag{29}$$

for the ‘standard state’, chosen above, with $M = S$. The ‘diagonal element’ of this quantity, obtained by putting $\mathbf{r}' = \mathbf{r}$, gives the density of spin angular momentum, around the z-axis, at point $\mathbf{r}$. It has been fully discussed elsewhere^4, along with other spin-dependent densities, and has been encountered already in (*14*) where it appeared as half the difference of the up-spin and down-spin components of the electron density $P(\mathbf{r}) = P_\alpha(\mathbf{r}) + P_\beta(\mathbf{r})$.

The numerical coefficient in (*28*) depends only on the nature of the spin coupling and may be expressed as an expectation value of the scalar product operator $\mathbf{S}^{\mathrm{A}} \cdot \mathbf{S}^{\mathrm{B}}$ in a spin state $\Theta_{S,M}$ with quantum numbers S, M. In fact[5]

$$f_1(S_{\mathrm{A}}, S_{\mathrm{B}}, S) = (S_{\mathrm{A}} S_{\mathrm{B}})^{-1} \langle \Theta_{S,M} | \mathbf{S}^{\mathrm{A}} \cdot \mathbf{S}^{\mathrm{B}} | \Theta_{S,M} \rangle \,. \tag{30}$$

It only remains to collect the terms in (*25*) and (*28*), which will give $\tilde{P}_0$ in the form (1 – Term 1 – Term 2), and to extend the analysis to $\tilde{P}_1$, again including all terms up to single interchanges. The results are recorded below

$$\begin{aligned} \tilde{P}_0 &= 1 - \frac{1}{2} \int P_1^{\mathrm{A}}(\mathbf{r}';\mathbf{r}) P_1^{\mathrm{B}}(\mathbf{r};\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' - \\ &\quad - 2 f_1(S_{\mathrm{A}}, S_{\mathrm{B}}, S) \int Q_S^{\mathrm{A}}(\mathbf{r}';\mathbf{r}) Q_S^{\mathrm{B}}(\mathbf{r};\mathbf{r}') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \end{aligned} \tag{31}$$

which is needed for normalization, and $\tilde{P}_1$, which gives the normalized one-electron density matrix as $P_1(\mathbf{r};\mathbf{r}') = \tilde{P}_0^{-1} \tilde{P}_1(\mathbf{r};\mathbf{r}')$, where

$$\begin{aligned} \tilde{P}_1(\mathbf{r};\mathbf{r}') &= P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') - \frac{1}{2} \int P_1^{\mathrm{A}}(\mathbf{r}_1';\mathbf{r}') P_1^{\mathrm{B}}(\mathbf{r};\mathbf{r}_1') \mathrm{d}\mathbf{r}_1' - \\ &\quad - 2 f_1(S_{\mathrm{A}}, S_{\mathrm{B}}, S) \int Q_S^{\mathrm{A}}(\mathbf{r}_1';\mathbf{r}') Q_S^{\mathrm{B}}(\mathbf{r};\mathbf{r}_1') \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}_1' - \\ &\quad - \frac{1}{2} \int P_2^{\mathrm{A}}(\mathbf{r}_1', \mathbf{r}; \mathbf{r}_1, \mathbf{r}') P_1^{\mathrm{B}}(\mathbf{r}_1; \mathbf{r}_1') \mathrm{d}\mathbf{r}_1' - \\ &\quad - 2 f_1(S_{\mathrm{A}}, S_{\mathrm{B}}, S) \int Q_{SL}^{\mathrm{A}}(\mathbf{r}_1', \mathbf{r}; \mathbf{r}_1, \mathbf{r}') Q_S^{\mathrm{B}}(\mathbf{r}_1; \mathbf{r}_1') \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_1' + \\ &\quad + [\text{similar terms with A} \leftrightarrow \text{B}]. \end{aligned} \tag{32}$$

Here Q_{SL} denotes a two-electron analogue of the spin density function defined in (*29*), the spin trace referring to the first of the two variables in the two-electron density $\rho_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2)$; in general

$$Q_{SL}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = \int_{s_1' = s_1} \mathrm{S}_z(1) \rho_2(\mathbf{x}, \mathbf{x}_2; \mathbf{x}', \mathbf{x}_2') \mathrm{d}s_1 \mathrm{d}\mathbf{x}_2 \,.$$

This function determines the spin-orbit coupling in a system and is thus aptly called the “spin-orbit coupling density”.

