REVIEWS OF MODERN PHYSICS VOLUME 34, NUMBER 2 APRIL, 1962

The Physical Nature of the Chemical Bond[*][†][‡]

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INTRODUCTION

Formulation of the Problem

As yet, the physical nature of the chemical bond is little understood in many essential details, and the reason for this must be seen in the mathematical difficulties which are encountered in solving molecular quantum-mechanical problems. The older concepts on the subject have suffered from being based on wave functions which, by virtue of their simplicity, permitted plausible interpretations (or so it was hoped), but turned out to be inadequate approximations to the true solutions. The recent progress towards better approxi-

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[*] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[†] Work supported by the National Science Foundation.

[‡] Parts of this paper were presented at the International Conference for Molecular Quantum Mechanics, held in June, 1959, at the University of Colorado, Boulder, Colorado, and at the Symposium of Molecular Structure and Spectroscopy, held in June, 1960, at the Ohio State University, Columbus, Ohio.

mations, on the other hand, is leading to increasingly complicated wave functions whose conceptual meaning is becoming less and less lucid.

While there used to exist hope of arriving at satisfactory results by supplementing mathematically unjustified approximations with chemical and physical intuition in such a way as to achieve an all-around cancellation of errors, it now seems to transpire that *bona fide* solutions of the mathematical problems, based on justified approximations only, cannot be sidestepped if quantitative reliability and unambiguous predictions are to be achieved in the absence of close analogies. It has furthermore become apparent that *bona fide* wave functions must be determined according to methods which are largely influenced by considerations of mathematical practicability and computational efficiency, and that they will have complex appearances of various forms. Thus, there has arisen the need for a uniform and generally applicable procedure of interpretation leading to a meaningful analysis of the physical and chemical significance of molecular wave functions.

In order to formulate such an analysis, it is necessary to define quantities referring to various parts of a given molecule so that total molecular quantities can be broken down into interpretable fragments. The actual value of such definitions depends upon whether analogous quantities assume similar numerical values in analogous situations (e.g., if two different molecules contain parts which for chemical or physical reasons are considered similar in character, then the quantities defined for the analogous portions in the two molecules should have similar values). If such is the case, then it is possible to formulate quantitatively meaningful comparisons of similar bonding situations in different molecules, and to use this information for interpolation and extrapolation to new cases. It is furthermore possible to analyze the physical similarities between different approximations and approaches to a given problem, and to spot "accidental" agreement with experiment. Last, but not least, an interpretation of the kind postulated should contribute towards bridging the gap presently existing between chemical concepts and rigorous mathematical treatments.

The question must be raised whether the isolation of fragments of the total energy, for example, is at all a physically meaningful objective. The answer would appear to be in the affirmative if it turns out that the defined fragments exhibit regular and illuminating behavior. If it should be so that, for series of molecules, the variation of the fragments follows certain curves whose parameters could be found empirically by considering enough members of the series, then these fragments would qualify as observables, or at least semiobservables, from an operational viewpoint.

The partitioning of molecular quantities has to be of a twofold nature. On the one hand, one expects to have available a partitioning into fragments corresponding to various "geographical regions" within the molecule, so that it becomes possible to assign quantitative meanings to such concepts as atoms and bonds within a molecule. On the other hand, one would like to obtain a partitioning according to physical significance so that the binding phenomenon can be quantitatively understood as the cooperative effect of such contributions as long-range Coulombic forces, short-range overlap forces, ionic and polarization effects, etc. The largest terms in such a conjunction of the regional and the physical partitioning have to be something akin to atomic valence states, but the analysis of the quantitatively smaller remainder is just as important in order to obtain an "anatomy of the bonds."

To be sure, the intuitive desire for such an understanding goes back to before the days of quantum mechanics, and fundamental insights in important aspects of the problem were gained by Lewis, Kossel, Heitler, London, Slater, Pauling, Lennard-Jones, Mulliken, Coulson, and others. *Here we wish to mark the succinct point, however, that no attempt has been made as yet to establish whether it is at all possible to extract from a rigorous wave function (or from a bona fide approximation to it), in a quantitative fashion, a partitioning of the energy which justifies conceptual interpretations.* There have been attempts to construct approximate forms for wave functions on the basis of certain preconceived notions concerning the physical or chemical character of interatomic forces, and how this character should be reflected in the wave functions. The valence bond theory in its simple form is one example, the additive introduction of van der Waals forces as intramolecular contributions is another. Unfortunately none of these synthetic approaches has been able to produce *bona fide* approximations to the true solutions, however, and one must therefore ask whether at least part of the concomitantly created concepts have not been forced artificially into the problem. Thus, these approaches do not answer the question raised here, viz., whether or not definite physical interpretations naturally emerge from the correct wave functions. They rather indicate that the *a priori* imposition of formalistic restrictions upon wave functions for the sake of interpretability may be a trap to be avoided.

Present Approach

The reason that it has not been possible to guess a generally valid, lucid form for molecular wave functions is, of course, that it is not yet known how best to deal with the many-body problem which arises due to the electronic interactions. Various formulations are useful at present to overcome this problem and it is therefore desirable that the interpretation sought should be based upon an analytic procedure, which is entirely independent of the synthetic forms by which specific wave functions take into account interelectronic interactions. This requirement is in harmony with the general quantum-mechanical principle that wave functions themselves are not physically observable and hence one is led to suspect that it may be best to also base molecular interpretations on quantities which qualify, at least in principle, as being observable. The most obvious property of this kind is the energy and its analysis is no doubt indispensable. However, if one observes that the energy as well as all other observable quantities are completely determined by two functions, viz., the density (first-order density kernel) and the pair density (second-order density kernel), then it appears natural to choose these two as the starting point for an interpretative analysis of molecules.

In view of these considerations, the aim of the following developments is a simultaneous regional and physical partitioning of the molecular density, the molecular pair density, and the molecular energy; a partitioning, moreover, which is such that meaningful concepts can be associated with the proposed fragments.

In such an analysis there are encountered many instances where definitions are needed which must fit in the mathematical framework as well as have a relation to physical intuition. All such formalistic definitions are, of course, arbitrary. The arbitrariness is *basically inherent in the objective* which we wish to achieve, viz., *to understand molecules in terms of atoms and bonds*. It has long been recognized that, within a molecule, an atom is best described as being to some degree modified; it is said to exist in a "promoted state." Thus, the conceptual isolation of atoms in molecules is paid for by granting that the atoms are somewhat changed to meet the demands of the valence situation, and it is clear that the appropriate valence state of an atom in a specific environment is by no means a unique invariant but, *within a certain range of physical reasonableness*, open to convenient choice.

This arbitrariness does not preclude, however, the usefulness of such definitions, if they are consistently adhered to in the comparison of different systems. The concept of atoms being the constituents of molecules has been so unquestionably successful in chemistry that attempts at a precise mathematical formulation of such an interpretation ought to be abandoned only when a cogent and definitive demonstration of their futility has been established.

The problems just mentioned are closely related to the fact that the molecular density and pair density differ profoundly from those of the constituent atoms, even if promoted and placed at the actual positions, because in the molecule electrons are *shared* between atoms. The detailed analysis of how electron sharing affects densities and energies is hoped to be a contribution of this investigation. It is suggested that a molecule differs from the juxtaposed promoted atoms in three major aspects, characterized by the concepts of *interference*, *penetration*, and *charge transfer*. The interference contributions embody the precise connections existing between overlap and chemical binding. The analysis shows that, contrary to a widely held misconception, the accumulation of charge in the bond associated with overlap does *not* provide the *potential* energy lowering which yields binding, but is accompanied by a crucial depression of the *kinetic* energy. The penetration contributions, on the other hand, describe how electron sharing modifies the electronic correlations. This important, *bond opposing*, aspect of electron sharing has not been fully appreciated previously. Finally, from an analysis of the hydrogen molecule and the hydrogen molecule-ion, it is concluded that electron sharing leads to chemical binding as the result of a subtle interplay between the uncertainty principle and the nuclear attractions: *Delocalization of the valence electrons from one atom to several atoms leads to a lowering of the kinetic-energy pressure and, as a consequence, there results a firmer attachment of these electrons to the nuclei with a concomitant lowering of the potential as well as the total energy.*

While the specific definitions of the individual terms representing the various contributions are subject to the arbitrariness mentioned earlier, limitations do exist in the form of conservation relations which must hold for the density and the pair density. To find, within these limits, physically sensible formulations which exhaustively account for all terms in the actual quantum-mechanical energy expression, is not altogether trivial.

Inevitably, the ideas advanced here can only be considered as a first step towards a fully adequate solution of the problem. While it has been possible to forge a seemingly complete chain of interpretative concepts to tie together all parts of the rigorous quantum-mechanical energy expression in a molecule, nobody could be more aware of the weak links than the author. It is hoped that these weaknesses may serve as a stimulus towards more careful thinking about these questions.

Purpose of Interpretative Physical Pictures

The objective of the present inquiry is the interpretation of given wave functions and not the proposal of new methods of calculation. On the other hand, it stands to reason that a meaningful method of interpreting general wave functions will also prove helpful for synthesizing good specific approximations. Moreover, the isolation of energy and density terms which show consistent trends under various conditions would improve the prospects for a more intimate welding of rigorous calculations and semi-empirical physicochemical considerations.

In the pursuit of this goal, we are going to be involved deeper and deeper into arguments concerning the interpretation of certain mathematical expressions. Many of these interpretations certainly are not "physical" in an operational sense, i.e., they have no direct relationship to specific experimental observations. They are however "physical" in the sense that they try to provide a *complete set of consistent physical pictures* which furnish a *correct facsimile of the mathematical* *workings of the Schrödinger equation.* Such pictures are useful in the field of molecular structure because they allow us to visualize and predict similarities and differences in the solutions of the Schrödinger equation for different molecules without continuous appeal to an electronic computer. As has already been indicated, the development of correct and useful pictures of this nature is a major, and largely still unsolved, objective of molecular calculations.

In this sense, then, one might say somewhat pointedly that we are interested in physical concepts which help to analyze and visualize electronic distributions and energies in molecules *"as long as they are unperturbed by measurement."* It is unavoidable that such interpretative concepts which are suitable to *describe* a system *in the absence* of observation and measurement (e.g., interference, sharing, exchange, correlation, penetration) differ from those interpretative concepts which are needed to *predict* properly *the results* of observation and measurement (the Copenhagen interpretation). This is undoubtedly connected with the fact that, in the *absence* of measurement, the *reversible Schrödinger equation* is the applicable law of nature, whereas, *during* a measurement, the Schrödinger equation ceases to apply and, instead, *irreversible statistical mechanisms* take over.[1]

It must be admitted that the way of thinking pursued here tends to consider molecular wavefunctions, or at least their densities and pair-densities, as fully representative description of the molecular "reality." The view that these quantities should *only* be considered as "potentialities" for the prediction of the "actuality" of certain physical experimental events,[1a] this extreme operational point of view is unlikely to find many *practical* followers among those who use wooden scale models of atomic and molecular wave functions to work out chemical structures.

1. BASIC CONCEPTS AND RELATIONS

1.1 Density Operator and Pair-Density Operator

Let

$$\mathbf{x}_i s_i = x_i y_i z_i s_i, \quad i = 1, 2, \cdots, N \tag{1.1}$$

denote the space-spin coordinates of the N electrons in a molecule; let

$$\begin{gathered} dV_i = dx_i dy_i dz_i, \quad d\tau_i = ds_i dV_i, \\ d\tau = d\tau_1 d\tau_2 d\tau_3 \cdots d\tau_N \end{gathered} \tag{1.2}$$

denote the corresponding volume elements; and let

$$\Psi(\mathbf{x}_1, s_1, \mathbf{x}_2, s_2, \cdots, \mathbf{x}_N, s_N) \tag{1.3}$$

denote the exact electronic wave function of the molecular system in question.

The second-order density matrix

$$\begin{aligned} &\Gamma(\mathbf{x}_1 s_1, \mathbf{x}_2 s_2 | \mathbf{x}_1' s_1', \mathbf{x}_2' s_2') \\ &\quad = N(N-1) \int (d\tau / d\tau_1 d\tau_2) \Psi(\mathbf{x}_1 s_1, \mathbf{x}_2 s_2, \mathbf{x}_3 s_3, \cdots, \mathbf{x}_N s_N) \\ &\qquad \times \Psi^*(\mathbf{x}_1 s_1, \mathbf{x}_2 s_2, \mathbf{x}_3 s_3, \cdots, \mathbf{x}_N s_N) \end{aligned} \tag{1.4}$$

and the first-order density matrix

$$\gamma(\mathbf{x}s | \mathbf{x}'s') = (N-1)^{-1} \int \mathrm{d}\tau_2 \Gamma(\mathbf{x}s, \mathbf{x}_2 s_2 | \mathbf{x}'s', \mathbf{x}_2 s_2) \tag{1.5}$$

were introduced and discussed by Löwdin and McWeeny.[2]

For the purpose of the present discussion, only the spinless density matrices

$$\rho(\mathbf{x} | \mathbf{x}') = \int ds \gamma(\mathbf{x}s | \mathbf{x}'s), \tag{1.6}$$

$$\pi(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1' \mathbf{x}_2') = \int ds_1 \int ds_2 \Gamma(\mathbf{x}_1 s_1, \mathbf{x}_2 s_2 | \mathbf{x}_1' s_1, \mathbf{x}_2' s_2), \tag{1.7}$$

are required. Their diagonal elements have the following physical significance:

$$\rho(\mathbf{x} | \mathbf{x}) = \rho(\mathbf{x}) = \text{total probable density of electrons at the space point } \mathbf{x} = (x, y, z), \tag{1.8}$$

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[1] See G. Ludwig, Z. Physik **135**, 483 (1953); P. Jordan, Phil. Sci. **16**, 269 (1949). See also G. Ludwig, *Die Grundlagen der Quantenmechanik* (Springer-Verlag, Berlin, Germany, 1954), Chap. V. A simple physical formulation is perhaps as follows. We define a measurement as the creation of an experimental effect *macroscopic enough to be perceptible to natural human observation* and therefore usable as a *classical record.*

To set up an atomistic measurement means to set up a thermodynamic trap. The system to be measured is brought into a situation where its state is highly improbable (e.g., a fast moving particle suddenly finds itself surrounded by a dense distribution of resting particles); hence a statistical interaction will take place (e.g., sooner or later the particle will suffer sufficient collisions to stop it or slow it down) which involves the system as a whole and causes it to impart its energy and momentum, or at least part of it, to the measuring device. Sometimes the statistical interaction does not involve the system itself but, e.g., a photon which is deflected by it.

The thermodynamic trap is moreover directly connected with a thermodynamic amplifier. An "inhibited statistical avalanche" has been dammed up independently (e.g., oversaturation in a cloud chamber; chemical reactions on a photographic plate inhibited in the absence of radiation). This avalanche is triggered by the relatively small energy and momentum received in the previously described trapping process. Sometimes several successive amplification stages are involved.

At the moment the system to be measured falls a victim to the thermodynamic trap, its wave function undergoes an irreversible change, which is known as the "reduction of the wave function" to the new state of the system.

In order to take into account the role of the trap, probability predictions could perhaps be written in the form: $P(x) = P_\psi(x) P_T(x)$, where $P(x)$ = probability of occurrence of the value x for the observable $\mathfrak{X}$, $P_\psi(x)$ = absolute square of the projection of the wave function ψ on the eigenfunction of $\mathfrak{X}$ corresponding to the eigenvalue x, $P_T(x)$ = statistical efficiency of the trap T for measuring the value x of the observable $\mathfrak{X}$. For example, one would have $P_T(x) = 0$ in the absence of a measuring device for $\mathfrak{X}$.

[1a] W. Heisenberg, *Niels Bohr and the Development of Physics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 12.

[2] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955); R. McWeeny, Proc. Roy. Soc. (London) **A232**, 114 (1955); **A235**, 496 (1956). We use McWeeny's definition but Löwdin's symbol **Γ**.

$$\pi(\mathbf{x}_1\mathbf{x}_2\,|\,\mathbf{x}_1\mathbf{x}_2)=\pi(\mathbf{x}_1\mathbf{x}_2)=\text{total pair density of electrons; i.e., the probable number of electron pairs which have one partner at the space point } \mathbf{x}_1=(x_1y_1z_1)\text{, the other at the space point } \mathbf{x}_2=(x_2y_2z_2). \tag{1.9}$$

Because of this physical significance the symbols ρ and π have been chosen. In the subsequent derivations certain *integrals over* ρ *and* π are important. For these, the name *populations* will be used. More specifically:

$$\int_V dV\rho(\mathbf{x})=\text{electron population in the volume } V, \tag{1.10}$$

$$\tfrac{1}{2}\int_V dV_1\int_V dV_2\pi(\mathbf{x}_1\mathbf{x}_2)=\text{electron-pair population in the volume } V.$$

The factor $\frac{1}{2}$ corrects for the fact that the double integration counts each pair of volume elements twice. From the definitions (1.4) to (1.7) follow the conservation relations

$$\int dV_2\pi(\mathbf{x}\mathbf{x}_2\,|\,\mathbf{x}'\mathbf{x}_2)=(N-1)\rho(\mathbf{x}\,|\,\mathbf{x}'), \tag{1.11}$$

$$\int dV\rho(\mathbf{x})=N, \tag{1.11$'$}$$

expressing the facts that the *total* population consists of N electrons and that the *total* pair population consists of $N(N-1)/2$ electron pairs.

Both $\rho(\mathbf{x}\,|\,\mathbf{x}')$ and $\pi(\mathbf{x}_1\mathbf{x}_2\,|\,\mathbf{x}_1'\mathbf{x}_2')$ must be considered as *kernels of Hermitian integral operators* $\boldsymbol{\rho}$ *and* $\boldsymbol{\pi}$ in the Hilbert spaces spanned by certain functions of the space coordinates of one and two electrons, respectively. These operators are defined by the identities

$$\boldsymbol{\rho}f(\mathbf{x})=\int\rho(\mathbf{x}\,|\,\mathbf{x}')dV'f(\mathbf{x}'), \tag{1.12}$$

$$\boldsymbol{\pi}f(\mathbf{x}_1,\mathbf{x}_2)=\int\int\pi(\mathbf{x}_1\mathbf{x}_2\,|\,\mathbf{x}_1'\mathbf{x}_2')dV_1'dV_2'f(\mathbf{x}_1',\mathbf{x}_2'), \tag{1.13}$$

where the f's denote arbitrary functions in the respective Hilbert spaces. In order to be consistent the following names will therefore be used: *density kernel, pair-density kernel* for the Schrödinger representations (1.6), (1.7); *density matrix, pair-density matrix* for matrix representations obtained by expansion in terms of discrete bases in the Hilbert spaces; *density operator, pair-density operator*, when reference to a particular representation is to be avoided. A similar nomenclature has been used previously by S. F. Boys.

Löwdin and McWeeny[2] pointed out that it is always possible to express $\boldsymbol{\rho}$ as a sum of projection operators arising from certain one-electron functions $\varphi_1(\mathbf{x})$, $\varphi_2(\mathbf{x})$, $\varphi_3(\mathbf{x})$, $\cdots$, the "natural molecular orbitals," as follows,

$$\rho(\mathbf{x}\,|\,\mathbf{x}')=\sum_{n=1}^{\infty}\rho_n(\mathbf{x}\,|\,\mathbf{x}'), \tag{1.14}$$

$$\rho_n(\mathbf{x}\,|\,\mathbf{x}')=N_n\varphi_n(\mathbf{x})\varphi_n^*(\mathbf{x}'). \tag{1.15}$$

In line with the interpretation given in Eqs. (1.8) and (1.9), the coefficients N_n are called the orbital occupation numbers. They fulfill the conservation relation

$$\sum_{n=1}^{\infty}N_n=N, \tag{1.16}$$

and, because of the antisymmetry of the wave function (1.3), are numbers between zero and two. In the case of the spinless density operator the existence of Eqs. (1.14) and (1.15) can be rigorously proven from the theory of integral equations. In fact, $\varphi_n(\mathbf{x})$ and N_n are defined as the solutions of the eigenvalue integral equation

$$\boldsymbol{\rho}\varphi_n(\mathbf{x})=N_n\varphi_n(\mathbf{x}), \tag{1.17}$$

$$\int dV'\rho(\mathbf{x}\,|\,\mathbf{x}')\varphi_n(\mathbf{x}')=N_n\varphi_n(\mathbf{x}). \tag{1.18}$$

Since it is easily shown that the density kernel is continuous, Hermitian, and non-negative, it follows from the theorem of Mercer for Fredholm integral equations of the first kind that the bilinear expansion

$$\rho(\mathbf{x}\,|\,\mathbf{x}')=\sum_{n=1}N_n\varphi_n(\mathbf{x})\varphi_n^*(\mathbf{x}')$$

exists and converges absolutely and uniformly. The bilinear expansion is, however, identical with Eqs. (1.14) and (1.15).

Similar arguments are valid for the pair density, for which "natural molecular pair orbitals" can be found from an analogous integral equation.

If an approximate wave function is known for a molecular system, such a wave function will give rise to approximate density operators. An approximation which is of some interest is that of *one* antisymmetrized product of N one-electron spin orbitals, i.e., the Hartree–Fock form. For the first-order density operator, this restriction has the consequence that only the values 0, 1, 2 occur for the occupation numbers N_n. A particular simplification arises for the self-consistent field approximation to a closed-shell state, an important special case. Here the occupation numbers are restricted to

$$N_n=\begin{cases}2, & n=1,2,\cdots,(N/2),\\ 0, & n>(N/2),\end{cases} \tag{1.19}$$

and the pair-density kernel can be expressed in terms of the density kernel by the relation[1]

$$\pi(\mathbf{x}_1\mathbf{x}_2\,|\,\mathbf{x}_1'\mathbf{x}_2') = \rho(\mathbf{x}_1\,|\,\mathbf{x}_1')\rho(\mathbf{x}_2\,|\,\mathbf{x}_2) - \tfrac{1}{2}\rho(\mathbf{x}_1\,|\,\mathbf{x}_2')\rho(\mathbf{x}_2\,|\,\mathbf{x}_1'), \quad (1.20)$$

$$\pi(\mathbf{x}_1\mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - (\tfrac{1}{2})\,|\rho(\mathbf{x}_1\,|\,\mathbf{x}_2)\,|^2. \quad (1.21)$$

The first term, commonly called the *Coulomb part*, would be the pair density for two independent sets of particles; the second term, called the *exchange part*, always represents the subtraction of a positive quantity and is discussed in Sec. 1.4. If the wave function is real, practically almost the only case of interest, then the density kernel is symmetric and the absolute-value signs can be dropped in Eq. (1.21).

In the general Hartree–Fock case, where the determinant consists of N different spin orbitals, each with occupation number 1, it is convenient to divide the sum (1.14) and (1.15) into a sum over the orbitals with (+) spin and a sum over the orbitals with (−) spin. If the two sums are denoted by ρ_+ and ρ_-, the density kernel can be written

$$\rho(\mathbf{x}_1\,|\,\mathbf{x}_2) = \rho_+(\mathbf{x}_1\,|\,\mathbf{x}_2) + \rho_-(\mathbf{x}_1\,|\,\mathbf{x}_2). \quad (1.22)$$

In this case the pair density is found to have the form

$$\pi(\mathbf{x}_1,\mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \rho_+^2(\mathbf{x}_1\,|\,\mathbf{x}_2) - \rho_-^2(\mathbf{x}_1\,|\,\mathbf{x}_2), \quad (1.22')$$

the previous Eq. (1.21) results from Eq. (1.22′) by putting $\rho_+ = \rho_- = \frac{1}{2}\rho$.

It is useful to introduce a decomposition similar to Eqs. (1.21) and (1.22′) for the *exact* pair density, namely,

$$\pi(\mathbf{x}_1,\mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \pi_x(\mathbf{x}_1,\mathbf{x}_2). \quad (1.23)$$

The term π_x may be called the generalized exchange term.

1.2 Molecular Energy

The density operators are sufficient to calculate the mean values of all spin-independent physical observables so far of interest. In particular, if

$$\mathcal{F} = \sum_{i=1}^{N} \mathbf{f}(\mathbf{x}_i)$$

is a sum of one-electron operators, and if

$$\mathcal{G} = \sum_{i=1}^{N}\sum_{j=1}^{N} \mathbf{g}(\mathbf{x}_i\mathbf{x}_j) \quad (i \neq j)$$

is a sum of two-electron operators, then the expectation values can be written

$$F = (\Psi\,|\,\mathcal{F}\,|\,\Psi) = \mathrm{Tr}(\mathbf{f}\boldsymbol{\rho}), \quad (1.24)$$

$$G = (\Psi\,|\,\mathcal{G}\,|\,\Psi) = \mathrm{Tr}(\mathbf{g}\boldsymbol{\pi}). \quad (1.25)$$

The energy to be discussed here is that obtained from nonrelativistic quantum mechanics, with the nuclei held in fixed positions, under neglect of interactions involving the electron spin. By virtue of Eqs. (1.24) and (1.25), it takes the form[2]

$$E = \sum_{A<B} Z_A Z_B R_{AB}^{-1} + \int dV h\rho + \frac{1}{2}\int dV_1 \int dV_2 r_{12}^{-1}\pi. \quad (1.26)$$

The following notation is used here. The capital letters $A, B, \cdots$ denote atoms; $Z_A, Z_B, \cdots$, denote the respective nuclear charges; $\mathbf{x}_A, \mathbf{x}_B, \cdots$, denote the respective nuclear positions; $R_{AB} = |\mathbf{x}_A - \mathbf{x}_B|$, etc., denote the various internuclear distances, finally,

$$h = \mathcal{T} + \mathcal{V} \quad (1.27)$$

$$\mathcal{T}(\mathbf{x}) = -\tfrac{1}{2}\nabla^2 \quad (1.28)$$

$$\mathcal{V}(\mathbf{x}) = -\sum_A Z_A/r_A = -\sum_A Z_A/|x - x_A| \quad (1.29)$$

denote the one-electron operators. Furthermore, the abbreviations

$$\mathcal{T}\rho = \{\mathcal{T}(\mathbf{x})\rho(\mathbf{x}\,|\,\mathbf{x}')\}_{\mathbf{x}'=\mathbf{x}}, \quad (1.30)$$

$$\mathcal{V}\rho = \mathcal{V}(\mathbf{x})\rho(\mathbf{x}) \quad (1.31)$$

$$\pi r_{12}^{-1} = \pi(\mathbf{x}_1\mathbf{x}_2)/\,|\mathbf{x}_1 - \mathbf{x}_2\,|, \quad (1.32)$$

have been used. Atomic units are understood: $a =$ one "Bohr" for length, and $(e^2/a) =$ one "Hartree" for energy. In conjunction with the meanings given in Eqs. (1.9) and (1.10). Formula (1.26) permits an obvious quasi-electrostatic interpretation.

It is helpful to rewrite the energy equation (1.26) in the form [Eq. (1.23) has been used]

$$E = T + V_c - V_x, \quad (1.33)$$

$$= \int dV T\rho + \int dV_1 \int dV_2 \omega(\mathbf{x}_1,\mathbf{x}_2)/r_{12} - \tfrac{1}{2}\int dV_1 \int dV_2 \pi_x(\mathbf{x}_1,\mathbf{x}_2)/r_{12},$$

with

$$\omega(\mathbf{x}_1,\mathbf{x}_2) = \sum_{A<B} \rho_A{}^N(\mathbf{x}_1)\rho_B{}^N(\mathbf{x}_2) + \tfrac{1}{2}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) + \tfrac{1}{2}\Big[\rho(\mathbf{x}_1)\sum_B \rho_B{}^N(\mathbf{x}_2) + \rho(\mathbf{x}_2)\sum_B \rho_B{}^N(\mathbf{x}_1)\Big], \quad (1.34)$$

where

$$\rho_A{}^N(\mathbf{x}) = -Z_A\delta(\mathbf{x} - \mathbf{x}_A) \quad (1.35)$$

denotes the nuclear point-charge distribution giving rise to the nuclear potential $(-Z_A/r_A)$.

The term V_c has the appearance of a classical electrostatic Coulombic energy in terms of the density $\rho(\mathbf{x})$. However, for the proper understanding and interpretation of the *actual form* of this density the recognition of wave-mechanical effects, in particular *interference*, is essential (see Sec. 3). The term V_x still looks like an electrostatic repulsion term, except that $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$ cannot be reduced to a one-particle density (see Sec. 4). The kinetic energy T, finally, can only be expressed in terms of a density *operator*, not in terms of a density *function*. It is via the kinetic energy that the *uncertainty principle* is known to influence the form of electronic wave functions (if we think in terms of the variation principle, say) and, as is seen, becomes essential for the typically quantum-mechanical phenomenon of covalent binding (see Sec. 7).

1.3 Preliminary Analysis of the Quasi-Classical Terms

It is instructive to analyze the potential energy part V_c which arises if one takes into account merely the Coulombic part

$$\pi_c=\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \tag{1.36}$$

of the pair density (1.23).[3] The distribution ω of Eq. (1.34) can be written

$$\omega=\tfrac{1}{2}[\sum_A \rho_A{}^N(\mathbf{x}_1)+\rho(\mathbf{x}_1)][\sum_B \rho_B{}^N(\mathbf{x}_2)+\rho(\mathbf{x}_2)] \\ -\tfrac{1}{2}\sum_A \rho_A{}^N(\mathbf{x}_1)\rho_A{}^N(\mathbf{x}_2), \tag{1.37}$$

and hence, except for the constant (infinite) self-energy of the nuclear point charges, the total potential energy of the molecule can be interpreted as the self-energy of the total molecular distribution $[\sum_A \rho_A{}^N(\mathbf{x})+\rho(\mathbf{x})]$. If one furthermore assumes that the total electronic charge $\rho(\mathbf{x})$ is expressible as a sum of atomic contributions,

$$\rho(\mathbf{x})=\sum_A \rho_A(\mathbf{x}), \tag{1.38}$$

then the distribution ω becomes a sum of monatomic and diatomic terms, and the potential energy can be split correspondingly,

$$V_c=\sum_A V_A+\sum_{A<B} V_{AB}. \tag{1.39}$$

Here

$$V_A=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)\rho_A(\mathbf{x}_2) \\ +\tfrac{1}{2}\rho_A(\mathbf{x}_1)\rho_A(\mathbf{x}_2)]/r_{12} \tag{1.40}$$

must be considered as the internal potential energy (nucleus-electron attraction and electronic repulsion) of atom A within the molecule, and

$$V_{AB}=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)+\rho_A(\mathbf{x}_1)] \\ \times[\rho_B{}^N(\mathbf{x}_2)+\rho_B(\mathbf{x}_2)]/r_{12} \tag{1.41}$$

represents the interaction energy between the total atom A (nucleus and electrons) and the total atom B.

In polar molecules it is to be expected that the total charge, given by the integral over ρ_A, is different from the nuclear charge Z_A on the same atom. Suppose that in such a case it is possible to give for all atoms a decomposition

$$\rho_A(\mathbf{x})=\rho_A{}^0(\mathbf{x})+\delta\rho_A(\mathbf{x}), \tag{1.42}$$

where $\rho_A{}^0$ can be considered as the density of the neutral atom A in the molecule and $\delta\rho_A$ as the charge density transferred to the atom, i.e.,

$$\int dV\rho_A{}^0(\mathbf{x})=Z_A, \tag{1.43}$$

$$\int dV\delta\rho_A(\mathbf{x})=\delta Z_A, \tag{1.44}$$

so that δZ_A represents the total charge transferred to A (a loss of charge being given by $\delta Z_A<0$). Substitution of this decomposition (1.42) into Eqs. (1.37) and (1.38) leads to the following, more detailed partitioning of the potential energy,

$$V_c=\sum_A V_A{}^0+\sum_{A<B} V_{AB}{}^0 \\ \sum_A V_A{}^{0i}+\sum_{A<B}[V_{AB}{}^{0i}+V_{BA}{}^{0i}] \\ +\sum_A V_A{}^i+\sum_{A<B} V_{AB}{}^i, \tag{1.45}$$

where the following meanings must be ascribed to the terms:

$$V_A{}^0=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)\rho_A{}^0(\mathbf{x}_2) \\ +\tfrac{1}{2}\rho_A{}^0(\mathbf{x}_1)\rho_A{}^0(\mathbf{x}_2)]/r_{12} \tag{1.46}$$

is the internal potential energy of the *neutral* atom A within the molecule;

$$V_{AB}{}^0=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)+\rho_A{}^0(\mathbf{x}_1)] \\ [\rho_B{}^N(\mathbf{x}_2)+\rho_B{}^0(\mathbf{x}_2)]/r_{12} \tag{1.47}$$

is the interaction energy between the *neutral* atoms A and B;

$$V_A{}^{0i}=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)+\rho_A{}^0(\mathbf{x}_1)]\delta\rho_A(\mathbf{x}_2)/r_{12} \tag{1.48}$$

is the electrostatic energy of the charge transferred to A in the field of neutral atom A;

$$V_{AB}{}^{0i}=\int dV_1\int dV_2[\rho_A{}^N(\mathbf{x}_1)+\rho_A{}^0(\mathbf{x}_1)] \\ \times\delta\rho_B(\mathbf{x}_2)/r_{12} \tag{1.49}$$

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[3] Different formulations of a similar character were given by P. O. Löwdin, Phil. Mag. Suppl. **5**, 12, 36 (1956).

is the electrostatic energy of the charge transferred to atom B in the field of another neutral atom A;

$$V_A{}^i=(\tfrac{1}{2})\int dV_1\int dV_2\delta\rho_A(\mathbf{x}_1)\delta\rho_A(\mathbf{x}_2)/r_{12} \quad (1.50)$$

is the self-energy of the charge transferred to atom A; and

$$V_{AB}{}^i=\int dV_1\int dV_2\delta\rho_A(\mathbf{x}_1)\delta\rho_B(\mathbf{x}_2)/r_{12} \quad (1.51)$$

is the interaction energy of the charge transferred to atom A with the charge transferred to atom B. Thus, Eq. (1.47) represents attractive long-range multipole forces and in most cases is negative. Equations (1.48) and (1.49) describe the energy changes occurring due to the fact that, in the usual terminology, different atoms have different electron affinities and ionization potentials, i.e., they are electronegativity terms. The term of Eq. (1.50) is positive, describing the electronic repulsion created by accumulating the additional charge $\delta\rho_A$ on atom A; it should be taken together with the electronegativity term of Eq. (1.48). Finally, Eq. (1.51) contains what might be called the naive ionic energy terms, which, taken together, will in general be negative.

The interpretations just discussed depend upon the incomplete expression (1.36) for the pair density and upon the hypothetical decompositions (1.38), (1.42) for the density. These interpretations can be termed "purely quasi-classical." Additional terms of typical quantum-mechanical character will appear in the energy decomposition when correct expressions are used for the density and the pair density.

