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# ANALYSES OF ELECTRONIC WAVE FUNCTIONS AND CHEMICAL BINDING IN SMALL MOLECULES

by

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# I. INTRODUCTION

Since the earliest days of the quantum mechanical theory of molecular structure, the independent particle model has held a dominating influence. It has been very successful qualitatively, and sometimes quantitatively, in explaining the properties of atoms and molecules. It is true that for many properties one must go beyond this very popular model to obtain even qualitatively correct conclusions, and the best way of refining the model is now the subject of much current investigation and debate in quantum chemistry. On the other hand, the independent particle model itself deserves close examination, and its results have not always been clearly understood.

In order to review the current situation, we will first discuss briefly the foundations of the independent particle model as applied to closed shell ground states. Approaches to refining the model will then be mentioned. Finally, the relations of each of the three main sections of this thesis to the general picture will be outlined.

## A. Brief Survey of the Independent Particle Model

The independent particle model in its simplest form ignores all interactions between electrons, and, for the total system's ground state, results in all electrons occupying the lowest one-electron orbital $\phi_1$, e.g., the 1s hydrogenic orbital for atoms. Because of the resulting separability of the hamiltonian operator, this corresponds to a simple product wave function for the N electrons, viz.,[1]

$$\psi_{s.p.} = \phi_1(1)\ \phi_1(2) \cdot \cdot \cdot \phi_1(n) \qquad \text{(I-1-1)}$$

If the average mutual coulombic interactions of the electrons were taken into account at this point, the electrons would come to occupy a somewhat expanded lowest orbital, with a total wave function of the same form as above. This corresponds to the ultimate independent particle model for Bosons.

However, since electrons are Fermions, effects much stronger than their mutual coulombic interactions take place between those with like spins, i.e., the effects of the Pauli exclusion principle, as expressed through the antisymmetry of the wave function and the resulting "Fermi holes". Thus a much better initial refinement of the simplest model is to neglect all coulombic interactions, but demand that the wave function be antisymmetric with respect to the interchange of coordinates of any two electrons. This applies to space and spin coordinates combined. The hamiltonian still demands that we use a product (or linear combination of products, with each of the products differing only in the permutation of electrons) of N orbitals for the one electron problem. The lowest energy wave function which satisfies both these requirements is the antisymmetrized product (Slater determinant) of the first N spin orbitals of the one electron problem (26):

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[1] This function actually applies to spinless particles, or can be interpreted as the space part only for particles of integer spins.

$$\Psi_{a.s.p.} = 1/\sqrt{N!}\begin{vmatrix} \phi_1(1) & \phi_1\beta(1) & \phi_2(1) & \phi_2\beta(1)\cdot\cdot & \phi_{N/2}(1) & \phi_{N/2}\beta(1) \\ \phi_1(2) & \phi_1\beta(2) & \phi_2(2) & \phi_2\beta(2)\cdot\cdot & \phi_{N/2}(2) & \phi_{N/2}\beta(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \phi_1(N) & \phi_1\beta(N) & \phi_2(N) & \phi_2\beta(N)\cdot\cdot & \phi_{N/2}(N) & \phi_{N/2}\beta(N) \end{vmatrix} \qquad \text{(I-1-2)}$$

The exclusion principle, acting through the required antisymmetry of the wave function, correlates the motions of electrons of like spin so that there is zero probability of finding any two of them at the same point in space. The main effects of these so-called Fermi holes result in electrons being "pushed" into higher states when the lower states are already occupied by electrons of like spin. The energy corresponding to $\Psi_{a.s.p.}$ is, as with the simple product, the sum of the one-electron orbital energies.

If we now considered the mutual coulombic interactions of the electrons to be "turned on", but keep the wave function fixed, we obtain (27) a somewhat more realistic energy value:[1]

$$E = 2\sum_i \langle\phi_i(1)|h(1)|\phi_i(1)\rangle + \sum_i \langle\phi_i^2(1)|1/r_{12}|\phi_i^2(2)\rangle$$

$$+ 2\sum_i\sum_{j\neq i} \langle\phi_i^2(1)|1/r_{12}|\phi_j^2(2)\rangle - \sum_i\sum_{j\neq i} \langle\phi_i(1)\phi_j(1)|1/r_{12}|\phi_i(2)\phi_j(2)\rangle$$

$$\text{(I-1-3)}$$

where

$$h(1) = -1/2\nabla_1^2 - \sum_k Z_k/r_{k1} \qquad \text{(I-1-4)}$$

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[1] This addition to the energy is, of course, the first order perturbation energy when the electronic coulombic interactions are the perturbation.

with $Z_k$ being the nuclear charge of nucleus k. This is not the true energy of the system because we have not allowed the wave function to readjust to the interelectronic repulsions. This adjustment would involve the formation of a "coulombic correlation hole" around each of the electrons, wherever it may be found in space. This is a region in which the probabilities of finding the other electrons are depressed as compared to those for the noninteracting model.

As indicated above, because we have used an antisymmetrized product (not a simple product) wave function, electrons already have Fermi correlation holes around them with respect to electrons of like spin. In this case the coulombic correlation holes are not needed so badly. Thus the antisymmetrized product wave function has a somewhat lower energy than its corresponding simple product wave function. This energy lowering is formally due to the so-called exchange integrals, which are brought into the energy expression in going from $\psi_{s.p.}$ to the corresponding $\psi_{a.s.p.}$ (27). These constitute the last sum on the right of Eq. I-1-3.

This is still not the most refined form of the independent particle model, since one can keep the form of $\psi_{a.s.p.}$ by allowing the orbitals to change due to the average interactions of the electrons. Thus, orbitals may be chosen which are solutions of one-electron Schrodinger-like equations which include an extra potential due to the average fields of the remaining electrons. This approach reaches its zenith in the Hartree-Fock (self-consistent-field) method in which the best possible orbitals are found. This is, of course, still not the true wave function, but it is as far as the independent particle model can be extended.[1] The energy expression remains that of Eq. I-1-3.

As with the previous case, in order to go on to the correct wave function we must allow the wave function to readjust to the "instantaneous" coulombic interactions of the electrons, bringing in the correlation holes. The magnitudes of these holes have now been somewhat lessened, but their energy effects (collectively called the correlation energy) are still very significant. The correlation energies for most molecules exceed their binding energies. Thus when correlation effects are quite different in the molecule from what they are in the separated atoms or ions (the $N_2$ molecule for example), one does not get good estimates of the binding energies by taking the difference between the SCF energy of the molecule and those of the atoms. The alkali halides are not of this type, so that reasonably good estimates of their ionic binding energies can usually be obtained.

At the present time SCF wave functions have been found for about half the atoms, and a few small molecules. These are usually found using the LCAO-MO (linear combination of atomic orbitals-molecular orbitals) SCF approach (22). The "minimal basis set" SCF wave functions which are dealt with in this thesis represent reasonable approximations to the true

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[1] The extension of the model to "different orbitals for different spins", sometimes called the unrestricted Hartree-Fock method, involves departure from a pure spin state, i.e., the resulting function is not an eigenfunction of the total spin operator. One can use the "extended Hartree-Fock method" and project out the pure spin state (take the component which is a pure spin state), but it is a linear combination of determinants, and so is quite different from the usual independent particle model.

ones (see for example Figure 10). For atoms, minimal basis set SCF wave functions use only as many analytic (usually Slater type) orbitals as there are SCF orbitals. In molecules a minimal basis set commonly includes only as many analytic orbitals as is necessary to describe the separated atoms in the minimal basis set approximation.

In the following section, we will briefly discuss some of the major methods which have been proposed to go beyond the independent particle model.

## B. Methods for Improving on the Independent Particle Model

The correlation hole has a cusp (discontinuous derivative) at the position of the electron it surrounds, and furthermore changes shape somewhat depending on the electron's position in space. These facts, among others, make it difficult to introduce into the wave function.

The most widely used technique for overcoming the correlation difficulty has been the configuration interaction method. Here one attempts to build the wave function from a linear combination of Slater determinants which differ from each other in the inclusion of at least one different orbital. This method is analogous to a Fourier expansion, and is based on the theorem that if the orbitals constitute a complete set in the one-electron space, then these determinants are a complete set in the antisymmetric N-electron space. If one uses suitable orbitals, he can obtain about 80-90 percent of the correlation energy with fairly short expansions. Since the orbitals do not have singularities in their derivatives except at their own nuclear centers, the cusps of the correlation holes must be built up by very long expansions. Thus the last few percent of the correlation energy are very hard to come by with this method.

Another major method of attack has been to introduce the interelectronic distances explicitly into the wave function. This acts to build the correlation hole directly, and the cusp is put in easily. Except for two electron systems, this has led to extremely difficult integrals involving three or more interelectronic distances in the same integral. This method is very successful on <u>some</u> two electron systems, but its application to larger systems is just beginning.

A third approach of relatively recent origin is that of the pair function theories. They attempt to break up the N electron problem into a combination of comparatively simple two electron ones. This approach, used in combination with either of the two previous ones for solving the two electron problems, appears to hold the greatest promise at present. Pair theories have arisen from the recognition that two electron "collisions" (two electrons coming within the range of each other's correlation holes) are much more probable than three, four, etc., electron collisions. This is particularly true because, for any three electrons, two must have the same spin and therefore tend to be kept apart by their Fermi holes.

Of the various pair theories, separated pair theory (11) (see also Reference 2 and earlier references given there) appears to hold the most promise. In this scheme the wave function is an antisymmetrized product of N/2 pair functions, each pair function replacing a doubly occupied molecular space orbital of the conventional SCF theory. This allows the greatest correlation effects, viz., those between a pair of electrons in the same space orbital, to be accounted for. The small interorbital correlation effects, neglected by this approach, can hopefully best be taken into account later on.

## C. Survey of Main Topics of Thesis

### 1. Chemical binding in $H_2O$ and $H_2^+$

In Secs. II and III of this thesis, we consider what can be learned about molecule formation from the independent particle model, e.g., from SCF wave functions. It was pointed out above that correlation errors in molecules are usually larger than their binding energies. Thus unless there is considerable cancellation between the separated atoms and the molecule, with respect to their correlation errors, good binding energies are not obtained. However, in most molecules about 50-70 percent of the binding energies are given by SCF calculations applied to both the separated atoms and the molecule. It is of course important that we understand where this part of the binding comes from, as well as the effects on binding due to correlation. Also the effects on binding due to correlation must generally await accurate wave functions, whereas the one-electron (independent particle model) effects can be studied now.

As indicated by the above percentages, the one-electron effects are generally the most important, and it is becoming increasingly evident that the correlation effects are not as complex conceptually.

In Sec. II we examine the chemical binding in $H_2O$ according to an analysis developed by Ruedenberg (24). It is shown that the commonly held belief that the binding comes about because of the build up of electronic charge in the bond region is almost surely false. The bonding is in fact much more complex and might best be interpreted as a complex interplay between interference effects (reflecting the wave character of the electron), and the usual electrostatic potentials. The analysis treats the binding energy in terms of these concepts.

In Sec. III the same analysis, which was applied to $H_2O$ in Sec. II, is applied to $H_2^+$. The major conclusions found to apply to $H_2O$ are found to apply to $H_2^+$. Although this analysis probably does not represent the final word in this complex picture, it nevertheless brings out many subtle effects which must be understood in order to really comprehend what makes up the chemical bond in the independent particle model. In Sec. III we also consider various ways of interpreting the concept of "charge shifted into the bond region" and the energy effects associated with this phenomenon.