The one-electron density matrix $P_1(\mathbf{r};\mathbf{r}')$, defined above, gives a completely general expression for the electron density (on putting $\mathbf{r}' = \mathbf{r}$), for any two colliding systems, atoms or molecules, given their exact wave functions in the absence of interaction. In practice it will be necessary to use approximate functions, usually expressed in orbital form, and this will provide a means of defining the region of interpenetration and of discussing the electron density changes taking place.

PARTITIONING OF THE ELECTRON DENSITY

Let us first use a Hartree–Fock approximation to the wave function of each system: this will take the form of a single determinant of spin-orbitals, with doubly-occupied orbitals $\phi_i\alpha,\phi_i\beta$ providing a closed-shell ‘core’ and singly-occupied orbitals $\phi_j\alpha$ providing an open shell in the ‘standard state’ of maximum multiplicity, $M = S$ = half the number of parallel-coupled spins. This approximation is intended only to illustrate the general nature of the results and in no way detracts from the generality of the approach.

For a single determinant of spin-orbitals $\rho_1(\mathbf{x}_1, \mathbf{x}') = \sum_p \psi_p(\mathbf{x})\psi^*_p(\mathbf{x}')$ and it is well known that ρ_1 then determines all other density functions. In particular,

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = \rho_1(\mathbf{x}_1; \mathbf{x}_1')\rho_1(\mathbf{x}_2; \mathbf{x}_2') - \rho_1(\mathbf{x}_2; \mathbf{x}_1')\rho_1(\mathbf{x}_1; \mathbf{x}_2') .$$

Integration of ρ_1 over spin gives the spinless density $P_1(\mathbf{r}_1;\mathbf{r}_2) = P_{\alpha,\alpha}(\mathbf{r}_1;\mathbf{r}_1') + P_{\beta,\beta}(\mathbf{r}_1;\mathbf{r}_1')$ and the standard spin density (*14*), as half the difference of $P_{\alpha,\alpha}$ and $P_{\beta,\beta}$. In what follows it is convenient to define, with an obvious abbreviation

$$P_1 = P_\alpha + P_\beta , \qquad Q_1 = P_\alpha - P_\beta = 2SD_S . \qquad (33)$$

With a similar notation, the spin-orbit coupling function (*3*) is more conveniently replaced by

$$Q_2(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') = 2SD_{SL}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1', \mathbf{r}_2') . \qquad (34)$$

In terms of P_1 and Q_1 it follows easily that

$$P_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) =$$

$$= P_1(\mathbf{r}_1;\mathbf{r}'_1)P_1(\mathbf{r}_2;\mathbf{r}'_2) - \frac{1}{2}[P_1(\mathbf{r}_2;\mathbf{r}'_1)P_1(\mathbf{r}_1;\mathbf{r}'_2) + Q_1(\mathbf{r}_2;\mathbf{r}'_1)Q_1(\mathbf{r}_1;\mathbf{r}'_2)] \qquad (35)$$

while the spin-orbit function becomes

$$Q_2(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}'_1,\mathbf{r}'_2) =$$

$$= Q_1(\mathbf{r}_1;\mathbf{r}'_1)P_1(\mathbf{r}_2;\mathbf{r}'_2) - \frac{1}{2}[P_1(\mathbf{r}_2;\mathbf{r}'_1)Q_1(\mathbf{r}_1;\mathbf{r}'_2) + Q_1(\mathbf{r}_2;\mathbf{r}'_1)P_1(\mathbf{r}_1;\mathbf{r}'_2)]\,. \qquad (36)$$