1.4. Sharing, Self-Pairing, and Correlation

Interpretation of the Generalized Exchange Term π_x

The conservation relations (1.11, 11′), in conjunction with Eq. (1.23), yield the separate identities

$$\int dV_2\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)=N\rho(\mathbf{x}_1), \quad (1.52)$$

$$\int dV_2\pi_x(\mathbf{x}_1,\mathbf{x}_2)=\rho(\mathbf{x}_1), \quad (1.52')$$

indicating that, for large systems, the simpler Coulomb term will yield the majority of the interelectronic interaction energy. This suggests that the decomposition (1.23) may be useful in isolating the more complicated aspects of the electronic interactions. For the interpretations in subsequent sections it is necessary to appreciate these aspects, i.e., to develop a physical feeling for the term $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$.

I.

First consider a wave function describing two atoms A and B, at a distance large enough so that the respective atomic wave functions have practically *vanishing overlap*. Suppose the wave function to be such that electrons 1, 2, $\cdots$, N_A are associated with atom A, whereas electrons N_A+1, N_A+2, $\cdots$, $N_A+N_B=N$, are associated with atom B. This separation of electrons will be preserved since according to the time-dependent Schrödinger equation the time required for an electron to tunnel from A to B will be infinitely long from the practical standpoint. Hence it is possible to distinguish the electrons on A from the electrons on B and to make the statement that the two atoms are occupied by different electrons.

Assume now furthermore that the atoms are far enough apart so that *long-range forces* between them are entirely *negligible.* Then the probability of finding an electron at a certain point on atom A is independent of whatever the electrons on atom B do, and vice versa. Under these conditions the identity

$$\pi(\mathbf{x}_1,\mathbf{x}_2)=\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)=\pi_c(\mathbf{x}_1,\mathbf{x}_2) \quad (1.53)$$

holds for the pair density, if $\mathbf{x}_1$ denotes a position on atom A and $\mathbf{x}_2$ denotes a position on atom B.

II.

Consider next the case of two *nonoverlapping* atoms between which *long-range forces are acting*. The electrons of the two atoms still form two distinguishable sets, but now the motions of the electrons on atom A are correlated with the motions of the electrons on atom B. Consequently, the identity (1.53) is no longer valid, i.e., even if $\mathbf{x}_1$ and $\mathbf{x}_2$ lie on atoms A and B, respectively. The generalized exchange term $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$ in Eq. (1.23) can now be nonvanishing. However, since no electrons are shared between the two atoms, it is still true that the total number of pairs having one partner on A and the other partner on B is given by

$$\int_{V(A)} dV_1\int_{V(B)} dV_2\pi(\mathbf{x}_1,\mathbf{x}_2)=q(A)q(B) \quad (1.54)$$

where

$$q(A)=\int_{V(A)} dV\rho(\mathbf{x})$$

$$q(B)=\int_{V(B)} dV\rho(\mathbf{x})$$

are the total populations of atom A and B, respectively [$V(A)$ and $V(B)$ denote volumes including the nonoverlapping atoms A and B, respectively].

Hence one finds that, under these circumstances, the pair density is given by Eq. (1.23) where, however, π_x

has the property that

$$\int_{V(A)} dV_1 \int_{V(B)} dV \pi_x(\mathbf{x}_1,\mathbf{x}_2)=0. \tag{1.55}$$

It follows that, for $\mathbf{x}_1$ on A and $\mathbf{x}_2$ on B, the term $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$ must assume negative as well as positive values.

These deviations of π_x from its mean value zero (for $\mathbf{x}_1$ on A and $\mathbf{x}_2$ on B), describe precisely the correlations which exist between the electrons on atom A and those on atom B, and which are the physical reasons for the lowering of energy giving rise to certain long-range forces. Thus, in the case of London forces such unshared correlations correspond to the classical situation where electrons on the atoms circle their respective centers in unison, so that the instantaneous positions of the electrons on A depend upon those of the electrons on B. There results an attractive dipole energy at all times without giving rise to an average dipole on either atom.

In this situation, then, the difference term $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$ deserves the name "correlative pair density between different electrons," as long as $\mathbf{x}_1$ belongs to atom A and $\mathbf{x}_2$ belongs to atom B.

III.

Consider now the case that two atoms are close to each other and form a molecule, so that they *share* certain electrons, i.e., the motions of such electrons extend around both nuclei. From the point of view of tunneling between A and B, it is clear that the sharing of electrons is necessarily connected with an appreciable overlap of the wave functions on the two atoms.

Now the electrons at $\mathbf{x}_1$ and those at $\mathbf{x}_2$, where $\mathbf{x}_1$ is close to nucleus A and $\mathbf{x}_2$ is close to nucleus B, say, no longer form two separate sets and, therefore, certain shared electrons are involved in building up both, the density $\rho(\mathbf{x}_1)$ as well as the density $\rho(\mathbf{x}_2)$. Hence the product $\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$ must contain pair contributions in which the density contributions of a certain electron at $\mathbf{x}_1$ is paired with a density contribution of the *same* electron at $\mathbf{x}_2$. Such self-pairings are however foreign to the actual pair density π. Thus we conclude that the Coulomb term treats the electrons at $\mathbf{x}_1$ and those at $\mathbf{x}_2$ as belonging to two different sets, and that it contains unphysical self-pairing contributions if electrons are shared between $\mathbf{x}_1$ and $\mathbf{x}_2$. This viewpoint is supported by the conservation relation

$$\tfrac{1}{2}\int dV_1 \int dV_2 \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)=\tfrac{1}{2}N^2, \tag{1.56}$$

which indicates that the Coulomb term not only counts the $N(N-1)/2$ pairs which are obtained by choosing two different electrons, but also those fictitious pairs which result by choosing the same electron as partners in one pair. These N self-pairs are mathematical artifacts of the counting procedure inherent in the Coulomb term.

Under the present conditions, the term π_x plays therefore a different role than in the previously considered case. Now it serves to eliminate the spurious self-pairings contained in the Coulombic term. In a situation where this would be the only function of π_x, this term would be positive for all argument values. It would then deserve the name "self-pair density."

IV.

It is to be expected however, that correlative interactions between different electrons exist between two points $\mathbf{x}_1$ and $\mathbf{x}_2$ also in the case that electrons are shared between them. Therefore the general situation is that both roles are played by $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$, that of subtracting out spurious self-pairing as well as that of describing unshared correlations. It is tempting to assume that π_x can be written as a sum,

$$\pi_x=\pi_{\text{self}}+\pi_{\text{corr}}, \tag{1.57}$$

where π_{self} represents the totality of all contributions in $\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$ arising from self-pairing of particles which are shared between the two points, whereas π_{corr} furnishes that modification of π which arises from the instantaneous correlations between different electrons at the two points, *due to forces contained in the Hamiltonian.*

The self-pair density π_{self} would be characterized by the condition

$$\pi_{\text{self}}(\mathbf{x}_1,\mathbf{x}_2)\geqslant 0, \qquad \text{for all } \mathbf{x}_1,\, \mathbf{x}_2, \tag{1.58}$$

$$\int dV_1 \int dV_2 \pi_{\text{self}}(\mathbf{x}_1,\mathbf{x}_2)=N. \tag{1.59}$$

The correlative pair density π_{corr} would be characterized by assuming negative as well as positive values in such a way that

$$\int dV_1 \int dV_2 \pi_{\text{corr}}(\mathbf{x}_1,\mathbf{x}_2)=0. \tag{1.60}$$

Interpretation of the Exchange Term π_x for an Antisymmetric Product of Molecular Spin Orbitals

I.

In the preceding discussion certain conditions had been quoted under which π_{self} vanishes, namely, between two atoms which do not share electrons. Are there other conditions, under which π_{corr} vanishes so that π_x accounts merely for self-pairing?

We suggest that this may be the appropriate interpretation for an antisymmetrized product of spin orbitals (molecular orbital approximation) such as was discussed for the Hartree–Fock approximation, in conjunction with Eqs. (1.19) to (1.22′). The following arguments can be given in support of this viewpoint.

The molecular orbital wave function is an exact solution for noninteracting particles. In the case of interacting particles, it represents an approximation which consists of imitating, as well as possible, the individual electronic interactions by an average potential (operator) acting on all electrons equally. Hence a single determinant may be taken to describe individually uncorrelated particles, and it is therefore known as the independent particle model.

Next, the exchange term π_x of such a wave function is always positive for any values of the arguments $\mathbf{x}_1$, $\mathbf{x}_2$, as is apparent from Eqs. (1.21, 22′). This is in agreement with the postulate (1.58) for the self-pairing term. In particular, it has the consequence that a Hartree–Fock type wave function is intrinsically incapable of describing long-range forces which result from unshared correlation and, as was discussed earlier, arise only if π_x assumes also negative values.

Finally, the present point of view appears to be in agreement with the two concepts "exchange term" and "correlation energy." In the first place, the *exchange* concept attempts to describe the same state of affairs as the sharing concept: Both express the fact that one and the same electron appears to be energetically active at different places in space, as far as the solution of the Schrödinger equation is concerned. The sharing concept is preferred here because it avoids the use of a pseudo-time-dependent picture, and a static picture seems more in line with the relevant properties of wave functions. The *correlation energy*, on the other hand, is defined as that energy difference which distinguishes the exact energy eigenvalue from the best possible approximation to it that can be attained by the molecular orbital approximation.

II.

It is sometimes expedient to write the Hartree–Fock pair density in the form

$$\pi(\mathbf{x}_1,\mathbf{x}_2)=\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)[1-s(\mathbf{x}_1,\mathbf{x}_2)]. \tag{1.61}$$

In our interpretation,

$$\begin{aligned}s(\mathbf{x}_1,\mathbf{x}_2)&=\rho^2(\mathbf{x}_1\,|\,\mathbf{x}_2)/\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\\&=\pi_x(\mathbf{x}_1,\mathbf{x}_2)/\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\leqslant 1\end{aligned} \tag{1.62}$$

represents that fraction of the Coulomb term which results from self-pairing. Hence it is natural to call it the *sharing fraction* between the points $\mathbf{x}_1$ and $\mathbf{x}_2$. This concept can also be illustrated in the following manner.

According to the present view, the Coulomb term

$$\pi_c(\mathbf{x}_1,\mathbf{x}_2)=\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \tag{1.63}$$

represents, for a Hartree–Fock type wave function, the number of "virtual pairs" between $\mathbf{x}_1$ and $\mathbf{x}_2$, where by "virtual" it is meant that the two partners of a pair may be different particles or the same particle. If, in analogy to Eq. (1.63), two densities $\rho_=$ and $\rho_{\neq}$ are defined by

$$\pi(\mathbf{x},\mathbf{x}_0)=\rho(\mathbf{x}_0)\rho_{\neq}(\mathbf{x}\|\mathbf{x}_0), \tag{1.64}$$

$$\pi_x(\mathbf{x},\mathbf{x}_0)=\rho(\mathbf{x}_0)\rho_=(\mathbf{x}\|\mathbf{x}_0), \tag{1.65}$$

then $\rho_{\neq}(\mathbf{x}\|\mathbf{x}_0)$ can be considered as that part of the total density at $\mathbf{x}$ which describes the average number of particles which are not shared with the point $\mathbf{x}_0$, whereas $\rho_=(\mathbf{x}\|\mathbf{x}_0)$ describes the average number of particles at $\mathbf{x}$ which are shared between $\mathbf{x}$ and $\mathbf{x}_0$. From Eqs. (1.63) to (1.65) and Eq. (1.23) it follows that

$$\rho(\mathbf{x})=\rho_=(\mathbf{x}\|\mathbf{x}_0)+\rho_{\neq}(\mathbf{x}\|\mathbf{x}_0), \tag{1.66}$$

i.e., the total density at the point $\mathbf{x}$ can be divided into a shared part and an unshared part with respect to an arbitrary point $\mathbf{x}_0$. If one considers $\rho_=$ and $\rho_{\neq}$ as a function of $\mathbf{x}$, for a fixed value of $\mathbf{x}_0$, then one can also say that *that* density at $\mathbf{x}$ which *interacts* with the density at $\mathbf{x}_0$, namely, $\rho_{\neq}(\mathbf{x}\|\mathbf{x}_0)$, differs from the *total* density at $\mathbf{x}$, namely, $\rho(\mathbf{x})$, by having subtracted out the "hole" $\rho_=(\mathbf{x}\|\mathbf{x}_0)$, which arises from those electrons which are shared with $\mathbf{x}_0$ at any given time.[4]

From Eqs. (1.63 to 1.65) follow the relations

$$\rho_=(\mathbf{x}\|\mathbf{x}_0)=\rho(\mathbf{x})s(\mathbf{x},\mathbf{x}_0), \tag{1.67}$$

$$\rho_{\neq}(\mathbf{x}\|\mathbf{x}_0)=\rho(\mathbf{x})[1-s(\mathbf{x},\mathbf{x}_0)], \tag{1.68}$$

which suggest the same interpretation of $s(\mathbf{x}_1,\mathbf{x}_2)$ as was given above, viz., that of a sharing fraction.

III.

Sometimes the term "correlation" is used to describe a different aspect of the pair density of antisymmetric wave functions. It is said that the exchange term in the Hartree–Fock pair density introduces modifications of the Coulomb term which result from *correlations between motions of different electrons* as a consequence of the mutual *exchange repulsions originating from the antisymmetry* of the wave function.[5] From the present point of view this matter looks as follows.

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[4] The following simple picture may serve to illustrate Eqs. (1.63)–(1.66). *If* at a particular time the density at the point $\mathbf{x}_2$ *were* due entirely to one given electron, then, at the point $\mathbf{x}_1$, the part $\rho_=(\mathbf{x}_1\|\mathbf{x}_2)$ would be due to the same electron and the part $\rho_{\neq}(\mathbf{x}_1\|\mathbf{x}_2)$ would be due to all other electrons. Note that

$$\int dV_1\rho_=(\mathbf{x}_1\|\mathbf{x}_2)=1,\qquad \int dV_1\rho_{\neq}(\mathbf{x}_1\|\mathbf{x}_2)=N-1.$$

From this picture follows indeed that, between $\mathbf{x}_1$ and $\mathbf{x}_2$,

$$\rho_=(\mathbf{x}_1\|\mathbf{x}_2)\rho(\mathbf{x}_2)=\pi_x(\mathbf{x}_1,\mathbf{x}_2)$$

is the self-pair density, and that

$$\rho_{\neq}(\mathbf{x}_1\|\mathbf{x}_2)\rho(\mathbf{x}_2)=\pi(\mathbf{x}_1,\mathbf{x}_2)$$

is the number of pairs with different electrons at that particular time.

[5] See, e.g., R. McWeeny, Revs. Modern Phys. **32**, 335 (1960). Thus, the function $s(\mathbf{x},\mathbf{x}')$, called the sharing fraction here, is called the "correlation function" there (aside from a change in sign).

In the first place, the existence of the term π_x is independent of the symmetry properties of wave functions. Consider for example the symmetric wave function obtained by placing all N electrons in the same spin orbital $\phi(\mathbf{x})$, viz.,

$$\Phi=\phi(\mathbf{x}_1)\phi(\mathbf{x}_2)\cdots\phi(\mathbf{x}_N)\alpha(1)\alpha(2)\cdots\alpha(N).$$

The density and the pair density are found to be

$$\pi(\mathbf{x}_1,\mathbf{x}_2)=N(N-1)\phi^2(\mathbf{x}_1)\phi^2(\mathbf{x}_2),$$

$$\rho(\mathbf{x}_1|\mathbf{x}_2)=N\phi(\mathbf{x}_1)\phi(\mathbf{x}_2),$$

so that

$$\pi(\mathbf{x}_1,\mathbf{x}_2)=\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)-\rho^2(\mathbf{x}_1|\mathbf{x}_2)/N.$$

In this case the concept of exchange repulsion is not very apt, but the identification of π_x with the self-pair density of shared electrons is still meaningful.

Secondly, the interpretation of the exchange term as a correlation correction is based upon the premise that the Coulomb term represents the pair density correctly if the motions of different electrons are truly independent. There exists however no argument which could be advanced in support of this hypothesis, and its validity is in fact excluded by virtue of the integral relationship (1.56).

Finally, let us consider in detail the specific characteristics of the pair density of an antisymmetric wave function. They are best discussed in the combined space of position and spin. For antisymmetric wave functions, the position-spin pair densities, i.e., the diagonal elements of the second-order density kernel (1.4), are characterized by the fundamental exclusion property, i.e., the closer $(\mathbf{x}_1s_1)$ and $(\mathbf{x}_2s_2)$ are together in position-spin space, the less likely it is, in general, to find at these points two different electrons. More specifically,

$$\Gamma(\mathbf{x}_1s_1,\mathbf{x}_1s_1)=0, \tag{1.69}$$

$$\Gamma(\mathbf{x}_1s_1,\mathbf{x}_2s_2)=o\{|(\mathbf{x}_1s_1)-(\mathbf{x}_2s_2)|^2\} \tag{1.70}$$

for $(\mathbf{x}_1s_1)\rightarrow(\mathbf{x}_2s_2)$.

This exclusion behavior does not result from any physical force, i.e., from a term in the Hamiltonian. Within the unrelativistic quantum mechanics of electrons, it stems from an independent *a priori* axiom, the Pauli principle.[6] As such, it plays in this part of quantum mechanics a role completely analogous to Aristotles' principle that "two bodies cannot be in the same place." (In fact, Aristotles' principle is a corollary of the Pauli principle; for the noninterpenetrability of "bodies" arises from the repulsion of closed shells which is a direct consequence of the exclusion principle.) The exclusion principle is static and not kinetic in character.

Now the position-spin pair density can be decomposed in analogy to Eq. (1.23):

$$\Gamma(\mathbf{x}_1s_1,\mathbf{x}_2s_2)=\gamma(\mathbf{x}_1s_1)\gamma(\mathbf{x}_2s_2)-\Gamma_x(\mathbf{x}_1s_1,\mathbf{x}_2s_2), \tag{1.71}$$

where $\gamma(\mathbf{x}_1s_1)$ is the diagonal element of the first-order position-spin density of Eq. (1.5). For a molecular orbital wave function, one finds

$$\gamma(\mathbf{x}s|\mathbf{x}'s')=\alpha(s)\alpha(s')\rho_+(\mathbf{x}|\mathbf{x}')+\beta(s)\beta(s')\rho_-(\mathbf{x}|\mathbf{x}'), \tag{1.72}$$

with ρ_+ and ρ_- having the same meaning as in Eq. (1.22), and[2]

$$\Gamma_x(\mathbf{x}_1s_1,\mathbf{x}_2s_2)=|\gamma(\mathbf{x}_1s_1|\mathbf{x}_2s_2)|^2\geqslant 0, \tag{1.73}$$

and the exclusion behavior is then expressed by

$$\Gamma_x(\mathbf{x}_1s_1,\mathbf{x}_2s_2)/\gamma(\mathbf{x}_1s_1)\gamma(\mathbf{x}_2s_2)$$
$$=1-0\{|(\mathbf{x}_1s_1)-(\mathbf{x}_2s_2)|^2\} \tag{1.74}$$

for $(\mathbf{x}_1s_1)\rightarrow(\mathbf{x}_2s_2)$. This equation says that the self-pairing part Γ_x constitutes a larger and larger fraction of the Coulomb term as the two points in position-spin space approach each other until, when the points coincide, the total Coulomb term is made up of spurious self-pairing. Thus the exclusion principle finds its natural expression in the fact that, for antisymmetric molecular-orbital functions, the position-spin sharing fraction has its maximum, viz., unity, on the surface $(\mathbf{x}_1s_1)=(\mathbf{x}_2s_2)$ and is reasonably compact around it. According to Eq. (1.67), the shared density $\rho_=$ has a quite similar behavior.[7]

Thus, inasmuch as (1) there is no reason to consider the Coulombic term as the general pair density for uncorrelated electrons, and (2) the exclusive behavior of spin-1/2 particles is not the result of forces contained in the Hamiltonian but rather the atomistic counterpart of Aristotles' principle, it seems more appealing to interpret the exchange term as being the subtractive correction which eliminates spurious self-pairing in the Coulomb term rather than representing a pseudo-kinetic correlation phenomenon.

IV.

Frequently, an "intermediate" point of view is taken: The exchange term of the Hartree–Fock approximation is considered to describe both, self-pairing corrections as well as interelectronic correlations arising from the antisymmetry requirement.

One version of this view is the following interpretation.[8] By expansion in molecular orbitals, the exchange term of Eq. (1.21) can be written

$$\tfrac{1}{2}\rho^2(\mathbf{x}_1|\mathbf{x}_2)=2\sum_n\sum_m\phi_n(\mathbf{x}_1)\phi_m(\mathbf{x}_1)\phi_n(\mathbf{x}_2)\phi_m(\mathbf{x}_2). \tag{1.75}$$

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[6] In general relativistic quantum mechanics, the antisymmetry requirement can of course be related to the statistical behavior and to the spin of the electron. Also there are bosons and, for these, symmetric wave functions are appropriate. These arguments show even more clearly that the Pauli exclusion does not stem from a force in the Hamiltonian.

[7] Thus, even in a set of delocalized orbitals, the individual electrons act *with respect to each other* as more or less localized clouds which dislike to penetrate each other. There is no conceptual reason why the instantaneous sharing distribution for a given point could not differ from the average electron distribution.

[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 240.

It has been suggested that the diagonal terms, which clearly cancel identical terms in the Coulomb part, eliminate spurious self-interactions, whereas the off-diagonal terms in Eq. (1.75) are different in character and describe correlations between different electrons. This view is unsatisfactory in that the division into diagonal and off-diagonal terms is not invariant against the permissible unitary transformations among the molecular orbitals. The misunderstanding of this interpretation lies in the identification of electrons with molecular orbitals. In fact, because of symmetrization or antisymmetrization, electrons cannot be identified with orbitals, but all electrons make use of all orbitals.

Another version consists in asking for that set of molecular orbitals, among the many equivalent sets, which exhibits maximum localization, e.g., for which the energy of the diagonal terms in Eq. (1.75) is greatest. These unique diagonal elements are then identified with the spurious self-interactions in the Coulomb term.[9]

Finally, it sometimes is argued that the spurious self-pairing contributions in the Coulomb term ought to be equated to $\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)/N$, i.e., to the Nth part of the Coulomb term.[10] This interpretation would be opposite to the point of view expressed in reference 7.

In the present investigation, we shall however preserve the Aristotelean idea that the Fermi hole, generated by the *total* invariant expression (1.75), represents a picture of how an electron keeps away others from the place it occupies itself, and that the *exclusion effect is therefore the consequence of a particularly compact self-pair density, typical for antisymmetric wave functions.* A related, though less radical, view was expressed by Slater in an earlier investigation.[11] Analyzing the Hartree–Fock equations of motion, he came to the conclusion that off-diagonal and diagonal terms together give rise to what must be considered as the self-repulsion of the electrons which are to be subtracted from the Coulomb terms.

General Relation between π_{corr} and π_{self}

For a complete analysis and understanding of rigorous molecular wave functions it will be necessary to differentiate quantitatively between self-pairing due to sharing and correlation due to electrostatic interactions. For Hartree–Fock self-consistent field approximations this is fortunately not necessary if the foregoing view is adopted.

It is an interesting question whether $\pi_x(1,2)$ ever has negative values within one molecule. Only if accurate molecular wave functions will furnish pair densities which exhibit such negative values, can we justifiably speak of London-type intramolecular forces.

There are two reasons why it is doubtful that forces arising from an unshared correlation play a major part within molecules. One is the fact that SCF wave functions appear to be reasonably good as first approximations. The other is the paramount importance of electron sharing in connection with strong chemical forces, as is seen later. It seems doubtful whether these strong forces permit the subtle rearrangements that are required to originate strong correlation forces

It does not appear to be easy to think of a simple partitioning of the pair density such as was postulated in Eq. (1.57), and we shall, therefore, not pursue the subject here. In the remainder of this investigation, unshared correlation will be omitted from consideration; it is hoped that this question can be analyzed in greater detail elsewhere.

Conclusion

The preceding discussions show that a completely satisfactory interpretation of the nonclassical contributions in the pair density will require more careful thought. It is therefore to be expected that similar problems will be encountered in interpreting the interelectronic contributions to the molecular binding energy.

2. EXPANSION IN ATOMIC ORBITALS

2.1 Choice of Atomic Orbitals

There exist several methods for constructing explicit expressions of electronic wave functions in molecules. Numerical and analytical formulations are possible and, in the case of analytical formulations, there exists a choice of basic functions in terms of which a wave function can be expanded. Physical and chemical intuition anticipates the expansion in terms of atomic orbitals to be an effective device for constructing solutions to the problem of electrons moving in the field of fixed nuclei, and also from the mathematical viewpoint this approach seems reasonable for a differential equation with simple poles at the nuclear positions. The numerical experience gained so far has confirmed these expectations and, vice versa, it suggests that expansions in atomic orbitals have physical significance.

An exception is the case of diatomic molecules where molecular orbitals in terms of elliptic coordinates appear to form a more convenient basis set (the explanation lies in the fact that, in this case, one has at hand *one* orthogonal, curvilinear coordinate system which exhibits singularities at the positions of *all* nuclei in the molecule). However, if molecules are to be understood in terms of atoms and bonds, then decompositions of the density operators into atomic building blocks are required; and if many electron wave functions are

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[9] The possibility of this interpretation was pointed out by Dr. G. G. Hall and Dr. S. F. Boys (personal communication). A method for approximating such orbitals has been suggested by S. F. Boys, Revs. Modern Phys. **32**, 300 (1960). See also Sec. 3.6 below.

[10] This possibility was pointed out by Dr. J. S. Pople (personal communication).

[11] J. C. Slater, Phys. Rev. **81**, 385 (1951). Similar views go back to E. Wigner and F. Seitz, *ibid.* **43**, 804 (1933); **46**, 509 (1934).

formed, in one way or another, from one-electron functions, then the expansion of the wave function in atomic orbitals appears to be the most appropriate point of departure for the interpretative analysis. If a wave function has been determined in terms of elliptic coordinates, its expansion in terms of atomic orbitals can always be carried out afterwards.

Thus, we start with *the postulate that there exists a physically significant expansion of the rigorous solution of the Schrödinger equation in terms of atomic orbitals on the participating atoms in the molecule.* Since all atomic orbitals on all atoms form an overcomplete set, there exist, of course, infinitely many ways of expanding the exact solution in terms of atomic orbitals. Some of these expansions however, converge more rapidly than others (e.g., the convergence is very slow if all AO's are chosen from the same atom). Exactly the same statements are valid for the density kernel derived from the wave function. We should like to believe that the requirement of *optimal convergence of the expansion of the first-order density kernel* in terms of atomic orbitals will select a particular sequence of AO's from the various atoms and thus lead to a shortest expansion, which then deserves the name "significant expansion" in atomic orbitals. It is conceivable that in some cases there may exist more than one significant expansion of roughly comparable speed of convergence, and they would then lead to several equivalent interpretations. It seems, however, likely that, in any specific case, an ambiguity of this kind would be limited to only a few alternatives. The actual selection of the significant expansion depends, of course, upon the mathematical formulation of the criterion of optimal convergence; this question is discussed in Sec. 2.3.

The following derivations practically presuppose wave functions which are expressed in terms of antisymmetrized products of one-electron orbitals. If and when it should become feasible to explicitly include in the wave functions many inter-electronic distances, then a corresponding modification of our developments will be in order.

The following notation for atomic orbitals is adopted throughout; $A, B, C, \cdots$ denote atoms and $a, b, c, \cdots$, are indices numbering the orbitals on the atoms $A, B, C, \cdots$, respectively; furthermore

$$\chi_{Aa}(x,y,z)=\chi_{Aa}(\mathbf{x})=(Aa) \tag{2.1}$$

denotes the ath orbital on atom A; e.g., $(N1s)$, $(N3d\delta)$, $(N2p\sigma)$ would denote the $1s$ orbital, the $3d\delta$ orbital, and the $2p\sigma$ orbital on the nitrogen atom in NH_3. But in the case of hybrid orbitals, the index a can represent any other kind of orbital identification on atom A which may be useful. Occasionally, it is convenient to number through *all* atomic orbitals in a molecule without reference to the atoms; for this purpose, the indices $r, s, t, \cdots$, will be used, so that each of these is equivalent to an index *pair* of the type Aa, Bb, Cc, $\cdots$, etc. Also the notation

$$\chi_{Aa}(x_1,y_1,z_1)=\chi_{Aa}(1)=(Aa)^{(1)} \tag{2.2}$$

is employed.

A given set of atomic orbitals determines a metric characterized by the overlap integrals

$$\Delta(r,s)=\int dV\chi_r\chi_s. \tag{2.3}$$

Since it is always assumed that atomic orbitals are normalized, and that those located on the same atom are mutually orthogonal, the *overlap matrix* can be written

$$\boldsymbol{\Delta}=\mathbf{I}+\mathbf{S}, \tag{2.4}$$

with

$$S(Aa,Bb)=(1-\delta_{AB})\int dV(Aa)(Bb), \tag{2.4'}$$

so that the matrix $\mathbf{S}$ has nonvanishing elements only if the two orbitals belong to different atoms. In order to keep the formulas free of asterisks, it is assumed that all atomic orbitals are chosen to be real, in practice the only case of importance.

2.2 Expansion of Density and Pair Density

Let

$$\begin{aligned}\rho(\mathbf{x}_1|\mathbf{x}_2)&=\sum_r\sum_s\chi_r(1)\chi_s(2)p(r|s)\\&=\sum_{Aa}\sum_{Bb}(Aa)^{(1)}(Bb)^{(2)}p(Aa|Bb),\end{aligned} \tag{2.5}$$

with

$$\sum_{Aa}\sum_{Bb}=\sum_A\sum_a\sum_B\sum_b, \tag{2.5'}$$

be the expansion of the first-order density. The expansion coefficients $p(Aa|Bb)$ form a Hermitian matrix $\mathbf{p}$ for which the name *bond-order matrix* will be used. More specifically, only the off-diagonal elements of $\mathbf{p}$ will be referred to as bond orders, whereas the diagonal elements are related to atomic populations to be discussed in a subsequent section. The name as well as the symbol $\mathbf{p}$ are chosen, because the quantities $p(r|s)$ are the natural generalizations of the "bond orders" used, with the symbol $\mathbf{p}$, in molecular orbital theory for two decades. Thus *the bond-order matrix is defined as the representation of the first-order density operator in the nonorthogonal basis of significant atomic orbitals.*[12]

According to Eq. (1.32) only the diagonal elements (1.9) of the pair-density kernel π enter in the molecular

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[12] We reserve the name "bond-order matrix" for a representation of the density operator in a basis of atomic orbitals. It is confusing to use this name for representations in other basis sets. For them the nomenclature proposed after Eq. (1.13) is adequate.

calculation. Hence, we introduce the expansion

$$\pi(\mathbf{x}_1\mathbf{x}_2)=\sum_r \sum_{\bar{r}} \sum_s \sum_{\bar{s}} \chi_r(1)\chi_{\bar{r}}(1)\chi_s(2)\chi_{\bar{s}}(2) \times p(r\bar{r}\,|\,s\bar{s}), \quad (2.6)$$

$$=\sum_{Aa} \sum_{\bar{A}\bar{a}} \sum_{Bb} \sum_{Bb} (Aa\bar{A}\bar{a})^{(1)}(Bb\bar{B}\bar{b})^{(2)} \times p(Aa\bar{A}\bar{a}\,|\,Bb\bar{B}\bar{b}),$$

where

$$(Aa\bar{A}\bar{a})^{(1)}=(Aa)^{(1)}(\bar{A}\bar{a})^{(1)}, \text{ etc.,} \quad (2.6')$$

and where the atomic orbitals are those used in Eq. (2.5). Frequently, in particular for computational purposes, it is convenient to consider the expansion coefficients $p(Aa\bar{A}\bar{a}\,|Bb\bar{B}\bar{b})$ as elements of a matrix $\mathfrak{p}$ wherein *each row corresponds to one index quadruple* $(Aa\bar{A}\bar{a})$ and *each column corresponds to one index quadruple* $(Bb\bar{B}\bar{b})$. This matrix is real and symmetric, i.e.,

$$p(Aa\bar{A}\bar{a}\,|Bb\bar{B}\bar{b})=p(Bb\bar{B}\bar{b}\,|Aa\bar{A}\bar{a}); \quad (2.7)$$

and furthermore it follows from Eq. (2.6) that it can be chosen such that

$$\begin{aligned} p(Aa\bar{A}\bar{a}\,|Bb\bar{B}\bar{b})&=p(\bar{A}\bar{a}Aa\,|Bb\bar{B}\bar{b}),\\ p(Aa\bar{A}\bar{a}\,|Bb\bar{B}\bar{b})&=p(Aa\bar{A}\bar{a}\,|\bar{B}\bar{b}Bb). \end{aligned} \quad (2.8)$$

By virtue of Eq. (2.8) it is permissible, in most numerical work, to omit the row $(\bar{A}\bar{a}Aa)$ and instead double the row $(Aa\bar{A}\bar{a})$, provided $(Aa)\neq(\bar{A}\bar{a})$; similar simplifications hold for the columns. The matrix $\mathfrak{p}$ will be called the *pair bond-order matrix.*

From the formal mathematical point of view, the grouping of indices inside the parentheses of the pair bond-orders would be unsuitable if it were intended to construct a representative of the operator π. The arrangement is however expedient for our analysis, whose object is the disentanglement of contributions arising from overlapping atomic orbitals.

The conservation relations (1.11) and (1.11′) generate corresponding relations for the bond-order matrix and for the pair bond-order matrix, viz.,

$$\mathrm{Tr}(\mathbf{\Delta p})=\sum_r \sum_s p(r\,|\,s)\Delta(r,s)=N, \quad (2.9)$$

$$\sum_s \sum_{\bar{s}} p(r\bar{r}\,|\,s\bar{s})\Delta(s,\bar{s})=(N-1)p(r\,|\,\bar{r}). \quad (2.10)$$

Considering the overlap matrix $\mathbf{\Delta}$ and the bond-order matrix $\mathbf{p}$ as vectors, one can write Eq. (2.10)

$$\mathfrak{p}\mathbf{\Delta}=(N-1)\mathbf{p}. \quad (2.11)$$

Combination of Eqs. (2.9) and (2.10) yields

$$\sum_{r\bar{r}} \sum_{s\bar{s}} \Delta(r,\bar{r})p(r\bar{r}\,|\,s\bar{s})\Delta(s,\bar{s})=N(N-1). \quad (2.12)$$

The derivation of Eqs. (2.9) and (2.10) is based on the assumption that the set of atomic orbitals selected by the significant expansion is *not* overcomplete.