## 2. Optimally localized orbitals

Orthogonal Hartree-Fock orbitals $\phi_i(1)$ are solutions of coupled equations of the type (27)

$$F(1)\phi_i(1) = \sum_j \lambda_{ij}\phi_j(1) \quad , \qquad \text{(I-3-1)}$$

where

$$F(1) = -1/2\nabla^2(1) - \sum_k Z_k/r_{k1} + \sum_j \int \phi_j(2)\ 1/r_{12}\phi_j(2)\ d\tau_2$$

$$- \sum_j \int \phi_j(2)\ 1/r_{12}\phi_i(2)\ d\tau_2 \qquad \text{(I-3-2)}$$

Any closed shell Slater determinant wave function is invariant with respect to a unitary (orthogonal, if the orbitals are real functions) transformation among the space orbitals.[1] The usual (canonical) Hartree-Fock orbitals are unique in that they correspond to a diagonal representation of the Hartree-Fock operator F(1), i.e., the $\lambda_{ij}$'s of Eq. I-3-1 are zero if $i \neq j$. Thus for these orbitals we have equations of the type

$$F(1)\phi_i(1) = \epsilon_i(1)\ \phi_i(1) \qquad \text{(I-3-3)}$$

This results in $\epsilon_i$ being interpretable as the negative of the ionization potential for ionization from the corresponding orbital $\phi_i$. Therefore, $\epsilon_i$ corresponds to those terms which would be missing from Eq. I-1-3 if $\phi_i$ suddenly became unoccupied. For ionization potentials, and similarly spectral transitions, the canonical orbitals are particularly suitable. For discussing and computing some other properties, a different set of SCF orbitals is often much more useful.

Sec. IV of this thesis discusses a method for finding that set of SCF orbitals which are localized so as to have the least total electronic interactions between them. For these orbitals the sum of the last two terms on the right of Eq. I-1-3 is a minimum. Further, each of the two terms is separately a minimum. The first term represents the coulombic interactions between the orbital charge densities, and the second the exchange interactions. Since the physical meaning (in particular the

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[1] Actually this applies to any linear transformation of the orbitals which leaves them linearly independent. We confine ourselves to orthogonal transformations, resulting in orthogonal orbitals, because the simple energy expression of Eq. I-1-3 holds for such orbitals.

total electronic interaction energy) of the wave function is not changed in going to this new orbital set, these orbitals have the maximum total "internal" electronic interactions (second sum on the right of Eq. I-1-3).

Because of these properties, the localized orbitals should exhibit very nearly minimum interorbital correlation effects, and therefore are best suited to be replaced by separated pair functions. They also have two other interesting properties. When the proper molecular or atomic symmetry exists, they usually turn out to be equivalent orbitals (7, 13), e.g., in $s^2p_x^2p_y^2$ state of the oxygen atom, the 2s, $2p_x$ and $2p_y$ canonical SCF orbitals hybridize to become three equivalent $sp^2$ trigonal hybrids. Perhaps partially due to the preceding property, for molecular ground states the localized orbitals usually end up to be either lone pair orbitals, bond orbitals, or fairly isolated inner shell orbitals.

Because of their maximum overall localization from each other, these orbitals can be expected to show the greatest achievable independence of each other, i.e., any one of them should be least influenced by changes in another, on the whole. Changes of this type occur when one proceeds from member to member of an isoelectronic series of molecules. Thus the series Ne, HF, $H_2O$, $NH_3$, and $CH_4$ can be visualized as created by successively "pulling" protons, from the central nucleus, out along the axes of the tetrahedral $sp^3$ hybrid localized orbitals of Ne. The proton should cause a large perturbation on the orbital along whose axis it is placed, but little effect on the other hybrids. Further, any change in this orbital will induce minimal changes in the other orbitals.

Thus one might hope to be able to estimate the localized orbitals for a given system from those of other members of the series, and a rough consideration of the perturbational effects. More importantly, by far, one might hope to similarly estimate changes in pair functions in going from molecule to molecule.

It should be pointed out that these ideas have been discussed since the early days of quantum mechanics, and were particularly revived by the discussions of equivalent orbitals (7, 13, 14, and 15). However these ideas have not been given quantitative application up to now because of the lack of a method for determining energy-localized orbitals, without the help of symmetry. Symmetry is not enough to determine the localized orbitals uniquely for any atomic or molecular system.

# II. CHEMICAL BINDING IN THE WATER MOLECULE

## A. Introduction

### 1. Method

The development and application, in recent years, of techniques for computing more accurate molecular electronic wave functions, has created the need for methods of interpreting such wave functions. Procedures capable of attributing quantitative meaning to concepts frequently used to describe chemical binding in a qualitative fashion would be desirable. Among these are such terms as hybrid orbitals, promotion, valence states, ionic and covalent binding contributions, electron sharing, and resonance. Recently, Ruedenberg has suggested such an analysis which can be applied to wave functions given as expansions in atomic orbitals (24).

This analysis partitions the electron density and the electronic pair density of the molecule into components corresponding to promoted atomic states, to quasiclassical coulombic interactions of these promoted states, and to interactions resulting from the sharing of electrons between atoms. If the molecule contains atoms of different electronegativities, resulting in a net transfer of electronic charge, components reflecting this effect are also found. From the various density parts, corresponding energy effects are derived. They lead to a decomposition of the molecular binding energy which is conceptually interpretable.

An application of this analysis to the $H_2$ molecule has been given in Reference 24, and discussions for $H_2^+$ are contained in the following section and Reference 25. Here the analysis is applied to the water molecule, in an effort to test it on a more complex system.

Considering the limitations imposed by the approximate character of the wave function analyzed, it is felt that the present investigation makes progress toward understanding the underlying physical basis of chemical binding in $H_2O$. It is possible to quantitatively define unique hybrid atomic orbitals, atomic coulombic interactions, and promoted valence states of atoms, all of which correspond surprisingly closely to the intuitive "pictures" of chemists. Furthermore, in contrast to several somewhat mysterious quantities used in the past to describe covalent binding, e.g., the "exchange energy" of valence bond theory, the energy contributions to covalent binding are shown to correspond to effects (mainly due to electron sharing) which are not at all mysterious.

The conclusions arrived at in connection with the $H_2O$ molecule substantiate the views on chemical binding which were reached in the cases of the $H_2$ and $H_2^+$ molecules. These hold that the shift of charge into the bond region, which accompanies binding, leads to a strong drop in kinetic energy, but little or no decrease in potential energy. Also it is maintained that even stronger energy effects occur in the regions close to the nuclei, which, however, are opposite in sign to those arising from the shift of charge into the region between the nuclei.

## 2. Molecule

The water molecule was selected not only because it is a molecule of great importance, but also because it is among the simplest of the general polyatomic molecules, i.e., while it contains relatively few electrons and has considerable symmetry, it contains atoms of different electronegativities, more than one bond, and is nonlinear.

The analysis is applied to the LCAO-MO (linear combination of atomic orbitals-molecular orbital) SCF (self-consistent field) wave function (22) of the $H_2O$ molecule obtained by Ellison and Shull (9). It is recognized that this wave function suffers from the approximate character of the SCF method, and also from the use of a very limited set of AO's for the expansion of the MO's. Furthermore, a number of the three center integrals involved were approximated, and the energy was not minimized with respect to the effective nuclear charges for the AO's, so that the virial theorem is not obeyed. Nevertheless, it was decided to carry out a detailed test of the analysis for this wave function, since it was the best at the time the analysis was carried out.

The atomic orbitals used as a basis for the molecular orbitals are the Slater 1s, orthogonalized 2s, 2px, 2py, and 2pz orbitals on the oxygen atom, and the 1s orbitals of each of the two hydrogen atoms. The 2 px orbital is perpendicular to the plane of the molecule, and the 2pz orbital is directed midway between the two hydrogen atoms. For our purposes, these orbitals are not the most suitable. The partitioning of the electron densities exhibits its greatest clarity in terms of certain hybrid atomic orbitals, to be described in Sec. II-C. These "valence atomic orbitals" are selected such that they have maximum or minimum valence activities.

The following discussion proceeds in two major parts. The first part combines a general description of the approach with a discussion of the gross results for $H_2O$, which illustrate the various concepts. The second part combines a more detailed characterization of the various density components with the orbital by orbital breakdown of the gross effects.

## B. Partitioning According to Physical Concepts

### 1. Basic considerations

As mentioned in the introduction the basis of the analysis is a partitioning of both the molecular electronic density, $\rho$, and the electronic pair density, $\pi$, into several components. These components are interpreted as corresponding to various conceptual steps required in changing the wave functions describing the component atoms in their ground states into the molecular wave function.[1] Since the molecular energy is completely determined by $\rho$ and $\pi$ ($\rho$ gives the kinetic and nuclear attraction energies of the electrons, and $\pi$ the interelectronic repulsion energies), the energy effects associated with each of our conceptual steps can be calculated from the density and pair density components, and in this way a breakdown of the molecular binding energy is also obtained. The binding energy associated with the present approximate wave function is taken as the difference of the total molecular energy and the energies of the atoms in their ground states, as calculated using the same intra-atomic integrals as in the molecular energy calculation. It is found to

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[1] These steps do not correspond to physically measurable processes, but are purely conceptual in nature.

be 7.87 ev.[1]

The interpretation of the partitioning makes use of two basic physical pictures. One picture is that of bringing the atoms from infinite separation into their equilibrium positions. The other picture is that of the electrons changing their motions from being associated with particular atoms to being shared between several atoms, i.e., in the molecule the various electrons attain substantial probabilities of being found on atoms other than the ones they were originally on. They can be said to have their probability charge clouds "spread" over several atoms.

For the actual physical system both these effects are of course intimately connected: the solutions of the Schrodinger equation describe more and more electron sharing the closer the atoms are situated with respect to each other. Nevertheless, it is possible to construct hypothetical electron densities and pair densities which do exhibit sharing at very large distances, and others which include no sharing even at small distances. Such a conceptual separation of positional approach and electron sharing appears to be a useful interpretative tool for analyzing the difference between atomic and molecular electronic arrangements.

In accordance with the preceding remarks, the series of steps which describe the transition from the separated atoms to the molecule are

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[1] After the work herein reported was completed, it was pointed out by R. McWeeny and K. A. Ohno (Proc. Roy. Soc. 255: 367. 1960) that, due to an error in the normalization factor of the Slater 2s orbital of the oxygen atom, the binding energy should have been found to be 5.7 ev instead of 7.7 ev. Due to the correction of some, but not all, of the errors involved, a binding energy of 7.87 ev was obtained in the present analysis.

classified according to the following scheme.

a. Non-sharing modifications These are modifications of $\rho$ and $\pi$ which bring them as close as possible to their molecular values, without the sharing of electrons between the atoms.

Effects at infinite separation: These are what we shall call promotional effects.

Effects due to moving the atoms from infinite separation to their actual separations in the molecule: These will be called quasiclassical electrostatic interactions.

b. Sharing modifications These are the modifications in $\rho$ and $\pi$ due to electron sharing.