Let us now introduce two quantities which will measure the degree of overlap between the charge and spin distributions in system A and those in system B.

$$M_P = \int P_1^{\mathrm{A}}(\mathbf{r}_1;\mathbf{r}'_1)P_1^{\mathrm{B}}(\mathbf{r}'_1;\mathbf{r}_1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}'_1 \qquad (37)$$

$$M_Q = \int Q_1^{\mathrm{A}}(\mathbf{r}_1;\mathbf{r}'_1)Q_1^{\mathrm{B}}(\mathbf{r}'_1;\mathbf{r}_1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}'_1 \qquad (38)$$

The integrands in these quantities allow us to define density ‘products’ such as

$$P_1^{\mathrm{A}}Q_1^{\mathrm{B}}Q_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') = \int P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}_1)Q_1^{\mathrm{B}}(\mathbf{r}_1;\mathbf{r}_2)Q_1^{\mathrm{A}}(\mathbf{r}_2;\mathbf{r}')\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \qquad (39)$$

where the intermediate variables follow a ‘chain rule’.

With these definitions the (un-normalized) electron density in the composite system A + B, given in (*32*), takes the form

$$\tilde{P}_1(\mathbf{r};\mathbf{r}') = (1 - \frac{1}{2}M_P)P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') - \frac{1}{2}P_1^{\mathrm{B}}P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') +$$

$$+ \frac{1}{4}P_1^{\mathrm{A}}P_1^{\mathrm{B}}P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') + \frac{1}{4}Q_1^{\mathrm{A}}P_1^{\mathrm{B}}Q_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') -$$

$$- \frac{1}{2}\theta[M_Q P_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}') + Q_1^{\mathrm{B}}Q_1^{\mathrm{A}}(\mathbf{r};\mathbf{r}')] +$$

$$+\frac{1}{4}\theta[P_1^{A}Q_1^{B}Q_1^{A}(\mathbf{r};\mathbf{r}')+Q_1^{A}Q_1^{B}P_1^{A}(\mathbf{r};\mathbf{r}')]+$$

$$+\ [\text{similar terms with A} \leftrightarrow \text{B}] \tag{40}$$

where only θ depends on the spin coupling, being given by

$$\theta=\frac{\langle \mathbf{S}^{A}\cdot\mathbf{S}^{B}\rangle}{S_A S_B}=\frac{S(S+1)-S_A(S_A+1)-S_B(S_B+1)}{2S_A S_B}\ . \tag{41}$$

It is easy to show that the normalized charge density $P_1(\mathbf{r})=\tilde{P}_0^{-1}\tilde{P}_1(\mathbf{r})$ integrates correctly to give the total number of electrons $N = N_A + N_B$. But what concerns us here is how much of the total charge remains distributed as it was in the free systems and how much has gone into the region of overlap between A and B. And the answer is given by separating the terms in $\int\tilde{P}_1(\mathbf{r})\mathrm{d}\mathbf{r}$ into parts referring to the A and B systems alone and those that come jointly from A and B system densities. With neglect of terms involving triple and higher products, the un-normalized density may be written

$$\tilde{P}_1(\mathbf{r})=P_1^{A}(\mathbf{r})+\ldots-\frac{1}{2}P_1^{B}(\mathbf{r})P_1^{A}(\mathbf{r})+\ldots$$

$$+\ P_1^{B}(\mathbf{r})+\ldots-\frac{1}{2}P_1^{A}(\mathbf{r})P_1^{B}(\mathbf{r})+\ldots\ .$$

On multiplying by the normalizing factor $(1-\tfrac{1}{2}M_P-\theta\tfrac{1}{2}M_Q)^{-1}$ the total electron density becomes

$$P=\frac{P_1^{A}+P_1^{B}-P_1^{A}P_1^{B}-\theta Q_1^{A}Q_1^{B}}{1-\tfrac{1}{2}M_P-\tfrac{1}{2}\theta M_Q}\ . \tag{42}$$