2.3 Significant Expansions

At present, even the most rigorous LCAO calculations use only a limited number of atomic orbitals. In these cases, it seems natural to consider the chosen set of atomic orbitals, or a suitable linear combination of them, as the significant expansion of this particular approximation.

For this reason there does not seem to be an urgent need for finding methods to determine significant expansions.[13] Hence the purpose of the subsequent suggestions is not to establish a practical method, but to show that criteria can be given by which a significant expansion can be defined, in principle, from the rigorous wave functions of a molecule.

A possible general procedure would be as follows:

(1) Find the natural orbitals by solving the Fredholm integral equation (1.18);
(2) Find the optimal expansions of the natural orbitals;
(3) By substituting into the bilinear expansion (1.14), (1.15), find the significant expansion of the density kernel.

In order to find the optimal expansion of a natural orbital $\varphi(\mathbf{x})$, suppose that

$$\varphi(\mathbf{x})=\sum_A \varphi_A(\mathbf{x}),$$

where $\varphi_A(\mathbf{x})$ is the contribution from atom A. Because of the overcompleteness, many such expansions can be found. If the equations[14]

$$\varphi_A(\mathbf{x})=\sum_{l,m} Y_{lm}(\theta_A,\phi_A)f_{lm}(r_A), \quad (2.13)$$

and

$$\sum_m \int_0^\infty drr^2 f_{lm}(r)=f_l^2, \quad (2.14)$$

define $f_{lm}(r)$ and f_l^2, then the "uncertainty" Δl_A, given by

$$(\Delta l_A)^2=\sum_{l=0}^{\infty}(l-\bar{l})^2 f_l^2, \quad (2.15)$$

with

$$\bar{l}=\sum_{l=0} l f_l^2, \quad (2.15')$$

would seem to be an appropriate measure for the length of the expansion of $\varphi_A(\mathbf{x})$ in terms of atomic orbitals on atom A.

An optimal expansion of $\varphi(\mathbf{x})$ could then be characterized by the minimum of the multiple uncertainty product[15]

$$\Delta l=\textstyle\prod_A(\Delta l_A). \quad (2.16)$$

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[13] Except in the case of those wave functions for diatomic molecules which have been calculated in elliptic coordinates.

[14] The $Y_{lm}(\theta,\phi)$ are spherical harmonics.

[15] It is also stipulated that $f_{lm}(r)$ is an *analytic* function of its argument in the whole range $0\leqslant r<\infty$.

Suppose then that an optimal expansion has been found for each natural orbital, i.e.,

$$\varphi_n(\mathbf{x})=\sum_{Aj}\bar{\chi}_{jn}{}^{A}c_{jn}{}^{A}. \tag{2.17}$$

In this way, one obtains many atomic orbitals $\bar{\chi}_{jn}{}^{A}$ on a given atom A. They form a nonorthogonal set with metric matrix

$$\mathbf{M}^{A}=\{M_{im,jn}{}^{A}\}, \tag{2.18}$$

and linear dependence, or at least near-linear dependence, is to be expected between them.

An effective way to eliminate the linear dependence is by canonical orthogonalization.[16] To this end, one finds the matrix $\mathbf{U}^{A}$ which diagonalizes $\mathbf{M}^{A}$, i.e.,

$$(\mathbf{U}^{A})^{\dagger}\mathbf{M}^{A}\mathbf{U}^{A}=\mathbf{d}^{A}$$

$$\sum_{i,m}\sum_{j,n}M_{im,jn}{}^{A}(U_{im,a}{}^{A})^{*}U_{jn,\bar{a}}{}^{A}=d_a{}^{A}\delta_{a\bar{a}} \tag{2.19}$$

and then constructs new orthogonal atomic orbitals χ_{Aa}, defined by the relation

$$\bar{\chi}_{jn}{}^{A}(\mathbf{x})=\sum_{a}(U_{jn,a}{}^{A})^{*}(d_a{}^{A})^{\frac{1}{2}}\chi_{Aa}(\mathbf{x}). \tag{2.20}$$

The occurrence of linear dependence (near linear dependence) among the original orbitals manifests itself by the appearance of vanishing (very small) eigenvalues $d_a{}^{A}$.

Substitution of the transformations (2.20) into the optimal expansions (2.17) and inserting the latter into the bilinear expansion (1.14), (1.15), yields for the density an expansion of the kind given in Eq. (2.5) with the bond-order matrix

$$p(Aa|Bb)=(d_a{}^{A}d_b{}^{B})^{\frac{1}{2}}\sum_{n}N_n\sum_{Ai}c_{in}{}^{A}(U_{in,a}{}^{A})^{*}$$
$$\times\sum_{Bj}c_{jn}{}^{B}(U_{jn,b}{}^{B})^{*}. \tag{2.21}$$

By omitting those terms in this series which are insignificant because of the smallness of the factors $(d_a{}^{A}d_b{}^{B})^{\frac{1}{2}}$, one selects the best set of linear independent atomic orbitals. They are found explicitly by inverting the Eq. (2.20).

3. DENSITY PARTITIONING AND SHARING INTERFERENCE

3.1 Interference Partitioning

From the expression (2.5), it is apparent that a decomposition of the density in terms of atomic contributions *only*, such as considered in Eq. (1.38), is *not* possible if the atomic contributions are derived, in some way, from *atomic orbitals*. A relation of the type of Eq. (1.38) could be obtained on the basis of a *cellular* subdivision; however, the *orbital* subdivision is unquestionably more appropriate if *atomic contributions* are to be isolated. Moreover, the cross terms between atomic orbitals from different atoms are actually of greatest interest since they are intimately connected with the overlap effect which is the chief cause for bond formation.

The presence of overlap terms in the density ρ is typical for the wave character of quantum mechanics. This kind of phenomenon occurs in *any* wave theory based on a homogeneous linear differential equation, whenever certain constituent wave functions combine linearly to form exact or approximate new solutions, and it is generally called the *interference effect.*

Whereas, in classical electrostatics one would *superpose densities to form new densities; in wave mechanics, wave functions are superposed to form new wave functions*, from which new densities are then obtained by squaring the absolute value. Hence, the resulting density differs from the sum of the densities of the constituent wave functions.

Consider the case of two atomic orbitals χ_A and χ_B forming a molecular orbital φ. The densities for the separate constituent atoms are given by

$$\rho_A(\mathbf{x})=\chi_A{}^2(\mathbf{x}),\quad \rho_B(\mathbf{x})=\chi_B{}^2(\mathbf{x}). \tag{3.1}$$

Suppose that the molecular wave function is of the form

$$\varphi=[2(1+S)]^{-\frac{1}{2}}(\chi_A+\chi_B), \tag{3.2}$$

with S being the overlap integral between the two atomic orbitals. Equation (3.2) indicates that each atomic orbital contributes 50% to the electron. In such a situation, a "quasi-classical" electrostatic approach would lead to the molecular density

$$\rho^{\mathrm{CL}}=\tfrac{1}{2}\rho_A+\tfrac{1}{2}\rho_B. \tag{3.3}$$

The equipartitioning follows from the symmetric linear combination chosen in Eq. (3.2) and *does not depend upon whether the two orbitals (3.1) are similar in range or character.* [The factors (1/2) originate from the fact that ρ, ρ_A, ρ_B all must be normalized to unity.] In contrast, the wave-mechanical density is given by

$$\rho=\rho^{\mathrm{CL}}+\rho^{\mathrm{I}}, \tag{3.4}$$

where

$$\rho^{\mathrm{I}}=[\chi_A\chi_B-\tfrac{1}{2}S(\chi_A{}^2+\chi_B{}^2)]/(1+S) \tag{3.5}$$

represents precisely the *modification of the quasi-classical density* ρ^{CL} *due to the interference effect.* A further characteristic of the wave nature of quantum mechanics is that it gives rise to two distinct possibilities:

(1) *Constructive interference* resulting in charge *accumulation* within the bond region, this is the case of Eq. (3.2);

(2) *Destructive interference* resulting in charge *diminution* within the bond region, this case is that of the antibonding orbital

$$\varphi'=[2(1-S)]^{-\frac{1}{2}}(\chi_A-\chi_B), \tag{3.6}$$

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[16] This method of eliminating linear dependencies is due to P. O. Löwdin (personal communication).

which is characterized by the density

$$\rho' = \rho^{\mathrm{CL}} + \rho'^{\mathrm{I}}, \tag{3.7}$$

with

$$\rho'^{\mathrm{I}} = -[\chi_A\chi_B - \tfrac{1}{2}S(\chi_A{}^2 + \chi_B{}^2)]/(1-S). \tag{3.8}$$

It is significant that ρ and ρ' differ in the interference parts ρ^{I}, ρ'^{I} and not in the quasi-classical part ρ^{CL}.

We proceed now to find an interference partitioning

$$\rho(\mathbf{x}) = \rho^{\mathrm{CL}}(\mathbf{x}) + \rho^{\mathrm{I}}(\mathbf{x}) \tag{3.9}$$

for the *general* density expansion

$$\rho(\mathbf{x}) = \sum_{Aa}\sum_{Bb} (Aa)(Bb)p(Aa|Bb), \tag{3.10}$$

which follows from Eq. (2.5). The two parts must have the following structure and meaning[17]:

$$\rho^{\mathrm{CL}}(\mathbf{x}) = \sum_A \rho_A(\mathbf{x}) = \text{quasi-classical density}, \tag{3.11}$$

$$\rho^{\mathrm{I}}(\mathbf{x}) = \sum_{A,B}{}' \rho_{AB}(\mathbf{x}) = \text{interference density}. \tag{3.12}$$

It is clear that the interference density ρ^{I} must *originate* from the cross terms

$$\sum_{A,B}{}' \sum_{a,b} (Aa)(Bb)p(Aa|Bb), \tag{3.13}$$

of Eq. (3.10). It cannot be identical with these terms, however, since the *total population* of ρ^{I} vanishes, i.e.,

$$\int dV\rho^{\mathrm{I}}(\mathbf{x}) = 0, \tag{3.14}$$

a relation which follows from the fact that the total classical population as well as the total wave-mechanical population, *both* must be equal to N, the total number of electrons. It is therefore necessary that the expression (3.13) be separated into two parts: One part *can* have nonvanishing total population, but *must* be a sum of atomic contributions only; the other part *must* have vanishing total population, but *can* have interatomic cross terms. If we now adopt the natural postulate that the *procedure of carrying out this separation does not depend upon the particular values which the bond orders $p(Aa|Bb)$ happen to have* in specific cases, then it follows that this separation *must be carried out for each orbital product $(Aa)(Bb)$ individually.* Hence a partitioning

$$\chi_{Aa}(\mathbf{x})\chi_{Bb}(\mathbf{x}) = c_{Aa}\chi_{Aa}{}^2(\mathbf{x}) + c_{Bb}\chi_{Bb}{}^2(\mathbf{x}) + f_{AaBb}(\mathbf{x}) \tag{3.15}$$

must be found, where

$$\int dV f_{AaBb}(\mathbf{x}) = 0,$$

and where c_{Aa} and c_{Bb} depend only upon the two orbitals and add up to $S(Aa,Bb)$. In the special case of the molecular orbitals (3.2) and (3.6), the expansion (3.10) reduces to

$$2(1\pm S)^{-1}(\chi_A{}^2 + \chi_B{}^2 \pm 2\chi_A\chi_B). \tag{3.16}$$

In order that the substitution of the decomposition (3.15) into the expressions (3.16) yields the previously discussed results (3.3) to (3.5), and (3.7), (3.8), it is necessary that the constants C_{Aa} and C_{Bb} must be equal, and in fact, equal $\frac{1}{2}S(Aa,Bb)$. Thus we find the basic interference partitioning for orbital products

$$(AaBb) = (Aa)(Bb) = \tfrac{1}{2}S(Aa,Bb)[(Aa)^2 + (Bb)^2] + \langle Aa,Bb\rangle, \quad A\neq B, \tag{3.17}$$

where $\langle Aa,Bb\rangle$, defined by

$$\langle Aa,Bb\rangle = (Aa)(Bb) - \tfrac{1}{2}S(Aa,Bb)[(Aa)^2 + (Bb)^2], \quad A\neq B, \tag{3.18}$$

is called the *interference-density part of the orbital product* $(Aa)(Bb)$. As was pointed out after Eq. (3.3), these results do not depend upon an assumption of similarity between the atomic orbitals.

Substitution of the interference partitioning (3.17) for orbital products into the expansion (3.10) leads now to an interference partitioning for the general electron density. This partitioning is of the kind expressed by Eqs. (3.9), (3.11), and (3.12), where now the terms ρ_A and ρ_{AB} are given by

$$\rho_A(\mathbf{x}) = \sum_{a,\bar{a}} (Aa)(A\bar{a}) \times [p(Aa|A\bar{a}) + \delta_{a\bar{a}}(\mathbf{Sp})_{AaA\bar{a}}] = \rho(A), \tag{3.19}$$

$$\rho_{AB}(\mathbf{x}) = \sum_a \sum_b \langle Aa,Bb\rangle p(Aa|Bb) = \rho(AB), \quad (A\neq B). \tag{3.20}$$

Note that the matrix $\mathbf{S}$, defined by Eq. (2.4′) has vanishing elements for $A = B$.

3.2 Interference Densities

In agreement with Eq. (3.14), interference densities satisfy the conservation relations

$$\int dV\langle Aa,Bb\rangle = 0, \qquad \int dV\rho(AB) = 0. \tag{3.20a}$$

These relations show that an interference density is positive in some regions and negative in other regions, a circumstance which characterizes it as a density *modification*: the addition of an interference density *rearranges* the quasi-classical density *without changing the total population*. Specifically, the constructive bond-

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[17] Here and in the rest of the paper a primed summation is defined by $\sum'_{i,j} = \sum_i\sum_j$, $(i\neq j)$.

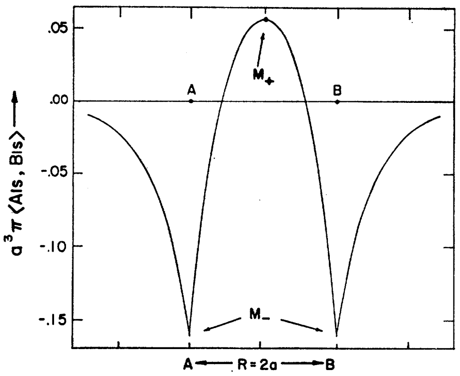

FIG. 1. Interference density in H_2^+. Values along the internuclear axis. $(A1s) = (1s)$ orbital on nucleus A with effective charge $\zeta = 1$ Similar for $(B1s)$.

ing interference takes away density from the atoms and puts it in the bond regions, whereas the destructive interference takes density out of the bond regions and puts it in the atom regions. In order to illustrate these statements a graphical representation is given for the interference density $\langle A1s,B1s\rangle$ arising in the case of the H_2^+ ion. The distance of the two centers A and B is chosen to be two Bohr, and the orbital exponent of the $(1s)$ function is chosen equal to unity. Figure 1 gives a plot of the value of the interference density along the internuclear axis; Fig. 2 gives a radial cut through the surfaces of constant density.

From the preceding derivations it appears likely, and the subsequent derivations make it explicit, that *the interference density* ρ^I *is responsible for the origin of the specific and substantial stabilization energy which cannot be understood in terms of a quasi-classical picture and which gives rise to the phenomenon of "covalent chemical binding."*

In previous approaches, referred to in the introduction, these nonclassical energy contributions have been variously characterized by such concepts as "exchange energy," "resonance," and "overlap forces," the latter giving rise to the "postulate of maximum overlap." Although in none of these cases a rigorous general formulation has been achieved, it is of interest to examine the relation between these concepts and those introduced here.

In Sec. 7.6, it is shown that the energy-lowering part of the *exchange energy* indeed arises from the interference density ρ^I. It is also found, however, that the exchange energy contains other terms which raise the energy. Its meaning is further confused by certain unjustified simplifications introduced in connection with the "approximation of perfect pairing."

Originally, the *resonance* concept was closely tied to the exchange picture of covalent binding, which is discussed in the last subsection of Sec. 7.6. More recently the chemical meaning of resonance appears to have been limited to describe simply the superposition principle for the construction of solutions to the Schrödinger equation. More specifically it denotes what may be called "structure interaction" in analogy to "configuration interaction." The present results show that, in a covalent bond, orbitals from different atoms are involved in interactions which may be compared to *acoustical resonance*, as the origin of the latter is precisely an enhancement (or attenuation) of the amplitudes of sound waves due to interference. In fact, we shall see that certain integrals over our interference densities lead directly to certain previously encountered "resonance integrals." Thus, it seems that the formalism of interference densities exhibits physical essentials lying behind the resonance idea.

The close connection between *overlap* and interference has already been elaborated. A further point must be made: At first sight it might have appeared tempting to hold the "overlap distribution"

$$\chi_{Aa}(\mathbf{x})\chi_{Bb}(\mathbf{x}) \tag{3.21}$$

responsible for the specific covalent binding effect between the orbitals (Aa) and (Bb), and hence to consider this effect roughly proportional to the overlap integral $S(Aa,Bb)$. This suggestion has been made repeatedly.[18] However, the present analysis suggests that the responsibility must be attributed to the interference density (3.18) rather than to the expression (3.21). The strength of this interference depends upon the amount of charge displaced, in Fig. 2, from the negative region into the positive central region. This *interference population* is roughly proportional to $S(1-S)$, in the case at hand. That this view is indeed the correct one becomes evident from the energy analysis in Sec. 6.2. Expressions related to the overlap distribution (3.21) will, however, be found useful for a somewhat more modest purpose, viz., to characterize the "valence activity" of atomic and molecular orbitals.

3.3 Quasi-Classical Densities

The quasi-classical atomic density contributions (3.19) can be written in the form[17]

$$\rho(A) = \sum_a (Aa)^2 q(Aa) + \sum_{a,\bar{a}}{}' (Aa)(A\bar{a})p(Aa|A\bar{a}), \tag{3.22}$$

where

$$q(Aa) = (\mathbf{\Delta p})_{Aa,Aa}, \tag{3.23}$$

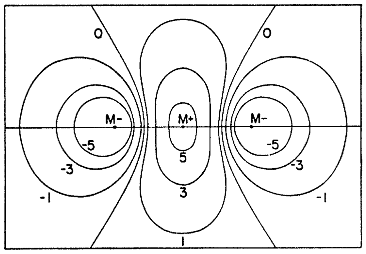

FIG. 2. Interference density in H_2^+. Contour lines in a plane containing the internuclear axis. The numbers characterizing the different contours represent

$$[a^3\pi\langle A1s,B1s\rangle \times 10^2].$$

Extrema: $M_+ = 5.642$, $M_- = -16.156$. (Compare Fig. 1).

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[18] R. McWeeny, J. Chem. Phys., **19**, 1614 (1951); **20**, 920 (1951); R. S. Mulliken, *ibid.* **23**. 1833, 1841, 2338, 2343 (1955).

or

$$q(Aa)=p(Aa)+v(Aa), \tag{3.24}$$

with

$$p(Aa)=p(Aa|Aa), \tag{3.25}$$

$$v(Aa)=(\mathbf{Sp})_{Aa,Aa}=\sum_{Bb} S(Aa,Bb)p(Bb|Aa). \tag{3.26}$$

The overlap matrices $\mathbf{\Delta}$, $\mathbf{S}$ are defined in Eqs. (2.4), and (2.4′). Integration yields the populations

$$\int dV\rho(A)=\sum_{a} q(Aa)=q(A), \tag{3.27}$$

which, according to Eq. (2.9), satisfy the conservation relation

$$\int dV\rho=\int dV\rho^{\mathrm{CL}}=\sum_{A} q(A)=\mathrm{Tr}(\mathbf{\Delta p})=N. \tag{3.28}$$

Thus the quantities $q(Aa)$ can be considered as the populations of the orbitals (Aa) in the quasi-classical density part ρ^{CL}. These quantities are the natural generalizations of certain quantities, which have been used, *with the symbol* q, for over a decade in "naive" molecular orbital theories, although in somewhat different context.[19] The names "atomic charges," "formal charges," and more recently, by Mulliken,[18] "gross atomic populations" have been used in that context. We shall call $q(Aa)$ simply the *population of the atomic orbital* (Aa) in the molecule considered.

From Eqs. (3.24) to (3.26) it is likely that the relative magnitude of the contribution of $v(Aa)$ to $q(Aa)$ furnishes a measure of the degree to which the orbital (Aa) participates in the formation of nonvanishing interference densities and, hence, contributes to binding or antibinding. For this reason we call

$p(Aa)=$ the *valence-inactive population* of (Aa),[20]
$v(Aa)=$ the *valence-active population* of (Aa).

Their sum is $q(Aa)$, the (gross) population of (Aa). The relative size of $v(Aa)$ can be considered as a measure of the *valence activity* of the orbital (Aa).

Equation (3.22) is not yet entirely satisfactory. Its conceptual simplicity is marred by the appearance of the second sum on the right-hand side, for which the preceding arguments have yielded no interpretation. These terms actually have the character of interference densities inasmuch as, because of the intra-atomic orthogonality of atomic orbitals, they merely modify the density without changing the total population. In fact, it is convenient for later purposes to extend the definition (3.18) of the interference densities $\langle Aa,Bb\rangle$ to the case that both orbitals are on the same atom. Because of orthonormality, one obtains in this case indeed

$$\langle Aa,A\bar{a}\rangle=(1-\delta_{a\bar{a}})(Aa)(A\bar{a}) \tag{3.29}$$

as *intra-atomic interference densities*. It may be noted that the decomposition (3.17) is also valid for them. The elimination of these terms from the quasi-classical density contributions (3.22) is achieved in the next section.

3.4 Valence Atomic Orbitals

General Discussion

In qualitative reasoning on molecules, it has become useful to assume certain atomic orbitals, generally of hybrid character, as rather valence active and others, such as lone-pair orbitals and inner shells, as more or less valence inactive. It is desirable to have a way to extract an orthogonal set of such hybrid atomic orbitals from a general molecular wave function.

The results of the preceding section suggest that, for the determination of such orbitals, it may be reasonable to demand that the valence-inactive parts $p(Aa)$ arising from the density of the molecule under study should be either as large as possible or as small as possible. The atomic hybrid orbitals which are derived from this *postulate of maximal or minimal valence activity* will be called *valence atomic orbitals* (VAO's, if an abbreviation is desired) of a given atom in a given molecule.

It is readily shown that this postulate of extremal valence activity is equivalent to the condition that *all intra-atomic parts of the bond-order matrix are diagonal*, i.e.,

$$p(Aa|A\bar{a})=p(Aa)\delta_{a\bar{a}}, \quad \text{for all } A. \tag{3.30}$$

Indeed: Let (Aa^0) be an arbitrary orthogonal set of atomic orbitals on atom A. Let (Aa) be another orthogonal basis on A, spanning the same function space so that

$$(Aa)=\sum_{\bar{a}}(A\bar{a}^0)T_{\bar{a}a}{}^{A}, \tag{3.31}$$

where $\mathbf{T}^A$ is an orthogonal matrix. If $\mathbf{p}^0$ and $\mathbf{p}$ are the bond-order matrices representing the molecular density in these two bases, then one has the relations

$$p(Aa|Bb)=\sum_{\bar{a},\bar{b}} p^0(A\bar{a}|B\bar{b})T_{\bar{a}a}{}^{A}T_{\bar{b}b}{}^{B}. \tag{3.32}$$

Our postulate requires the extremization of the quadratic form

$$p(Aa|Aa)=\sum_{\rho,\sigma} p^0(A\rho|A\sigma)T_{\rho a}{}^{A}T_{\sigma a}{}^{A}, \tag{3.33}$$

considered as function of the variables $T_{\rho a}{}^{A}$ ($\rho=1, 2, \cdots$), for each atom A. The result is that the components of the valence orbitals (Aa), in terms of the original orbitals (Aa^0), are the eigenvectors of that intra-atomic part of the bond-order matrix $\mathbf{p}^0$ which refers to the atom A. Hence, the matrix of these eigenvectors

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[19] C. A. Coulson and H. C. Longuet-Higgings, Proc. Roy. Soc. (London) **A191**, 39 (1947).

[20] Mulliken suggested the name "net" populations for the $p(Aa)$'s. However, he made no use of these quantities.

$\mathbf{T}^A$ diagonalizes the intra-atomic bond-order matrix, i.e.,

$$\sum_{\rho,\sigma} T_{\rho a}{}^{A} p^0(A\rho|A\sigma) T_{\sigma a}{}^{A} = p(Aa)\delta_{a\bar{a}}. \tag{3.34}$$

If the matrix $\mathbf{T}$ denotes the direct sum of all eigenvectors matrices $\mathbf{T}^A$, i.e.,

$$T(Aa,Bb)=\delta_{AB}T_{ab}{}^{A}, \tag{3.35}$$

then the Eq. (3.34), *for all A*, can be expressed by the *one* matrix equation

$$\mathbf{T}^{\dagger}\mathbf{p}^0\mathbf{T}=\mathbf{p}, \tag{3.36}$$

where the intra-atomic parts of $\mathbf{p}$ are given by Eq. (3.30). We shall say that the bond-order matrix in terms of valence atomic orbitals is *locally diagonal.*

This property makes the valence orbitals particularly suited for the interference partitioning, since it leads to the disappearance of the intra-atomic interference densities (3.29). Thus, Eq. (3.22) for the quasi-classical density simplifies to

$$\rho^{\mathrm{CL}}=\sum_A \rho(A)=\sum_A \sum_a (Aa)^2 q(Aa), \tag{3.37}$$

so that the populations $q(Aa)$ can now also be interpretated as orbital occupation numbers. *In the following discussions we always assume that, in any given molecule, the valence atomic orbitals have been chosen as basis of expansion on each atom,* unless explicitly stated otherwise.[21]

Examples

We illustrate the physical significance of valence hybrids by two examples: First, we consider the wave function calculated by Scherr for the N_2 molecule by means of the LCAO-SCF-MO method.[22] The following basis of unhybridized atomic orbitals was used in this work: $(A1s)$, $(A2s)$, $(A2p\sigma)$, $(A2p\pi)$, $(A2p\bar{\pi})$; $(B1s)$, $(B2s)$, $(B2p\sigma)$, $(B2p\pi)$,$(B2p\bar{\pi})$, where A and B denote the two centers. Diagonalization of the intra-atomic bond-order matrix leaves the π orbitals unchanged, but leads to six σ-valence hybrids:

$$(Ai\sigma),\ (Al\sigma),\ (Ab\sigma);\ (Bi\sigma),\ (Bl\sigma),\ (Bb\sigma);$$

which are related to the spherical orbitals[23] as follows:

	$(1s)$	$(2s)$	$(2p)$
$(i\sigma)$	0.961959	−0.251794	0.105998
$(l\sigma)$	0.271779	0.842545	−0.465031
$(b\sigma)$	0.027784	0.476149	0.878926

(3.38)

(for A and B). It is apparent that the hybrid orbital $(b\sigma)$ points to the other atom, whereas the hybrid orbital $(l\sigma)$ points away from it. Table I lists the gross orbital populations and their partitioning in valence-active and valence-inactive parts for both the spherical and the valence orbitals. The exhibited quantitative clarification effected by transformation to valence hybrids is remarkable and justifies the choice of the names:

$$\left.\begin{array}{l}(i\sigma),\ \text{inner-shell valence—AO}\\ (l\sigma),\ \text{lone-pair valence—AO}\\ (b\sigma),\ \text{bonding valence—AO}\end{array}\right\}\ \begin{array}{l}\text{of the } N \text{ atom in the N}_2\\ \text{molecule, within the}\\ \text{chosen approximation.}\end{array}$$

TABLE I. Populations of spherical AO's and valence AO's in N_2.

	$1s$	$2s$	$2p\sigma$	$i\sigma$	$l\sigma$	$b\sigma$	$2p\pi$	$2p\bar{\pi}$
p	2.01	1.81	0.984	2.00	2.16	0.64	0.78	0.78
v	−0.01	−0.07	0.276	0.00	−0.11	0.31	0.22	0.22
q	2.00	1.74	1.26	2.00	2.05	0.95	1.00	1.00

Secondly, we consider the wave function for the water molecule calculated by Ellison and Shull within the LCAO-MO-SCF approximation.[24] The basis of unhydrized orbitals is

$$(O1s),\ (O2s),\ (O2px),\ (O2py),\ (O2pz),\ (H1s),\ (H'1s).$$

Here, $(O2px)$ is perpendicular to the molecular plane; $(O2py)$ is parallel to the H—H′ bond; and $(O2pz)$ points to the midpoint of the H—H′ bond. Due to the molecular symmetry, the "local" bond-order matrix is already diagonal in $(2px)$ and $(2py)$, so that the formation of valence hybrids merely mixes $(1s)$, $(2s)$, and $(2pz)$. Again one finds valence hybrids $((Oi\sigma)$, $(Ol\sigma)$, $(Ob\sigma)$. They are related to the unhybridized atomic orbitals as follows:

	$(O1s)$	$(O2s)$	$(O2pz)$
$(Oi\sigma)$	0.988077	−0.144001	0.054465
$(Ol\sigma)$	0.149955	0.820012	−0.552353
$(Ob\sigma)$	0.034878	0.553935	0.831829

(3.39)

It is obvious that the method of local diagonalization furnishes valence atomic orbitals which transform according to irreducible representations of the molecular symmetry group and, hence, do not point in the direction of the OH and OH′ bonds. Each of these single bonds appear divided into a σ-type contribution and a π-type contribution. It seems reasonable now to construct *bond atomic orbitals* on oxygen by the definitions,[25]

$$\begin{aligned}(ObH)&=[(Ob\sigma)+(O2py)]/\sqrt{2},\\ (ObH')&=[(Ob\sigma)-(O2py)]/\sqrt{2}.\end{aligned} \tag{3.40}$$

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[21] After completion of this work the author learned that R. McWeeny had previously expressed the conjecture that it might be useful to choose atomic orbitals which diagonalize the intra-atomic parts of the bond-order matrix. See: R. McWeeny, Tech. Rept. No. 7, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (1955), p. 33; also Revs. Modern Phys. **32**, 335 (1960). No relation to a maximum–minimum principle was given.

[22] C. W. Scherr, J. Chem. Phys. **23**, 569 (1955).

[23] Spherical atomic orbitals = atomic orbitals which are proportional to spherical harmonics.

[24] F. O. Ellison and H. Shull, J. Chem. Phys. **23**, 2348 (1955).

[25] Equation (3.40) defines the only superpositions of $(Ob\sigma)$ and $(O2py)$ which are each other's mirror images. Furthermore, the 1:1 mixing ratio seems reasonable since, according to Table II, both are equally valence active.

The angle enclosed by *these* two atomic orbitals is found to be 100° 30′, slightly less than 105°, the assumed HOH′ angle. This compares rather favorably with previous attempts of defining "bond hybrids." One definition, proposed by Pople,[26] if applied to the Ellison–Shull calculation, yields bond hybrids enclosing an angle of 68°47′! Another definition, proposed by McWeeny,[27] if applied to this calculation yields bond hybrids enclosing an angle of 154°! It may also be mentioned that these other definitions are based upon a transformation of *molecular orbitals* and, in contrast to the procedure proposed here, are therefore inapplicable outside the MO approximation (one-determinant wave function).

Tables II and III list the gross populations, valence-active populations, and valence-inactive populations for H_2O. As in the case of N_2, it exhibits the conceptual advantage in choosing the valence orbitals as basis for interpreting populations.

3.5 Expectation Values of One-Electron Operators; Dipole Partitioning

In order to be able to calculate expectation values of the kind given by Eq. (1.24), we generalize the interference partitioning, in terms of valence orbitals, to the density kernel

$$\rho(\mathbf{x}_1|\mathbf{x}_2)=\rho^{\mathrm{CL}}(\mathbf{x}_1|\mathbf{x}_2)+\rho^{\mathrm{I}}(\mathbf{x}_1|\mathbf{x}_2), \tag{3.41}$$

$$\rho^{\mathrm{CL}}(\mathbf{x}_1|\mathbf{x}_2)=\sum_A \rho_A(\mathbf{x}_1|\mathbf{x}_2)=\sum_{Aa} q(Aa)\chi_{Aa}(1)\chi_{Aa}(2), \tag{3.42}$$

$$\begin{aligned}\rho^{\mathrm{I}}(\mathbf{x}_1|\mathbf{x}_2)&=\sum_{A,B}{}' \rho_{AB}(\mathbf{x}_1|\mathbf{x}_2)\\ &=\sum_{A,B}{}'\sum_{a,b} p(Aa|Bb)\langle Aa^1Bb^2\rangle,\end{aligned} \tag{3.43}$$

where

$$\begin{aligned}\langle Aa^1Bb^2\rangle=\tfrac{1}{2}\{&[\chi_{Aa}(1)\chi_{Bb}(2)+\chi_{Bb}(1)\chi_{Aa}(2)]\\ &-S(Aa,Bb)[\chi_{Aa}(1)\chi_{Aa}(2)+\chi_{Bb}(1)\chi_{Bb}(2)]\}\\ &=\langle Bb^1Aa^2\rangle,\end{aligned} \tag{3.44}$$

so that

$$\langle Aa^1Bb^1\rangle=\langle Aa,Bb\rangle.$$

Table II. Populations of spherical AO's and valence AO's on oxygen in H_2O.

	O1s	O2s	O2pz	Oiσ	Olσ	Obσ	O2py	O2px
p	2.00	1.84	1.41	2.00	2.22	1.045	0.59	2.00
v	0.00	0.00	0.18	0.00	−0.15	0.315	0.33	0.00
q	2.00	1.84	1.59	2.00	2.07	1.36	0.92	2.00

Table III. Populations of valence AO's and bond AO's on oxygen in H_2O.

	Obσ	O2py	ObH	ObH′
p	1.045	0.59	0.82	0.82
v(OH)	0.158	0.165	0.34	−0.02
v(OH′)	0.158	0.165	−0.02	0.34
q	1.36	0.92	1.14	1.14

The expectation value (1.24) can be written

$$F=\sum_A F_A+\sum_{A<B} F_{AB}, \tag{3.45}$$

exhibiting the difference between quasi-classical and wave-mechanical contributions.

According to the Hellman-Feynman theorem, the operator

$$f(\mathbf{x})=Z_Ae^2\,\mathrm{grad}_A|\mathbf{x}_A-\mathbf{x}| \tag{3.46}$$

yields the force acting on nucleus A. In this case, the interference term gives the deviation of the internuclear forces from a purely classical description, e.g., the nonbonded repulsion between two closed-shell atoms or molecules.