Effects at infinite separation: Here there are no effects on $\rho$, but there are effects on $\pi$, which we shall call sharing penetration effects.

Effects due to moving the atoms to their actual molecular positions: This leads to effects on both $\rho$ and $\pi$, which we shall refer to as interference (overlap) effects.

The following sections explain the individual parts of this scheme in terms of the concepts just mentioned. At the same time, the actual magnitudes of the energy contributions will be illustrated by discussing the gross quantitative results found for $H_2O$. These are collected in Figure 1. A more detailed discussion of the individual entries will be pursued in Sec. II-C. It should be understood that the arguments given are not meant to justify any of the mathematical formulations. Rather, they represent interpretations which are found to be useful and

Figure 1. Binding energy partitioning for the $H_2O$ molecule. The rows for the O atom and H atom, the OH and HH' bonds, represent the totals from Figures 4 and 5 respectively.

## BINDING ENERGY PARTITIONING

| | | Promotion | | Quasi-classical | | Sharing Penetration | | Sharing Interference | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Intra-bond | | Interbond | | |
| | | PRH | PRC | QCN | QCT | SPN | SPT | SIN | SIT | SIN | SIT | TOTAL |
| O | KIN | 2.53 | - | | 22.44 | | | | | | | 22.44 |
| | SNA | .94 | - | | -18.82 | | | | | | | -18.82 |
| | OEI | 4.49 | - | | 1.41 | 14.18 | -8.40 | | | | | 7.19 |
| | TOT | 7.95 | - | | 5.03 | 14.18 | -8.40 | | | | | 10.81 |
| H | KIN | - | - | | -2.39 | | | | | | | -2.39 |
| | SNA | - | - | | 1.79 | | | | | | | 1.79 |
| | OEI | - | - | | .26 | 4.71 | .12 | | | | | 5.09 |
| | TOT | - | - | | -.34 | 4.71 | .12 | | | | | 4.49 |
| OH BOND | KIN | | | | | | | -13.14 | | | | -13.14 |
| | SNA | | | -2.17 | .39 | | | 2.89 | -.52 | 1.07 | .10 | 1.70 |
| | OEI | | | | -.84 | -8.75 | 1.97 | -.54 | | .26 | | -7.90 |
| | TOT | | | -2.17 | -.46 | -8.75 | 1.97 | -10.79 | -.52 | 1.33 | .10 | -19.28 |
| HH' BOND | KIN | | | | | | | 3.88 | | | | 3.88 |
| | SNA | | | -.22 | .12 | | | -1.52 | -.04 | .16 | -.24 | -1.73 |
| | OEI | | | | .28 | .18 | .11 | .01 | | .20 | | .79 |
| | TOT | | | -.22 | .40 | .18 | .11 | 2.37 | -.04 | .36 | -.24 | 2.93 |
| $H_2O$ | KIN | 2.53 | - | | 17.66 | | | -22.41 | | | | -2.22 |
| | SNA | .94 | - | -4.57 | -14.34 | | | 4.27 | -1.05 | 2.30 | -.04 | -12.50 |
| | OEI | 4.49 | - | | .53 | 6.30 | -4.12 | -1.07 | | .73 | | 6.85 |
| | TOT | 7.95 | - | -4.57 | 3.83 | 6.30 | -4.12 | -19.21 | -1.05 | 3.03 | -.04 | -7.87 |

reasonable for the understanding of the mathematical breakdown to be described subsequently.

## 2. Pre-sharing modifications

a. Promotion To begin with, we can hypothetically think of the atoms as being in their ground states at infinite internuclear separations. At this stage the molecular electronic density is given by

$$\rho^G = \sum_A \rho^G(A) \tag{II-1-1}$$

where $\rho^G(A)$ is the electron density of atom A in its ground state. The molecular pair density at this stage is given by

$$\pi^G = \sum_A \pi^G(A) + \sum_{A,B}{}' \pi^G(A,B) \tag{II-1-2}$$

where $\pi^G(A)$ is the ground state pair density of atom A, and $\pi^G(A,B)$ is the pair density arising from electron pairs with one partner on atom A and the other on atom B. Since the electrons composing the charge distributions ($\rho^G(A)$'s) of the different atoms are different, the $\pi^G(A,B)$'s are simple products of the form

$$\pi^G(A,B) = \rho^G(A)\rho^G(B) \ . \tag{II-1-3}$$

Each atom is now considered to be promoted to a certain "promoted state" which can, in form at least, be represented as a superposition of the ground and excited states of the isolated atom. Each atom in being promoted suffers a change in its electron density and pair density, so that the molecular electron density now becomes

$$\rho^P = \sum_A \rho^P(A) \qquad \text{(II-1-4)}$$

where $\rho^P(A)$ is the promotion state density of atom A. The pair density of the molecule becomes

$$\pi^P = \sum_A \pi^P(A) + \sum_{A,B}{}' \pi^P(A,B) \qquad \text{(II-1-5)}$$

where $\pi^P(A)$ is the promotion state pair density of atom A, and $\pi^P(A,B)$ is the pair density arising from electron pairs with one partner on the promoted atom A, and the other on the promoted atom B. By the same reasoning as for Eq. II-1-3

$$\pi^P(A,B) = \rho^P(A)\rho^P(B) \qquad \text{(II-1-6)}$$

b. Promotion effects in $H_2O$ The promotion effects for $H_2O$ are given in the first two columns of Figure 1. Unfortunately, the wave function does not allow for variation of the effective nuclear charges of the atomic orbitals which it involves, so that contraction (or clustering) type promotion is not allowed for. The second column (PRC) therefore contains no entries.

Hybridization promotion (first column, (PRH)) raises the energy of the oxygen atom 7.95 ev. This is due to a "distortion" of the atom in such a way that its valence shell electron density can be represented as a simple superposition of the electron densities of two lone pair orbitals and two bonding orbitals. The two lone pair orbitals are directed away from the hydrogen atoms, and the two bonding orbitals generally toward them. The largest contribution to the oxygen promotion energy is seen to be due to an increase in electronic repulsion energy (4.49 ev), due to the fact that in the promotion state the electrons are forced together somewhat more than in the ground state. Promotion raises the kinetic energy of the oxygen atom by 2.53 ev, and the nuclear attraction energy by .94 ev. All these effects will be examined in detail in Sec. II-C-6. We will see that they are considerably different from what would be expected, due to the fact that the wave function tries to compensate for the unallowed contraction promotion by excessive mixing in of the ls orbital with its very strong energies.

In the present wave function, even hybridization promotion is not allowed for the hydrogen atoms, since these are described in the wave function by a single fixed ls orbital.

The construction of hybrid orbitals for the oxygen atom will be described in detail in Sec. II-C-1.

c. Quasiclassical interactions of the promoted atoms If the atoms are moved to their actual positions in the molecule, without being modified by the resulting interaction, they will interact with one another quasiclassically, i.e., their electronic and nuclear charge distributions interact in a purely coulombic fashion. This is analogous to the interactions of fixed charge distributions in classical electrostatics. If atoms were actually composed of fixed classical-like charge distributions, these quasiclassical interactions would constitute the extent of bond formation in molecules.

In the past, similar types of interaction have frequently been referred to as "coulombic" as opposed to "exchange" interactions. We prefer the name "quasiclassical", since all electronic interactions must in fact be considered as coulombic in nature.

The quasiclassical interactions are of three types. There are the nuclear repulsions, computed by considering the nuclei as point charges. The attractions of the nuclei for the electrons on other atoms are obtained by considering the electrons of an atom A to be represented by the charge distribution $\rho^P(A)$, as defined in connection with Eq. II-1-4. The interactions of the electrons of different atoms are given by the classical electrostatic interactions of the atomic charge distributions $\rho^P(A)$, and are represented by the $\pi^P(A,B)$'s of Eq. II-1-6.

d. Quasiclassical interactions in $H_2O$ The energies for these interactions are given in the third column (QCN) of Figure 1.

In completely analogous fashion it is possible to compute the quasiclassical interactions of the atoms in their ground states at the molecular nuclear configuration. Their sum is found to be -6.60 ev.[1] This is larger than the interactions between the promoted atoms, i.e., -4.57 ev, because promotion of the oxygen atom results in a general shift of its electronic charge away from the hydrogen atoms, due to the formation of the lone pairs. This decreases the repulsion between the atomic

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[1] Two neutral atoms with spherically symmetric electronic charge distributions always interact quasiclassically with an attractive effect up to very close separations: the repulsion of the electronic clouds is weak enough that, even combined with the repulsion of the two nuclei (the strongest interaction), the attractions of the nuclei for the electrons of other atoms predominate. The oxygen atom in its ground state does not have a spherically symmetric electronic charge cloud, but for the orientation which we have chosen (one electron in each of the 2py and 2pz orbitals, and two in the 2px orbital), the attractive effect for a spherical distribution is only slightly lessened.

charge clouds less than the attraction of the hydrogen nuclei for the oxygen electrons. The attractive interaction (-.22 ev) between the hydrogen atoms remains unchanged, since they suffer no promotional change.

### 3. Sharing modifications

a. Interference effects on the density If the atoms are at infinite separations, it is possible to pass from a wave function describing no sharing of electrons to one describing shared electrons, without changing the first order density $\rho^P$. This is so because the contributions to the first order density arising from different electrons are indistinguishable.

However, if the atoms are in their actual molecular positions, sharing of electrons is accompanied by a redistribution of the electron density $\rho^P$, because of non-vanishing overlap between orbitals of different atoms. This redistribution will be called the "interference" effect.

It is well known that the electron density of a molecule is not even roughly approximated by a superposition of the electron densities of the separated atoms. However, a wave function made by superposing atomic wave functions yields a bona fide approximation to the actual electron density, especially if the component atomic wave functions can be modified (promoted) by polarization and scaling (minimization of the molecular energy with respect to the effective nuclear charges of the orbitals involved). Thus the molecular electron density is given much more closely by the square of a sum of atomic wave functions, rather than by a sum of squared atomic wave functions. Because of this, it will differ from the promotion state density $\rho^P$, if the atomic wave functions overlap each other.

One can interpret this as an "interference" between the promoted atomic wave functions, similar to that observed with classical waves.

Interference acts to redistribute the electron density of the promoted atoms by either increasing the electron density between the atoms at the expense of the densities on the atoms (constructive interference) or by increasing the electron densities on the atoms at the expense of the regions between the atoms (destructive interference).

Among the various concepts used in the past in connection with chemical binding, the idea of "resonance" comes nearest to what we define here as interference. For, in the original sense, resonance as well as interference both describe the enhancement or attenuation of resultant wave amplitudes generated by the superposition of component wave amplitudes. This typical wave phenomenon leads to the chemical effects of bonding and antibonding resultant states. No close relationship exists however between our approach and the valence bond theory, where "resonance" is used to describe interactions of any type of "structure wave functions". Our method of defining interference energies is based specifically on the interaction of atomic orbitals only, and hence is quite different from that used for obtaining valence bond resonance energies. It is superior in that it can be applied with rigor to any molecular wave function.

The redistribution of electron density which results from interatomic interference in the case of nonvanishing overlap, can be described by a density term $\rho^I$ which is added to the promotion state density $\rho^P$. This change due to interference will be denoted by

$$\rho^I = \sum_{A,B} \rho^I(A,B) \qquad \text{(II-1-7)}$$

where $\rho^I(A,B)$ is the interference density arising from electron sharing between atoms A and B.