The partitioning of the total charge, of $N = N_A + N_B$ electrons, is obtained by integrating over all space: the amount of charge migrating from the separate systems, before interaction, into their region of overlap easily follows as

$$\Delta N = \frac{M_P + \theta M_Q}{1 - \frac{1}{2} M_P - \frac{1}{2}\theta M_Q} . \qquad (43)$$

The analogy with the results of Heitler and London[1] is clear. The extreme values of θ, corresponding to parallel and antiparallel coupling of the total spins of the two systems, follow from (*41*): they are, using S_{A} for the greater of the two spins,

$$\theta_{\max} = 1, \qquad \theta_{\min} = -(1 + S_{\mathrm{A}}) / S_{\mathrm{A}}$$

and the corresponding values of the charge migration are then (to first order in the small quantities M_P, M_Q)

$$\Delta N_{\text{parallel}} = -(M_P + M_Q), \qquad \Delta N_{\text{antiparallel}} = (M_Q + M_P) + (M_Q / S_{\mathrm{A}}) . \qquad (44)$$

For two closed-shell systems, the spin density terms are absent and the interaction leads to repulsion at all distances: this is often described as the "exchange repulsion" between closed-shells, but in fact has nothing to do with electron exchange, arising simply because electron density is 'pushed out' from the overlap region. On the other hand, with non-zero spin densities, θ may take negative values, giving an attraction between the systems, roughly in proportion to the degree of overlap of their spin distributions.

CONCLUSION

It has been shown that the interaction of two systems, atoms or molecules of arbitrary size and complexity, may be described formally in terms of a coupling between their total spins, thus extending and generalizing the simple model first proposed by Heitler and London[1] 80 years ago. In general, the energy of interaction arising from the overlap of the two systems, A and B, may be expressed as the expectation value of a spin Hamiltonian of the form

$$\mathsf{H}_{\text{spin}} = E_0 + E_1 (\mathbf{S}^{\mathrm{A}} \cdot \mathbf{S}^{\mathrm{B}}) + E_2 (\mathbf{S}^{\mathrm{A}} \cdot \mathbf{S}^{\mathrm{B}})^2 + \ldots \qquad (45)$$

within a manifold of pure spin states $|S,M\rangle$. Only the numerical coefficients depend on the many-electron wave functions of the two systems and the series is rapidly convergent in terms of the degree of overlap between their electron and spin distributions.

The present paper has emphasized the qualitative interpretation of the interaction, in terms of the Hellmann–Feynman forces called into play by the electron density changes in the overlap region: it applies only in the early stages of interaction but allows us to discuss quantitatively, and without making approximations of any kind, the factors responsible for cohesion. The basic question is: If two systems collide, will they simply bounce? Or will they stick? And the answer is determined mainly by the spin-coupling factor θ, along with the geometry of the approach configuration, which fixes in turn the overlap parameters M_P and M_Q.

There are many potential applications of the approach. In particular, with much current interest in 'lock and key' chemistry, it is important to be able to discuss, on a rigorous quantum mechanical basis, the encounter between a large molecule A, say, and a small reactant species B. System A may have free-radical character, described by a spin density extending over the whole molecule, and one needs to characterize its response to the attacking reagent. A detailed and accurate energy calculation is often out of the question; but an approach along the lines proposed in this note makes no heavy computational demands, little more than an evaluation of the parameters M_P, M_Q in Partitioning of the Electron Density, which depend only on overlap integrals and can be estimated using quite simple wave functions.

Applications involving the concept of 'molecular similarity' may be found elsewhere[7]. It must be stressed that the present note is concerned only with the close approach of two systems, where their electron distributions interpenetrate and are significantly distorted. More generally, other factors become important, e.g., the polarization and dispersion interactions first identified by London[8]. A more complete discussion, including such terms, is available elsewhere[9] and the whole approach has been illustrated in numerical calculations on some simple dimers[10]. A general review, emphasizing the physical interpretation of the interactions, has been given by Magnasco and McWeeny[11].

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