Consider now the dipole moment operator. Decompositions of the dipole moment of a molecule into atomic moments, bond moments, etc., have been used traditionally on an empirical basis. All theoretically defined decompositions proposed so far have been unsatisfactory, however, in that the magnitudes of the various contributions in them are very sensitively dependent upon the choice of the origin with respect to which the moment is calculated. In contrast, the total dipole moment $\mathbf{D}$ of a neutral molecule is *independent* of the choice of the origin, and it seems therefore logical to look for a *decomposition of* $\mathbf{D}$ *into parts whose magnitudes, too, are invariant against changes of the origin. Such a partitioning is furnished by Eq.* (3.45).

The molecular dipole is defined by

$$\mathbf{D}=\sum_A Z(A)\mathbf{x}_A-\int dV\rho(\mathbf{x})\mathbf{x}. \tag{3.47}$$

The total atomic population $q(A)$, defined by Eq. (3.27) for the valence orbitals, is in general different from $Z(A)$ the nuclear charge, where

$$q(A)=Z(A)+\Delta q(A). \tag{3.48}$$

Since we consider neutral molecules, the $Z(A)$ represent also the populations of the separated neutral atoms, and Eq. (3.48) therefore defines the *total population transfers* $\Delta q(A)$. Substituting the interference partitioning in Eq. (3.47) and expressing $Z(A)$ by means of Eq. (3.48), one obtains

$$\mathbf{D}=\mathbf{D}^{\mathrm{T}}+\sum_A \mathbf{D}_A+\sum_{A<B} \mathbf{D}_{AB}, \tag{3.49}$$

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[26] J. A. Pople, Proc. Roy. Soc. (London) **A202**, 323 (1950).

[27] R. McWeeny, Tech. Rept. No. 7, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (1955), p. 101.

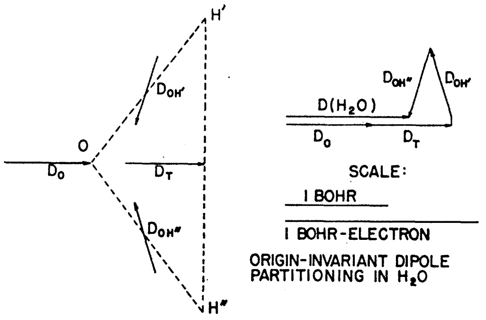

FIG. 3. Dipole partitioning of water.

where

$$\mathbf{D}_A=q(A)\mathbf{x}_A-\int dV\rho(A)\mathbf{x}, \tag{3.50}$$

$$\mathbf{D}_{AB}=-2\int dV\rho(A,B)\mathbf{x}, \tag{3.51}$$

$$\mathbf{D}^{\mathrm{T}}=-\sum_A \Delta q(A)\mathbf{x}_A. \tag{3.52}$$

The expression (3.50) represents atomic moments and Eq. (3.51) represents bond moments. The moment of Eq. (3.52) would be obtained by placing the total charges transferred to the various atoms on the respective nuclear positions and it may be called the *charge transfer dipole*, or *formal ionic dipole.*

It is easily seen that in each of the cases (3.50), (3.51), and (3.52), the partial dipoles are calculated from charge densities whose total populations vanish, and hence their magnitudes are indeed invariant against displacements of the origin.

Consequently, it is permissible to choose different origins for the different partial dipoles. For the atomic moments (3.50) it is convenient to choose the respective atomic center as origin; thus Eq. (3.50) becomes

$$\mathbf{D}_A=-\sum_a q(Aa)\mathbf{D}(Aa), \tag{3.53}$$

with

$$\mathbf{D}(Aa)=\int dV(Aa)^2(\mathbf{x}-\mathbf{x}_A). \tag{3.54}$$

For the bond moments (3.51) it is convenient to choose the bond midpoint as origin. Thereby one deduces

$$\mathbf{D}_{AB}=\sum_a v_B(Aa)\mathbf{D}(Aa)+\sum_b v_A(Bb)\mathbf{D}(Bb)-2\sum_{a,b} p(Aa|Bb)\mathbf{D}(Aa,Bb), \tag{3.55}$$

where $\mathbf{D}(Aa)$ and $\mathbf{D}(Bb)$ are the moments defined by Eq. (3.54) with respect to *atomic* centers and

$$\mathbf{D}(Aa,Bb)=\int dV(Aa)(Bb)[\mathbf{x}-\tfrac{1}{2}(\mathbf{x}_A+\mathbf{x}_B)] \tag{3.56}$$

are moments calculated with respect to the bond midpoint $\frac{1}{2}(\mathbf{x}_A+\mathbf{x}_B)$. Moreover,

$$v_B(Aa)=\sum_b p(Aa|Bb)S(Aa,Bb) \tag{3.57}$$

is that part of the valence-active population (3.26) of orbital (Aa) which originates from the bond between A and B.

As an example, Fig. 3 shows the dipole partitioning found for the water molecule according to the calculation mentioned earlier.[24] It illustrates the large contribution of the lone-pair electrons on oxygen and the fact that both bonds contain considerably larger moments than their contributions to the total dipole betray.

3.6 Valence Molecular Orbitals

We consider now the special, but at present rather frequent situation, that the wave function is given in the MO approximation, with all MO's having the same occupation number [see Eq. (1.19)]. In this case there exists the possibility of an arbitrary unitary transformation among the (filled) MO's. Lennard-Jones has therefore suggested that this freedom be exploited to construct molecular orbitals of a form which exhibits most clearly the origin of chemical binding.[28]

Specifically, Lennard-Jones and Pople[29] proposed for this purpose the construction of *equivalent orbitals* which are determined by the condition that, in the invariant exchange energy, those contributions which arise from the diagonal terms of Eq. (1.75) become as large as possible so that the contributions coming from the off-diagonal terms become as small as possible. The conditions defining these equivalent MO's become very complicated however.

On the other hand, the procedure employed above for finding the valence atomic orbitals suggests the possibility of finding different MO's which are likely to elucidate the bonding effects. Moreover, these MO's are determined by a simple procedure.

In the MO theory we have

$$\begin{aligned}\varphi_n&=\sum_{Aa}(Aa)c_{Aa,n},\\ \rho&=\sum_n N_n\varphi_n^2.\end{aligned} \tag{3.58}$$

Consequently

$$p(Aa|Bb)=\sum_n p_n(Aa|Bb),$$

with $p_n(Aa|Bb)$ defined by

$$N_n\varphi_n^2=\sum_{Aa}\sum_{Bb} p_n(Aa|Bb)(Aa)(Bb)$$

$$p_n(Aa|Bb)=N_nc_{Aa,n}c_{Bb,n}.$$

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[28] J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, **1**, 14 (1949); J. Chem. Phys. **20**, 1024 (1952).

[29] J. Lennard-Jones and J. A. Pople, Proc. Roy. Soc. (London) **A202**, 166 (1950).

Moreover, we consider only the case that all N_n's are identical. The total electron population can now be written

$$N=\sum_n N_n \tag{3.59}$$

$$N_n=p_n+v_n \tag{3.60}$$

$$p_n=\sum_{Aa} p_n(Aa|Aa) \tag{3.61}$$

$$v_n=\sum_{Aa}\sum_{Bb} p_n(Aa|Bb)S(Aa,Bb). \tag{3.62}$$

The population partitioning given by Eqs. (3.59) to (3.62) is analogous to that given by Eqs. (3.24), (3.27), and (3.28) for atomic orbitals and can therefore be similarly interpreted, viz., the molecular orbital population N_n consists of the valence-inactive part p_n and the valence-active part v_n.

This parallelism then suggests the introduction of *valence molecular orbitals based on the requirement of maximal or minimal valence activity.* We therefore define as valence MO's those molecular orbitals for which the valence-inactive populations

$$p_n=N_n\sum_{Aa} c_{Aa,n}c_{Aa,n} \tag{3.63}$$

are extremal. It is readily seen that this condition is equivalent to the requirement that the matrix

$$p_{nm}=N_n\sum_{Aa} c_{Aa,n}c_{Aa,m}, \quad (\text{Note } N_n=N_m), \tag{3.64}$$

be diagonal.

Indeed, suppose that the molecular orbitals

$$\varphi_\nu{}^0=\sum_{Aa}(Aa)c_{Aa,\nu}{}^0 \tag{3.65}$$

give rise to the matrix

$$p_{\nu\mu}{}^0=N_\nu\sum_{Aa} c_{Aa,\nu}{}^0c_{Aa,\mu}{}^0. \tag{3.66}$$

Let

$$\varphi_n=\sum_\nu \varphi_\nu{}^0T_{\nu n} \tag{3.67}$$

be another set of molecular orbitals, related to the original ones by the linear transformation $\mathbf{T}$, and giving rise to the matrix p_{nm} of Eq. (3.64). Then the relation

$$p_{nm}=\sum_{\nu\mu} p_{\nu\mu}{}^0T_{\nu n}T_{\mu m} \tag{3.68}$$

holds, and the extremization of the expression (3.63) is equivalent to constructing the columns of $\mathbf{T}$ from the eigenvector of $\mathbf{p}^0$; hence, $\mathbf{p}$ will be diagonalized and the transformation $\mathbf{T}$ will be unitary.

It is easily shown that the valence molecular orbitals, obtained in this way, are invariant against unitary transformations among the orbitals on any one atom, in Eq. (3.58). *Thus, they depend only upon the choice of the total function space on each atom, but not upon the choice of a basis in each of these atomic spaces.*[29a]

TABLE IV. Gross populations of spherical AO's and SCF MO's in H_2O.

	$O1s$	$O2s$	$O2pz$	$O2py$	Hh	$H'h$	Total
$1a_1$	2	0	0	0	0	0	2
$2a_1$	0	1.64	0.05	0	0.155	0.155	2
$3a_1$	0	0.21	1.54	0	0.125	0.125	2
$1b_1$	0	0	0	0.92	0.54	0.54	2
Total	2	1.85	1.59	0.92	0.82	0.82	8

As an example, we consider again the water calculation of reference 24. Aside from the $(O2px)$ orbital perpendicular to the molecular plane, four doubly filled MO's are found from the SCF equations:

$$(1a_1),\ (2a_1),\ (3a_1) \text{ of symmetry } A_1,$$
$$\text{and } (1b_2) \text{ of symmetry } B_2.$$

Diagonalization of the matrix $\mathbf{p}^0$ leads to the four valence MO's

$$(mia_1),\ (mla_1),\ (mba_1),\ (mbb_2),$$

related to the original MO's according to

	$(1a_1)$	$(2a_1)$	$(3a_1)$	$(1b_2)$
(mia_1)	0.986044	−0.142674	0.085795	0
(mla_1)	−0.145950	−0.492880	0.857769	0
(mba_1)	0.080095	0.858320	0.506824	0
(mbb_2)	0	0	0	1

(3.69)

The properties of these MO's are best recognized if one considers the populations

$$q_n(Aa)=\sum_{Bb} p_n(Aa|Bb)\Delta(Bb,Aa), \tag{3.70}$$

which represent the contributions of the molecular orbitals φ_n to the populations of the atomic orbitals (Aa) and also the contributions of the atomic orbitals (Aa) to the populations of the molecular orbitals φ_n; i.e.,

$$\sum_n q_n(Aa)=q(Aa), \quad \sum_{Aa} q_n(Aa)=N_n. \tag{3.71}$$

Table IV furnishes the partitioning of the total popula-

TABLE V. Gross populations of valence AO's and valence MO's in H_2O.

	$Oi\sigma$	$Ol\sigma$	$Ob\sigma$	$O2py$	Hh	$H'h$	Total
mi	2	0	0	0	0	0	2
mla_1	0	2.01	0.03	0	−0.02	−0.02	2
mba_1	0	0.06	1.33	0	0.305	0.305	2
mbb_1	0	0	0	0.92	0.54	0.54	2
Total	2	2.07	1.36	0.92	0.825	0.825	8

[29a] This was pointed out by R. Rue of this laboratory.

TABLE VI. Gross populations of bond AO's and bond MO's in H_2O.

	ObH	*ObH'*	*Olσ*	*Hh*	*H'h*	Total
mOH	1.12	0.01	0.03	0.90	−0.06	2
mOH'	0.01	1.12	0.03	−0.06	0.90	2
Total	1.13	1.13	0.06	0.84	0.84	4

tion in terms of the *spherical* AO and SCF-MO populations; Table V gives the partitioning of the total population in terms of the *valence* AO and MO populations. The clarification achieved by the transformation to valence orbitals is too evident to need further elaboration.

In analogy to Eq. (3.40) it is possible to define *bond molecular orbitals* in terms of the valence MO's, viz.,

$$\begin{aligned}(m\mathrm{OH}) &= [(mba_1)+(mbb_2)]/\sqrt{2}\\ (m\mathrm{OH}') &= [(mba_1)-(mbb_2)]/\sqrt{2}.\end{aligned} \tag{3.72}$$

The population partitioning using these bond MO's and bond AO's is given in Table VI.

4. PAIR-DENSITY PARTITIONING AND SHARING PENETRATION

4.1 Interference Partitioning

Although the second-order density operator has a more complex structure than the first-order density operator, the results of the preceding section still determine a partitioning of the pair density into an interference part and a noninterference part.

This is most clearly seen by first considering the "Coulombic fragment" given by Eq. (1.36). Substituting into this equation the expressions for the first-order density in the partitioned form (3.9), one obtains

$$\pi_c(1,2)=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)+2\mathcal{S}\rho^{\mathrm{CL}}(1)\rho^{\mathrm{I}}(2)+\rho^{\mathrm{I}}(1)\rho^{\mathrm{I}}(2). \tag{4.1}$$

Here and in the following, $\mathcal{S}$ denotes the two-electron symmetrizer defined by

$$\mathcal{S}fg=\mathcal{S}f(\mathbf{x}_1)g(\mathbf{x}_2)=\tfrac{1}{2}[f(\mathbf{x}_1)g(\mathbf{x}_2)+g(\mathbf{x}_1)f(\mathbf{x}_2)] \tag{4.2}$$

for two arbitrary functions f and g. Equation (4.1) exhibits three characteristically different terms, and the analysis of the molecular energy in Sec. (6.1) will evince that such a tripartition is conceptually satisfactory.

In analogy to Eq. (4.1), it is to be expected that a general pair density π will be amenable to a similar tripartition, viz.,

$$\pi(1,2)=\pi^{\mathrm{VS}}(1,2)+\pi^{\mathrm{I}}(1,2)+\pi^{\mathrm{II}}(1,2), \tag{4.3}$$

into

an interference-free pair density π^{VS},
a primary interference pair density π^{I},
and a secondary interference pair density π^{II}.

The superscript "VS" stands for "valence state" and is explained in Sec. 4.2.

In order to find the decomposition (4.3), we observe that Eq. (4.1) could have been derived by substituting the Eq. (3.17) into the expanded form of π_c (1.36). Hence the interference partitioning of the general pair density should be obtained by substituting the orbital interference partitioning, as given by Eqs. (3.17), (3.18), and (3.29), into the expansion (2.6) of the general pair density in terms of atomic orbitals. This substitution leads to the decomposition

$$\pi=\pi^0+\pi'+\pi'', \tag{4.3'}$$

$$\pi^0=\sum_r\sum_s q(r|s)\mathcal{S}(\chi_r^2)(\chi_s^2), \tag{4.4}$$

$$\pi'=\sum_{r\bar{r}}\sum_s 2p(r\bar{r}|s)\langle\chi_r\chi_{\bar{r}}\rangle(\chi_s^2), \tag{4.5}$$

$$\pi''=\sum_{r\bar{r}}\sum_{s\bar{s}} p(r\bar{r}|s\bar{s})\langle\chi_r\chi_{\bar{r}}\rangle\langle\chi_s\chi_{\bar{s}}\rangle, \tag{4.6}$$

where

$$p(r\bar{r}|s)=\sum_{\bar{s}} p(r\bar{r}|s\bar{s})\Delta(s,\bar{s}), \tag{4.7}$$

$$\begin{aligned}q(r|s)&=\sum_{\bar{r}}\Delta(r,\bar{r})p(r\bar{r}|s)\\ &=\sum_{\bar{r}}\sum_{\bar{s}}\Delta(r,\bar{r})p(r\bar{r}|s\bar{s})\Delta(s,\bar{s})=q(s|r).\end{aligned} \tag{4.8}$$

The definitions of the functions $\langle\chi_r\chi_{\bar{r}}\rangle$ and $(\chi_r^2)=(\chi_r\chi_r)$ are those of Eq. (3.17), and Eq. (3.29).

By virtue of Eqs. (2.9) and (2.10), the quantities introduced in Eqs. (4.7) and (4.8) satisfy the conservation relations

$$\sum_s p(r\bar{r}|s)=(N-1)p(r|\bar{r}), \tag{4.9}$$

$$\sum_s q(r|s)=(N-1)q(r), \tag{4.10}$$

where $q(r)$ are the atomic orbital populations of Eq. (3.23). These relations, in conjunction with Eqs. (3.11), (3.37) and Eqs. (3.12), (3.20), mean that the total conservation relation for π, Eq. (1.11), can be split into the following three equations:

$$\int dV_2\pi^0(\mathbf{x}_1,\mathbf{x}_2)=(N-1)\rho^{\mathrm{CL}}(\mathbf{x}_1), \tag{4.11}$$

$$\int dV_2\pi'(\mathbf{x}_1,\mathbf{x}_2)=(N-1)\rho^{\mathrm{I}}(\mathbf{x}_1), \tag{4.12}$$

$$\int dV_2\pi''(\mathbf{x}_1,\mathbf{x}_2)=0. \tag{4.13}$$

The total pair population, as defined by Eq. (1.10), becomes

$$\tfrac{1}{2}N(N-1)=\frac{1}{2}\int dV_1\int dV_2\pi(\mathbf{x}_1,\mathbf{x}_2)$$

$$=\frac{1}{2}\int dV_1\int dV_2\pi^0(\mathbf{x}_1,\mathbf{x}_2)=\tfrac{1}{2}\sum_{rs}q(r|s), \quad (4.14)$$

and hence the following connotations are adopted:

$q(r|s)$ = electron pair population of the orbital pair χ_r, χ_s, $(r\neq s)$,

$\frac{1}{2}q(r|r)$ = electron pair population of the orbital χ_r.

A physical interpretation of the coefficients $p(r\bar{r}|s)$ is given in Sec. 6.2. [See Eq. (6.17″) ff.]

In order to obtain a partitioning of the type (4.3), it is necessary to decompose the pair density into contributions according to atoms. To this end, the Eqs. (4.4) to (4.6) are expanded as follows:

$$\pi^0=\sum_{A,B}\pi^0(A,B), \quad (4.15)$$

$$\pi'=\sum_{A,B}\pi'(A,B)+\sum_{A\bar{A}}{}'\sum_{B}\pi'(A\bar{A},B), \quad (4.16)$$

$$\pi''=\sum_{A,B}\pi''(A,B)+\sum_{A\bar{A}}{}'\sum_{B}\pi''(A\bar{A},B)$$
$$+\sum_{A\bar{A}}{}'\sum_{B\bar{B}}{}'\pi''(AA,BB), \quad (4.17)$$

where the constituent parts are given by

$$\pi^0(A,B)=\sum_{a}\sum_{b}q(Aa|Bb)\mathcal{S}(Aa^2)(Bb^2), \quad (4.18)$$

$$\pi'(A,B)=\sum_{a\bar{a}}{}'\sum_{b}2p(AaA\bar{a}|Bb)$$
$$\times\mathcal{S}(AaA\bar{a})(Bb^2), \quad (4.19)$$

$$\pi'(A\bar{A},B)=\sum_{a\bar{a}}\sum_{b}2p(Aa\bar{A}\bar{a}|Bb)$$
$$\times\mathcal{S}\langle Aa\bar{A}\bar{a}\rangle(Bb^2), \quad (A\neq\bar{A}), \quad (4.20)$$

$$\pi''(A,B)=\sum_{a\bar{a}}{}'\sum_{b\bar{b}}{}'p(AaA\bar{a}|BbB\bar{b})$$
$$\times\mathcal{S}(AaA\bar{a})(BbB\bar{b}), \quad (4.21)$$

$$\pi''(A\bar{A},B)=\sum_{a\bar{a}}\sum_{b\bar{b}}{}'2p(Aa\bar{A}\bar{a}|BbB\bar{b})$$
$$\times\mathcal{S}\langle Aa\bar{A}\bar{a}\rangle(BbB\bar{b}), \quad (A\neq\bar{A}), \quad (4.22)$$

$$\pi''(A\bar{A},B\bar{B})=\sum_{a\bar{a}}\sum_{b\bar{b}}p(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})$$
$$\times\mathcal{S}\langle Aa\bar{A}\bar{a}\rangle\langle Bb\bar{B}\bar{b}\rangle, \quad (A\neq\bar{A},\ B\neq\bar{B}). \quad (4.23)$$

By rearrangement, the pair density can then be written in the form (4.3), where the three parts are now defined by

$$\pi^{\mathrm{VS}}=\sum_{A}\sum_{B}\pi(A,B), \quad (4.24)$$

$$\pi^{\mathrm{I}}=\sum_{A\bar{A}}{}'\sum_{B}\pi(A\bar{A},B), \quad (4.25)$$

$$\pi^{\mathrm{II}}=\sum_{A\bar{A}}{}'\sum_{B\bar{B}}{}'\pi(A\bar{A},B\bar{B}), \quad (4.26)$$

with

$$\pi(A,B)=\pi^0(A,B)+\pi'(A,B)+\pi''(A,B), \quad (4.27)$$

$$\pi(A\bar{A},B)=\pi'(A\bar{A},B)+\pi''(A\bar{A},B), \quad (A\neq\bar{A}), \quad (4.28)$$

$$\pi(A\bar{A},B\bar{B})=\pi''(A\bar{A},B\bar{B}), \quad (A\neq\bar{A},\ B\neq\bar{B}). \quad (4.29)$$

The conservation relations (4.11) to (4.13) can be narrowed down to

$$\int dV_2\pi''(A\bar{A},B\bar{B})=\int dV_2\pi''(A\bar{A},B)$$
$$=\int dV_2\pi''(A,B)=0, \quad (4.30)$$

$$\int dV_2\sum_{A,B}\pi'(A,B)=0, \quad (4.31)$$

$$\int dV_2\sum_{A\bar{A}}{}'\sum_{B}\pi'(A\bar{A},B)=(N-1)\rho^{\mathrm{I}}, \quad (4.32)$$

$$\int dV_2\sum_{A,B}\pi^0(A,B)=(N-1)\rho^{\mathrm{CL}}, \quad (4.33)$$

where Eq. (4.31) is a consequence of choosing valence atomic orbitals as a basis of expansion.

It should be noted that a summation of the type $\sum'_{A\bar{A}}$ represents in effect a summation over all formal "bonds" between all atoms, the bond between each atom pair taken twice (note that $A\neq\bar{A}$).

4.2 Valence State

In Sec. 3 the view was taken that, within a molecule, the atoms themselves possess the electron densities $\rho(A)$, whereas the density terms $\rho(A,B)$ were ascribed to interference between atoms due to finite overlap. Similarly, we now consider the atomic pair-density contributions of Eq. (4.27), $\pi(A,B)$, as the pair density due to the atoms themselves and ascribe the pair-density terms $\pi(A\bar{A},B)$, $\pi(A\bar{A},B\bar{B})$ of Eqs. (4.28) and (4.29) to an interaction between atoms, caused by mutual overlapping.

These concepts are somewhat clarified by imagining the atoms being removed "infinitely" far apart, to the "separated positions" A_∞, B_∞, $\cdots$, while keeping the wave function such that

the electron populations $q(Aa)$, (4.34)

the pair populations $q(Aa|Bb)$, (4.34′)

and also the two-atom pair-density coefficients

$$p(AaA\bar{a}|Bb),\quad p(AaA\bar{a}|BbB\bar{b}),\tag{4.35}$$

remain "frozen" at the values they had in the molecule. During this process all overlap-dependent interference terms would vanish, and the terms

$$\rho^{\mathrm{VS}}=\rho^{\mathrm{CL}}=\sum_A \rho(A),\tag{4.36}$$

$$\pi^{\mathrm{VS}}=\sum_A\sum_B \pi(A,B),\tag{4.37}$$

would be the only one surviving. We shall call the ensemble of atoms characterized by the density (4.36) and the pair density (4.37) the "atoms in the valence state corresponding to the molecule in question."

This definition of the valence state differs from previous ones in that it is based upon the density and the pair density and not upon any wave function. One could, of course, try to construct a wave function which would yield the densities (4.36) and (4.37) and this problem is discussed in Sec. 4.7.

For the present purpose we consider it however more realistic to leave the valence-state wave function undefined and to stipulate that the word "state" implies, in this context, density and pair density only. The valence state is merely a model in order to visualize more clearly the interference-free parts of the molecular densities.

4.3 Promotion State and Sharing Penetration in the Absence of Charge Transfer

General Considerations

The valence state is essentially a molecular and not an atomic entity. It must be distinguished from the ensemble of separated atoms, each in a "promoted" state by itself.

In order to appreciate what is involved here, consider a molecule without charge transfer, i.e., where all atomic populations are equal to the number of electrons occurring in the neutral atoms, i.e.,

$$\int dV\rho(A)=q(A)=\sum_a q(Aa)=Z(A),\quad\text{for all } A,\tag{4.38}$$

where $Z(A)$ is the nuclear charge on atom A. Construct the valence state density and pair density of this molecule according to Eqs. (4.36) and (4.37).

In distinction from this process, suppose now each atom isolated by itself with $q(A)$ whole electrons; suppose furthermore each atom in a promoted state, such that its electron density is identical with the density $\rho(A)$ in the valence state of the aforementioned molecule.[30] Let $\pi^{\mathrm{P}}(A,A)$ be the pair densities of the atoms, each in its promoted state. Since each electron is confined to one atom, these pair densities will satisfy the individual conservation relations

$$\int dV_2\pi^{\mathrm{P}}(A,A)=[q(A)-1]\rho(A),\tag{4.39}$$

$$\tfrac{1}{2}\int dV_1\int dV_2\pi^{\mathrm{P}}(A,A)=\tfrac{1}{2}[q(A)-1]q(A).\tag{4.40}$$

Let ρ^{P} be the density and π^{P} the pair density of the total system of *all* promoted atoms. According to construction one has

$$\rho^{\mathrm{P}}=\sum_A \rho(A)=\rho^{\mathrm{VS}}.\tag{4.41}$$

The total pair density can be written

$$\pi^{\mathrm{P}}=\sum_A\sum_B \pi^{\mathrm{P}}(A,B),\tag{4.42}$$

where the *intra*atomic terms $\pi^{\mathrm{P}}(A,A)$ are those for which Eqs. (4.39) and (4.40) hold, whereas the *inter*atomic terms are given by

$$\pi^{\mathrm{P}}(A,B)=\mathcal{S}\rho(A)\rho(B),\quad (A\neq B),\tag{4.43}$$

since the electrons on atom A and those on atom B belong to two different sets and, hence, the reasoning leading to Eq. (1.53) applies (in the present context the symmetrized form is more convenient). Equations (4.39), (4.41), and (4.43) are in harmony with the over-all conservation relation (1.11), since

$$\begin{aligned}\int dV_2\pi^{\mathrm{P}}&=\sum_A [q(A)-1]\rho(A)\\&\quad+\sum_{A,B}{}'\,\tfrac{1}{2}[q(A)\rho(B)+q(B)\rho(A)]\\&=[\sum_B q(B)-1]\sum_A \rho(A)=(N-1)\rho^{\mathrm{P}}.\end{aligned}\tag{4.44}$$

The state characterized by $\rho^{\mathrm{P}}=\rho^{\mathrm{VS}}$ and π^{P} will be called the *promotion state* of the ensemble of atoms.

We now compare the pair density of the promotion state with that of the valence state. Whereas the densities of these two states are identical, such an equality does not exist between π^{P} and π^{VS}, no matter how the promotion state is chosen. This conclusion follows from the fact that, in all practical cases, one has

$$\int dV_2\pi^{\mathrm{VS}}(A,A)\neq[q(A)-1]\rho^{\mathrm{VS}}(A),\tag{4.45}$$

$$\tfrac{1}{2}\int dV_1\int dV_2\pi^{\mathrm{VS}}(A,A)>\tfrac{1}{2}q(A)[q(A)-1],\tag{4.46}$$

$$\int dV_2\pi^{\mathrm{VS}}(A,B)\neq\tfrac{1}{2}[q(A)\rho^{\mathrm{VS}}(B)+q(B)\rho^{\mathrm{VS}}(A)],\tag{4.47}$$

$$\int dV_1\int dV_2\pi^{\mathrm{VS}}(A,B)<q(A)q(B).\tag{4.48}$$

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[30] For simplicity it is assumed that $\rho(A)$ can be expressed as a density of an atomic wave function. This assumption is discussed further in Sec. 4.7.

The over-all conservation relation

$$\int dV_2 \pi^{\mathrm{VS}} = (N-1)\rho^{\mathrm{VS}} \tag{4.48'}$$

is, of course, satisfied.

Example

The difference between π^{P} and π^{VS} is most easily understood by considering the case of the H_2 molecule. In the promotion state, each atom has an electron for itself and its atomic pair density vanishes. Within the molecule, however, *both electrons are shared by both atoms* and there results a finite probability of finding both electrons on the same nucleus, giving rise to a nonvanishing atomic pair density and thus to a positive atomic pair population.

It is instructive to analyze this simple case in quantitative detail. Let A and B be the atomic orbitals on the two nuclei of H_2 and suppose that the normalized space-part of the molecular wave function is given in the Weinbaum form[31]

$$\Phi(\mathbf{x}_1,\mathbf{x}_2) = (\tfrac{1}{2}N)^{\frac{1}{2}}\{\cos\gamma[A(1)A(2)+B(1)B(2)] + \sin\gamma[A(1)B(2)+B(1)A(2)]\} \tag{4.49}$$

with

$$N = (1+S^2+2S\sin 2\gamma)^{-1}. \tag{4.49'}$$

Here, S is the overlap integral and γ determines the mixing of "covalent" and "ionic" terms:

$\gamma = 0$: pure "ionic wave function,"
$\gamma = \pi/4$: molecular orbital wave function,
$\tan\gamma = 3.9$: Weinbaum's result for ($1s$) atomic orbitals with effective charges of 1.193, (4.50)
$\gamma = \pi/2$: pure covalent wave function.

For Weinbaum's wave function the overlap integral has the value $S = 0.6720263$.
From Eq. (4.49) one finds

$$\pi^{\mathrm{VS}} = q(A\,|\,A)[A^2(1)A^2(2)+B^2(1)B^2(2)] + 2q(A\,|\,B)\mathcal{S}A^2(1)B^2(2), \tag{4.51}$$

$$\pi^{\mathrm{I}} = 4p(AB\,|\,A)\{\mathcal{S}\langle AB\rangle\langle A^2\rangle + \mathcal{S}\langle AB\rangle\langle B^2\rangle\}, \tag{4.51'}$$

$$\pi^{\mathrm{II}} = 4p(AB\,|\,AB)\mathcal{S}\langle AB\rangle\langle AB\rangle, \tag{4.51''}$$

with

$$q(A\,|\,A) = \quad q(B\,|\,B) = \tfrac{1}{2}(1+N\cos 2\gamma), \tag{4.52}$$

$$q(A\,|\,B) = \tfrac{1}{2}(1-N\cos 2\gamma), \tag{4.53}$$

$$p(AB\,|\,A) = \quad p(AB\,|\,B) = \tfrac{1}{2}p(A\,|\,B), \tag{4.54}$$

$$p(AB\,|\,AB) = \tfrac{1}{2}N; \tag{4.55}$$

and furthermore

$$\rho = q(A)[A^2+B^2] + 2p(A\,|\,B)\langle AB\rangle, \tag{4.56}$$

with

$$q(A) = q(B) = 1, \tag{4.57}$$

$$p(A\,|\,B) = N(S+\sin 2\gamma). \tag{4.58}$$

The pair density of the promotion state is given by

$$\begin{aligned} \pi^{\mathrm{P}}(A,A) &= \pi^{\mathrm{P}}(B,B) = 0, \\ \pi^{\mathrm{P}}(A,B) &= \mathcal{S}A^2(1)B^2(2). \end{aligned} \tag{4.59}$$

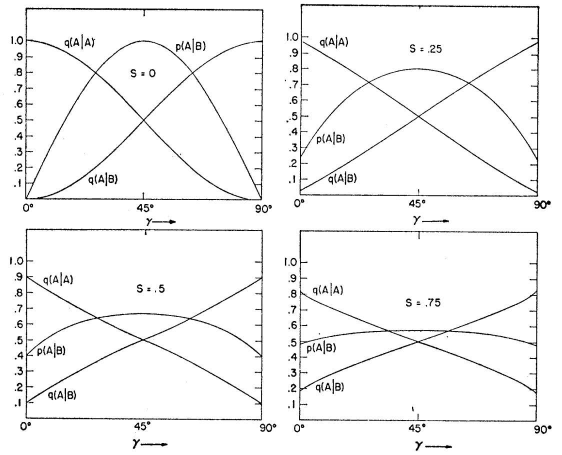

FIG. 4. Bond orders and pair populations in H_2 for $S=0$, $S=0.25$, $S=0.5$, and $S=0.75$. [Function of Eq. (4.49) with effective charge 1.193.] $\tan\gamma$ = covalent-ionic mixing ratio.

Figure 4 shows the variation of $q(A\,|\,A)$, $q(A\,|\,B)$, and $p(A\,|\,B)$ with γ for various values of the overlap integral S. It is seen that the pair population of each atom, $\frac{1}{2}q(A\,|\,A)$, increases with increasing admixture of ionic terms. Thus the effect of ionic terms in a homonuclear situation is to change the atomic pair population without changing the atomic population $q(A)$ itself, which remains always unity in the present case. The result is easiest to visualize in the molecular orbital case ($\gamma = \pi/4$): here it is obvious that each of the two electrons, *separately*, belongs half to atom A and half to atom B; hence, there should be a probability of $\frac{1}{4}$ to find both electrons at the same nucleus, and this value agrees with $\frac{1}{2}q(A\,|\,A)$ from Eq. (4.52). However, *even for a purely covalent function* ($\gamma = \pi/2$) *there exists a nonvanishing atomic pair population which must be ascribed to electron sharing.* Only for $S=0$ does the pure covalent function correspond exactly to the case of two isolated atoms; $q(A\,|\,A)=0$, $q(A\,|\,B)=1$.