As mentioned earlier, constructive interference acts to shift electronic charge into the bond region from the atoms. Therefore the additive term $\rho^I(AB)$ has in general a region of negative charge in the bond and regions of positive charge on the atoms; the total charge of the negative region being equal in magnitude to the sum of those for the positive regions. For an antibonding destructive interference, usually the opposite situation exists for $\rho^I(AB)$.

Constructive interference is typical of covalent binding situations, and leads to a strong lowering of the energy of the system. In the following section dealing with $H_2^+$, it is pointed out that this energy lowering has a physical interpretation quite different from that generally conjectured by previous writers. It is essentially due to a strong decrease in kinetic energy, the effects on the potential energy being relatively weak. The effect on the kinetic energy occurs because of a strong decrease in the gradient of the wave function, especially on the atoms, as a result of the shift of charge from the atoms into the bond region.[1]

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[1] It is well known that the kinetic energy corresponding to a given wave function is proportional to the square of the gradient of the function, summed over all configuration space.

The results for $H_2O$, which are to be discussed a little further on, confirm again the detailed discussion given in the preceding sections, and show that the accumulation of charge in the bond, due to interference, does not lower the potential energy appreciably.

b. Penetration effect on the pair density   There is an important difference between the density and the pair density of a hypothetical wave function which exhibits electron sharing between atoms whose overlap can be neglected. This is due to the fact that, while it is possible to construct a promotion state density $\rho^P$ which remains unaffected by electron sharing in this situation, this is impossible for any promotion state pair density $\pi^P$.

In fact it is not difficult to see that the interelectronic interactions will be substantially affected by the sharing. Thus before electrons are shared, the entire electronic charge cloud of one atom repels the entire electronic charge cloud of another atom, since the two clouds contain different sets of electrons. After electron sharing, a substantial part of the interaction between the charge clouds of different atoms disappears, due to the fact that parts of both atomic charge clouds are now due to the same electrons. There is of course no interaction of a single electron with itself. Thus, sharing gives rise to a decrease in interatomic electronic repulsion energy.

Inside the atoms an opposite effect occurs. Here, before electron sharing occurs, the actual electronic repulsion energy is much less than that which would correspond to the classical self-interaction of the density $\rho^P(A)$. This is due to the fact that many of the different parts of the charge cloud $\rho^P(A)$ are due to the same electron, and hence are noninteracting. After sharing, although the total atomic charge cloud $\rho^P(A)$ is not changed, more different electrons now make up this charge distribution. Hence, parts of the atomic charge cloud which previously originated from the same electron now originate from different electrons, so that the electronic repulsion on the atoms is increased.

It is thus clear that sharing induces changes in the pair density even in the absence of overlap, because it leads to a greater penetration of the electrons from different atoms. These changes will be denoted as follows

$$\pi^{SP} = \sum_A \pi^{SP}(A) + \sum_{A,B}{}' \pi^{SP}(A,B) \qquad \text{(II-1-8)}$$

where $\pi^{SP}(A)$ is the change in the pair density of atom A due to sharing penetration, and $\pi^{SP}(A,B)$ is the change in pair density between atoms A and B due to sharing penetration.

These sharing penetration effects remain when the atoms are brought into their actual molecular positions, the only difference being that the interatomic electronic repulsion energies arising from $\pi^{SP}(A,B)$ become considerably larger in magnitude. But even then, the increase in intra-atomic electronic repulsions corresponding to the first term of Eq. II-1-8 is larger than the decrease due to the second term.

c. Penetration effects in $H_2O$ In the case of $H_2O$, this effect is exhibited in the fifth column of Figure 1, labeled SPN. Since sharing penetration affects only the electronic interactions, these terms are given in the row (OEI), i.e., other electronic interactions. The energies of the promoted atoms are raised 14.18 ev for the oxygen and 4.71 ev for each of the hydrogens, due to sharing penetration. However the energy of each OH bond is lowered 8.75 ev. The very slight increase in energy of the HH' bond is anomalous, in that this indicates a very slight decrease in sharing from a situation in which there is no sharing. Actually we would expect very little sharing penetration to take place between the hydrogen atoms, so that this small deviation from zero could easily be due to the lack of accuracy of the wave function, our method of analysis, or some other little understood effect.

d. Interference modifications of the pair density. When the atoms are brought together, the overlap between atomic orbitals introduces further modifications of the pair density. These are of the same character as those found for the first order density, and therefore are considered to be due to interference. We denote these changes by

$$\pi^{IP} + \pi^{II} \qquad \text{(II-1-9)}$$

with

$$\pi^{IP} = \sum_{A} \sum_{\underline{B},\bar{B}}' \pi^{IP}(B\bar{B}|A) \qquad \text{(II-1-10)}$$

and

$$\pi^{II} = \sum_{\underline{A},\bar{A}}' \sum_{\underline{B},\bar{B}}' \pi^{II}(A\bar{A}|B\bar{B}) \quad . \qquad \text{(II-1-11)}$$

Here, $\pi^{IP}$ can be thought of as the change in the pair density for which one partner of the electron pair is associated with $\rho^I$, and the other with $\rho^P$. $\pi^{IP}$ therefore has components of the form $\pi^{IP}(B\bar{B}|A)$ where one partner is associated with $\rho^I(B,\bar{B})$ and the other with $\rho^P(A)$. $\pi^{II}$ represents the change in the pair density, where both partners of the electron pair are associated with $\rho^I$. It therefore has components of the form $\pi^{II}(A\bar{A}|B\bar{B})$, where one partner of the electronic pair can be thought of as being associated with $\rho^I(A\bar{A})$ and the other with $\rho^I(B\bar{B})$.

The energy effects associated with $\pi^{IP} + \pi^{II}$ are combined with the kinetic and nuclear attraction energy effects of $\rho^I$ to give the total interference energy effects for the interaction of the neutral promoted atoms. Furthermore, the energies associated with $\pi^{IP}$ are combined with the nuclear attraction energies from $\rho^I$ to give "shielded nuclear attraction" (SNA) terms which represent, in one type of term, the interaction between the interference density and the promoted atoms. The energies arising from $\pi^{II}$ are referred to as "other electronic interactions" (OEI) and the kinetic energy terms (KIN) constitute a third type of term.

e. Interference effects in $H_2O$ In Figure 1 all interference energy contributions arising from $\rho^I$ and $\pi^I$ are divided into intra-bond contributions (listed in the seventh column (SIN)), and inter-bond contributions (ninth column (SIN)).

The intra-bond contributions arise from the $\rho^I(A,B)$'s of Eq. II-1-7, and also from the $\pi^{IP}(B\bar{B}|A)$'s and $\pi^{II}(A\bar{A}|B\bar{B})$'s of Eqs. II-1-10 and II-1-11 where A=B and $\bar{A}=\bar{B}$.

The contributions for the OH bonds are seen to be large and negative

(-10.79 ev for each bond), and in fact constitute the main contributions to the total binding energy, in agreement with the general reasoning given previously.

As discussed at that point, this energy lowering is entirely due to the kinetic energy. Its contribution (KIN) is -13.14 ev. It arises from the kinetic energy of $\rho^{I}(OH)$, and corresponds to a strong reduction in the average gradient of the wave function due to interference. This is to be expected, since the shift of charge into the bond region from the atoms strongly decreases the large gradient on the atoms and also somewhat the gradient in the bond region (24).

The shielded nuclear attraction (SNA) terms correspond to the interaction of $\rho^{I}(OH)$ with the promoted atoms O and H. They arise from the attractions of the nuclei for $\rho^{I}(OH)$ plus the electronic repulsion energies coming from $\pi^{IP}(OH|O)$ and $\pi^{IP}(OH|H)$ respectively. In the interactions of a charge distribution such as $\rho^{I}(OH)$ with the promoted atoms, the interaction with the nucleus usually predominates over that with the diffuse electronic charge cloud of the atom (provided the center of gravity of the latter is not very much closer to the charge distribution than is the nucleus). This is so in all cases occurring here, so that the promoted neutral atoms always attract electronic charge.

A further essential fact is that these shielded attractions for $\rho^{I}(OH)$ consist of two opposing contributions, owing to $\rho^{I}(OH)$ having regions of both negative and positive charge. As mentioned earlier, any constructive interference density is of positive charge on the atoms and of negative charge in the bond. For the OH bond in particular, these regions are not located symmetrically with respect to the atoms, but instead the central negative-charge region is displaced strongly toward the H nucleus. The reason for this is that the oxygen atom interacts appreciably only with its valence orbitals which are in the outer regions of the atom, whereas the hydrogen atom is intimately involved as a whole in the interference and bonding situation. This asymmetry of $\rho^I(OH)$ leads to characteristic differences in its interactions with the O and H atoms.

The interaction of $\rho^I(OH)$ with the shielded O atom (6.45 ev) is positive, due to the predominance of the repulsion of the O atom for that positive region of $\rho^I(OH)$ which lies on it, over its attraction for the negative region which lies much further away. The repulsion of the O atom for the other positive region on the H atom would be still smaller, and can usually be disregarded in qualitative reasoning.

The interaction term for $\rho^I(OH)$ with the shielded H atom (-3.56 ev) is negative, due to the greater attraction of the H atom for the central negative-charge region of $\rho^I(OH)$ which lies very close to it, as opposed to its repulsion for that positive-charge region of $\rho^I(OH)$ which lies on it. This predominance occurs because the negative region has approximately twice the total charge of either of the two positive regions, since its charge is equal in magnitude to the combined charges of both positive regions.

The electronic interaction energy arising from $\pi^{II}(OH|OH)$, (OEI), is -.54 ev. We will see in Sec. II-C-4 that this energy is mainly due to interactions which arise from oxygen orbitals which are of lone-pair or inner-shell type, and in addition overlap appreciably with the hydrogen 1s orbitals. These electronic interactions are similar to those which lower the triplet state below the singlet state in multiplet theory, giving rise to Hund's rule.

The energy of the HH' bond is raised 3.27 ev due to interference between the hydrogen atoms, mainly because of an increase of 3.88 ev in the kinetic energy. This indicates a destructive antibonding interference between the atoms, in which charge is taken from the bond region and forced onto the atoms, thereby increasing even more the already large gradient of the wave function on the atoms, and also the gradient between the atoms.

The interaction of the hydrogen atoms with $\rho^{I}(HH')$ i.e., the shielded nuclear attraction (SNA), is attractive (-.76 ev for each atom) as would be expected, since $\rho^{I}(HH')$ has its regions of negative charge on the atoms.

The interaction arising from $\pi^{II}(HH'|HH')$ appears to be very slightly repulsive (.01 ev), but this figure is almost certainly subject to revision when a better wave function is found.

The inter-bond contributions are of two types. The first involves the interaction of a promoted atom A with an interference density $\rho(B,\bar{B})$ between the two other atoms, and arises from the $\pi^{IP}(B,\bar{B}|A)$'s of Eq. II-1-10, where A is neither B nor $\bar{B}$, and the attraction of the nucleus of A for $\rho^{I}(B,\bar{B})$. The interactions of the OH bonds with the H atoms opposite them are quite large and positive (1.07 ev). This is to be expected, since the positive region of $\rho^{I}(O,H)$ lies closest to the H' atom (as pointed out above, the negative region of $\rho^I(O,H)$ lies almost on the H atom, which is considerably further from the H' atom than is the O atom). On the other hand, the interaction of the O atom with the HH' bond is .16 ev. This represents the predominance of the repulsion of the O atom for the positive region of $\rho^I(H,H')$ compared to its attraction for the negative regions on the H atoms. This occurs because of the closer proximity to the O atom of the center of the HH' bond than the H atoms.

The second type of inter-bond contributions are those representing the interactions of the interference densities of different bonds, and arise from the $\pi^{II}(A,\bar{A}|B,\bar{B})$'s of Eq. II-1-11 where $A \neq B$ and $\bar{A} \neq \bar{B}$. In $H_2O$ these interactions are gratifyingly small, the largest being that between the two OH bonds (.16 ev). That this interaction is positive is reasonable, since the positive regions of $\rho^I(O,H)$ and $\rho^I(O,H')$ are both on or near the O atom. The slight positive interaction between $\rho^I(H,H')$ and $\rho^I(O,H)$ (.10 ev) must be due to the slight predominance of the repulsion of the negative region of $\rho^I(H,H')$ for that of $\rho^I(O,H)$ combined with the repulsion of the positive regions (which also are close), over the attractions of the negative regions of $\rho^I(H,H')$ for the positive regions of the $\rho^I(O,H)$'s on the H atoms.

It is pleasing that all the inter-bond contributions are not very large (the largest being only about 10 percent of the total binding energy), since this not only confirms the empirically observed approximate additivity of bond energies, but also allows one to make estimates of the possible errors in such additive schemes.

## 4. Charge transfer effects

Any effects associated with a gross electronic charge transfer from atom to atom within the molecule have been ignored so far. Such effects undoubtedly exist and are important in polar molecules. In $H_2O$ there is a gross "shift" of electronic charge (.3515 electrons--see the ninth column of Figure 2) toward the oxygen atom and away from the hydrogen atoms, due to the greater electronegativity of the oxygen atom. These effects will be referred to as charge transfer effects.

### a. Changes in the density

Charge transfer gives rise to a change in the electron density $\rho^P$ which is given by:

$$\rho^T = \sum_A \rho^T(A) \qquad \text{(II-1-12)}$$

where $\rho^T(A)$ is the change in the electron density of the promoted atom A due to charge either being transferred to it, or away from it. It should be noted that we have here considered charge transfer to cause only a modification of $\rho^P$ and not $\rho^I$, i.e., we consider $\rho^T$ and $\rho^I$ to be independent modifications of $\rho^P$. This simplifying assumption is considered to be justifiable since $\rho^T$ and $\rho^I$ represent redistributions of different character: whereas $\rho^I$ is associated with covalent binding, $\rho^T$ is related to ionic binding. It is an empirical fact that additive-decompositions of binding energies into covalent and ionic contributions are markedly successful.[1]

b. Changes in the interatomic pair density terms Since charge transfer results in a modification of $\rho^P(A)$ to give $\rho^P(A) + \rho^T(A)$, the pair density for the quasiclassical interaction between the promoted states of atoms A and B [$\pi^P(A,B)$, which depends upon the $\rho^P(A)$'s according to Eq. II-1-6] will be modified by the obvious change

$$\pi^{QCT}(A,B) = [\rho^P(A) + \rho^T(A)][\rho^P(B) + \rho^T(B)] - \rho^P(A)\rho^P(B)$$

$$= \rho^T(A)\rho^P(B) + \rho^T(A)\rho^P(B) + \rho^T(A)\rho^T(B) \quad . \qquad \text{(II-1-13)}$$

But charge transfer also gives rise to a change in the sharing situation between the atoms. This must be so since only a fraction of an electronic charge is transferred, which can only be accomplished by a partial shift of the shared electrons. Consequently, the sharing penetration interaction between the two atoms A and B will be changed, i.e., $\pi^{SP}(A,B)$ will be modified by the addition of a transfer term $\pi^{SPT}(A,B)$.

Finally, the pair density contributions to the total interference energy will also be affected. In analogy to the term $\pi^{IP}$ of Eq. II-1-10, there will be changes in the pair density of the form

$$\pi^{IT} = \Sigma\ \Sigma'\pi^{IT}(A|BB) \quad . \qquad \text{(II-1-14)}$$

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[1] This discussion, in which for the purposes of the analysis, $\rho^I$ and $\rho^T$ are effectively defined to be mutually independent, is typical of a number of assumptions which are unavoidable in order to proceed. The real test of all definitions of this analysis is their ability to correlate and predict the properties of similar molecules.

Here, $\pi^{IT}(A|B\bar{B})$ can be thought of as the pair density contribution arising from electron pairs in which one partner of the pair is associated with $\rho^{T}(A)$ and the other with $\rho^{I}(B\bar{B})$. These changes correspond to changes in the interactions between the interference densities and the promoted atoms, due to the changes in the shielding electron densities of the promoted atoms as a consequence of charge transfer.

c. Interatomic quasiclassical effects    The total change in interatomic quasiclassical effects between atoms A and B, caused by charge transfer, involves the attraction of the nucleus of B for $\rho^{T}(A)$, and vice versa, plus the electronic interactions arising from the $\pi^{QCT}(A,B)$ of Eq. II-1-13. These interactions can be regrouped into two types of contributions. The first is the interaction of $\rho^{T}(A)$ with the promoted atom B on the other end of the bond, or vice versa, and is referred to as a "shielded nuclear attraction" term (SNA). It involves the attraction of the nucleus of B for $\rho^{T}(A)$, plus the electronic interaction from the first term of the right side of Eq. II-1-13. The second type of contribution is called the "other electronic interactions" (OEI), and involves the electronic interactions arising from the third term of the right side of Eq. II-1-13.

d. Interatomic quasiclassical effects in $H_2O$    The interaction of the promoted O atom with $\rho^{T}(H)$ is seen from Figure 1 to be 1.20 ev, which is to be expected since the O atom is repulsive to a positive charge distribution (due to the greater repulsion of the O nucleus than the attraction of its diffuse electronic cloud). The interaction of the

H atom with $\rho^T(O)$ is seen to be -.81 ev, again as would be expected since $\rho^T(O)$ is a negative charge distribution. The interaction of $\rho^T(H)$ with $\rho^T(O)$ (OEI) is attractive (-.84 ev) as would be expected. The interactions in the HH' bond are seen to follow well in terms of the above reasoning for the OH bond.

e. Interatomic sharing penetration effects in $H_2O$ It is seen from Figure 1 that the change in sharing penetration due to charge transfer increases the energy of each OH bond 1.97 ev, which can be understood in terms of the following. When electrons are "shifted" toward the oxygen atom it is most advantageous, energy wise, that these electrons be predominantly those which are already mainly associated with that atom, i.e., what we refer to as the "oxygen electrons". This is due to the fact that while the kinetic and nuclear attraction energies are indifferent to which electrons are "shifted", the electronic repulsion energy on the oxygen atom is not increased nearly so strongly if the shifted electrons are the ones which are already mainly present on that atom. Since, as was pointed out earlier, the electronic repulsions on the atoms are considerably stronger than those between atoms, the result of charge transfer is that the oxygen atom mainly withdraws its own electrons. Thus there is a decrease in the sharing of electrons by the oxygen atom with the hydrogens, and an associated partial elimination of the strong decrease in energy of the OH bond which occurred upon neutral sharing by the promoted atoms.

An examination of the intra-atomic sharing penetration changes will reveal that the hydrogen atoms have little or no tendency to withdraw their electrons, which would be expected since the general shift of charge is toward the oxygen atom.

There is also a slight indicated decrease in sharing penetration between the two H atoms (.11 ev), which is open to question because of the antisharing effect observed in the neutral sharing situation.

f. Charge transfer effects on interference in $H_2O$ The effects of charge transfer on interference, which arise from the $\pi^{IT}$ of Eq. II-1-14, in the case of $H_2O$ are given in the eighth and tenth columns of Figure 1.

For a bonding situation such as in the OH bonds, interference shifts charge from the atoms into the bond. This leaves a net positive region on each of the atoms, and a net negative region between them. If we imagined momentarily that our atoms were of about equal size, so that the negative region of the interference density would lie about equally between them, we would expect a charge on one of the atoms to interact somewhat more strongly with the positive region on the same atom than with the negative region in the center. However in the OH bond the negative region lies close to the H atom, so that the above situation is reversed to give a .40 ev energy lowering for the interaction of $\rho^T(H)$ with $\rho^I(O,H)$. The interaction of $\rho^T(O)$ with $\rho^I(OH)$ is negative as expected (-.12 ev), but is not as large as would probably be expected on the basis of the close proximity of the positive region of $\rho^I(OH)$ and $\rho^T(O)$.

The interaction of $\rho^I(HH')$ with both $\rho^T(H)$ and $\rho^T(H')$ gives slight negative contributions (-.02 ev), as would be expected in view of the fact that the negative regions of $\rho^I(HH')$ lie on the H atoms.

There is one type of inter-bond interaction involving charge transfer and interference. This is the interaction of the $\rho^T(A)$ of an atom A with an interference density $\rho^I(B\bar{B})$ between two other atoms. The interaction of $\rho^T(H)$ with $\rho^I(OH')$ (.10 ev) is repulsive due to the closer proximity of $\rho^T(H')$ to the positive region of $\rho^I(OH)$ which lies on the O atom, than to its negative region which lies near the H atom. The closer proximity of the H atoms to the O atom, than to each other, has already been pointed out. The interaction of $\rho^T(O)$ with $\rho^I(HH')$ (-.24 ev) is attractive, again as would be expected, since the positive region of $\rho^I(HH')$ lies closest to $\rho^T(O)$.

g. Intra-atomic effects on the pair density The intra-atomic changes in the pair density, due to transfer, can be treated in a way completely analogous to that used for the interatomic changes: namely, by dividing them into quasiclassical and penetration parts.

The quasiclassical part will have the pair density

$$\begin{aligned} \pi^{QCT}(A) &= [\rho^P(A) + \rho^T(A)]^2 - [\rho^P(A)]^2 \\ &= 2\rho^P(A)\rho^T(A) + \rho^T(A)\rho^T(A) \quad . \qquad \text{(II-1-15)} \end{aligned}$$

It represents the difference between the quasiclassical interaction of $\rho^P(A) + \rho^T(A)$ with itself, and that of $\rho^P(A)$ with itself.

That charge transfer also changes the intra-atomic sharing penetration (given by the pair density term in Eq. II-1-8) is a necessary consequence of the change in the general sharing situation associated with charge transfer. For, just as interatomic sharing penetration between the promoted atoms originally gave rise to changes in the intra-atomic as well as the interatomic pair densities, the change in sharing penetration, due to transfer, also gives rise to intra-atomic changes in the pair density. As with $\pi^{SP}$, these changes are not associated with a change in the electron density $\rho$, and so are not included in the quasi-classical changes of Eq. II-1-14. For an atom A, these changes will be denoted by $\pi^{SPT}(A)$.

h. Intra-atomic quasiclassical effects The total intra-atomic quasiclassical effects of charge transfer involve the electronic interaction energies arising from Eq. II-1-15, and the nuclear attraction terms for the $\rho^T(A)$'s. As with the interatomic terms, the electronic interaction and nuclear attraction contributions are combined into "shielded nuclear attraction" terms (SNA), and "other electronic interactions" terms (OEI). The shielded nuclear attraction terms represent the attractions of the neutral promoted atoms for the charges transferred to them. Thus the term for an atom A includes the attraction of its nucleus for $\rho^T(A)$, plus the electronic interactions of the first term of the right side of Eq. II-1-15. The "other electronic interactions" represent the quasiclassical self-interaction of the charge transferred to an atom with itself. They arise from the second term of the right side of Eq. II-1-15, and are in general small.