Because of the pair conservation relation,

$$q(A\,|\,A) + q(A\,|\,B) = 1, \tag{4.60}$$

it is clear that an increase in intra-atomic pair population is coupled with a decrease in the interatomic pair population $q(A\,|\,B)$, which is related to the probability of finding one electron on A and the other on B. This correlation is also exhibited in the plots [it may be noted that, except in the case $S=0$, $q(A\,|\,B)$ does not vanish even for a purely "ionic function"]. As a conse-

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[31] S. Weinbaum, J. Chem. Phys. 1, 593 (1933).

quence, *some interatomic electronic repulsion is replaced by some intra-atomic electronic repulsion as the atoms proceed to share their electrons in forming a molecule.* In other words, *electron sharing causes a greater penetration of the two electrons.* Since the intra-atomic repulsion is much larger than the interatomic repulsion (the electrons being much closer to each other), it is evident that *this sharing penetration of the pair density will raise the total energy and thus be unfavorable to bond formation.*

Why then is this effect further increased in the Weinbaum function by the admixture of "ionic terms?" The answer is that the bond-forming energy depression is furnished by the interference terms, as discussed in Sec. 3.2, and that *interference cannot arise without electron sharing.* The interdependence between the interference effect of the first-order density matrix and the sharing-penetration effect of the second-order density matrix is quantitatively illustrated in Fig. 4 by the plot of the bond order $p(A|B)$, which, according to Eq. (4.56), determines the degree of influence of the orbital interference density $\langle AB\rangle$. It indicates that the bond order is strongest when intra-atomic and interatomic pair density differ least. Since the bond order is largest for the molecular orbital wave function, the Weinbaum result means that, in this specific case, the sharing-penetration repulsion overcomes the interference attraction before the latter reaches its maximal value.

Conclusions

The analysis of other molecules has shown that the physically significant arguments in the foregoing example remain largely valid under more complicated conditions; we therefore infer the following general conclusions.

The transition from free atoms to a molecule formed by them can be visulaized in terms of the following steps.[32]

(1) Each of the separated atoms individually assumes its promotion state density and pair density. This is as near as each atom, by itself, can come to its status in the molecule.

(2) Valence electrons are shared between the separated atoms to form the pair densities of the valence state. The latter therefore involves all atoms simultaneously; one can speak of an atom in a valence state only within an ensemble of atoms corresponding to a molecule.

(3) The atoms are then moved from their separated positions to their actual positions, where their orbitals overlap. Thereby interference terms arise because there are electrons which, individually, are shared between different atoms.

Alternatively, the transition from free atoms to a molecule can be visualized in terms of the following steps.[32]

(1) (a) Each of the separated atoms assumes its promotion-state density and pair density.

(b) The atoms are then moved from the separated positions to the actual positions.

(2) Now valence electrons are shared between the atoms; this gives rise to two effects.

(a) *Interference.* Since each valence electron, individually, makes use of overlapping atomic orbitals from different atoms, interference terms are generated in the first-order density.

(b) *Sharing penetration.* The valence electrons from different atoms penetrate each other much more thoroughly than before, and the average distance between them is decreased. Hence the valence-state pair density favors interelectronic approaches more than the promotion-state pair density (both taken for the actual atomic positions). This fact is expressed by the inequalities

$$\tfrac{1}{2}\int dV_1\int dV_2\pi(A,A)-\tfrac{1}{2}q(A)[q(A)-1]>0, \quad (4.61)$$

$$\int dV_1\int dV_2\pi(A,B)-q(A)q(B)<0. \quad (4.62)$$

The first of the two pictures given stresses the difference between the *overlap-free* terms (steps 1 and 2) which contain the *long-range* (Coulombic) *interaction energies* between atoms, and the *overlap-dependent* terms (step 3), which contain to *short-range interaction energies* between atoms. The second picture emphasizes the *coupling* which exists between the *interference* effect, which *favors* binding, and the *penetration* effect, which *opposes* binding, since both are generated when electrons are *shared.*

It should be mentioned that the difference between valence state and promotion state is *not* a consequence of our particular valence state definition. The same problem arises in the valence-bond approach to the valence state as soon as ionic structures are included. Since the latter are indispensible for obtaining accurate results, even within the "atoms in molecules" procedure,[33] Hurley has in fact recently introduced molecular valence states in which the states of the constituent atoms are interdependent. In the valence-bond theory, the "ionic structures" clearly serve two purposes; (1) to enhance interference by effecting electron sharing, (2) to effect charge transfer induced by differences in electronegativities of the atoms.

The energetic considerations advanced in the present section have been qualitative in character. Quantitative

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[32] These steps merely represent a conceptual "taking apart" which serves to differentiate between the roles played by various terms in the *actual* density and pair density. They have nothing to do with the variation of ρ and π which would result from solving the Schrödinger equation for larger and larger internuclear distances. The latter question is discussed in Sec. 7.5.

[33] The method was first proposed by W. Moffitt. Recent reviews are found in: T. Arai, Revs. Modern Phys. **32**, 370 (1960); A. C. Hurley, *ibid.* **32**, 400 (1960).

formulations, which justify the foregoing conclusions in detail, are derived in Sec. 6.

4.4 Inter-Atomic Sharing Penetration and Self-Pair Density

In Sec. 1.4 it was found that there exists an intrinsic relationship between the electron sharing phenomenon and the self-pair density discussed in Sec. 1.4. As mentioned at the end of that section we simplify the interpretation by equating the self-pair density with the generalized exchange term, $\pi_x(\mathbf{x}_1,\mathbf{x}_2)$, defined in Eq. (1.23). Hence, it is to be expected that the latter will be a convenient quantity for the analysis of electron sharing between atoms.

Our first step is to combine the decomposition of the pair density into Coulombic pair density and self-pair density, as given by Eq. (1.23), with the partitioning of the pair density into valence-state pair density and interference pair densities, as given by Eq. (4.3). In Eq. (4.1), there was given the interference partitioning of the Coulombic pair density. The analogous partitioning π_x is obtained by comparing (4.1) and (4.3), whence

$$\pi_x=\pi_x{}^{\mathrm{VS}}+\pi_x{}^{\mathrm{I}}+\pi_x{}^{\mathrm{II}}, \qquad (4.63)$$

where the parts are defined by

$$\pi^{\mathrm{VS}}(1,2)=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)-\pi_x{}^{\mathrm{VS}}(1,2), \qquad (4.64)$$

$$\pi^{\mathrm{I}}(1,2)=2\mathcal{S}\rho^{\mathrm{CL}}(1)\rho^{\mathrm{I}}(2)-\pi_x{}^{\mathrm{I}}(1,2), \qquad (4.65)$$

$$\pi^{\mathrm{II}}(1,2)=\rho^{\mathrm{I}}(1)\rho^{\mathrm{I}}(2)-\pi_x{}^{\mathrm{II}}(1,2). \qquad (4.66)$$

The conservation relation (1.52′) can then be decomposed into the equations

$$\int dV_2\pi_x{}^{\mathrm{VS}}(1,2)=\rho^{\mathrm{CL}}(1), \qquad (4.67)$$

$$\int dV_2\pi_x{}^{\mathrm{I}}(1,2)=\rho^{\mathrm{I}}(1), \qquad (4.68)$$

$$\int dV_2\pi_x{}^{\mathrm{II}}(1,2)=0. \qquad (4.69)$$

In the preceding section, attention was focused on the fact that, due to electronic rearrangements, the amount of electron sharing in the valence state differs from that in the promotion state. Equations (4.64) to (4.66) show that this difference can be analyzed by examining the valence-state self-pair density $\pi_x{}^{\mathrm{VS}}$. In the following we use the term *interatomic sharing-penetration effect* to denote this specific phenomenon, which does not include the sharing effects inherent in the terms $\pi_x{}^{\mathrm{I}}$, $\pi_x{}^{\mathrm{II}}$.

In the case of the H_2 calculation, discussed in Eqs. (4.49) ff., the self-pair densities for valence state and promotion state become

$$\pi_x{}^{\mathrm{P}}=\pi_x{}^{\mathrm{P}}(A,A)+2\pi_x{}^{\mathrm{P}}(A,B)+\pi_x{}^{\mathrm{P}}(B,B), \qquad (4.70)$$

$$\pi_x{}^{\mathrm{VS}}=\pi_x{}^{\mathrm{VS}}(A,A)+2\pi_x{}^{\mathrm{VS}}(A,B)+\pi_x{}^{\mathrm{VS}}(B,B), \qquad (4.70')$$

where

$$\pi_x{}^{\mathrm{P}}(A,A)=\rho(A)\rho(A),\quad \pi_x{}^{\mathrm{P}}(B,B)=\rho(B)\rho(B),\quad \pi_x{}^{\mathrm{P}}(A,B)=0, \qquad (4.71)$$

$$\pi_x{}^{\mathrm{VS}}(A,A)=q(A\,|\,B)\rho(A)\rho(A),$$

$$\pi_x{}^{\mathrm{VS}}(B,B)=q(A\,|\,B)\rho(B)\rho(B), \qquad (4.72)$$

$$\pi_x{}^{\mathrm{VS}}(A,B)=q(A\,|\,A)\mathcal{S}\rho(A)\rho(B). \qquad (4.72')$$

Equation (4.71) shows again that there is no sharing between atoms A and B in the promotion state, and the population on atom A is due to electrons different from those populating atom B. Equations (4.72) and (4.72′) show that, in the valence state, the *population* on atom A, viz., $q(A)=1$, consists of the two parts $q(A\,|\,B)=q_x(A\,|\,A)$ and $q(A\,|\,A)=q_x(A\,|\,B)$; the part $q_x(A\,|\,B)$ is shared with atom B, the part $q_x(A\,|\,A)$ is *not* shared with atom B. Figure 4 shows that, for the covalent case and the Weinbaum case, the *intra*-atomic sharing is $>\frac{1}{2}$ and the *inter*atomic sharing is $<\frac{1}{2}$, that is to say, the electrons stay predominantly on one of the two atoms. For the molecular orbital case both are equal to $\frac{1}{2}$.

Consider now the interatomic electron-sharing effect for a general molecule without charge transfer. Since promotion state and valence state are assumed to have the same density $\rho^{\mathrm{CL}}=\rho^{\mathrm{VS}}$, the two will also agree as regards the Coulombic pair density, so that

$$\pi^{\mathrm{P}}(1,2)=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)-\pi_x{}^{\mathrm{P}}(1,2), \qquad (4.73)$$

$$\pi^{\mathrm{VS}}(1,2)=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)-\pi_x{}^{\mathrm{VS}}(1,2). \qquad (4.74)$$

Hence, one can write

$$\pi^{\mathrm{VS}}(1,2)=\pi^{\mathrm{P}}(1,2)+\pi^{\mathrm{SP}}(1,2), \qquad (4.75)$$

where the difference

$$\pi^{\mathrm{SP}}(1,2)=\pi_x{}^{\mathrm{P}}(1,2)-\pi_x{}^{\mathrm{VS}}(1,2) \qquad (4.76)$$

will be called the *sharing-penetration pair density* in the molecule. Let

$$\pi^{\Sigma}=\sum_{A,B}\pi^{\Sigma}(A,B), \qquad (4.77)$$

$$\pi_x{}^{\Sigma}=\sum_{A,B}\pi_x{}^{\Sigma}(A,B), \qquad (4.77')$$

where the superscript Σ may be

$\Sigma=$ VS for the valence-state pair density,
$\Sigma=$ P for the promotion state pair density,
$\Sigma=$ SP for the sharing-penetration pair density.

[Note that, according to Eq. (4.24),

$$\pi^{\mathrm{VS}}(A,B)=\pi(A,B),\quad \pi_x{}^{\mathrm{VS}}(A,B)=\pi_x(A,B); \qquad (4.78)$$

and, according to Eq. (4.76),

$$\pi^{\mathrm{SP}}(1,2)=-\pi_x{}^{\mathrm{SP}}(1,2).] \qquad (4.78')$$

Since there are no interatomic sharing terms in the promotion state [see Eq. (4.43)], the *interatomic* parts of π^{SP} in Eq. (4.77′) are determined by

$$\pi^{\mathrm{SP}}(A,B)=-\pi_x{}^{\mathrm{VS}}(A,B),\quad A\neq B. \tag{4.79}$$

For the *intra-atomic* parts of π^{SP} a relation can be derived as follows. From Eqs. (4.44), (4.48′), and (4.75) it follows that π^{SP} satisfies

$$\int dV_2\pi^{\mathrm{SP}}(1,2)=0. \tag{4.80}$$

Substituting Eq. (4.79) into Eq. (4.77′), and Eq. (4.77′) into Eq. (4.80), one obtains

$$\int dV_2\pi^{\mathrm{SP}}(A,A)=\sum_{(B\neq A)}{}' \int dV_2\pi_x{}^{\mathrm{VS}}(A,B), \tag{4.80′}$$

where, by virtue of Eq. (4.67),

$$\int dV_2\pi^{\mathrm{SP}}(A,A)=\rho^{\mathrm{CL}}(A)-\int dV_2\pi_x{}^{\mathrm{VS}}(A,A). \tag{4.81}$$

Carrying out the double integration $\frac{1}{2}\int dV_1\int dV_2$ on Eqs. (4.79) and (4.81), one obtains the expressions for the pair population changes which were discussed previously in Eqs. (4.61) and (4.62). Hence, the terms $\pi^{\mathrm{SP}}(A,B)$ of Eq. (4.79) describe the *decrease in interatomic pair density due to the creation of interatomic electron sharing* as one proceeds from the promotion state to the valence state, and the terms $\pi^{\mathrm{SP}}(A,A)$ *describe the increase in intra-atomic pair density due to the decrease in intra-atomic electron sharing*, which according to the conservation relations (4.80), (4.80′), is necessarily connected with the increase in interatomic sharing.

The transition from the promotion state to the valence state can also be characterized by stating that the character of the self-pair density term π_x changes from purely atomic to being partly molecular. This interpretation is particularly obvious in the Hartree–Fock approximation. The fact that the self-energy of genuine molecular orbitals is necessarily smaller than that of the constituent atomic orbitals furnishes then another visualization of the energy increase associated with the sharing penetration.

4.5 Sharing-Penetration Partitioning in the Absence of Charge Transfer

In the simple case of Eq. (4.49), the promotion-state pair density, and hence also the sharing pair density were known; the partitioning (4.75) was therefore completely determined. In more complicated molecules the interatomic parts only are fixed, as given by Eq. (4.79). Is it possible to give specifications which, in conjunction with the conservation relation (4.81) would determine the intra-atomic parts and thereby completed the partitioning (4.75) for the general case?

In analogy with Eqs. (4.18), (4.19), (4.21), and (4.27) let

$$\begin{aligned}\pi^{\Sigma}(A,B)&\\ =&\sum_a\sum_b q^{\Sigma}(Aa|Bb)\mathcal{S}(Aa^2)(Bb^2)\\ &+\sum_{a\bar{a}}{}'\sum_b 2p^{\Sigma}(AaA\bar{a}|Bb)\mathcal{S}(AaA\bar{a})(Bb^2)\\ &+\sum_{a\bar{a}}{}'\sum_{b\bar{b}}{}' p^{\Sigma}(AaA\bar{a}|BbB\bar{b})\mathcal{S}(AaA\bar{a})(BbB\bar{b}).\end{aligned} \tag{4.82}$$

From Eqs. (4.73) and (4.74) it follows that

$$\begin{aligned}\pi_x{}^{\Sigma}(A,B)&\\ =&\sum_a\sum_b q_x(Aa|Bb)\mathcal{S}(Aa^2)(Bb^2)\\ &-\sum_{a\bar{a}}{}'\sum_b 2p^{\Sigma}(AaA\bar{a}|Bb)\mathcal{S}(AaA\bar{a})(Bb^2)\\ &-\sum_{a\bar{a}}{}'\sum_{b\bar{b}}{}' p^{\Sigma}(AaA\bar{a}|BbB\bar{b})\mathcal{S}(AaA\bar{a})(BbB\bar{b}),\end{aligned} \tag{4.82′}$$

where

$$q_x{}^{\Sigma}(Aa|Bb)=-q^{\Sigma}(Aa|Bb)+q(Aa)q(Bb),\quad \text{for } \Sigma=\mathrm{P, VS}, \tag{4.82″}$$

$$q_x{}^{\mathrm{SP}}(Aa|Bb)=-q^{\mathrm{SP}}(Aa|Bb). \tag{4.82‴}$$

According to Eq. (4.79), the interatomic coefficients of π^{SP} are determined by [Note that the superscript VS can be omitted, see Eq. (4.78)]

$$q^{\mathrm{SP}}(Aa|Bb)=-q_x(Aa|Bb), \tag{4.83}$$

$$p^{\mathrm{SP}}(AaA\bar{a}|Bb)=p(AaA\bar{a}|Bb),\quad (A\neq B) \tag{4.83′}$$

$$p^{\mathrm{SP}}(AaA\bar{a}|BbB\bar{b})=p(AaA\bar{a}|BbB\bar{b}). \tag{4.83″}$$

For the intra-atomic coefficients of π^{SP}, Eqs. (4.80′), (4.81) furnish the relations

$$\sum_{a'} p^{\mathrm{SP}}(AaA\bar{a}|Aa')=\sum_{a'} p(AaA\bar{a}|Aa'), \tag{4.84}$$

$$\sum_{\bar{a}} q^{\mathrm{SP}}(Aa|A\bar{a})=q^{\mathrm{SP}}(Aa), \tag{4.85}$$

where

$$\begin{aligned}q^{\mathrm{SP}}(Aa)&=q(Aa)-\sum_{\bar{a}} q_x(Aa|A\bar{a})\\ &=\sum_{\substack{Bb\\(B\neq A)}}{}' q_x(Aa|Bb).\end{aligned} \tag{4.85′}$$

This quantity can be considered as a measure of the *interatomic sharing-activity of the valence orbital* (Aa) in the valence state of the molecule. Equation (4.85) signifies that, in passing from the promotion state to the valence state, the gain in interatomic electron sharing (right-hand member) equals the loss in intra-atomic electron sharing (left-hand member) for each atomic orbital (Aa).

The simplest supposition which satisfies this conservation relation and, moreover, takes into account the interatomic sharing activity of the various orbitals in a proportionate fashion, is given by

$$q^{\mathrm{SP}}(Aa|A\bar{a})=q^{\mathrm{SP}}(Aa)q^{\mathrm{SP}}(A\bar{a})/q^{\mathrm{SP}}(A), \quad (4.86)$$

where $q^{\mathrm{SP}}(Aa)$ is defined by Eq. (4.85′) and $q^{\mathrm{SP}}(A)$ by

$$q^{\mathrm{SP}}(A)=\sum_{a} q^{\mathrm{SP}}(Aa)=q(A)-\sum_{a\bar{a}} q_x(Aa|A\bar{a})$$
$$=\sum_{a\bar{a}} q(Aa|A\bar{a})-q(A)[q(A)-1]. \quad (4.86')$$

Hence, $\frac{1}{2}q^{\mathrm{SP}}(A)$ is the pair population transfer into atom A, as given in Eq. (4.61).

The simplest way to satisfy Eq. (4.84) is to assume

$$p^{\mathrm{SP}}(AaA\bar{a}|Aa')=p(AaA\bar{a}|Aa'). \quad (4.87)$$

Moreover, it seems natural to put

$$p^{\mathrm{SP}}(AaA\bar{a}|Aa'A\bar{a}')=0. \quad (4.88)$$

It would be desirable, if it should prove possible, to find a more profound analysis of the pair density leading to a more cogent choice of the intra-atomic coefficients of π^{SP}. The rather modest approach adopted here is, however, far from arbitrary. Among a variety of definitions examined in detail, the one given in Eq. (4.86) appeared to be the only one which (1) satisfied the conservation relation (4.80); (2) embodied physically plausible weighting factors for the various intra-atomic contributions; (3) yielded reasonable quantitative results in those cases which were carried through numerically. As was discussed in the introduction, the overriding criterion in judging all definitions introduced here must be their usefulness for the comparison of series of molecules.

In accordance with the final remarks in Sec. 1.4, the effect of electrostatic interelectronic correlation has been ignored in the foregoing. An appropriate complementation in this direction will be necessary for a perfect interpretation of non-SCF wave functions.

4.6 Molecular-Orbital Pair Bond Orders

In view of the frequency of SCF-MO calculations for closed shell structures, it is of interest to particularize the general results for this special case. The simplifications introduced by this approximation lead to the form

$$\pi_x(1,2)=\tfrac{1}{2}\rho^2(1,2) \quad (4.89)$$

for the exchange part of the pair density [See Eq. (1.21)].

Accordingly, the pair-bond orders assume the form

$$p(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})$$
$$=p_c(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})-p_x(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b}), \quad (4.90)$$

with

$$p_c(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})=p(Aa|\bar{A}\bar{a})p(Bb|\bar{B}\bar{b}), \quad (4.90')$$

$$p_x(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})=\tfrac{1}{4}\{p(Aa|Bb)p(\bar{A}\bar{a}|\bar{B}\bar{b})$$
$$+p(Aa|\bar{B}\bar{b})p(\bar{A}\bar{a}|Bb)\}. \quad (4.90'')$$

For the quantities in Eqs. (4.82) to (4.82″) one obtains

$$q_x(Aa|Bb)=\tfrac{1}{4}\{p(Aa|Bb)(\mathbf{\Delta p\Delta})_{Aa,Bb}$$
$$+(\mathbf{\Delta p})_{Aa,Bb}(\mathbf{p\Delta})_{Aa,Bb}\}, \quad (4.91)$$

$$p(Aa\bar{A}\bar{a}|Bb)=-\tfrac{1}{4}\{p(Aa|Bb)(\mathbf{p\Delta})_{\bar{A}\bar{a},Bb}$$
$$+p(\bar{A}\bar{a}|Bb)(\mathbf{p\Delta})_{Aa,Bb}\}, \quad (4.91')$$

$$p(AaA\bar{a}|BbB\bar{b})=-p_x(AaA\bar{a}|BbB\bar{b}). \quad (4.91'')$$

For valence AO's, the intra-atomic parts of Eq. (4.91″) are still diagonal, viz.,

$$p(AaA\bar{a}|Aa'A\bar{a}')=-\tfrac{1}{4}p(Aa|Aa)p(A\bar{a}|A\bar{a})$$
$$\times[\delta_{aa'}\delta_{\bar{a}\bar{a}'}+\delta_{a\bar{a}'}\delta_{\bar{a}a'}]. \quad (4.91''')$$

By virtue of the special form (4.89), the conservation relation (1.52′) yields

$$\int dV\rho(\mathbf{x}_1|\mathbf{x})\rho(\mathbf{x}|\mathbf{x}_2)=2\rho(\mathbf{x}_1|\mathbf{x}_2)$$
$$\varrho\varrho=2\varrho, \quad (4.92)$$

indicating that $(\frac{1}{2}\rho)$ is a projection operator. From this relation follow the identities

$$\mathbf{p\Delta p}=2\mathbf{p}, \quad (4.93)$$

$$(\tfrac{1}{2}\mathbf{p\Delta})(\tfrac{1}{2}\mathbf{p\Delta})=(\tfrac{1}{2}\mathbf{p\Delta}), \quad (4.93')$$

$$(\tfrac{1}{2}\mathbf{\Delta p})(\tfrac{1}{2}\mathbf{\Delta p})=(\tfrac{1}{2}\mathbf{\Delta p}), \quad (4.93'')$$

which are related to Eqs. (4.9) and (4.10).

4.7 Wave Functions for Promotion State and Valence State

It is a fundamental hypothesis of the present investigation that densities and pair densities are more significant for purposes of interpretation than are wave functions. In view of past approaches, it is nevertheless of interest to ask whether it may be possible to formulate wave functions for valence states and/or promotion states on the basis of the partitioning carried out here.

In order to discuss this problem, let us write a molecular wave function in the form used in the "atoms in molecules" method, viz.,[33]

$$\Psi=\sum_{K} \Phi_K\Gamma_K, \quad (4.94)$$

where the Φ_K are the so-called "composite functions,"

$$\Phi_K=\mathcal{A}\prod_{A} \Phi_K{}^A. \quad (4.94')$$

Here $\Phi_K{}^A$ represents a particular neutral or ionic state of atom A. Hence, Φ_K is an antisymmetric wave function describing the ensemble of all constituent atoms, each in a particular state.

It is clear that a given composite function must contain atomic ionic states $\Phi_K{}^A$ in such a way that the total system is neutral, assuming a neutral molecule is to be described. In general, there will be several different composite functions Φ_K which agree as regards the state of ionization of all *individual* atoms. Let us say, they are composite functions corresponding to the same state of ionization within the molecule.

For the present purpose it is convenient to rewrite Eq. (4.94) in the form

$$\Psi=\sum_K C_K\Psi_K, \quad \sum_K C_K{}^2=1, \tag{4.95}$$

where the Ψ_K represent partial sums collecting all those terms which belong to the same state of ionization within the molecule. *If we now let the nuclei of the atoms be located at the "separated positions"* A_∞, B_∞, $\cdots$, then Ψ represents a "valence state wave function" and each Ψ_K represents a "promotion state wave function" for the molecule.

The density of a promotion state Ψ_K is found to have the form

$$\rho_K=\sum_A \rho_K(A), \tag{4.96}$$

where

$$\int dV\rho_K(A)=Z_K(A)=Z(A)-Q_K(A),$$

the integer $Q_K(A)$ giving the state of ionization of atom A in Ψ_K. The pair density of Ψ_K is found to have the form

$$\pi_K=\sum_{A,B} \pi_K(A,B), \tag{4.97}$$

where $\pi_K(A,A)$ satisfies the relation

$$\int dV\pi_K(A,A)=[Z_K(A)-1]\rho_K(A),$$

and $\pi_K(A,B)$ is given by

$$\pi_K(A,B)=\mathcal{S}\rho_K(A)\rho_K(B), \quad (A\neq B).$$

Furthermore, the total density and pair density of the valence state become

$$\rho(\Psi)=\sum_K C_K{}^2\rho_K=\sum_A \rho_\psi(A), \tag{4.98}$$

$$\pi(\Psi)=\sum_K C_K{}^2\pi_K=\sum_{A,B} \pi_\psi(A,B), \tag{4.98$'$}$$

where

$$\rho_\psi(A)=\sum_K C_K{}^2\rho_K(A), \tag{4.99}$$

$$\pi_\psi(A,B)=\sum_K C_K{}^2\pi_K(A,B). \tag{4.99$'$}$$

Suppose now that the valence state and promotion-state density and pair density of a molecule have been determined by the partitioning described in the preceding sections. Two questions can then be raised:

(1) Is it possible to find a valence-state wave function of the type given in Eqs. (4.94) and (4.95) which would reproduce the valence-state density and pair density found from the partitioning?

(2) Is it possible to find, for a given atom A, an atomic promotion state wave function which would reproduce the atomic promotion state density and pair density found from the partitioning? The chances are against this being the case in general, because there is no guarantee that the density and pair density constructed by our method of partitioning will fulfill the conditions which must be satisfied by such quantities in order to be derivable from antisymmetric wave functions. For example, Tables I and II show that some orbital populations $q(Aa)$ slightly exceed the value 2, a situation which cannot arise for a first-order density derived from an antisymmetric wave function constructed by means of normalized atomic orbitals.

The nonexistence of such wave functions is not, in itself, an objectionable feature. Not only are they unnecessary for carrying out our analysis, but also from quite general considerations they would have the character of artifacts. In the "atoms in molecules" method too, *it is impossible to assign a promoted wave function to an atom in a molecule*, because the expansion (4.95) of the molecular valence state necessarily contains several terms, corresponding to various states of ionization, even in the absence of charge transfer. This is indispensable for a proper description of the electron-sharing effect, as can be seen from the following consideration.

Let

$$\rho_Z(A), \quad \rho_{Z+1}(A), \quad \rho_{Z-1}(A);$$
$$\pi_Z(A,A), \quad \pi_{Z+1}(A,A), \quad \pi_{Z-1}(A,A)$$

be special cases of Eq. (4.96) and (4.97) for a specific atom, where Z, $(Z+1)$, and $(Z-1)$ correspond to neutral atom, singly positive, and negative ion, respectively. Suppose that the Eqs. (4.99) and (4.99′) have the following form:

$$\rho_\psi(A)=C_0{}^2\rho_Z(A)+C_1{}^2[\rho_{Z+1}(A)+\rho_{Z-1}(A)],$$
$$\pi_\psi(A,A)=C_0{}^2\pi_Z(A,A)+C_1{}^2[\pi_{Z+1}(A,A)+\pi_{Z-1}(A,A)],$$
$$C_0{}^2+2C_1{}^2=1.$$

One finds then the following intra-atomic electron population and pair population:

$$\int dV\rho_\psi(A)=Z,$$

$$\tfrac{1}{2}\int dV_1\int dV_2\pi_\psi(A,A)=\tfrac{1}{2}Z(Z-1)+C_1{}^2,$$

showing that the admixture of positive- and negative-ionic states in equal amounts serves as a means to modify the atomic pair population without affecting the atomic electron population itself.

Since an atom in a molecule cannot be given a promotion state wave function, Moffit[34] was forced to consider a "condition" of the atom in the molecule, represented by a symbolic sum of several atomic wave functions containing different numbers of electrons. This impasse is avoided if the analysis is based upon the density and pair-density partitioning.

The present approach could be modified so as to permit the construction of a promotion-state wave function. One could decompose the atomic contribution $\rho(A)$ of the quasi-classical density (3.37) into a part which *can* be derived from an atomic wave function and a remainder which could be attributed to electron sharing. In a number of actual cases, it was found that this objective can be achieved with an extremely small remainder.[35] Once such a promotion-state wave function is found, it does furnish a definite promotion state pair density, so that the sharing-penetration partitioning of Sec. 4.5 is no longer needed. However the general construction of a wave function for a prescribed first-order density is a difficult problem, since it involves the solution of set of simultaneous nonlinear equations in many variables.

In the present investigation the terms "valence state" and "promotion state" imply merely the existence of density and pair density, and not the existence of a wave function.

5. CHARGE TRANSFER

5.1 Integral Transfer and Fractional Transfer

In most molecules, the total charge associated with a particular atom, i.e., the quantity $q(A)$ defined by Eq. (3.27), is different from that atom's nuclear charge $Z(A)$. In such cases the quantity $\Delta q(A)$, defined by Eq. (3.48), represents the total population transfer into atom A, and

$$Q(A) = -\Delta q(A) = Z(A) - q(A) \tag{5.1}$$

is the total "ionic charge" of this atom in the molecule.

If this total population transfer is an *integral* number of electrons, then it is convenient to consider the ion with the charge $Q(A)$, rather than the corresponding neutral atom, as the natural building block for the particular molecule. In such a case, all derivations given in the preceding sections remain directly applicable. One has merely to keep in mind that $Z(A)$ and $q(A)$ are different. The atom must then be thought of as entering the molecule in the form of a *promoted ion.*

Considerably more complicated relationships arise when the atomic population transfers $\Delta q(A)$ are fractions of an electronic unit. *Fractional population transfer*, i.e., *partial electron transfer*, is possible *since valence electrons are shared*, and it is in fact the most common situation. In this condition it is impossible to conceive of a promotion state, i.e., a state with *unshared* electrons, which has the identical atomic populations $q(A)$, and one cannot follow the procedure of Eq. (4.41), i.e., to take $\rho(A)$ as the promotion state density.

One has to be satisfied with constructing "the most closely related promotion state," i.e., one has to find atomic promotion-state densities $\rho^{\mathrm{P}}(A)$ which have *integral* populations

$$q^{\mathrm{P}}(A) = \int dV \rho^{\mathrm{P}}(A), \tag{5.2}$$

and differ from the quasi-classical atomic densities $\rho(A)$ as little as possible, in a sense which remains to be examined. With this promotion-state density one may then proceed in a manner similar to that applied in Sec. 4.

The most appropriate values for the promotion state populations $q^{\mathrm{P}}(A)$ are not necessarily identical with those of the nuclear charges $Z(A)$. In view of the interatomic character of charge transfer and electron sharing, it seems that all atoms in a molecule ought to be considered simultaneously. Hence, we define the $q^{\mathrm{P}}(A)$ as those *integers* which satisfy the conditions

$$\sum_A [q^{\mathrm{P}}(A) - q(A)]^2 = \mathrm{Min}, \tag{5.3}$$

while

$$\sum_A q^{\mathrm{P}}(A) = \sum_A q(A) = N = \mathrm{const.} \tag{5.3'}$$

When these equations have been solved, one can write the decompositions

$$q(A) = q^{\mathrm{P}}(A) + q^{\mathrm{T}}(A), \tag{5.4}$$

with

$$\sum_A q^{\mathrm{T}}(A) = 0. \tag{5.4'}$$

The quantity $q^{\mathrm{T}}(A)$ will be called *transfer population* for the atom A. If it should turn out that the promotion state population $q^{\mathrm{P}}(A)$ corresponds to that of an ion, then $q^{\mathrm{T}}(A)$ will differ from the total population transfer $\Delta q(A)$ discussed in the beginning of this section and in Sec. 3.5.

5.2 Transfer Partitioning of the Density

It is our aim to define the partitioning

$$\rho(A) = \rho^{\mathrm{P}}(A) + \rho^{\mathrm{T}}(A) \tag{5.5}$$

for each atom in a molecule. If the *promotion state density* $\rho^{\mathrm{P}}(A)$ and the *transfer density* $\rho^{\mathrm{T}}(A)$ are expanded in terms of atomic orbitals

$$\rho^{\mathrm{P}}(A) = \textstyle\sum_a q^{\mathrm{P}}(Aa)(Aa^2), \tag{5.6}$$

$$\rho^{\mathrm{T}}(A) = \textstyle\sum_a q^{\mathrm{T}}(Aa)(Aa^2), \tag{5.7}$$

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[34] W. Moffitt, Repts. Progr. in Phys. **17**, 173 (1954), Eq. (3.6) ff.

[35] The promotion state is of course *not* a stationary state of the free atom.

then Eq. (5.5) can be expressed by the orbital decompositions

$$q(Aa)=q^{\mathrm{P}}(Aa)+q^{\mathrm{T}}(Aa), \tag{5.8}$$

which, moreover, define the corresponding partitioning for the density *operator*. From Eqs. (5.2), (5.5) to (5.7) follow the conservation relations

$$\textstyle\sum_a q^{\mathrm{P}}(Aa)=q^{\mathrm{P}}(A), \tag{5.9}$$

$$\textstyle\sum_a q^{\mathrm{T}}(Aa)=q^{\mathrm{T}}(A). \tag{5.10}$$

Is there a physically reasonable way of implementing the partitioning (5.8) with the side conditions (5.4), (5.9), and (5.10)?

Since valence-active atomic orbitals are expected to carry a larger share of electron transfer and electron sharing, it seems reasonable to assume the orbital transfer populations $q^{\mathrm{T}}(Aa)$ proportional to the $v(Aa)$, the valence-active parts of the gross orbital populations. If the proportionality constant is considered the same for all orbitals on one atom, then the necessary validity of Eq. (5.10) yields

$$q^{\mathrm{T}}(Aa)=v(Aa)q^{\mathrm{T}}(A)/v(A), \tag{5.11}$$

where

$$v(A)=\textstyle\sum_a v(Aa) \tag{5.11$'$}$$

is the total valence-active population of atom A.

The following different line of reasoning might also seem plausible. According to Eq. (3.24), the amount $v(Aa)$ is taken from the bond region to form, together with $p(Aa)$, the *total* orbital population $q(Aa)$. In order to obtain the *promotion state* orbital-populations $q^{\mathrm{P}}(Aa)$, the amounts taken from the bond regions should be modified, though still in the relative proportions determined by the valence-active parts $v(Aa)$, i.e.,

$$q^{\mathrm{P}}(Aa)=p(Aa)+c_Av(Aa),$$

where c_A is the same for all orbitals on one atom. The required validity of relation (5.9) now yields

$$q^{\mathrm{P}}(Aa)=p(Aa)+v(Aa)[q^{\mathrm{P}}(A)-p(A)]/v(A), \tag{5.12}$$

with

$$p(A)=\textstyle\sum_a p(Aa). \tag{5.12$'$}$$

By virtue of Eq. (5.8), the two definitions, (5.11) and (5.12) are equivalent; hence, both kinds of arguments lead to the same partitioning of $q(Aa)$.

These definitions seem, however, reasonable only if $v(Aa)>0$, i.e., in the case of an over-all bonding atomic orbitals, but not for an antibonding atomic orbital where $v(Aa)<0$. An example is the lone-pair hybrid orbital ($Ol\sigma$) of oxygen in water (see Table II). Since there is an over-all charge transfer unto oxygen, Eq. (5.11) would yield the unlikely result that some charge leaves the lone-pair orbital and is transferred into the binding oxygen VAO's. We therefore modify the definition (5.11) by replacing the valence-active populations $v(Aa)$ with their absolute values. Thus, the relation

$$q^{\mathrm{T}}(Aa)=|v(Aa)|q^{\mathrm{T}}(A)/|v(A)|_{\mathrm{av}}, \tag{5.13}$$

with

$$|v(A)|_{\mathrm{av}}=\textstyle\sum_a|v(Aa)|, \tag{5.13$'$}$$

is proposed as definition of the transfer populations. Another possibility would be to use the squares $|v(Aa)|^2$ instead of the absolute values $|v(Aa)|$.

On the other hand, by comparison with bonding and antibonding orbitals in heteronuclear diatomics, it may be argued that the choice (5.11) is not unreasonable.

If one defines

$$\rho^{\mathrm{P}}=\sum_A\rho^{\mathrm{P}}(A),\quad \rho^{\mathrm{T}}=\sum_A\rho^{\mathrm{T}}(A), \tag{5.14}$$

then the Eqs. (5.5) can be written as [see Eq. (4.36)]

$$\rho^{\mathrm{VS}}=\rho^{\mathrm{CL}}=\rho^{\mathrm{P}}+\rho^{\mathrm{T}}. \tag{5.15}$$

In the case of partial electron transfer, this definition of ρ^{P} replaces the previous Eq. (4.41).

5.3 Transfer Partitioning of the Pair Density

Valence-State Pair Density

There is no reason why the interference partitioning of the pair density described in Sec. 4.1 should not be carried through when there exists partial electron transfer. Assuming then that one has obtained the three parts π^{VS}, π^{I}, π^{II}, of Eq. (4.3), let us first consider the further partitioning to which the valence-state pair density π^{VS} must be subjected as a consequence of fractional population transfer.

Let π^{P} be a promotion-state pair density, whose exact definition is discussed below, but which *is* related to the promotion-state density ρ^{P} by Eqs. (4.39) to (4.44), except that Eq. (4.41) is now replaced by Eq. (5.15). One would then expect the difference $(\pi^{\mathrm{VS}}-\pi^{\mathrm{P}})$ to account for two effects:

(1) A modification of π^{P} arising from straight electron sharing, irrespective of charge transfer;

(2) An additional modification which is inseparably tied up with the fractional population transfer ρ^{T}. Let us therefore attempt a partitioning of the type

$$\pi^{\mathrm{VS}}=\pi^{\mathrm{P}}+\pi^{\mathrm{SP}}+\pi^{\mathrm{T}}, \tag{5.16}$$

where the following conceptual significance is attached to π^{SP} and π^{T}: π^{SP} is due to the sharing-penetration effect *while the density remains that of the promotion state*, viz., ρ^{P}; π^{T} is concomitant with the *subsequent* transfer of charge, which changes ρ^{P} into $\rho^{\mathrm{P}}+\rho^{\mathrm{T}}$. From Eqs. (4.44), (4.48$'$), and (5.15) follow the conservation relations

$$\int dV_2\pi^{\mathrm{P}}(\mathbf{x}_1,\mathbf{x}_2)=(N-1)\rho^{\mathrm{P}}(\mathbf{x}_1), \tag{5.17}$$

$$\int dV_2\pi^{\mathrm{SP}}(\mathbf{x}_1,\mathbf{x}_2)=0, \tag{5.17$'$}$$

$$\int dV_2\pi^{\mathrm{T}}(\mathbf{x}_1,\mathbf{x}_2)=(N-1)\rho^{\mathrm{T}}(\mathbf{x}_1). \tag{5.17$''$}$$

In order to implement the partitioning (5.16), we first find a suitable definition of the transfer pair density π^{T}. Then the difference

$$\pi^{\mathrm{VS}}-\pi^{\mathrm{T}}=\pi^{\mathrm{P}}+\pi^{\mathrm{SP}} \qquad (5.18)$$

can be formed. Thereupon the procedure developed in Secs. 4.4 and 4.5 is applied to separate π^{P} from π^{SP}.

It is convenient to decompose the various terms in Eq. (5.16) into Coulomb and self-pair density parts [Compare Eqs. (4.73), (4.74)]:

$$\pi^{\mathrm{VS}}(1,2)=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)-\pi_x{}^{\mathrm{VS}}(1,2), \qquad (5.19)$$

$$\pi^{\mathrm{P}}(1,2)=\rho^{\mathrm{P}}(1)\rho^{\mathrm{P}}(2)-\pi_x{}^{\mathrm{P}}(1,2), \qquad (5.20)$$

$$\pi^{\mathrm{SP}}(1,2)= \qquad -\pi_x{}^{\mathrm{SP}}(1,2) \qquad (5.21)$$

$$\pi^{\mathrm{T}}(1,2)=\pi_c{}^{\mathrm{T}}(1,2)-\pi_x{}^{\mathrm{T}}(1,2), \qquad (5.22)$$

where

$$\begin{aligned}\pi_c{}^{\mathrm{T}}(1,2)&=\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)-\rho^{\mathrm{P}}(1)\rho^{\mathrm{P}}(2)\\&=\rho^{\mathrm{T}}(1)\rho^{\mathrm{M}}(2)+\rho^{\mathrm{M}}(1)\rho^{\mathrm{T}}(2),\end{aligned} \qquad (5.22')$$

and

$$\rho^{\mathrm{M}}(\mathbf{x})=\tfrac{1}{2}[\rho^{\mathrm{P}}(\mathbf{x})+\rho^{\mathrm{CL}}(\mathbf{x})]=\sum_A \rho^{\mathrm{M}}(A). \qquad (5.22'')$$

Here, the *median atomic density*

$$\rho^{\mathrm{M}}(A)=\tfrac{1}{2}[\rho^{\mathrm{P}}(A)+\rho^{\mathrm{CL}}(A)]=\rho^{\mathrm{P}}(A)+\tfrac{1}{2}\rho^{\mathrm{T}}(A) \qquad (5.22''')$$

is the mean value of the quasi-classical atomic density before and after charge transfer. The problem at hand is now to propose a definition for $\pi^{\mathrm{T}}(1,2)$ or, alternatively, for $\pi_x{}^{\mathrm{T}}(1,2)$. It is preferable to use the latter term, since it is about N times smaller than the former in magnitude. Hence, the unavoidable arbitrariness will be of less consequence if it is limited to the self-pair density part of the transfer pair density.

Consider again decompositions of the kind given in Eqs. (4.77) and (4.77′), where the superscript Σ can now be one of the following:

$$\Sigma=\mathrm{VS,\ P,\ SP,\ T}. \qquad (5.22a)$$

For the terms in these decompositions, orbital expansions of the type given in Eqs. (4.82) and (4.82″) are again valid. It is readily seen that Eqs. (5.17) to (5.17″) yield, among others, the conservation relations

$$\sum_{Bb} p^{\Sigma}(AaA\bar{a}\,|\,Bb)=0, \quad \text{for} \quad \mathrm{VS,\ P,\ SP,\ T}, \qquad (5.23)$$

$$\sum_{Bb} q_x{}^{\mathrm{T}}(Aa\,|\,Bb)=q^{\mathrm{T}}(Aa). \qquad (5.24)$$

Since there arise no other conditions as regards $\pi_x{}^{\mathrm{T}}$, it is simplest to put

$$p^{\mathrm{T}}(AaA\bar{a}\,|\,Bb)=p^{\mathrm{T}}(AaA\bar{a}\,|\,BbB\bar{b})=0, \qquad (5.25)$$

so that $\pi_x{}^{\mathrm{T}}$ contains only the principal terms $q_x{}^{\mathrm{T}}(Aa\,|\,Bb)$, which represent essentially the change, caused by partial population transfer, in the self-pair density of those electrons which are shared between different atoms.

Now, if two orbitals (Aa) and (Bb) share *one* electron, then we would estimate the change, due to charge transfer, in the self-pair density of this electron to be given by

$$q_x{}^{\mathrm{T}}(Aa\,|\,Bb)=q^{\mathrm{T}}(Aa)q^0(Bb)+q^0(Aa)q^{\mathrm{T}}(Bb), \qquad (5.26)$$

where $q^0(Aa)$ is the mean value of the population fraction due to the shared electron in (Aa) before and after transfer [compare the similar expression (5.22′) for $\pi_c{}^{\mathrm{T}}$]. Actually, several electrons are involved in electron sharing between two atoms. It remains, however, true that the charge transfer is effected by the shared electrons only. Thus, we feel justified in trying Eq. (5.26) as an approximation, provided suitable values can be found for the quantities $q^0(Aa)$.

On the other hand, we note that the quantity

$$v_x(Aa\,|\,Bb)=q_x(Aa\,|\,Bb)-p_x(AaAa\,|\,BbBb), \qquad (5.27)$$

with

$$\begin{aligned}&p_x(AaAa\,|\,BbBb)\\&\quad=p(AaAa\,|\,BbBb)-p(Aa\,|\,Aa)p(Bb\,|\,Bb),\end{aligned} \qquad (5.27')$$

indicates how much of the exchange term $q_x(Aa\,|\,Bb)$ must be ascribed to interference. By adhering to the kind of reasoning advanced in Sec. 5.2 in connection with the transfer partitioning of the density, we take the quantity (5.27) also as a measure of the effect which charge transfer has on $q_x(Aa\,|\,Bb)$. In analogy to Eq. (5.13), it seems therefore reasonable to put $q_x{}^{\mathrm{T}}(Aa\,|\,Bb)$ proportional to the absolute value of $v_x(Aa\,|\,Bb)$.

In this way, one arrives at the supposition

$$\begin{aligned}&q_x{}^{\mathrm{T}}(Aa\,|\,Bb)\\&\quad=|v_x(Aa\,|\,Bb)|\,\{q^{\mathrm{T}}(Aa)\lambda(Bb)+q^{\mathrm{T}}(Bb)\lambda(Aa)\},\end{aligned} \qquad (5.28)$$

where the coefficients $\lambda(Aa)$ are as yet undetermined. Substitution in the conservation relations (5.24) yields the following system of linear equations

$$\begin{aligned}&q^{\mathrm{T}}(Aa)\sum_{Bb}|v_x(Aa\,|\,Bb)|\,\lambda(Bb)\\&\qquad+\lambda(Aa)\sum_{Bb}|v_x(Aa\,|\,Bb)|\,q^{\mathrm{T}}(Bb)=q^{\mathrm{T}}(Aa)\end{aligned} \qquad (5.29)$$

which determines the $\lambda(Aa)$ completely. Since, in general, some of the $q^{\mathrm{T}}(Aa)$ are very small (e.g., for inner shells), it is convenient to put

$$\lambda(Aa)=q^{\mathrm{T}}(Aa)y(Aa). \qquad (5.29')$$

One then finds

$$q_x{}^{\mathrm{T}}(Aa\,|\,Bb)=M(Aa\,|\,Bb)[y(Aa)+y(Bb)], \qquad (5.30)$$

with

$$M(Aa\,|\,Bb)=|v_x(Aa\,|\,Bb)|\,q^{\mathrm{T}}(Aa)q^{\mathrm{T}}(Bb), \qquad (5.30')$$

and the $y(Aa)$ are determined by the linear equations

$$\sum_{Bb} \{M(Aa|Bb) + \delta_{Aa,Bb} \sum_{Cc} M(Aa|Cc)\} y(Bb) = q^{\mathrm{T}}(Aa), \quad (5.31)$$

or

$$\sum_{Bb} \{ |v_x(Aa|Bb)| q^{\mathrm{T}}(Bb) + \delta_{Aa,Bb} \sum_{Cc} |v_x(Aa|Cc)| q^{\mathrm{T}}(Cc)\} y(Bb) = 1. \quad (5.31')$$

By virtue of the definitions (5.25,28), the exchange part of the quantity (5.18) can now be obtained explicitly [the Coulomb part follows from Eqs. (5.19) to (5.22)]. Its orbital expansion coefficients [see (4.82′)] will be:

$$q_x^{\mathrm{P}}(Aa|Bb) + q_x^{\mathrm{SP}}(Aa|Bb) = q_x(Aa|Bb) - q_x^{\mathrm{T}}(Aa|Bb), \quad (5.32)$$

$$p^{\mathrm{P}}(Aa A\bar{a}|Bb) + p^{\mathrm{SP}}(Aa A\bar{a}|Bb) = p(Aa A\bar{a}|Bb), \quad (5.32')$$

$$p^{\mathrm{P}}(Aa A\bar{a}|Bb B\bar{b}) + p^{\mathrm{SP}}(Aa A\bar{a}|Bb B\bar{b}) = p(Aa A\bar{a}|Bb B\bar{b}). \quad (5.32'')$$

Hence, the partitioning into π_x^{P} and π_x^{SP} can now be carried out by means of the Eqs. (4.83)–(4.88), if only one substitutes in these equations $(q_x^{\mathrm{P}} + q_x^{\mathrm{SP}})$ for q_x.

Interference Pair Density

The primary interference pair density π^{I} resulting from the partitioning (4.3) is also effected by partial electron transfer. That this will be so is evident from the decomposition in Coulomb and exchange term given in Eq. (4.65), since it contains the quasi-classical density ρ^{CL} which involves charge transfer.

We, therefore, define the following partitioning of π^{I}:

$$\pi^{\mathrm{I}} = \pi^{\mathrm{IP}} + \pi^{\mathrm{IT}}, \quad (5.33)$$

where

$$\pi^{\mathrm{IP}}(1,2) = 2\mathcal{S}\rho^{\mathrm{P}}(1)\rho^{\mathrm{I}}(2) - \pi_x^{\mathrm{IP}}(1,2), \quad (5.34)$$

$$\pi^{\mathrm{IT}}(1,2) = 2\mathcal{S}\rho^{\mathrm{T}}(1)\rho^{\mathrm{I}}(2) - \pi_x^{\mathrm{IT}}(1,2). \quad (5.35)$$

In the next section, it is seen that π^{I} gives rise to relatively small energy contributions; moreover, it is to be expected that π_x^{I} is about $(N-1)$ times smaller in magnitude than π^{I}. Hence, we tentatively simplify Eqs. (5.34) and (5.35) by the approximation

$$\pi_x^{\mathrm{IT}} = 0, \quad \pi_x^{\mathrm{IP}} = \pi_x^{\mathrm{I}}. \quad (5.36)$$

This assumption is compatible with the conservation relation (4.68) and its counterpart

$$\int dV_2 \pi_x^{\mathrm{IP}}(1,2) = \rho^{\mathrm{I}}(1). \quad (5.37)$$

While it is believed that the present definitions of transfer densities and pair densities represent reasonable first approximations, they clearly require considerable improvements by a more careful analysis.

A more fundamental approach would consist in resolving the molecular problem under the additional side conditions that all atomic populations $q'(A)$ resulting from *that* calculation keep the values $q^{\mathrm{P}}(A)$ found from Eqs. (5.3) and (5.3′) for the actual molecule. The density and pair density resulting from such a calculation might be considered as the most satisfying definitions for ρ^{P} and $(\pi^{\mathrm{P}} + \pi^{\mathrm{SP}})$.

6. ENERGY PARTITIONING

The objective of the present section is to understand the physical significance of the partitioning of the molecular energy which results from substituting into the energy formula (1.26) the density partitioning and the pair-density partitioning which were derived in the preceding sections.

6.1 Characterization of the Interference Partitioning

Analysis of the Coulomb Term

As in Sec. 4.1, it is again instructive first to consider the terms which arise if one merely includes the "Coulombic fragment" (1.36) of the pair density. Insertion of the interference partitioning for the density, Eq. (3.9), and the corresponding pair density, Eq. (4.1), into the energy expression (1.26) yields

$$E = E^0 + E' + E'', \quad (6.1)$$

with

$$E^0 = \sum_{A<B} Z_A Z_B R_{AB}^{-1} + \int dV h \rho^{\mathrm{CL}} + \frac{1}{2}\int dV_1 \int dV_2 \frac{\rho^{\mathrm{CL}}(1)\rho^{\mathrm{CL}}(2)}{r_{12}}, \quad (6.2)$$

$$E' = \int dV h \rho^{\mathrm{I}} + \int dV_1 \int dV_2 \frac{\rho^{\mathrm{CL}}(1)\rho^{\mathrm{I}}(2)}{r_{12}}, \quad (6.2')$$

$$E'' = \frac{1}{2}\int dV_1 \int dV_2 \frac{\rho^{\mathrm{I}}(1)\rho^{\mathrm{I}}(2)}{r_{12}}. \quad (6.2'')$$

Since the quasi-classical density ρ^{CL} can be expressed by the atomic expansion (3.37), the results derived in Eqs. (1.38) to (1.41) become applicable for E^0, and one obtains, in a slight generalization of Eq. (1.39),

$$E^0 = \sum\nolimits_A E_A{}^0 + \sum\nolimits_{A<B} V_{AB}, \quad (6.3)$$

where $E_A{}^0$ is related to V_A of Eq. (1.40) by

$$E_A{}^0 = \int dV \mathcal{T}\rho(A) + V_A, \quad (6.3')$$

and represents the total intra-atomic energy of atom A in this approximation. Thus, the term E^0 represents that part of the energy which can be given the *quasi-*

classical interpretation which was discussed in considerable detail in Sec. 1.3.

The terms E' and E'' represent two of the quantum-mechanical additions whose existence was mentioned at the end of Sec. 1.3.

Of these two, the term E' is the more substantial one. If one inserts again the atomic decomposition (3.37) for ρ^{CL}, one finds

$$E'=\int dV(\mathcal{T}+U)\rho^{\mathrm{I}}, \tag{6.4}$$

with

$$U=\sum_{A} U_A, \tag{6.4$'$}$$

$$U_A(\mathbf{x})=\left(\frac{-Z_A}{|\mathbf{x}-\mathbf{x}_A|}\right)+\int dV'\frac{\rho_A(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}. \tag{6.4$''$}$$

The potential $U_A(x)$ clearly represents the attraction of the *atom* A, i.e., the nuclear attraction shielded by the repulsion due to the electronic density $\rho(A)$. Thus the term E' must be understood as the total energy, kinetic and potential, of the interference density ρ^{I} under the influence of the *shielded* potentials of all atoms. It should be noted moreover, that according to Eq. (3.12), the term E' is a sum of contributions from the various bonds of the molecule. *The term E' is the prototype of the interference-energy terms which represent the primordial source for the positive or negative stabilization energy which leads to chemical binding and antibinding.*

The term E'' represents the self-interaction of the interference density and its most notable quality is its smallness. According to Eq. (3.12) it is the *only* term which contains interactions *between different bonds*. For reasons which soon become clear, it incorporates a considerable amount of *internal cancellation* and is therefore much smaller than the individual multi-center electron-repulsion integrals which it contains. It is obviously extremely desirable that the interactions between different bonds appear embedded in such "packages" so that their quantitative contributions are reduced to a minimum. If this minimum is small enough, then there exists hope of understanding the phenomenon of approximate additivity of bond energies, which is experimentally so firmly established and theoretically so little explained.

Characterization by Energy Integrals

The three types of energies, E^0, E', and E'' can also be characterized by the type of *energy integrals between atomic orbitals* which they contain. Let

$$T(f,g)=\int dV f(\mathbf{x})\mathcal{T}g(\mathbf{x}), \tag{6.5}$$

$$[f|g]=\int dV_1\int dV_2\frac{f(\mathbf{x}_1)g(\mathbf{x}_2)}{r_{12}}, \tag{6.6}$$

$$[f|\mathrm{Nu}A]=-Z_A\int dV\frac{f(\mathbf{x})}{|\mathbf{x}-\mathbf{x}_A|}. \tag{6.7}$$

The definitions (6.6) and (6.7) are consistent, if (NuA) signifies the nuclear pointcharge distribution $-Z_A\delta(\mathbf{x}-\mathbf{x}_A)$ defined in Eq. (1.35).

There are two kinds of kinetic-energy contributions: (1) The intra-atomic integrals,

$$T(Aa,A\bar{a}) \tag{6.8}$$

belong to the intra-atomic energy E_A which is a part of the quasi-classical energy E^0; (2) the interatomic integrals

$$T\langle Aa,Bb\rangle=\int dV\,\mathcal{T}\langle Aa,Bb\rangle=T(Aa,Bb)$$

$$-\tfrac{1}{2}S(Aa,Bb)[T(Aa,Aa)+T(Bb,Bb)],\quad (A\neq B), \tag{6.8$'$}$$

represent the kinetic energies of the orbital interference densities and belong to the interference energy E'.

There are three kinds of orbital nuclear attraction contributions: (1) The intra atomic integrals

$$[AaA\bar{a}|\mathrm{Nu}A] \tag{6.9}$$

are part of the intra-atomic energy E_A; (2) the "Coulombic" interatomic integrals

$$[AaA\bar{a}|\mathrm{Nu}B],\quad (A\neq B), \tag{6.9$'$}$$

describe attractive interatomic potential energies between the quasi-classical electron density on one atom and the nucleus of another; both (6.9) and (6.9′) belong to the quasi-classical energy E^0; (3) the interatomic integrals

$$\begin{aligned}[\langle AaBb\rangle|\mathrm{Nu}C]&=[AaBb|\mathrm{Nu}C]\\&\quad-\tfrac{1}{2}S(Aa,Bb)\{[Aa^2|\mathrm{Nu}C]+[Bb^2|\mathrm{Nu}C]\},\\&\qquad(A\neq B),\end{aligned} \tag{6.9$''$}$$

on the other hand, represent the potential energy of the interference density $\langle AaBb\rangle$ in the bond A–B, in the field of the nuclear charge at C. These contributions belong to the interference energy E'.

There are four kinds of orbital electronic repulsion contributions: (1) The one-center integrals

$$[AaA\bar{a}|Aa'A\bar{a}'] \tag{6.10}$$

represent intra-atomic electronic repulsions contributing to E_A. (2) The "two-center Coulomb integrals,"

$$[AaA\bar{a}|BbB\bar{b}],\quad (A\neq B), \tag{6.10$'$}$$

describe the shielding repulsion between the quasi-classical electron densities on different atoms; both terms are part of E^0. (3) On the other hand, the integrals

$$\begin{aligned}[\langle AaBb\rangle|CcC\bar{c}]&=[AaBb|CcC\bar{c}]\\&\quad-\tfrac{1}{2}S(Aa,Bb)\{[Aa^2|CcC\bar{c}]+[Bb^2|CcC\bar{c}]\},\\&\qquad(A\neq B),\end{aligned} \tag{6.10$''$}$$

express the shielding of the nuclear attractions, due to the repulsions by atomic electrons, as acting with respect to the orbital interference density $\langle AaBb\rangle$ in the bond A–B; they belong to the interference energy E'. The terms (6.10″) contain the two- and three-center hybrid integrals. (4) Finally, there are the interactions between orbital interference densities,

$$\begin{aligned}[\langle AaBb\rangle|\langle CcDd\rangle]=&[AaBb|CcDd]\\ &+\tfrac{1}{4}S(Aa,Bb)S(Cc,Dd)[Aa^2+Bb^2|Cc^2+Dd^2]\\ &-\tfrac{1}{2}S(Aa,Bb)[Aa^2+Bb^2|CcDd]\\ &-\tfrac{1}{2}S(Cc,Dd)[AaBb|Cc^2+Dd^2],\\ &\qquad (A\neq B),\ (C\neq D). \quad (6.11)\end{aligned}$$

These are the only kind of integrals occurring in E'', the self-energy of the interference density.

It is thus apparent that the individual integrals between atomic orbitals and their interference densities are characteristic for the different energy terms E^0, E', E''.

It can furthermore be understood why the interference self-interaction E'' is small. Many-electron repulsion integrals between atomic orbitals satisfy "Mulliken's approximation,"[36] viz.,

$$[f|AaBb]\approx\tfrac{1}{2}S(Aa,Bb)\{[f|Aa^2]+[f|Bb^2]\},\qquad (A\neq B),\quad (6.12)$$

surprisingly closely. This circumstance explains immediately why the integrals (6.11) are found to be an order of magnitude smaller than the "bare" two-, three-, and four-center repulsion integrals $[AaBb|CcDd]$, $(A\neq B, C\neq D)$. There are, moreover, reasons to expect that the approximation (6.12) is better for the valence atomic orbitals, defined in Sec. 3.4, than for spherical atomic orbitals (i.e., those which are proportional to spherical harmonics). Thus, the orbital interference densities $\langle AaBb\rangle$, $(A\neq B)$, seem to be particularly suited to minimize the electronic interactions between bonds.

Mulliken's approximation (6.12) applies also to the integrals (6.10″), but not to the nuclear attraction integrals (6.9″).

6.2 Interference Partitioning

Partitioning

Let us now insert the *exact* expressions for density and pair density in the molecular energy formula (1.26). The density decomposition is given by Eqs. (3.9), (3.12), (3.20), and (3.37); the pair-density decomposition is given by Eqs. (4.3) and (4.18) to (4.29). By examining the occurring integrals between atomic orbitals and their interference densities, and assigning to them the physical significance discussed in the preceding section, it is then possible to partition the rigorous energy expression into a sum of three terms which are analogous to those found in Eqs. (6.2) to (6.2″). The result is

$$E=E^{\mathrm{VS}}+E^{\mathrm{I}}+E^{\mathrm{II}},\quad (6.13)$$

with

$$E^{\mathrm{VS}}=\sum_{A<B}Z_AZ_BR_{AB}{}^{-1}+\sum_{A}\int dVh\rho(A)$$
$$+\sum_{A}\sum_{B}\tfrac{1}{2}\int dV_1\int dV_2\pi(A,B)/r_{12},\quad (6.14)$$

$$E^{\mathrm{I}}=\sum_{A\bar{A}}{}'\int dVh\rho(A,\bar{A})$$
$$+\sum_{A\bar{A}}{}'\sum_{B}\tfrac{1}{2}\int dV_1\int dV_2\pi(A\bar{A},B)/r_{12},\quad (6.14')$$

$$E^{\mathrm{II}}=\sum_{A\bar{A}}{}'\sum_{B\bar{B}}{}'\tfrac{1}{2}\int dV_1\int dV_2\pi(A\bar{A},B\bar{B})/r_{12}.\quad (6.14'')$$

Interference Energies

I

Since it is convenient to discuss the various terms in order of increasing complexity, consider first the *interference self-interaction* E^{II}. It can be written

$$E^{\mathrm{II}}=\sum_{A<\bar{A}}E^{\mathrm{II}}(A\bar{A},A\bar{A})+\sum_{A\bar{A}<B\bar{B}}E^{\mathrm{II}}(A\bar{A},B\bar{B}),\quad (6.15)$$

with

$$E^{\mathrm{II}}(A\bar{A},B\bar{B})=\epsilon(A\bar{A},B\bar{B})\sum_{a\bar{a}}\sum_{b\bar{b}}p(Aa\bar{A}\bar{a}|Bb\bar{B}\bar{b})$$
$$\times[\langle Aa\bar{A}\bar{a}\rangle|\langle Bb\bar{B}\bar{b}\rangle],\quad (A\neq\bar{A},\ B\neq\bar{B}),\quad (6.15')$$

where

$$\epsilon(A\bar{A},B\bar{B})=\begin{cases}2, & \text{if}\quad A\bar{A}=B\bar{B}\\ 4, & \text{if}\quad A\bar{A}\neq B\bar{B},\end{cases}\quad (6.15'')$$

and

$$\sum_{A\bar{A}<B\bar{B}}=\tfrac{1}{2}\sum_{A<\bar{A}}\sum_{B<\bar{B}},\quad (A\bar{A}\neq B\bar{B}),\quad (6.15''')$$

is a sum over all *bond pairs* (adopting the convention that each pair of different atoms determines a formal bond), each bond pair taken *once*, and excluding terms of the type $E^{\mathrm{II}}(A\bar{A},A\bar{A})$.

Equation (6.15) represents a "regional" partitioning according to bond pairs; there are three types of terms: self-interactions of individual bonds, interactions of bonds having one atom in common, and interactions of nonoverlapping bonds. The contributions can be expected to decrease in this order; also bonds between neighbor atoms will furnish larger contributions than "bonds" between non-neighbor atom pairs. Within each bond, the contributions to the term (6.15′) will decrease with the amount of overlap associated with the interacting orbital pairs. All contributions will be small for the reasons discussed in the preceding section.

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[36] R. S. Mulliken, J. chim. phys. 46, 500, 521 (1949); see also K. Ruedenberg, J. Chem. Phys. 19, 1433 (1951); P. O. Löwdin *ibid*, 21, 374 (1953).

II

The *interference energy* E^{I} is the source for covalent binding and antibinding. It can be written

$$E^{\mathrm{I}}=\sum_{A<\bar{A}} E^{\mathrm{I}}(A\bar{A}), \qquad (6.16)$$

$$E^{\mathrm{I}}(A\bar{A})=2\sum_{a\bar{a}} p(Aa|\bar{A}\bar{a})E\langle Aa,\bar{A}\bar{a}\rangle, \quad (A\neq\bar{A}), \qquad (6.16')$$

$$E\langle Aa,\bar{A}\bar{a}\rangle=T\langle Aa,\bar{A}\bar{a}\rangle+U\langle Aa,\bar{A}\bar{a}\rangle, \qquad (6.16'')$$

where

$$U\langle Aa,\bar{A}\bar{a}\rangle=\sum_{B} U_B\langle Aa,\bar{A}\bar{a}\rangle. \qquad (6.17)$$

$$U_B\langle Aa,\bar{A}\bar{a}\rangle=[\langle Aa\bar{A}\bar{a}\rangle|(\mathrm{Nu}B)] +\sum_{b\bar{b}} q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bb)[\langle Aa\bar{A}\bar{a}\rangle|BbB\bar{b}], \qquad (6.17')$$

with the definitions

$$q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bbb)=p(Aa\bar{A}\bar{a}|Bb)/p(Aa|\bar{A}\bar{a}),$$
$$q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bb\bar{b})=p(Aa\bar{A}\bar{a}|BbB\bar{b})/p(Aa|\bar{A}\bar{a}), \qquad (6.17'')$$
$$(b\neq\bar{b}).$$

Clearly $U_B\langle Aa,\bar{A}\bar{a}\rangle$ represents the potential energy of the orbital interference density $\langle Aa\bar{A}\bar{a}\rangle$ in the field of the nucleus B, shielded by the electronic *interference shielding density*

$$\sigma^{\mathrm{I}}(Aa\bar{A}\bar{a}|B)=\sum_{b\bar{b}} q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bb\bar{b})\chi_{Bb}(\mathrm{x})\chi_{B\bar{b}}(\mathrm{x}) \qquad (6.18)$$

on atom B. The *total interference shielding density specific for the interference density* $\langle Aa\bar{A}\bar{a}\rangle$ is apparently

$$\sigma^{\mathrm{I}}(Aa\bar{A}\bar{a})=\sum_{B} \sigma^{\mathrm{I}}(Aa\bar{A}\bar{a}|B). \qquad (6.18')$$

Its population becomes, by virtue of the definitions (6.17″) and the conservation relation (4.9),

$$\int dV\sigma^{\mathrm{I}}(Aa\bar{A}\bar{a})=\sum_{B}\sum_{b} q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bbb)=N-1, \quad \text{for all } \langle Aa\bar{A}\bar{a}\rangle, \qquad (6.19)$$

expressing the fact that the total amount of shielding experienced by any one electron is due to the $(N-1)$ other electrons. The quantities $q^{\mathrm{I}}(Aa\bar{A}\bar{a}|Bbb)$ will therefore be called *interference shielding populations;* this interpretation answers the question as to the physical significance connected with the quantities $p(r\bar{r}|s)$, referred to earlier after Eq. (4.14).

The conservation relation (6.19) also substantiates the intuitively obvious fact that the *average* shielding per (shielded) atom or per (affected) bond will decrease with the size of the molecule. In H_2, for example, each nucleus is only shielded by $\frac{1}{2}$ electron (as far as the interference energy is concerned), whereas in large aromatics each atom is shielded by nearly a whole electron. This result shows that it is really not justified to carry over such parameters as resonance integrals from diatomics (as e.g., the pi bond in ethylene) to large systems.

Discussion

(1) The total interference energy (6.16) contains contributions from all *atom* pairs. The energy $E^{\mathrm{I}}(A,\bar{A})$ arising from any *one* atom pair is a sum of contributions from all *orbital* pairs which have one partner on each of the two atoms. The various interference energy contributions can be divided into three categories; bonding contributions with negative interference energy, contributions from noninteracting partners with vanishing interference energy, and antibonding contributions with positive interference energy. It is to be expected that, within certain limits, the interference energies as well as the bond orders can assume any numerical value, and in practice this is found to be the case. The situation is therefore more general than that conceived in the "valence-bond approximation of perfect pairing" where one anticipates only strong bonding attractions, strong antibonding repulsions, and weak nonbonded repulsions. From the viewpoint of the present analysis, this tripartition appears as an artifact of the perfect-pairing formalism. *Actually there exists an almost continuous graduation of repulsive as well as attractive interference terms.* Some of them are easily understood as bonding or antibonding interactions of atomic orbitals, others can be appropriately termed nonbonded repulsions or nonbonded attractions, for a third group however these categories appear to be too narrow.