There is also a kinetic energy term arising from $\rho^T(A)$. It is convenient to group these kinetic energy contributions together with the quasiclassical terms just mentioned (although they are of course not quasiclassical) for the following reason. The shielded nuclear attraction term represents the potential energy of the additional transferred charge $\rho^T(A)$ in the field of the nucleus of A as shielded by $\rho^P(A)$. Hence, in the case where $\rho^T(A)$ represents a negative charge distribution, the shielded nuclear attraction energy plus the kinetic energy of $\rho^T(A)$ is a quantity similar in character to the electron affinity of atom A. This is seen by comparison with the one-electron model[1] for the latter.

One might therefore expect that the total contribution from these terms would be close to $q^T(A)$ times the electronic affinity of atom A, where $q^T(A)$ is the total electronic charge in $\rho^T(A)$. The similarity is limited, however, in that $\rho^T(A)$ and $\rho^P(A)$ do not represent the optimal distributions for the free negative ion, and this alters the quantitative results.

In the case that $\rho^T(A)$ represents a positive charge distribution, such as with $\rho^T(H)$, the resulting terms are best considered as analogous to the electronic affinity of the atom for a "positive electronic charge".

In conclusion then, it is seen that the intra-atomic quasiclassical and kinetic energy terms represent those contributions in the analysis which are most similar to the familiar concept of electronegativity. However, the severe restrictions imposed upon $\rho^T(A)$ and $\rho^P(A)$ by

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[1] The one-electron model for electron affinities considers the negative ion as consisting of the additional electron moving in the field generated by a neutral core. For best results, the additional electronic distribution should be determined by the variation principle, and the distribution of the shielding electrons might need semi-empirical adjustment.

their specific definitions (to be discussed in Sec. II-C-3), along with the restricted form and limitations of the original wave function, result in the energies obtained in the case of $H_2O$ being quite different from the electron affinities of the O and H atoms. Presumably, if an accurate wave function were available, and if our definitions of $\rho^T(A)$ and $\rho^P(A)$ were the best possible, the resulting energies would correspond quite closely to the electron affinities of the atoms involved.

i. Intra-atomic effects in $H_2O$ We see from Figure 1 that the energy of the O atom is raised 5.03 ev due to the kinetic energy and quasiclassical effects. The energy of each of the hydrogen atoms is lowered .34 ev by the same effects.

The effects on both types of atoms are seen to be due essentially to a predominance of the kinetic energy of $\rho^T(A)$, over the shielded nuclear attraction of the atom for it ($\rho^T(A)$ is seen to have a relatively small quasiclassical interaction with itself). This result can be understood by noting that electron affinities are relatively small compared to the kinetic or potential energy of the additional electron, as given by the one-electron model. Thus the kinetic and potential energies of the additional electron are about equal in absolute magnitude, and, except for the small electron affinity residue, cancel each other.[1] It is

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[1] This is not in contradiction to the virial theorem, since in the one-electron model the shielded potential for the additional electron is not homogeneous of degree (-1), i.e., due to the fact that it moves through the charge clouds of the other electrons, the field which it experiences is not that of a point charge. For a rigorous many-electron calculation of the electron affinity, the virial theorem must of course hold.

therefore not difficult to see that our restricted choices of $\rho^P(A)$ and $\rho^T(A)$ might increase the one-electron energy of $\rho^T(A)$ so that it actually becomes positive, i.e., the kinetic energy of $\rho^T(A)$ comes to predominate over its potential energy. This situation exists in both the O and H atom cases, but the signs of the energies in the case of the H atom must be reversed since $\rho^T(H)$ represents a "positive electronic charge".[1]

Figure 1 indicates a decrease in sharing penetration energy of 8.40 ev for the O atom due to charge transfer. This clearly shows that the oxygen withdraws its own electrons in preference to those of the hydrogen atoms, which is in complete agreement with the diminished sharing of electrons between the O and H atoms indicated by the increase in interatomic penetration energy observed earlier.

The H atoms suffer a very slight rise in energy (.12 ev) due to the change in sharing penetration, indicating that they are not effective in withdrawing their electrons from the sharing situation, as was the O atom. This is probably to be expected, since the general movement of charge is toward the O atom.

The net result of charge transfer is therefore a lowering in energy of 3.37 ev for the O atom, and a lowering in energy of .22 for each of the H atoms. The effect for the O atom is probably to be expected, due to its large electronegativity (assuming this has not changed too

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[1] The case of adding charge to the 1s orbital of a simple H atom illustrates clearly these effects, since the additional electronic charge, in being shielded by the original electron, cannot experience a lowering of potential energy corresponding to that of the original electron. However in being forced into a 1s orbital, it gains a corresponding amount of kinetic energy.

drastically in going to the promoted state), but the effects for the H atoms have been reversed from that of free atoms, no doubt due to the above discussed effect of shielding on the potential energy.

## 5. Summary

Elsewhere (24) it has been shown that the density and energy contributions discussed in the foregoing, if properly defined, exhaust the modifications required in changing the electronic distributions of the atoms to that of the molecule.

From a formal point of view, this implies that the following additive decompositions exist for the total molecular density $\rho$ and the total molecular pair density $\pi$. For the density:

$$\begin{aligned}\rho &= \rho^P + \rho^T + \rho^I \\ &= \rho^G + \rho^{P-G} + \rho^T + \rho^I \qquad \text{(II-1-16)}\end{aligned}$$

where $\rho^G$, $\rho^P$, $\rho^I$ and $\rho^T$ are defined in Eqs. II-1-1, II-1-4, II-1-7 and II-1-12, and

$$\rho^{P-G} = \rho^P - \rho^G \qquad \text{(II-1-17)}$$

is the density modification due to promotion. Similarly for the pair density:

$$\begin{aligned}\pi &= \pi^P + \pi^{SP} + \pi^{QCT} + \pi^{SPT} + \pi^{IP} + \pi^{IT} + \pi^{II} \\ &= \pi^G + \pi^{P-G} + \pi^{SP} + \pi^{QCT} + \pi^{SPT} + \pi^{IP} + \pi^{IT} + \pi^{II} \qquad \text{(II-1-18)}\end{aligned}$$

where $\pi^G$, $\pi^P$, $\pi^{SP}$, $\pi^{QCT}$, $\pi^{IP}$, $\pi^{IT}$ and $\pi^{II}$ are defined in Eqs. II-1-2,

II-1-5, II-1-8, II-1-13, II-1-15, II-1-10, II-1-14, and II-1-11, and

$$\pi^{P-G} = \pi^{P} - \pi^{G} \qquad \text{(II-1-19)}$$

is the pair density modification due to promotion.

From a conceptual point of view, the conclusions of the preceding sections can be synthesized to give the following over-all picture of the major aspects of chemical binding in $H_2O$.

In the ground state the valence electrons of the oxygen atom doubly occupy the 2s and the 2px orbitals, and singly occupy the 2py and 2pz orbitals. Hybridization promotion results in the formation of two 2s-2pz valence hybrid orbitals, of which the lone pair orbital is doubly occupied and the bonding orbital contains somewhat more than one electron (1.221 electrons). Correspondingly, the 2py orbital contains less than one electron (.772 electrons).[1] This distortion has only small effects on the kinetic and nuclear attraction energies, but causes a relatively large increase in the electronic repulsion energy, due to the slightly greater "squeezing together" of the electrons, particularly in the bonding orbital.

The quasiclassical interactions between the promoted atoms are all attractive, although the O-H interactions are not quite so strong as

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[1] In Sec. II-C-1 the formation of these valence hybrids will be discussed. Also, since the valence lone pair orbital has a population of almost exactly two electrons, it can be linearly combined with the 2px orbital without introducing cross terms into the intra-atomic part of the density expansion. Thus can be formed two equivalent lone pair orbitals above and below the plane of the molecule, which represent the electron distribution of the lone pairs in a completely equivalent fashion to that of the former orbitals.

they would be between the atomic ground states, due to the general shift of electronic charge to the back of the oxygen atom upon its promotion.

The sharing of electrons across the OH bonds greatly lowers the energy, due to the constructive interference which is thereby established. The sharing across the HH' bond increases the energy due to destructive interference. Both interference effects are mainly due to the kinetic energy contributions.

However, sharing also raises the energy somewhat due to the increase in penetration between the valence electrons of the oxygen atom and those of the hydrogen atoms. Composing this rise in energy are energy increasing intra-atomic contributions, which are only partially balanced by the energy lowering interatomic contributions.

Finally, charge transfer from the H atoms to the O atom lowers the energy. The largest contribution to this arises from a decrease in the energy of the oxygen atom, although the hydrogen atoms also have their energies decreased somewhat by loosing electronic charge. This latter is due to the greatly changed character of the hydrogen atoms as a result of the electronic shielding established on them by electron sharing.

The only interatomic quasiclassical transfer effects of appreciable consequence are the attractive interactions of the transferred charges across the OH bonds, which are often naively associated with the energy lowering of charge transfer. Since however the modification of the covalent bonds by charge transfer is largely accomplished by the oxygen atom's pulling back of a fraction of its shared electrons, there also results an increase in interatomic energy due to the decrease in penetration. This latter effect is considerably stronger than the interatomic quasiclassical effect, but considerably weaker than the effect on the oxygen atom.

Finally, the remaining small interactions between interference and charge transfer have been seen to be understandable in terms of the spatial charge distributions characteristic for the two effects.

## C. Partitioning According to Atomic Orbitals

In order to illustrate how an orbital partitioning of the various densities and energies becomes possible, we must refer to the specific definitions for the various partitionings of $\rho$ and $\pi$. Since they are treated in detail elsewhere, (24), we will describe them here only briefly. While it is believed that the basic partitioning, as discussed in Sec. II-B, pinpoints the typical features of molecular wave functions which are essentially associated with chemical binding, it is realized that the particular definitions to be discussed in the following, and used in this analysis, are open to modification and improvement.

As in the preceding section, we shall discuss the general principles and definitions as well as the specific results in the case of $H_2O$. The latter are given in Figures 2, 3, 4, and 5, to which repeated reference will be made.

### 1. The valence atomic orbitals of the oxygen atom in $H_2O$

An orbital breakdown of the gross energy effects and the electron densities discussed in the preceding section would seem to be particularly instructive if it were based on atomic hybrid orbitals which conform naturally to the actual valence situation. In the following, the actual molecular electron density will be used to construct such a set of "valence atomic orbitals".

The electron density resulting from a calculation based on certain atomic orbitals $\chi_r$ has a unique expansion in terms of them, viz.,[1]

$$\rho = \sum_{r,s} p(r,s)\,\chi_r \chi_s \; . \qquad \text{(II-2-1)}$$

The coefficient p(r,s), which indicates the weight of the contribution of the orbital product $\chi_r \chi_s$, is called a bond-order if $\chi_r$ and $\chi_s$ are on different atoms.