(2) *The contribution of each orbital pair is the product of the bond order $p(Aa|\bar{A}\bar{a})$ and the "resonance integral"* $E\langle Aa,\bar{A}\bar{a}\rangle$. Equation (6.16′) represents the first rigorous formula exhibiting this characteristic structure for the essential ingredients of chemical binding energies. Since expressions *formally* similar to Eq. (6.16′) occur in certain simple approximative treatments, they have been used in semi-empirical reasoning since the early days of quantum chemistry. The present derivation shows that, first, the bond order concept (if derived from the first-order density, as discussed in Sec. 2.2) has a rightful place in a rigorous energy analysis and that, second, the true resonance integrals are more complicated than the quantities considered in semi-empirical approaches.

(3) In the case of conjugated systems, there has been some argument as to which bond orders are appropriate when overlap is included. When the present results are particularized to that situation, it becomes evident that the proper bond orders in the resonance energy are those denoted by p' in recent papers by this author.[37] They are related to a bond-order definition by Mulliken. On the other hand, Chirgwin–Coulson–Löwdin bond

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[37] K. Ruedenberg, J. Chem. Phys. 34, 1861, 1878, 1884, 1892, 1897, 1907 (1961); see also N. S. Ham and K. Ruedenberg, *ibid.* 29, 1215 (1958).

orders[38] are not appropriate in conjunction with resonance integrals. A more detailed discussion of the relations between the different bond-order definitions is given in reference 37.

(4) Passing on to the resonance integrals, let us suppose for a moment that the total interference shielding density of Eq. (6.18′) is not too different for the various interference densities $\langle Aa,\bar{A}\bar{a}\rangle$ occurring in the molecule, i.e., that one can write

$$q^{\mathrm{I}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b})=q^{\mathrm{I}}(Bb\bar{b})+\delta q^{\mathrm{I}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b}), \quad (6.20)$$

$$\delta q^{\mathrm{I}}(Aa\bar{A}\bar{a}\,|\,Bbb)\ll q^{\mathrm{I}}(Bb\bar{b}),$$

where

$$E\langle Aa,\bar{A}\bar{a}\rangle=E_0\langle Aa,\bar{A}\bar{a}\rangle+\delta E\langle Aa,\bar{A}\bar{a}\rangle, \quad (6.20')$$

The major part E_0 can now be expressed by means of the "effective interference Hamiltonian"

$$h^{\mathrm{I}}=\mathcal{T}+U^{\mathrm{I}},$$

$$U^{\mathrm{I}}(\mathbf{x})=\sum_B\left\{\left(\frac{-Z_B}{|\mathbf{x}-\mathbf{x}_B|}\right)+\sum_{b\bar{b}}q^{\mathrm{I}}(Bb\bar{b})\times\int dV'\frac{\chi_{Bb}(\mathbf{x}')\chi_{B\bar{b}}(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}\right\}. \quad (6.21)$$

One obtains then

$$E_0\langle r,s\rangle=\gamma(r,s)=\beta(r,s)-\tfrac{1}{2}S(r,s)[\alpha(r,r)+\alpha(s,s)], \quad (6.22)$$

with

$$\beta(r,s)=\int dV\chi_r h^{\mathrm{I}}\chi_s, \quad (r\neq s) \qquad (6.22')$$

$$\alpha(r,r)=\int dV\chi_r h^{\mathrm{I}}\chi_r. \quad (6.22'')$$

Now we shall see in the subsequent sections that the kinetic energy is considerably larger than the potential energy in $E\langle Aa,\bar{A}\bar{a}\rangle$ and hence represents the major part of the interference energy. From the approximate validity of the Mulliken approximation (6.12) follows, furthermore, that in the potential part of the interference energy, the shielding term is small compared to the nuclear attraction term. It can therefore be anticipated that, in many cases, the substitution of E_0 [Eq. (6.22)] for the exact expression (6.20′) will be approximately justified and that, under favorable conditions, the shielding terms may be altogether neglected in the potential term (6.17): The shielding effect appears to be of limited importance for the interference energy.

Particularly favorable circumstances exist in the pi-electronic approximation to large conjugated organic molecules, where each atom is assumed to contribute only one $2p\pi$ orbital. Since these atomic orbitals are known to satisfy the Mulliken approximation very well, the use of Eq. (6.22), and even the neglect of the shielding terms in Eq. (6.21), would appear to be *bona fide* quantitative approximations.[37]

(5) The appearance of expressions formally identical to that of Eq. (6.22) had been observed previously by Mulliken in an analysis carried out essentially within a one-electron approximation involving unspecified effective potentials.[39] Nevertheless, it has not been realized that the peculiar form (6.22) constitutes a demonstration of the essential role played by *interference densities* and thereby disagrees with Mulliken's more recent suggestion, namely, that *overlap distributions* [See Eq. (3.21)] are the essential quantities.[40]

Formally, one could, of course, write

$$p(r\,|\,s)E\langle r,s\rangle=[S(r,s)p(r\,|\,s)][E\langle r,s\rangle/S(r,s)],$$

where $[S(r,s)p(r\,|\,s)]$ would be generalized overlap populations. Such an introduction of overlap integrals seems questionable, however, since the ratios $[E\langle r,s\rangle/S(r,s)]$ are in fact *not* approximate constants. The analysis of simple cases[41] seems to indicate that, in agreement with the remarks at the end of Sec. 3.2, the interference energy is roughly proportional to the *interference population* rather than to the *overlap population.*

Transfer Partitioning

The effect of partial electron transfer upon the shielding coefficients (6.17″) is determined by Eqs. (5.33) to (5.36). They yield the decomposition

$$q^{\mathrm{I}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b})=q^{\mathrm{IP}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b})+q^{\mathrm{IT}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b}), \quad (6.23)$$

where q^{IT} is defined by

$$q^{\mathrm{IT}}(Aa\bar{A}\bar{a}\,|\,Bb\bar{b})=\delta_{b\bar{b}}q^{\mathrm{T}}(Bb). \quad (6.23')$$

For the interference energies there results the partitioning

$$E\langle Aa,\bar{A}\bar{a}\rangle=E^{\mathrm{P}}\langle Aa,\bar{A}\bar{a}\rangle+E^{\mathrm{T}}\langle Aa,\bar{A}\bar{a}\rangle, \quad (6.24)$$

with

$$E^{\mathrm{T}}\langle Aa,\bar{A}\bar{a}\rangle=\sum_{Bb}q^{\mathrm{T}}(Bb)[\langle Aa\bar{A}\bar{a}\rangle\,|\,Bb^2]. \quad (6.24')$$

Insertion of Eq. (6.24) into Eq. (6.16′) yields the partitioning

$$E^{\mathrm{I}}(A\bar{A})=E^{\mathrm{IP}}(A\bar{A})+E^{\mathrm{IT}}(A\bar{A}). \quad (6.24'')$$

6.3 Valence-State Partitioning

The major energy term (6.14) can be written in the form

$$E^{\mathrm{VS}}=\sum_A E^{\mathrm{VS}}(A)+\sum_{A<B}E^{\mathrm{VS}}(A,B), \quad (6.25)$$

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[38] B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) **A201**, 196 (1950); P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[39] R. S. Mulliken, J. chim. phys. **46**, 497 (1949); the formula $(\beta-S\alpha)$, which results if $\alpha(rr)=\alpha(ss)$, was already given by R. S. Mulliken, J. Chem. Phys. **3**, 373 (1935); R. S. Mulliken, C. A. Rieke, W. G. Brown, J. Am. Chem. Soc. **63**, 41 (1941) (note that Mulliken uses β and γ with the reverse meanings).

[40] R. S. Mulliken, J. Chem. Phys. **23**, 1842 (1955).

[41] K. Ruedenberg and E. Mehler (to be published).

where

$$E^{\mathrm{VS}}(A)=\int dV[\mathcal{T}-Z(A)r_A^{-1}]\rho(A)+\frac{1}{2}\int dV_1\int dV_2\pi(A,A)/r_{12}, \quad (6.25')$$

$$E^{\mathrm{VS}}(A,B)=Z(A)Z(B)R_{AB}^{-1}-\int dV[\rho(A)Z(B)r_B^{-1}+\rho(B)Z(A)r_A^{-1}]+\int dV_1\int dV_2\pi(A,B)/r_{12}, \quad (A\neq B). \quad (6.25'')$$

The expression (6.25) represents the total energy of the valence state of the ensemble of atoms as defined in Sec. 4.2. It must now be decomposed according to the sharing-penetration partitioning and the charge-transfer partitioning discussed in Secs. 4 and 5. According to Eqs. (5.5) and (5.16), (4.77), (5.22a) this breakdown is characterized by the basic formulas

$$\rho(A)=\rho^{\mathrm{P}}(A)+\rho^{\mathrm{T}}(A), \quad (6.26)$$

$$\pi(A,B)=\pi^{\mathrm{P}}(A,B)+\pi^{\mathrm{SP}}(A,B)+\pi^{\mathrm{T}}(A,B). \quad (6.27)$$

The various resulting energy contributions will be discussed in turn.

Promotion

The insertion of ρ^{P} and π^{P} into Eq. (6.25′) yields the intra-atomic energy of the promotion state of atom A. In this context, and in the following discussion, the expression "atom A" does not necessarily imply the neutral atom but may mean an atomic ion, as discussed in Sec. 5.1. We denote the energy of this promoted ion by $[E^{\mathrm{G}}(A)+E^{\mathrm{P}}(A)]$, so that

$$E^{\mathrm{G}}(A)+E^{\mathrm{P}}(A)=\int dV[\mathcal{T}-Z(A)r_A^{-1}]\rho^{\mathrm{P}}(A)+\tfrac{1}{2}\int dV_1\int dV_2\pi^{\mathrm{P}}(A,A)/r_{12}. \quad (6.28)$$

Here $E^{\mathrm{G}}(A)$ shall denote the energy of the atomic ion in its ground state, characterized by the density ρ^{G} and the pair density π^{G}, say. The *promotional energy* $E^{\mathrm{P}}(A)$ is therefore given by

$$E^{\mathrm{P}}(A)=\int dV[\mathcal{T}-Z(A)r_A^{-1}][\rho^{\mathrm{P}}(A)-\rho^{\mathrm{G}}(A)]+\tfrac{1}{2}\int dV_1\int dV_2[\pi^{\mathrm{P}}(A,A)-\pi^{\mathrm{G}}(A,A)]/r_{12}. \quad (6.29)$$

In the case that $E^{\mathrm{G}}(A)$ refers to the ground state of an ion, one may write

$$E^{\mathrm{G}}(A)=E^{\mathrm{G}}(A_0)+\Delta E^{\mathrm{G}}(A), \quad (6.29')$$

where $E^{\mathrm{G}}(A_0)$ is the ground state of the neutral atom and $\Delta E^{\mathrm{G}}(A)$ is the ionization energy or electron affinity associated with the transition from the neutral atom to the ion in question.

Quasi-Classical Interactions between Promoted Atoms

The insertion of ρ^{P} and π^{P} into the interatomic terms (6.25″) yields the quasi-classical electrostatic interactions $E^{\mathrm{CLP}}(A,B)$ occurring between the promoted atoms. Taking into account the expression (4.43) for the pair density terms $\pi^{\mathrm{P}}(A,B)$, one obtains

$$E^{\mathrm{CLP}}(A,B)=[(\mathrm{Nu}A)+\rho^{\mathrm{P}}(A)\,|\,(\mathrm{Nu}B)+\rho^{\mathrm{P}}(B)], \quad (6.30)$$

where $(\mathrm{Nu}A)=-Z(A)\delta(\mathbf{x}-\mathbf{x}_A)$, as used in Eq. (6.7).

Let

$$Q^{\mathrm{P}}(A)=Z(A)-q^{\mathrm{P}}(A) \quad (6.31)$$

be the ionic charge of atom A. Then one can write

$$(\mathrm{Nu}A)+\rho^{\mathrm{P}}(A)=(Q^{\mathrm{P}}A)+\sigma^{\mathrm{P}}(A) \quad (6.32)$$

where

$$(Q^{\mathrm{P}}A)=-Q^{\mathrm{P}}(A)\delta(\mathbf{x}-\mathbf{x}_A) \quad (6.32')$$

corresponds to a point charge of the magnitude $Q^{\mathrm{P}}(A)$, and

$$\sigma^{\mathrm{P}}(A)=\sum_a q^{\mathrm{P}}(Aa)\sigma(Aa), \quad (6.33)$$

with

$$\sigma(Aa)=(Aa^2)-\delta(\mathbf{x}-\mathbf{x}_A), \quad (6.33')$$

is a *perfectly shielded* atomic charge distribution (i.e., its total charge vanishes). With these definitions, the quasi-classical interaction (6.30) can be decomposed into an *ionic interaction*

$$E^{\mathrm{IoP}}(A,B)=[Q^{\mathrm{P}}A\,|\,Q^{\mathrm{P}}B]=Q^{\mathrm{P}}(A)Q^{\mathrm{P}}(B)/R_{AB}, \quad (6.34)$$

a *multipole interaction*

$$E^{\mathrm{MP}}(A,B)=[\sigma^{\mathrm{P}}(A)\,|\,\sigma^{\mathrm{P}}(B)], \quad (6.34')$$

and an *ion-multipole interaction*

$$E^{\mathrm{IoMP}}(A,B)=[Q^{\mathrm{P}}A\,|\,\sigma^{\mathrm{P}}(B)]+[Q^{\mathrm{P}}B\,|\,\sigma^{\mathrm{P}}(A)]. \quad (6.34'')$$

One finds

$$E^{\mathrm{CLP}}(A,B)=E^{\mathrm{IoP}}(A,B)+E^{\mathrm{IoMP}}(A,B)+E^{\mathrm{MP}}(A,B). \quad (6.35)$$

If the promotion states of A and B correspond to neutral atoms, then the multipole interaction (6.34) is the only one present.

Sharing Penetration between Promoted Atoms

Insertion of the sharing pair densities into Eq. (6.25) yields the contributions

$$E^{\mathrm{SP}}(A)=\tfrac{1}{2}\int dV_1\int dV_2\pi^{\mathrm{SP}}(A,A)/r_{12}=\tfrac{1}{2}\sum_{a\bar{a}} q^{\mathrm{SP}}(Aa\,|\,A\bar{a})[Aa^2\,|\,A\bar{a}^2]+\tfrac{1}{2}\sum_{a\bar{a}}{}'\sum_{a'} p^{\mathrm{SP}}(AaA\bar{a}\,|\,Aa')[AaA\bar{a}\,|\,(Aa')^2], \quad (6.36)$$

and

$$
\begin{aligned}
E^{\mathrm{SP}}(A,B)=&\int dV_1\int dV_2\pi^{\mathrm{SP}}(A,B)/r_{12},\quad (A\neq B)\\
&=\sum_{a,b} q^{\mathrm{SP}}(Aa|Bb)[Aa^2Bb^2]\\
&\quad+\sum_{a\bar{a}}{}'\sum_{b\bar{b}}{}' p^{\mathrm{SP}}(AaA\bar{a}|BbB\bar{b})[AaA\bar{a}|BbB\bar{b}]\\
&\quad+\sum_{a\bar{a}}{}'\sum_{b} p^{\mathrm{SP}}(AaA\bar{a}|Bb)[AaA\bar{a}|Bb^2]\\
&\quad+\sum_{b\bar{b}}{}'\sum_{a} p^{\mathrm{SP}}(BbB\bar{b}|Aa)[BbB\bar{b}|Aa^2].
\end{aligned}
\tag{6.37}
$$

The terms $E^{\mathrm{SP}}(A)$, $E^{\mathrm{SP}}(A,B)$ represent the *increase* in *intra*-atomic electronic repulsion and the *decrease* in *inter*atomic repulsion, respectively, both resulting from the sharing of electrons between atoms (see discussion in Sec. 4.3 and 4.4) "*before charge transfer has taken place*" (see discussion in Sec. 5.3).

Quasi-Classical Terms Due to Fractional Charge Transfer

According to Eq. (5.22), the transfer pair density is decomposed into a Coulombic term $\pi_c{}^{\mathrm{T}}$ and an exchange term $\pi_x{}^{\mathrm{T}}$.

Consider first the contributions resulting from inserting ρ^{T} and the Coulombic term $\pi_c{}^{\mathrm{T}}$ into Eq. (6.25). The intra-atomic terms can be written

$$
E^{\mathrm{CLT}}(A)=\int dV[\mathcal{T}-Z(A)r_A{}^{-1}]\rho^{\mathrm{T}}(A)+[\rho^{\mathrm{M}}(A)|\rho^{\mathrm{T}}(A)],\tag{6.38}
$$

$$
=\int dV\mathcal{T}\rho^{\mathrm{T}}(A)+[(Q^{\mathrm{P}}A)|\rho^{\mathrm{T}}(A)]+[\sigma^{\mathrm{P}}(A)|\rho^{\mathrm{T}}(A)]+\tfrac{1}{2}[\rho^{\mathrm{T}}(A)|\rho^{\mathrm{T}}(A)].\tag{6.38$'$}
$$

It is evident that, in the present analysis, these terms $E^{\mathrm{CLT}}(A)$ play a role which, in semi-empirical reasoning about binding energies, is generally assigned to the ionization potentials and electron affinities of the atoms. It is that place where the influence of the electronegativity tendencies of the participating atoms on the formation of the molecule becomes apparent. It is also clear however that the *charge addition energies* defined in Eq. (6.38) differ considerably from the ionization potentials and electron affinities of free atoms.

The interatomic terms give the quasi-classical interactions between different atoms arising from fractional charge transfer. They can be expressed in the form

$$
E^{\mathrm{CLT}}(A,B)=[\rho^{\mathrm{T}}(A)|(\mathrm{Nu}B)+\rho^{\mathrm{M}}(B)]+[\rho^{\mathrm{T}}(B)|(\mathrm{Nu}A)+\rho^{\mathrm{M}}(A)],\tag{6.39}
$$

$$
=[\rho^{\mathrm{T}}(A)|(Q^{\mathrm{P}}B)+\sigma^{\mathrm{P}}(B)]+[\rho^{\mathrm{T}}(B)|(Q^{\mathrm{P}}A)+\sigma^{\mathrm{P}}(A)]+[\rho^{\mathrm{T}}(A)|\rho^{\mathrm{T}}(B)].\tag{6.39$'$}
$$

In these equations, $\rho^{\mathrm{M}}(A)$ denotes the "median atomic density" of Eq. (5.22‴), and $\sigma^{\mathrm{P}}(A)$ represents the perfectly shielded atomic charge distribution of Eq. (6.33). Furthermore, $(Q^{\mathrm{P}}A)$ is the ionic point charge of the promotion state, defined in Eq. (6.32′), which vanishes in most cases.

The quasi-classical interpretations suggested by the formal structure of Eqs. (6.38), (6.38′), (6.39), and (6.39′) for the potential energy terms are evident and need no verbal elaboration. Equation (6.38) contains of course a nonclassical element, namely, the kinetic energy. Its inclusion here, together with the nuclear attraction, is clearly convenient.

Sharing Penetration Terms Due to Fractional Charge Transfer

Insertion of the transfer self-pair density $\pi_x{}^{\mathrm{T}}$ into Eq. (6.25) will yield those energy changes which result from modifications in the sharing penetration of electrons concomitant with the partial transfer of electrons [see text after Eq. (5.25)]. Hence they may be characterized as *sharing penetration effects of fractional population transfer*. By virtue of Eqs. (5.25) and (5.28) one obtains the intra-atomic terms

$$
E^{\mathrm{SPT}}(A)=-\tfrac{1}{2}\int dV_1\int dV_2\pi_x{}^{\mathrm{T}}(A,A)/r_{12}=-\sum_{a,\bar{a}} q_x{}^{\mathrm{T}}(Aa|A\bar{a})[Aa^2|A\bar{a}^2],\tag{6.40}
$$

and the interatomic terms

$$
E^{\mathrm{SPT}}(A,B)=-\int dV_1\int dV_2\pi_x{}^{\mathrm{T}}(A,B)/r_{12}=-\sum_{a,b} q_x{}^{\mathrm{T}}(Aa|Bb)[Aa^2|Bb^2].\tag{6.41}
$$

Partial transfer of electrons is caused by the strength of the nuclear attraction of the more electronegative atoms, and in spite of an increase in over-all kinetic energy and electronic repulsion incurred in the process. The negative of the sharing terms (6.40) and (6.41) can be interpreted as the *change in self-repulsion of the shared electrons* (see Sec. 1.4 and 4.4). If before transfer shared electrons are about evenly divided between two neighbor atoms, then partial transfer will increase this self-repulsion. The quasi-classical electronic repulsion will increase considerably more strongly however.

6.4 Total Energy

Collecting the results of the two preceding sections, one can now formulate a partitioning of the total molecular energy. Let

$$
E^{\mathrm{G}}=\sum_A E^{\mathrm{G}}(A)=\sum_A [E^{\mathrm{G}}(A_0)+\Delta E^{\mathrm{G}}(A)]\tag{6.42}
$$

be the sum of the ground-state energies of the separated atomic ions which are considered as the building blocks

TABLE VII. Partitioning of molecular binding energy E^B.

	P	CLP	CLT	SP	SPT	IP	IT	II	Total
$\Sigma(A)$	$E^P(A)$	$\cdots$	$E^{CLT}(A)$	$E^{SP}(A)$	$E^{SPT}(A)$	$\cdots$	$\cdots$	$\cdots$	E (Intra-atomic)
$\Sigma(A<B)$	$\cdots$	$E^{CLP}(A,B)$	$E^{CLT}(A,B)$	$E^{SP}(A,B)$	$E^{SPT}(A,B)$	$E^{IP}(A,B)$	$E^{IT}(A,B)$	$E^{II}(AB,AB)$	E (Inter-atomic)
$\Sigma(A\bar{A}<B\bar{B})$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$E^{II}(A\bar{A},B\bar{B})$	E (Inter-bond)
Total	E^P	E^{CLP}	E^{CLT}	E^{SP}	E^{SPT}	E^{IP}	E^{IT}	E^{II}	E^B
Definitions of individual terms in the breakdown:									
Definitions for:	P	CLP	CLT	SP	SPT	IP	IT	II	
In Eqs.:	(6.29)	(6.30 *ff*)	(6.38, 39)	(6.36, 37)	(6.40, 41)	(6.16′–17″, 23–24″) (4.7), (2.5)		(6.15), (2.6)	
Definitions of quantities occurring in quoted equations:									
Definitions for:		ρ^P, ρ^T, ρ^M				π^{SP}, $\pi_x{}^T$			π^P
In Eqs.:		(5.8, 13, 22‴), (3.23–26, 37)				(5.28), text after (5.32″), (4.86–88), (4.8)			(4.73–78), (4.8)

of the molecule, as discussed in connection with Eqs. (6.28)–(6.29′). Then the *binding energy E* , defined by

$$E = E^G + E^B, \tag{6.43}$$

can be written as the sum

$$E^B = E^P + \begin{Bmatrix} +E^{CLP} + E^{SP} + E^{IP} \\ +E^{CLT} + E^{SPT} + E^{IT} \end{Bmatrix} + E^{II}. \tag{6.44}$$

Here, E^P represents the total promotional energy, E^{II} represents the secondary interference interaction, and the six middle terms furnish quasi-classical (CL), sharing-penetration (SP), and interference (I) interactions *before* fractional charge transfer (P) and *due* to fractional charge-transfer (T).

The eight terms can be written as sums of intra-atomic, interatomic, and interbond contributions. The resulting decomposition can be tabulated according to the scheme shown in Table VII. Also given in the table are references to the major definitions of the various contributions. By means of these definitions it is possible to carry out a more detailed breakdown which will furnish the involvement of the individual atomic orbitals in the binding process.

Much of the general form of the energy partitioning given by Eq. (6.44) and Table VII should keep its physical significance, even if the individual parts would be redefined on the basis of a more thorough re-examination.

As an illustration, the results will be given for the Weinbaum type H_2 calculation discussed in Sec. 4.3.[31] In this case the breakdown of Table VII simplifies to that of Table VIII(a). Let $(A1s)$ and $(B1s)$ be the two atomic orbitals with $\zeta = 1.193$, and let $E_H = \frac{1}{2}$ be the energy of a free hydrogen atom. Then the contributions in Table VIII(a) are given by the following equations:

$$E^P(A) = E^P(B) = \int dV(1s) \times [-\tfrac{1}{2}\Delta - r^{-1}](1s) - E_H, \tag{6.45}$$

$$E^{CL}(A,B) = [\sigma(A1s) | \sigma(B1s)],$$
$$\sigma(A1s) = (A1s)^2 - \delta(\mathbf{x} - \mathbf{x}_A), \tag{6.46}$$

$$E^{SP}(A) = E^{SP}(B) = \tfrac{1}{2} q(A|A)[(A1s)^2 | (A1s)^2], \tag{6.47}$$

$$E^{SP}(A,B) = -q(A|A)[(A1s)^2 | (B1s)^2], \tag{6.48}$$

$$E^I(A,B) = 2p(A|B)\{T\langle A,B\rangle + [\langle AB\rangle | \sigma^I]\}. \tag{6.49}$$

$$E^{II}(AB) = 2p(AB|AB)[\langle AB\rangle | \langle AB\rangle]. \tag{6.50}$$

TABLE VIII. Binding energy partitioning for H_2 (in ev).

(a)

	P	CL	SP	I	II	Total
A	$E^P(A)$	$\cdots$	$E^{SP}(A)$	$\cdots$	$\cdots$	$E(A)$
B	$E^P(B)$	$\cdots$	$E^{SP}(B)$	$\cdots$	$\cdots$	$E(B)$
AB	$\cdots$	$E^{CL}(AB)$	$E^{SP}(AB)$	$E^I(AB)$	$E^{II}(AB)$	$E(AB)$
Total	E^P	E^{CL}	E^{SP}	E^I	E^{II}	E^B

(b)

	P	CL	SP	I	II	Total
A	0.507	$\cdots$	2.953	$\cdots$	$\cdots$	3.460
B	0.507	$\cdots$	2.953	$\cdots$	$\cdots$	3.460
AB	$\cdots$	−0.582	−4.398	−6.006	0.051	−10.935
Total	1.014	−0.582	1.508	−6.006	0.051	− 4.015

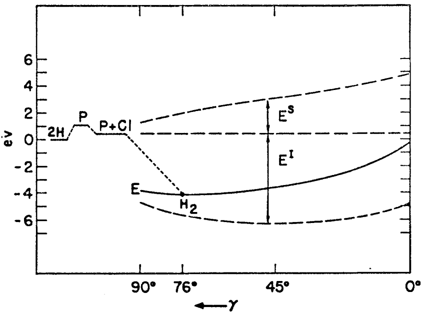

FIG. 5. Quantitative breakdown of binding energy in H_2 (Weinbaum calculation). $\tan\gamma$ = covalent–ionic mixing ratio [See Eq. (4.49)]. Note: E^S in the figure $\equiv E^{SP}$ in the text.

The interference shielding density in Eq. (6.49) is given by

$$\sigma^I = \{-\delta(\mathbf{x}-\mathbf{x}_A)+\tfrac{1}{2}(A1s)^2\} + \{-\delta(\mathbf{x}-\mathbf{x}_B)+\tfrac{1}{2}(B1s)^2\}. \quad (6.51)$$

The kinetic interference energy in (6.49) is defined by Eq. (6.8′). The bond order $p(A|B)$ and the pair population $q(A|A)$ were calculated in Sec. 4.3.

For the value of γ which yields the energy minimum ($\tan\gamma = 3.9$), one obtains the quantitative breakdown given in Table VIII(b). From the preceding equations it is obvious that these figures already incorporate the internal cancellation due to electrostatic shielding effects; e.g., the terms E^{CL}, E^I, E^{II} contain individual interatomic energy effects as large as ±20 ev. However, even after this shielding cancellation has taken place, so the breakdown shows, there remain several conceptually distinct contributions which counteract each other.

A graphical representation is given in Fig. 5 for all values of the angle γ. This figure illustrates the competition between the sharing penetration energy and the interference energy. It is particularly lucid in this case, since these two represent the only contributions which depend upon the covalent–ionic mixing ratio, if the orbital exponent $\zeta = 1.193$ is held constant (promotion energy and quasi-classical energy are independent of γ, and E^{II} is insignificantly small). The figure shows the opposition of E^I and E^{SP} as a function of γ. While the interference energy lowering would be greatest for $\gamma = \pi/4$ (the MO wave function), this minimum is clearly too flat to be very effective against the steady increase of the sharing-penetration repulsion in going from the covalent to the ionic extreme. *For this reason* Weinbaum's minimum lies far on the covalent side.

As a second example, Table IX gives the energy partitioning for the water calculation considered in Sec. 3. Here, the same general pattern is found as in the H_2 case. The full results for this molecule will be discussed elsewhere.[42]

It is natural to ask whether the formalism developed here lends itself to the introduction of semi-empirical elements.

It would be extremely gratifying if, for a given atom, one would find similar promotion-state densities and pair densities in many molecules. In that case it might be possible to assign certain empirical values to corresponding intra-atomic energies. In contrast to the "atoms in molecules" procedure, it would seem unnecessary to establish a connection with spectroscopic atomic states. Rather it would appear preferable to look for optimal values of the intra-atomic expressions by comparing different molecules, thereby avoiding the problem of finding appropriate wave functions for atomic states.

7. ORIGIN OF CHEMICAL BINDING

7.1 Interpretation of Energy Partitioning

The energy partitioning embodied in Eq. (6.44) and Table VII furnishes a more intimate analysis of the chemical bond than has been previously available. According to it, the stabilization which accounts for the formation of bonds can be pictured as occurring in the following steps:

(1) *Promotion* of the separated atoms *raises* the total energy.

(2) *Quasi-classical electrostatic* interactions between atoms furnish a slight energy *lowering* for neutral molecules, and a slight energy *rise* for some molecule ions.

TABLE IX. Partitioning of binding energy in H_2O (in ev).

						Interference						
		Quasiclassical		Sharing penetration		intrabond		interbond		Total		
	Promotion	P	T	P	T	P	T	P	T	P	T	P+T
O	7.95		5.03	14.18	−8.40					22.13	−3.37	18.76
H			−0.34	4.71	0.12					4.71	−0.22	4.50
H′			−0.34	4.71	0.12					4.71	−0.22	4.50
OH		−2.17	−0.46	− 8.75	1.97	−10.78	−0.52	1.34	0.10	−20.37	1.09	−19.28
OH′		−2.17	−0.46	− 8.75	1.97	−10.78	−0.52	1.34	0.10	−20.37	1.09	−19.28
HH′		−0.22	0.40	0.18	0.11	2.37	−0.03	0.37	−0.24	2.70	0.24	2.93
H_2O	7.95	−4.57	3.84	6.30	−4.12	−19.21	−1.07	3.03	−0.04	− 6.50	−1.37	**− 7.87**

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[42] C. Edmiston and K. Ruedenberg (to be published).

Between atoms which overlap, valence electrons are shared, causing two effects.

(3) *Interference* of atomic orbitals used by the same electrons; this effect yields the large energy *lowering* which is crucial for formation of covalent bonds.

(4) Increased *penetration* of electrons originating from different atoms; this effect *raises* the electronic repulsion energy moderately.

When there exist large differences in electronegativities, then there will be a substantial

(5) *Charge transfer* between atoms, associated with a *lowering* of the energy. Its effects are distributed over the previous terms (2)–(4).

While the main purpose of the energy partitioning is the establishment of a scheme for the comparison of specific molecules, a number of general conclusions can be drawn from the results so far derived.

7.2 Cohesive Effect of Constructive Interference

Relative Importance of Kinetic and Potential Contribution

The calculations quoted indicate that the quasi-classical ("Coulombic") energy is only a fraction of the interference energy, a result which was found in other cases too. Only if the molecular situation develops rather unusual features, is it possible for the quasi-classical energy to become a major contribution.[43] In H_2 it does not even compensate for the promotion energy. Indeed, since the chemical bond is known to be intimately connected with overlap, the interference energy is bound to be the essential ingredient.

While the interference energy has emerged as the decisive influence for bonding and anti-bonding, we have yet to answer the basic question: *Why is the interference energy strongly negative?* The answer will show that certain current opinions as regards the origin of the chemical bond need revision.

There have been two seemingly incompatible schools of thought on the physical reasons for chemical binding. One school goes back to Hellmann.[44] It holds that interatomic binding is due to a lowering of the *kinetic* energy upon molecule formation. This idea is suggested by the comparison between molecular wave functions and harmonic waves, and it is closely related to the various free-electron models for certain types of molecules.[45]

The other, currently more fashionable, school criticizes[46] this approach by pointing out that the *virial theorem* is known to hold for the molecule (in the equilibrium position) as well as for the free atoms, so that the binding energy has the form

$$E^B = \Delta V + \Delta T < 0; \quad \Delta V < 0, \Delta T > 0; \quad |\Delta V| = 2\Delta T. \tag{7.1}$$

Hence, the energy lowering comes about *because* of a drop in *potential* energy and *in spite* of an increase in *kinetic* energy. The proponents of this critique then go on to conjecture that the quantum-mechanical overlap effect accumulates *in the bond* extra charge (as compared with a classical model) and that *this* extra charge, being attracted by both nuclei, gives rise to the negative potential ΔV.[47]

The correct answer is obtained immediately by decomposing the partitioning for H_2 of Table VIII(b) into kinetic and potential contributions. One finds (in ev)

	E^P	E^I	Other	E^B
Kinetic	11.51	−7.48	···	4.03
Potential	−10.50	1.47	0.98	−8.05
Total	1.01	−6.01	0.98	−4.02

The graphical representation in Fig. 6(a) gives a more detailed plot for the kinetic and potential parts of the four contributions to the binding energy of H_2. This quantitative analysis shows that *the validity of the virial theorem not withstanding, the interference energy owes its binding effect entirely to a lowering of the kinetic energy*, and that *the fallacy of the previously mentioned arguments lies in the omission of the promotion effect from consideration.*

The promotion we are concerned with here is of a special kind; it consists merely in the change of the orbital exponent from 1 to 1.193 in the (1*s*) atomic orbital. We propose the name *cluster promotion* or *contractive promotion* for this phenomenon. From the variation principle, the uncertainty principle, and the form of the nuclear potential it is quite obvious that contractive promotion must lead to a large drop in potential energy and a more than compensating rise in kinetic energy, so that the virial theorem is far from valid in the promotion state. In fact, after the promotion state is formed, the potential energy is not too far from, and

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[43] An interesting case is the Li_2 molecule where there seems to occur an extensive cancellation of interference energies so that the weaker quasi-classical terms become more decisive. See, for example, S. Fraga and R. S. Mulliken, Revs. Modern Phys. **32**, 254 (1960).