Integration of $\rho$ over all space yields a completely analogous breakdown of the total electronic population, viz.,

$$N = 10 = \sum_{r,s} p(r,s)S(r,s) \qquad \text{(II-2-2)}$$

where S(r,s) is the overlap integral between $\chi_r$ and $\chi_s$. Since the orbitals on the same atom are orthogonal, intra-atomic contributions exist only for r=s. If we assume, with Mulliken (19) and McWeeny (17), that the interatomic contribution p(r,s)S(r,s) "owes its existence" in equal measure to the two interacting orbitals $\chi_r$ and $\chi_s$, then one can say that a given orbital $\chi_r$ is responsible for the fraction

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[1] For a MO wave function, the density $\rho$ is the sum of the electron densities of the doubly occupied MOs, viz., $\sum_n \phi_n^2$ where $\phi_n$ is the n^th MO. Hence an equation of the form of Eq. II-2-1 results upon substitution of the LCAO-MOs.

$$q(r) = p(r) + v(r) \qquad \text{(II-2-3)}$$

of the total population. Here the interatomic contribution

$$v(r) = \sum_{s} p(r,s)S(r,s) \qquad \text{(II-2-4)}$$

will be referred to as the valence active fraction, whereas

$$p(r) = p(r,r) \qquad \text{(II-2-5)}$$

shall be called the valence inactive fraction of the orbital population q(r). This is done because the interatomic contributions are indicative of chemical interactions, with a positive v(r) corresponding to a binding interaction and a negative one being associated with an antibonding interaction.[1] The reasons for this will be discussed in the next section.

It is possible to select, for a given atom, a set of unique orthogonal hybrid-atomic-orbitals which have the property that the first one has the largest possible valence inactive fractional population p(r), the second one has the next largest possible p(r), etc. In this way a separation into valence active and valence inactive orbitals is largely attained. Furthermore, these orbitals have the additional property that the intra-atomic coefficients p(r,s)(r≠s) vanish, which causes them to be identical with certain hybrid orbitals proposed by McWeeny (18).

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[1] This association of the signs of the v(r)'s with binding or antibinding interactions has been recognized for some time, particularly by Mulliken, but the underlying reasons have never been clearly elucidated, being usually attributed incorrectly to the build-up or decrease in charge density in the so-called "low potential" region between the nuclei.

a. Valence hybrids in $H_2O$ In the case of $H_2O$ the formation of valence hybrid orbitals affects only the oxygen atom and, because the valence hybrid orbitals diagonalize parts of the density matrix, they preserve symmetry, so that only the 1s, 2s, and 2pz orbitals mix to give an inner (Oi), lone pair ($O\ell$), and bonding orbital (Ob). The expansions for these hybrid orbitals in terms of the Slater orbitals are given in Figure 2. The overlap integrals between these orbitals and the hydrogen 1s orbitals are also given here. The $p(\chi_i)$'s, $v(\chi_i)$'s, and $q(\chi_i)$'s for the hybrid orbitals are given in Figure 2.

Examination of the $p(\chi_i)$'s, $v(\chi_i)$'s, and $q(\chi_i)$'s for the valence hybrids indicates the lone pair and nonbonding character of the 2px orbital. The $O\ell$ orbital is seen to have a population of almost two, and so is nearly a lone pair orbital. It is also seen to have some antibonding character in that $v(O\ell)$ is negative giving rise to a decrease in electron density in the bond regions where the contributions of the orbital products $O\ell Hh$ and $O\ell H'h'$ are the greatest. As would be expected, the Oi orbital, which is essentially still the 1s orbital, has very little valence active population, indicating its essentially nonbonding character. The 2py and Ob orbitals are seen to be strongly binding in character, in that they have fairly large positive valence active populations, giving rise to an accumulation of electronic density in the bond regions.

b. Bonding hybrids in $H_2O$ It is possible to form from the 2py and Ob orbitals two orthonormal "bonding atomic orbitals",

| Valence | Expansion in Spherical Orbitals | | | Overlap | Bondorders and Populations | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| A.O., X | k | s | z | S(X,h) | p | v | q | $q^N$ | $q^T$ | p(X,h) |
| i | .988077 | -.144001 | .054465 | .00056 | 2.000 | .000 | 2.000 | 2.000 | .000 | .000 |
| $\ell$ | .149955 | .820012 | -.552353 | .29774 | 2.215 | -.144 | 2.071 | 2.007 | .064 | -.242 |
| b | .034878 | .553935 | .831829 | .45228 | 1.046 | .316 | 1.362 | 1.221 | .141 | .350 |
| y | | (unhybridized) | | .27601 | .589 | .329 | .918 | .772 | .146 | .596 |
| x | | (unhybridized) | | 0 | 2.000 | 0 | 2.000 | 2.000 | 0 | 0 |
| h' | | (unhybridized) | | .37459 | .745 | .079 | .824 | 1.000 | -.176 | -.459 |

Figure 2. Density partitioning for the valence AO's, in the $H_2O$ molecule.

Figure 3. Exchange contributions to the pairpopulations for the $H_2O$ molecule.

|  |  | i | ℓ | b | y | x | h | h' |
|---|---|---|---|---|---|---|---|---|
| i | PR | 2.000 | .000 | .000 | .000 | .000 | .000 | .000 |
|  | SPN | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
|  | SPT | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
|  | TOT | 2.000 | .000 | .000 | .000 | .000 | .000 | .000 |
| ℓ | PR | .000 | 1.997 | -.034 | -.015 | .000 | .030 | .030 |
|  | SPN | .000 | .001 | .014 | .015 | .000 | -.015 | -.015 |
|  | SPT | .000 | .170 | .009 | .000 | .000 | -.058 | -.058 |
|  | TOT | .000 | 2.168 | -.011 | .000 | .000 | -.043 | -.043 |
| b | PR | .000 | -.034 | .418 | -.273 | .000 | .556 | .556 |
|  | SPN | .000 | .014 | .268 | .273 | .000 | -.278 | -.278 |
|  | SPT | .000 | .009 | .247 | .000 | .000 | -.058 | -.058 |
|  | TOT | .000 | -.011 | .933 | .000 | .000 | .220 | .220 |
| y | PR | .000 | -.015 | -.273 | -.072 | .000 | .565 | .565 |
|  | SPN | .000 | .015 | .273 | .278 | .000 | -.283 | -.283 |
|  | SPT | .000 | .000 | .000 | .215 | .000 | -.034 | -.034 |
|  | TOT | .000 | .000 | .000 | .421 | .000 | .248 | .248 |
| x | PR | .000 | .000 | .000 | .000 | 2.000 | .000 | .000 |
|  | SPN | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
|  | SPT | .000 | .000 | .000 | .000 | .000 | .000 | .000 |
|  | TOT | .000 | .000 | .000 | .000 | 2.000 | .000 | .000 |
| h | PR | .000 | .030 | .556 | .565 | .000 | -.110 | -.041 |
|  | SPN | .000 | -.015 | -.278 | -.283 | .000 | .555 | .020 |
|  | SPT | .000 | -.058 | -.058 | -.034 | .000 | -.014 | -.012 |
|  | TOT | .000 | -.043 | .220 | .248 | .000 | .431 | -.033 |
| h' | PR | .000 | .030 | .556 | .565 | .000 | -.041 | -.110 |
|  | SPN | .000 | -.015 | -.278 | -.283 | .000 | .020 | .555 |
|  | SPT | .000 | -.058 | -.058 | -.034 | .000 | -.012 | -.014 |
|  | TOT | .000 | -.043 | .220 | .248 | .000 | -.033 | .431 |

$$(\mathrm{ObH}) = 1/\sqrt{2}(\mathrm{Ob}+2\mathrm{py}) \quad \text{and} \quad (\mathrm{ObH}') = 1/\sqrt{2}\,(\mathrm{Ob}-2\mathrm{py}), \qquad \text{(II-2-6)}$$

which are unique in that they are "mirror images" of each other in the xz symmetry plane of the molecule. These are found to point generally toward the hydrogen atoms, with an angle of 100.5° between their maxima. ObH and ObH' do not however represent the corresponding valence inactive electron density of the oxygen atom as a simple sum of their individual contributions, as did the 2py and Ob orbitals.

## 2. Interference I

a. Interference partitioning of the density Of the three parts of $\rho$, both $\rho^P$ and $\rho^T$ are intra-atomic in nature. Only $\rho^I$ contains inter-atomic character, and thus the inter-atomic terms of $\rho$, as given in Eq. II-2-1, must belong to $\rho^I$. Since however $\rho^I$ represents a density modification, and hence is characterized by a vanishing population, it cannot be identical with the interatomic terms of $\rho$, whose population usually does vanish. It must also contain certain intra-atomic terms, $\rho'$ say, which, together with the interatomic terms, yield a vanishing population. This corresponds to the fact that interference shifts charge from the atoms into the bond or vice-versa. By virtue of Eq. II-2-1, it is also clear that subtraction of the same intra-atomic terms $\rho'$ from the intra-atomic terms of $\rho$ will yield the atomic densities $\rho^P + \rho^T$, whose population thus becomes equal to the total molecular population.

Among the various possible intra-atomic contributions $\rho'$ to $\rho^I$ which would serve the purpose, those are chosen which, besides being physically reasonable, also have the virtue of simplicity.

It is assumed that the total interference interaction between two atoms is the sum of the interactions between all the atomic orbital pairs, where one orbital of the pair is on one of the atoms and the other on the other atom. It is also assumed that the interference interaction between two atomic orbitals Aa[1] and Bb is independent of any other orbitals which might be present, and depends only on the orbitals themselves and their relative positions with respect to each other.[2] Finally, it is assumed that, in all cases, the two orbitals must be considered to enter equivalently into the interaction, even though they may not be of the same type, i.e., the two orbitals must be treated in the same way in the mathematical formalism.

The first part of the above assumption necessarily results in $\rho^I$ being given as a sum of orbital-pair contributions $\rho^I(AaBb)$. The second part of the assumption causes the intra-atomic contributions to $\rho^I(AaBb)$ to have distributions in space which are proportional to the density distributions of the two respective orbitals, i.e., proportional to $Aa^2$ and $Bb^2$ respectively. The final part of the assumption forces the populations of the two intra-atomic contributions to $\rho^I(AaBb)$ to be equal.

Combining the interatomic density terms with the intra-atomic terms thus obtained, we see that $\rho^I$ is given by:

---

[1] Here "A" denotes the atom and "a" designates one of its orbitals such as 1s, 2px, etc. or a hybrid orbital such as [.6(2s) + .8(2pz)].

[2] This is seen to be equivalent to treating the bond-orders merely as weighting factors, with the "nature" of the interference being determined by the properties of the orbitals involved.

$$\rho^{I} = \sum_{Aa,Bb} \rho^{I}(AaBb) = \sum_{Aa,Bb} p(AaBb) \langle AaBb\rangle \tag{II-2-7}$$

where the "orbital interference density" $\langle AaBb\rangle$ is defined by

$$\langle AaBb\rangle = AaBb - \frac{1}{2} S(AaBb)[Aa^2+Bb^2] \; . \tag{II-2-8}$$

It is seen that the definition of $\rho^P + \rho^T$ which is concomitant with this definition of $\rho^I$ will be:

$$\rho^P + \rho^T = \sum_{A} \sum_{a} q(Aa)Aa^2 \tag{II-2-9}$$

where the q(Aa)'s are just the "orbital populations" defined previously in Eq. II-2-3.