[44] H. Hellmann, Z. Physik **35**, 180 (1933); see also H. Hellmann, *Quantenchemie* (Deuticke 1937); R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1955), p. 101.

[45] See the recent review by J. R. Platt on "The Chemical Bond," *Encyclopedia of Physics* (Springer-Verlag, Berlin, German, 1961), Vol. 37/2, p. 173.

[46] See e.g., K. S. Pitzer, *Quantum Chemistry* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1953), p. 141; W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), pp. 245, 382, 390; P. O. Löwdin, Mol. Spectroscopy **3**, 46 (1959), reference on p. 51.

[47] J. C. Slater, J. Chem. Phys. **1**, 687 (1933); H. Eyring, J. Walter, and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 198; J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), p. 203 and p. 218; C. A. Coulson, *Valence* (Clarendon Press, Oxford, England, 1952), p. 82; K. S. Pitzer, *Quantum Chemistry* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1953), p. 134 and p. 140; W. Kauzmann, *Quantum Chemistry* (Academic Press Inc., New York, 1957), p. 382 and p. 390; R. Daudel, R. Lefebre, and C. Moser, *Quantum Chemistry* (Interscience Publishers, Inc., New York, 1959), p. 20–21; see also R. S. Mulliken in reference 52.

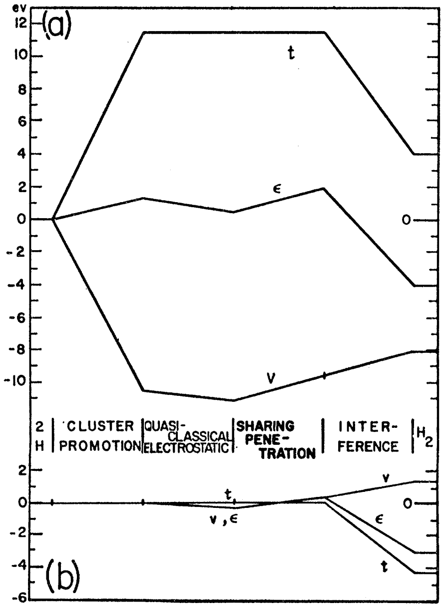

FIG. 6. (a) Kinetic and potential contributions to the binding energy in H_2 (Weinbaum calculation). (b) Kinetic and potential contributions to the binding energy in H_2 (Heitler-London calculation). In both cases: $t=T-T(2H)$; $v=V-V(2H)$; $\epsilon=E-E(2H)$.

actually lower than, its final value; but the kinetic energy is much too high. The drop in kinetic energy connected with interference in the process of bond-formation re-establishes the 2:1 ratio. From the point of view of the virial theorem it may be said that this "final" drop in kinetic energy *permits* the "initial" cluster promotion and thereby a more effectual exploitation of the available potentials *near* the nuclei.

Potential Interference Energy

An understanding of the interference energy can be gained by considering the upper two plots on Fig. 7. They represent, for the Weinbaum function, the density ρ of the molecule and the quasi-classical density ρ^{CL} of the promoted atoms.

They illustrate why the interference energy has a positive potential part; the interference effect *cannot create new charge between the atoms, but merely transfers charge from the atomic regions into the bond region* (see also Figs. 1 and 2 in Sec 3.2). Since the electrostatic potential is much lower near the nuclei than at the bond midpoint, *the interference process is unfavorable as regards the potential energy. The ubiquitous statement that overlap accumulation of electrons in a bond leads to a lowering of the potential energy is based on fallacious reasoning.*

Let us critically analyze some of the arguments which are commonly advanced.

(1) Most frequently the argument is made by an appeal to physical insight.[47] First, it is correctly observed that the potential energy function of the molecular Hamiltonian operator is more negative everywhere, in particular between the nuclei, as compared with the free atoms. Hence, it can be considered as intermediate between the separated atoms and a united atom of much higher charge. Secondly, it is correctly observed that there is an accumulation of charge in the bond due to overlap.

It is overlooked, however, that this last statement *implies a comparison* with a charge distribution lacking overlap effects; that is to say, the quantity which ought to be considered is the *difference* between the actual density and some quasi-classical density which has the same population. When *this* is done, accumulation in the bond goes hand in hand with depopulation near the nuclei, and a rise in potential energy results as discussed above.

It is true that the total *electronic* potential energy is lowered when each electron is attracted by two nuclei rather than by one. The crucial question is however, whether or not this additional attraction can outweigh the nuclear repulsions and the additional electronic repulsions. A considerable cancellation between attractive and repulsive terms is to be expected. This electrostatic cancellation is isolated in a clean fashion in the form of our quasi-classical energy. Thus, all that can be gained from the lowering of the potential between the atoms is contained in the quasi-classical energy and not in the interference energy. It has, therefore, little to do with the overlap effect and, in general, is much less than the interference energy arising from the latter.

(2) Another reason for misinterpreting the role of the potential energy appears to be a particular way of writing the molecular energy formulas for H_2 and H_2^+ in a simple approximation.[48] In this peculiar arrangement, the difference between the molecular energy and the energy of the free atoms appears to be determined by the so-called "Heisenberg exchange integral," which

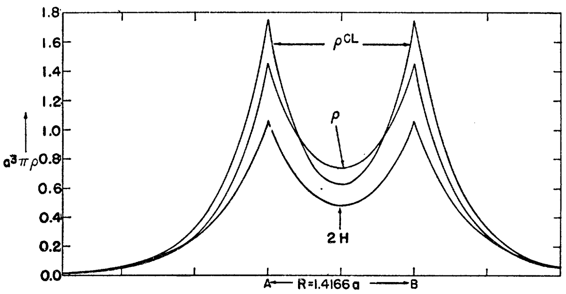

FIG. 7. Densities along the internuclear axis in H_2 (Weinbaum calculation). Curve denoted $2H$: Sum of densities of two H atoms: each in its ground state. Curve denoted ρ_{CL}: Sum of densities of two H atoms, each in the promoted state. Curve denoted ρ: Density of H_2 molecule.

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[48] These formulas go back to W. Heitler and F. London, Z. Physik **44**, 455 (1927) and L. Pauling, Chem. Revs. **5**, 173 (1928). See also the interaction-operator formalism of H. M. James, J. Chem. Phys. **2**, 794 (1934).

is totally potential in character.[49] Mistakenly, this fact is frequently considered as physically significant.

The confusion originates from the use of the *intra*-atomic Schrödinger equation for the simplification of *inter*atomic integrals. As a consequence, the quantity which, finally, is supposed to represent the energy of the free atoms in fact does not, *to the extent that it contains kinetic and potential energy in a wrong proportion*, and the same holds therefore for the quantity which is supposed to represent the binding energy. That such a purely potential expression for the binding energy cannot possibly be significant follows already by comparison with an early investigation of Hirschfelder and Kincaid.[50]

(3) A third misunderstanding appears to be involved, namely an overrating of the implications of the Hellmann-Feynman theorem.[51] This theorem states that the *forces* acting between the nuclei in a molecule are exactly identical with the forces which would arise from the nuclear point charges and the electronic space charge $\rho(x)$ *according to classical electrostatics*. Thus, in a diatomic molecule,

$$F(R)=(dE/dR)=\int dV\rho(\mathbf{x};R)[\partial v(\mathbf{x};R)/\partial R], \tag{7.2}$$

where R is the internuclear distance and v is the potential energy function in the Hamiltonian. Hence the binding energy is given by the integral

$$E=\int_{\infty}^{R_e} dRF(R), \tag{7.3}$$

where R_e is the equilibrium distance.

Superficial examination of Eq. (7.3) might give the impression that the total binding energy is a sum of many small potential contributions, and hence is itself potential in character. Moreover, Mulliken[52] has observed that the overlap effect tends to transfer electronic charge into regions which, according to an analysis of Berlin,[53] furnish attractive contributions to the *force* of Eq. (7.2). Since these regions lie essentially in the bond, Mulliken concludes that "at least so far as potential *energy* contributions are concerned" overlap accumulation in the bond leads to covalent binding.

Such a conclusion is unwarranted however, because Eq. (7.2) does *not* imply that the *energy change*

$$dE=E(R+dR)-E(R)=F(R)dR$$

is purely potential in character. In fact Berlin has also shown that because of the change in the wave function, in going from R to $(R+dR)$, *a certain amount of potential energy is transformed internally, so to speak, into kinetic energy* (or vice versa, depending upon the direction of dR),[54] an effect about which the Hellmann-Feynman theorem gives no information. For this reason it does *not* permit *any* conclusion concerning the potential and kinetic parts of the total binding energy.

Kinetic Interference Energy

The reason for the negative value of the kinetic part of the interference energy must be seen in the fact that the molecular density ρ is *flattened out* as compared with the quasi-classical density ρ^{CL}: the steepness of the peaks at the nuclei as well as the strong curvature at the bond-midpoint, are both softened. *By virtue of the uncertainty principle, it is to be expected that this smoothing of the density, inherent in the interference effect, is associated with a lowering of the kinetic energy.* It is related in character to the lowering of the kinetic energy of free electrons when the containing box is increased in size.

The free-electron picture is therefore appropriate as a model for changes which happen *after the atoms have been brought into their respective promotion states.* The energetic results derived from free-electron models must, therefore, be interpreted with reference to the promotion state. It is exactly in this sense that the model is used in the theory of conjugated systems.[55]

7.3 Covalent Binding

Formulation in Terms of Atomic Orbitals

Our energy partitioning has led to the following interpretation of the covalent bond:

Atoms form promotion states in which valence electrons contract towards the nucleus, thereby achieving a substantial decrease in potential energy. The concomitant excessive increase in kinetic energy (leading to an over-all "promotion") can be afforded, from the point of view of the virial theorem, since the subsequent interference of atomic wave functions from different atoms causes a large, compensating lowering of the kinetic energy. The interference effect is limited by a concomitant increase in potential energy and an enhancement of electronic repulsion as a consequence of sharing penetration. In neutral molecules, quasi-classical effects result in slightly attractive contributions, about large enough to balance the promotion energy. The nature of the promotion state depends upon the available atomic orbitals and upon the number of electrons present to make use of them in accordance with the Pauli principle. Although the bulk of the binding energy is potential in character, it must be said that the phenomenon

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[49] Eyring-Walter-Kimball (reference 47), Eqs. (11.26), (12.7); C. Slater (reference 47), Eq. (8.3.10); C. A. Coulson (reference 47), Eq. (18) on p. 83, Eq. (13) on p. 114; K. S. Pitzer (reference 47), Eq. (8.5); W. Kauzmann (reference 47), Eq. (A.21) on p. 380; R. Daudel *et al.* (reference 47), pp. 404, 419. See also L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), Eqs. (42.13), (43.11).

[50] J. O. Hirschfelder and J. F. Kincaid, Phys. Rev. **52**, 658 (1937).

[51] H. Hellmann, *Quantenchemie* (Franz Deuticke, Leipzig, Germany, 1937), p. 285; R. P. Feynman, Phys. Rev. **56**, 340 (1939).

[52] R. S. Mulliken, J. Chem. Phys. **23**, 1841 (1955), end of Sec. 1.

[53] T. H. Berlin, J. Chem. Phys. **19**, 208 (1951).

[54] Reference 53, Eq. (5) ff.

[55] K. Ruedenberg, J. Chem. Phys. **22**, 1878 (1954); N. S. Ham and K. Ruedenberg, *ibid.* **25**, 1, 13 (1956).

of covalent binding hinges upon the lowering of the virtual kinetic energy by interatomic interference.

Formulation without Atomic Orbitals

While the preceding formulation is expressed in terms of atomic orbitals, its essence can be formulated, without such reference, as follows.

The fundamental *causa prima* existing in a molecule is the tendency of the nuclei to attract the electrons as closely as possible. As electrons are pulled toward the nuclei, their potential energy V falls but their kinetic energy T increases in accordance with the uncertainty principle, because their wave function contracts. Finally this increase offsets the gain of further approach, and the point at which the rate of increase in T equals the rate of decrease in V determines the actual state in accordance with the variation principle. If the molecule is in equilibrium, this state is reached when T has increased up to the value $\frac{1}{2}|V|$.[56]

Compare now an electron which is shared by two nuclei and attracted simultaneously by both, with an electron which is attracted by one of the two nuclei only. The *specific cause for covalent binding* lies in the following circumstance: *As the electron is pulled towards the attractive center(s), the kinetic energy of the shared electron increases less rapidly than that of the unshared electron.* As a consequence the shared electron can cluster around each of the two nuclei more tightly before T reaches the value $\frac{1}{2}|V|$. Therefore, $|V|$ will be larger, and hence, E more negative, than in the case of the unshared electron.

The behavior of the kinetic energy is understood by dividing the total kinetic energy integral roughly into contributions from regions near the nuclei and contributions from bond regions. As seen below, the *contributions from the bond regions change very little when a shared electron approaches the nuclei more closely.* Bond contributions exist only in molecules, however, and not in free atoms. Hence, the total kinetic energy of a molecule will increase somewhat slower with increasing clustering of the electrons.

The reason for the behavior of the bond contributions can be seen by comparing, in Fig. 7, the molecular density ρ with the quasiclassical density of the two atoms in their ground states ($\zeta=1$), denoted by "2H": *In the bond region, the curve of* ρ *is only slightly steeper than the curve of* $\rho(2H)$, *although it rises to much higher values near the nuclei.*

Implicit in the foregoing reasoning is the premise that the two electrons acquire about the same amount of (negative) potential energy for a given approach to the attractive center(s). This is indeed the case because, for the shared electron, the virial theorem applies only after inclusion of the nuclear repulsion energy, which just about cancels the energy lowering due to the presence of the second nucleus, if the wave function is similar to the actual solution.

In summary, it can be said that delocalization of the valence electrons from one atom to two atoms reduces the virtual kinetic-energy pressure and that, as a consequence, there results a firmer attachment of these electrons to the nuclei with a concomitant lowering of the potential, and hence, the total energy.

The wave mechanical kinetic behavior, which differs typically from the classical behavior and is characterized by the cue "uncertainty principle," is a fundamentally essential element of covalent binding. Any explanation of chemical binding based essentially on an electrostatic, or any other nonkinetic concept, misses the very reason why quantum mechanics can explain chemical binding, whereas classical mechanics cannot.

The general description given here is necessarily somewhat vague; a more precise formulation necessarily entails a detailed comparison with atomic quantities, and thereby leads back to our previous discussion.

The arbitrariness in definition, discussed earlier for the sharing terms and the transfer terms, is absent from the H_2 calculation analyzed here, and therefore does not affect our conclusions.

A Model for the Hydrogen Molecule Ion

The following oversimplified model-calculation may serve as an illustration. Assuming the wave function $(\alpha^3\pi)^{-\frac{1}{2}}\exp(-r/\alpha)$ for the H atom, the variable parameter α represents a measure of the diameter of the electron cloud [In fact $\langle r^{-1}\rangle_{\text{av}}=\alpha^{-1}$.] For kinetic and potential energy, one finds

$$T(\alpha)=E_H(a/\alpha)^2,\quad V(\alpha)=-E_H 2(a/\alpha), \tag{7.4}$$

[a = Bohr radius, E_H = ionization potential of hydrogen atom] illustrating the competition between potential energy and uncertainty principle. The minimum total energy is reached for

$$\begin{gathered}(\alpha/a)=1;\quad T_H=E_H,\quad V_H=-2E_H,\\ T_H+V_H=-E_H.\end{gathered} \tag{7.5}$$

Consider now the hydrogen-molecule ion with its electron cloud equally divided between the two nuclei. Let α be a suitable measure of approach to either one of the two nuclei. We suppose now that Eq. (7.4) can still be used to calculate T and V, provided the following *one* modification is made: we wish to introduce the assumption that the "bond region" furnishes no kinetic energy contributions and that this entails a loss of (1/6) of the total kinetic energy as compared with Eq. (7.4). Hence, we have

$$T_+(\alpha)=(5/6)T(\alpha),\quad V_+(\alpha)=V(\alpha). \tag{7.6}$$

---

[56] Here and in the following it is said that the electrons are "sucked towards the nucleus by the potential, against the resistance of the kinetic-energy pressure." This picture is, of course, merely a vivid description of the selection made by the variation principle among the possible wave functions, by imagining a "virtual" process.

In this case the variation principle yields

$$\begin{aligned}(\alpha/a)&=(5/6); \quad T_+=(6/5)T_H,\\ V_+&=(6/5)V_H, \quad E_+=-(6/5)E_H,\end{aligned} \tag{7.7}$$

whence follows the binding energy

$$E_+-E_H=-\tfrac{1}{5}E_H=-2.7 \text{ ev.} \tag{7.8}$$

The assumptions (7.6) represent in fact a rather faithful model of the essential features of the actual H_2^+ calculation of Finkelstein and Horowitz.[57] The model clearly shows that the crucial change in the kinetic energy is the cause of the binding phenomenon, in spite of the binding energy having a positive kinetic and negative potential contribution. A detailed discussion of binding in the hydrogen-molecule ion will be given elsewhere.[41]

Covalent Binding in Solids

It can reasonably be expected that, qualitatively, the present results apply also to the cohesion of covalent solids. The theory of this subject goes back to the work by Wigner and Seitz.[58] It must be acknowledged that Seitz seems to be the only author who expresses the view that valence electrons lower their potential energy, at least partly, by "shifting their center of gravity nearer to the nuclei." [59] However, following Hellmann he holds, incorrectly, that part of the binding energy is due to a decrease in kinetic energy in contradiction to the virial theorem.[59] There may also exist a disagreement with the present results as regards the effects of those electronic repulsion terms which survive after the quasi-classical shielding contributions have been separated out. Wigner and Seitz seem to imply that these terms favor the binding process,[60] in a case like the alkali metals, say, whereas our results in the case of H_2 show that these terms oppose chemical binding because of the sharing-penetration effect.

7.4 Covalent Binding and Contractive Promotion

(1) The foregoing analysis explains a paradox which has puzzled quantum chemists in connection with the Heitler-London treatment of H_2.[61] In this calculation binding is obtained by a *drop* in kinetic energy and in spite of an *increase* in potential energy, in violation of the virial theorem. The partitioning of this calculation, analogous to that of the Weinbaum calculation, is plotted in Fig. 6(b).

This shows that the violation of the virial theorem arises from the lack of contractive promotion. The latter is missing, since the calculation does not admit a variation of the effective charge. That the inclusion of contractive promotion is essential for the validity of the virial theorem is a direct consequence of a theorem by Fock which states that minimization with respect to a scale parameter is a necessary and sufficient condition for an approximate wave function to satisfy the virial theorem.[62]

Figure 6(b) also shows that the Heitler-London calculation gives a qualitatively correct account of quasi-classical, sharing-penetration, and interference interactions. Thus, it seems that the energy partitioning separates out valid portions from invalid portions in this calculation.

(2) A similar situation exists in the water calculation partitioned in Table IX. Here too, the orbital exponents were kept fixed. We expect therefore that all terms, *except* the promotion terms, can be considered as typical. The breakdown in kinetic and potential energy contributions is given in Table X. It is seen that the binding character of the interference energy is again kinetic in origin. The nonbonded repulsions between the hydrogen atoms will be commented upon below. A detailed interpretation of all entries in Table X will be given elsewhere.[42]

Table X shows that the energy lowering which leads to molecule formation is the result of many positive and negative contributions. Hence, the question arises, whether it is justified to single out any one of them as *the* cause of the binding phenomenon. It would seem that the interference effect deserves this distinction for the following reason.

The essential energy gain results from the contractive effect. This effect, in turn, is only possible because of the behavior of the kinetic energy in the bond region. This latter, finally, is intrinsically related to the fact that the molecular wave function can be approximated by superposing atomic wave functions, whereas the molecular density cannot be approximated by a superposition of atomic densities.

(3) If it is correct that the bulk of the covalent binding energy is picked up close to the nuclei as a consequence of an increased concentration of valence electrons near the nuclear positions, then it follows that, in any molecule, the electron density near a bonded nucleus is higher than in the corresponding free atom.

It is, therefore, to be expected that any property which sensitively depends upon the electron density near the nucleus will exhibit a characteristic change when the atom is incorporated in a molecule. Hence,

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[57] The factor (5/6) in Eq. (7.6) has of course been chosen so that Eq. (7.8) comes out close to the correct binding energy of 2.78 ev. However, a remarkable *nontrivial* result of this crude calculation is that it yields the effective charge $\zeta=(a/\alpha)=1.20$ which is close to the value $\zeta=1.228$, found by M. Finkelstein and M. Horowitz, Z. Physik **48**, 118 (1928).

[58] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934); E. Wigner, *ibid.* **46**, 1002 (1934); see also F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Sec. 77–84, in particular Sec. 78. By covalent solids we mean solids held together by electron sharing, including metals.

[59] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 352 and 258.

[60] Reference 59, pp. 656 and 365.

[61] See, e.g., W. Kauzmann, reference 47.

[62] V. Fock, Z. Physik **63**, 855 (1930). An extensive discussion of the virial theorem has been given by P. O. Löwdin, Mol. Spectroscopy **3**, 46 (1959).

TABLE X. Kinetic and potential energy contributions to the binding energy in H_2O (in ev).

			Quasiclassical electrostatic		Sharing penetration		Interference					Total	
							intrabond		interbond				
		Promotion	P	T	P	T	P	T	P	T	P	T	P+T
O	KiE	2.55		22.44							2.55	22.44	24.99
	PoE	5.40		−17.41	14.18	−8.40					19.58	−25.81	−6.23
	Total	7.95		5.03	14.18	−8.40					22.13	−3.37	18.76
H	KiE	0		−2.39							0	−2.39	−2.39
	PoE	0		2.05	4.71	0.12					4.71	2.17	6.89
	Total	0		−0.34	4.71	0.12					4.71	−0.22	4.50
OH	KiE						−13.14		0		−13.14	0	−13.14
	PoE		−2.17	−0.46	−8.75	1.97	2.36	−0.52	1.34	0.10	−7.24	1.10	−6.14
	Total		−2.17	−0.46	−8.75	1.97	−10.78	−0.52	1.34	0.10	−20.37	1.09	−19.28
HH′	KiE						3.88		0		3.88	0	3.88
	PoE		−0.22	0.40	0.18	0.11	−1.51	−0.03	0.37	−0.24	−1.19	0.24	−0.95
	Total		−0.22	0.40	0.18	0.11	2.37	−0.03	0.37	−0.24	2.70	0.24	2.93
H_2O	KiE	2.55		17.66			−22.41		0		−19.86	17.66	−2.20
	PoE	5.40	−4.57	−13.81	6.30	−4.12	3.21	−1.07	3.03	−0.04	13.36	−19.03	−5.67
	Total	7.95	−4.57	3.84	6.30	−4.12	−19.21	−1.07	3.03	−0.04	−6.50	−1.37	**−7.87**

theoretical calculations of such properties should be based on molecular wave functions which properly describe the contractive effect. It seems questionable, for example, to try to predict effects due to nuclear magnetic resonance by using electron densities obtained from wave functions for free atoms.

7.5 Variation of Covalent Binding with Internuclear Distance

The present viewpoint also helps to understand the characteristic behavior of the curves which represent the total energy, the kinetic energy, and the potential energy as functions of the internuclear distance, i.e., the Morse curve and its kinetic and potential components. With the help of his generalization of the virial theorem. Slater showed early that these curves conform to a general pattern.[63]

The origin of this pattern becomes clear when one compares these curves with the curves which represent the optimal orbital exponents in H_2 and H_2^+ as functions of the internuclear distance.[64] This comparison leads to the following conclusions.

At internuclear distances larger than about $2.5R_e$ (where R_e= the equilibrium distance), but small enough so that there is some overlap, there exists a *pure interference effect without contracting*. This region is characterized as follows: (i) No change in orbital exponent, hence no contraction occurs. (ii) The energy lowering is due to a drop in kinetic energy in spite of an increase in potential energy; this is typical for the interference effect. (iii) A pure interference effect is possible here, because the kinetic energy T does not have to be equal to $-\frac{1}{2}V$ in this region.

The region from about $2.5R_e$ to R_e exhibits a gradual transition from the situation just described to the situation at the equilibrium position, which has been the object of our previous discussions. This transition is characterized as follows: (i) The orbital exponent increases from unity to its value at the equilibrium position; hence the amount of clustering increases steadily. (ii) The potential energy change ΔV falls. Beginning with a positive value, it ends up with the negative value of the equilibrium position. (iii) The kinetic energy change ΔT rises. Starting with a negative value, it finally reaches the positive value $\frac{1}{2}|\Delta V|$ at the equilibrium position. Clearly, the effects (ii) and (iii) are consequences of the clustering (i). In this region the interference effect, although present and essential, is covered up by the larger energy changes due to clustering.

In the region below R_e the following observation is of interest. At the equilibrium distance, the resistance against further compression arises from a further increase in kinetic energy, in spite of a further decrease in potential energy. Hence, this resistance is not an effect of the potential energy, but it arises from the further localization of the electronic wave function near the nuclei, in accordance with the uncertainty principle.

7.6 Covalent Binding and Electronic Interaction

Sharing Energy

From the valence-bond theory stems the idea that covalent binding is expressed by the "exchange energy." Although this theory has never been formulated with proper inclusion of all overlap terms, the results of our energy partitioning indicate that the sum of the interference energy E^{I} and the sharing-penetration energy E^{SP} must correspond essentially to what the exchange energy is supposed to represent; it embodies

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[63] J. C. Slater, J. Chem. Phys. **1**, 687 (1933). See also H. Eyring, J. Walter, and G. Kimball (reference 47), p. 358.

[64] N. Rosen, Phys. Rev. **38**, 2099 (1931); C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937). See also reference 47, p. 85.

the energy effects resulting from sharing, as contrasted to the quasi-classical terms. Hence, we must consider

$$E^{\mathrm{I}}+E^{\mathrm{SP}}=\textit{sharing energy},$$
$$\approx \textit{equivalent to valence-bond exchange energy}, \quad (7.9)$$

and it thus emerges that this quantity actually contains two antagonistic elements.

We wish to stress again that the *binding contribution* E^{I} is essentially determined by the first-order density (aside from minor shielding terms) and hence represents a *one-electron* effect, whose origin has become clear in the preceding discussion. In contrast, the *electron-interaction* term E^{SP} *opposes binding*, as we have seen. It arises essentially from the change in the self-pair density π_x, occurring when the transition is made from the free atoms to the molecule. Its existence shows that it is incorrect to imagine the electronic correlation in a molecule to be identical with that found in the separated atoms.

Competition between Interference and Penetration

The analysis of the Weinbaum calculation shows that, even beyond the SCF approximation, the relation between sharing-penetration effect and interference effect represents a dominant feature of the "correlation problem" *as far as molecule formation is concerned.* The two effects are linked together, yet opposing each other. *Useful wave functions must have enough flexibility to allow a maximum of interference attraction with a minimum of sharing-penetration repulsion.* Since this requirement is less than the correct prediction of the total "correlation energy," there may be hope that the explicit introduction of all interelectronic distances can be avoided.

The penetration repulsion is an unavoidable side effect of the sharing process. In order to minimize it, the true wave function adjusts itself as well as possible so that the pair density is characterized by a relatively low probability of finding different shared electrons close to each other. One consequence is the well-known tendency of the electrons in a pair bond always to be at opposite ends of the bond.

Competition between Kinetic Energy and Potential Energy

In view of the nature of the interference energy, it is clear that the competition between E^{I} and E^{SP} represents a competition between a lowering of the kinetic energy and a lowering of the electronic repulsion energy. Thus, in the case of the H_2 molecule, Fig. 5 shows that the molecular-orbital wave function would have the lowest kinetic energy; this is understandable because, in this approximation, both electrons independently try to lower their interference energy as much as possible. However, due to this uncorrelated action, the probability of being close to each other in the bond region becomes too large, so that the actual energy minimum is reached for a somewhat higher kinetic energy, again in agreement with the virial theorem. A similar more favorable adjustment of the subtle balance between kinetic energy and electronic repulsion energy is observed in all cases where *bona fide* SCF wave functions are being improved by further refinements.[65]

On the other hand, it is clear from the preceding discussions that the *bulk of the over-all increase in kinetic energy and of the over-all drop in potential energy, both are consequences of the one-electron contractive effect. They are not correlation effects.*

Exchange Picture of Chemical Binding

(1) It is frequently stated that covalent binding results because electrons are "exchanged" between different atoms. This idea has originated from a *formal* interpretation of valence-bond wave functions, and the sharing energy discussed in the beginning of this section would have to represent the energetic consequence of the effect.

It must be realized that, in discussions of this nature, the exchange concept is used with, at least, three different meanings. (i) The name exchange energy is used for a specific mathematical expression obtained for the nonclassical energy lowering in the "valence-bond theory of perfect pairing." It is now generally recognized that the assumptions in this theory, such as neglect of all overlap integrals, are inadequate for a *bona fide* approximation. (ii) It is postulated that the picture of electron exchange as cause of covalent binding has general validity beyond the valence-bond approximation. In the preceding subsection we have seen that the quantity $(E^{\mathrm{I}}+E^{\mathrm{SP}})$ would have to represent the corresponding energy effect. (iii) After Eqs. (1.21) and (1.23) and in Sec. 1.4 we saw that the electron-interaction energy is frequently divided into a Coulombic energy and an exchange energy. The latter is a result of the generalized exchange density π_x, and its change upon molecule formation is largely given by E^{SP}. Thus, the change in the "electron-interaction exchange energy" represents a bond-opposing part of the "valence-bond exchange energy."

(2) Can the general physical picture of electron exchange between atoms be considered as an *explanation* of covalent binding?

Basically the picture describes merely the fact that valence electrons are shared, i.e., that they give rise to energy contributions at widely separated points in space as was already discussed in Sec. 1.4. In order to appreciate the drawbacks of the exchange picture it suffices to recall the enormous confusion which has been created among chemists by the incorrect interpretation that exchange implies a truly time-dependent

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[65] See also the related remarks by P. O. Löwdin, Revs. Modern Phys. 34, 82 (1962) Sec. 3.

phenomenon, namely the "jumping back and forth" of electrons between atoms.[66,67]

Actually the pseudotime dependent picture of an electron being constantly exchanged between atoms expresses no more and no less than the static picture of the electron (i.e., *its "charge cloud") being shared between the atoms. Hence it is clear that "exchange" does not explain covalent binding any more than "sharing" does. Both merely try to describe a characteristic property of the electronic distribution in general terms.*

(3) In some expositions which ascribe covalent binding to "exchange forces," the impression is created that the *exchange of places between identical particles* is an essential ingredient for the resulting attraction, so that there seems to be a causal relation between covalent binding and inter-electronic effects. From this point of view, the one-electron bond in H_2^+ appears to have a qualitatively different character.

Such an interpretation of the exchange energy is incorrect. For, from Eq. (7.9) we learn that the exchange picture, if used, must be interpreted as follows:

The binding part E^{I} of the exchange energy results from the fact that *individual* valence electrons *independently* jump back and forth. The tendency to minimize the bond-opposing part E^{SP} (see preceding subsection), on the other hand, is the reason for *synchronizing* the exchange of the two electrons in a pair bond; if one jumps forth, the other tends to jump back. Thus, the "exchange of places" of the two *merely* results from the effort to *minimize an undesirable side effect of sharing*, viz., *penetration.*

Equation (7.9) also shows that the bond in H_2^+ is different only in that the bond-opposing term E^{SP} is missing. The binding term E^{I} is quite similar in character to analogous terms in a pair bond.

Moreover, there can be little doubt that two *nonidentical* negative light particles (two electrons with somewhat different masses, say, would they exist) could also form a bond between two protons.

In conclusion, it seems difficult to avoid the feeling that the exchange concept may be a Procrustean bed for the theory of chemical binding.

7.7 Antibinding and Destructive Interference

Kinetic and Potential Energy

The simplest example for antibonding is the $\sigma_u 1s$ state in H_2^+. From the discussion in Sec. 3.1, it is clear that the energy increase is due to a positive interference energy, i.e., we have *an anti-bonding effect due to destructive interference.* The explanation is analogous to the bonding effect of constructive interference and again contrary to common belief.[47] In the present case, charge is taken away from the bond region and placed near the atomic nuclei, as compared with a classical model. This rearrangement is associated with a moderate *drop in potential energy.* It also entails a considerable *increase in kinetic energy,* which can be understood in terms of an increased amount of slope of the density, in the bond, in accordance with the uncertainty principle.

The very same phenomenon is responsible for the "nonbonded repulsion" between the two hydrogen atoms in the water molecule, as can be seen from Table X.

Expansive Promotion

Since the $\sigma_u 1s$ state of H_2^+ is the lowest of its symmetry, its energy may be minimized with respect to the orbital exponents of the $1s$ atomic orbitals, and Coulson has shown that the optimal exponent is lower than unity, the free-atom value.[64] This decrease mitigates the steepness of the wave function between the atoms and thereby lowers the kinetic energy without undue increase of the potential energy.

In general, destructive interference will tend to cause the participating atomic orbitals to *expand*, i.e., it will lead to an *expansive* promotion.

Atomic Orbitals Involved in Binding As Well As Antibinding

In more complex molecules, some atomic orbitals are being used by binding as well as by antibinding electrons. In such cases it would seem essential to introduce at least two atomic orbitals of the same type with independently variable scaling parameters, e.g., two ($2s$) orbitals with independent orbital exponents, so that one of them can provide the contractive effect necessary for binding and the other can take care of the expansive effect associated with antibinding. In a recent calculation which, partially, has been carried out in this way, Richardson finds indeed that one orbital exponent falls below the free atom value and the other rises above this value.[68]

These arguments show that there is a need for several atomic orbitals of the same kind in a molecule, quite apart from the fact that SCF atomic orbitals are superpositions of Slater orbitals. *Even if atomic self-consistent-field orbitals (or equivalent superpositions of Slater orbitals), are used in a molecular calculation, it would appear necessary to introduce at least two independently variable scaling factors for each "SCF AO" which is involved in both, binding and antibinding.*

ACKNOWLEDGMENTS

The calculations in Secs. 3 and 6 were carried out by C. Edmiston, E. M. Layton, R. Rue, and D. Wilson. I wish to express my thanks for their cooperation and for many challenging discussions.

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[66] See, e.g., G. W. Wheland, *Resonance in Organic Chemistry* (John Wiley & Sons, Inc., New York, 1955), pp. 608–625, for a very sound discussion of the subject.

[67] See also the remarks on resonance preceding Eq. (3.21).

[68] J. W. Richardson, J. Chem. Phys. **35**, 829 (1961).