A closer look at the definition of Eq. II-2-8 shows that the interference term $p(HhOa)\langle HhOa\rangle$ represents either a shift of charge from the atoms into the bond region, or from the bond onto the atoms, depending on the signs of the orbitals and of p(HhOa). Which of the two possibilities actually occurs for a particular Oa is indicated by the sign of its valence active population v(Oa) (see Eq. II-2-4). If v(Oa) is positive, a shift of charge from the Oa orbital into the overlap region is indicated; if it is negative, a removal of charge from the region occurs. In the present case the S(HhOa)'s are all positive, as seen from Figure 2, so that the sign of v(Oa) is the same as that of the corresponding p(HhOa) which are given in the same table. Thus in the present case, a positive p(HhOa) is associated with a positive v(Oa) and therefore with a constructive interference interaction, with a destructive interference being associated with a negative p(HhOa).

It should be understood that the actual charge shifted is not identical with v(Oa), but is of course given by the integration of $\rho^I$(HhOa) over the regions where it is positive (which is equal to the integral over the negative regions, with opposite sign). This latter is more closely approximated by v(Oa)[1 - S(HhOa)], but, since S(HhOa) is always smaller in absolute magnitude than unity, the v(Oa)'s always indicate the direction of the charge shift by their signs.

Fairly large positive bondorders are found for the HhOy and HhOb orbital pairs, since the Oy and Ob orbitals are directed generally toward the hydrogen atoms, and therefore interact strongly with them. The somewhat larger bondorder for the Oy case presumably reflects the fact that the lobes of this orbital lie somewhat closer to the hydrogen atoms than does the main lobe of the Ob orbital. The value of p(HhO$\ell$) is weak and negative, indicating that the O$\ell$ orbital, in lying toward the back of the oxygen atom, and thereby having a lone pair character, has a smaller but antibonding interaction with the hydrogen atoms.

b. Kinetic interference energies in $H_2O$ In Sec. II-B it was pointed out that a shift of charge into the bond region is associated with a negative kinetic interference energy, which must be considered a primary cause of covalent binding. A shift of charge out of the bond leads to a positive kinetic interference energy, which results in antibonding effects.

These conclusions are further illustrated by the kinetic interference energies arising from the $\rho^I$(AaBb)'s for the individual orbital pairs. These kinetic energies are given in the seventh column of Figure 5. In the preceding section it was pointed out that a positive bond order p(HhOa) is associated with a positive v(Oa) or v(Oa)[1 - S(HhOa)], and therefore with a shift of charge into the bond: the reverse holds for a negative p(HhOa). A positive p(HhOa) is therefore associated with negative interference kinetic energy, and a negative p(HhOa) with a positive one.

In the cases of the HhOb and HhOy orbital pairs, these energies are very strongly negative, due to the fact that the corresponding interference densities are of the constructive, bonding type. The kinetic energy of $\rho^{I}(\mathrm{HhO}\ell)$ is strongly positive, since the interference is of the destructive, anti-bonding type. The fact that this latter energy is only about half as strong as the two former ones is to be expected since the Hh and $\mathrm{O}\ell$ orbitals overlap considerably less than do the orbitals in the other cases, so that the resulting interference density $\rho^{I}(\mathrm{HhO}\ell)$ is correspondingly less. The $\mathrm{HhO}_i$ orbital pair gives essentially no interference density, and therefore no interference kinetic energy contribution, since the overlapping of these orbitals is very small. The HhOx orbital pair gives no interference kinetic energy, not because of little overlap and therefore little interference, but because the 2px orbital has vanishing bond orders with all the other orbitals because of its unique symmetry. Even if it had a nonvanishing bond order with the Hh orbital, the kinetic and potential energies of $\rho^{I}(\mathrm{HhOx})$ would vanish because the antibonding destructive interference on one side of the plane would be exactly canceled, energy wise, by the bonding interference on the other side.

It should be noted that the kinetic energy contributions determine the character of the total interference energy, since the potential energy contributions are always considerably smaller. Furthermore, in $H_2O$ they are seen to cancel one another partially. These latter terms will be discussed in detail in Sec. II-C-4.

### 3. Quasiclassical interactions

#### a. Transfer and promotion state densities in $H_2O$

Since we have defined $\rho^I$ in such a way that $\rho^P + \rho^T$ is given as a simple sum of orbital contributions, according to Eq. II-2-9, it seems to be desirable that we also define $\rho^T$, and therefore $\rho^P$, to be of this form. Thus:

$$\rho^T = \sum_A \sum_a q^T)Aa)Aa^2 \qquad \text{(II-2-10)}$$

$$\rho^P = \sum_A \sum_a q^P(Aa)Aa^2 \quad . \qquad \text{(II-2-11)}$$

Not only does this greatly aid the interpretation of the results obtained, but it also simplifies the reasoning involved in obtaining a specific definition of $\rho^T$. Eqs. II-2-9, II-2-10 and II-2-11 imply the decomposition

$$q(Aa) = q^P(Aa) + q^T(Aa) \qquad \text{(II-2-12)}$$

for the orbital populations $q(Aa)$.

From the sum of the orbital populations we know the total population of each atom, and therefore in sample cases such as $H_2O$ we know how much total charge is transferred from atom to atom, assuming no transfer of charge between like atoms in identical situations, such as the two H atoms. Also since the two H atoms each have only one orbital, $\rho^T(H)$ for those atoms is already uniquely determined.

In order to ascertain what $\rho^T(O)$ is, we must decide how much of the electronic charge which is transferred to the oxygen atom, viz. $q^T(O) = .35154$ electrons, is given to each oxygen orbital, i.e. the $q^T(Oa)$'s of Figure 2. Since in the promoted and neutral sharing situation the oxygen atom is promoted and furthermore sharing electrons with the hydrogen atoms, we have no a priori knowledge of what the populations of these orbitals would be without charge transfer, i.e., the $q^P(Oa)$'s of Figure 2. However, since the more valence active orbitals are more involved in electron sharing, we would expect them to receive proportionally more of the transferred charge. Therefore, since the absolute values of the valence active populations ($v(Oa)$'s of Eq. II-2-4) for the various orbitals provide at least a rough measure of their valence activities, we consider it reasonable to set

$$q^T(Oa) = K|v(Oa)| = |v(Oa)|\, q^T(O)/\sum_a |v(Oa)| \quad . \qquad \text{(II-2-13)}$$

It is seen that the proportionality constant K is chosen such that

$$\sum_a q^T(Oa) = q^T(O) \quad . \qquad \text{(II-2-14)}$$

The results of the above method are given in Figure 2. This method gives about equal transferred charge to both the Ob and 2py orbitals, and about half this amount to the $O\ell$ orbital. The Oi and 2px orbitals receive essentially no transferred charge.

It should be noted that $q^P(O\ell)$ is almost exactly two, indicating that in its promoted state the oxygen atom has two lone pair orbitals $O\ell$ and 2px. Furthermore, the sum of $q^P(Ob)$ and $q^P(Oy)$ becomes almost exactly two, so that the two equivalent bonding orbitals ObH and ObH' of Eq. II-2-6 each become singly occupied, in the promoted state.

Having defined $\rho^P$ and $\rho^T$ in terms of orbital contributions, we can now examine (1) the quasiclassical interactions of the promoted atoms in terms of contributions from orbital pairs, (2) the changes in these interactions due to charge transfer, and (3) the intra-atomic quasiclassical effects of charge transfer in terms of orbital contributions.

b. Quasiclassical interactions of the promoted atoms in $H_2O$ The quasiclassical interaction of the promoted oxygen atom with one of the hydrogen atoms is broken down according to orbital pairs in the first column of Figure 5. As pointed out in Section II-B, there are three types of interactions involved in these terms, i.e., nuclear-nuclear repulsion, electronic repulsions between the atoms, and the attractions of the nuclei for electrons on the other atoms. In order to obtain a reasonable partitioning by orbital pairs, it seems best to consider the interactions of neutral fragments of the total atomic charge density, i.e., fragments consisting of an orbital and a fraction of the nucleus having a charge equal in magnitude, but opposite in sign, to the orbital population. In this way the very large magnitudes of the interactions largely cancel one another, and we have situations analogous to the total interactions of the neutral promoted atoms. Thus, in $H_2O$, the nuclear charge of the oxygen atom is divided among the oxygen orbitals according to the orbital populations ($q^P$) given in Figure 2, and each of the resulting fractional nuclear charges is associated with the corresponding orbital to give a neutral "orbital atom-fragment" for calculating the three types of interaction energies.

Two neutral spherically symmetric orbital fragments from different atoms, whose electronic charges overlap, always interact with an attractive effect, up to very close separations. If the overlap is small, this interaction will be very small. This explains the very small attractive effect for the orbital pair HhOi, since the Oi orbital is almost entirely of 1s character, and therefore overlaps the hydrogen 1s orbital very little.

Those oxygen orbitals which are not spherically symmetric about the oxygen atom in general have their charge densities shifted either closer to or further away from the hydrogen atom, as compared with a spherically symmetric distribution. In order to understand the interaction energies from these orbital fragments and the hydrogen atom, we must consider the changes in the three contributing types of interactions when this situation exists instead of the spherically symmetric charge density. For a given interaction distance, the nuclear-nuclear repulsion is the strongest type of interaction, the nuclear-electronic attraction the next strongest type of interaction, and the electronic-electronic repulsion the weakest type interaction. Since all these interactions rise monotonically from zero at large interaction distances (up to very close separations), the changes of the three types of interactions occurring with changing interaction distance have the same relative ordering of magnitudes as the effects themselves, i.e., the electronic-electronic interaction changes most slowly with interaction distance, the electronic-nuclear interaction changes more rapidly and the nuclear-nuclear repulsion changes most rapidly.

Now the interaction energy of the H atom with an orbital fragment on the oxygen will differ from that of a comparable spherically symmetric distribution in the contributions arising from the interaction of the oxygen electrons with the hydrogen electrons and the hydrogen nucleus. In view of the preceding discussion, it is the latter, i.e., the attraction between the oxygen electrons and the hydrogen nucleus, which predominates, so that the total difference follows this effect.

In the case of the HhOℓ interaction, where the charge density of the Oℓ orbital lies toward the back of the oxygen atom, the slight attractive effect which would exist for a spherically symmetric orbital, such as a 2s orbital, is seen to have been converted to a fairly strong repulsive effect, due to the predominence of the decrease in the aforementioned attraction.

The small repulsive effect for the HhOx interaction arises also because the charge cloud of the 2px orbital is not as close, on the average, to the H atom as in the case of a spherically symmetric orbital. The effect is not nearly so large, however, as in the HhOℓ case, since the two lobes of the 2px orbital are not so strongly directed away from the H atom as is the principal lobe of the Oℓ orbital.

The strong attractive effects for the HhOb and HhOy interactions occur for analogous reasons because the Ob and Oy orbitals are generally directed toward the hydrogen atom. That the HhOb interaction is about twice as strong as that for HhOy reflects the fact that the Oy orbital has only one of its two identical lobes close to the hydrogen atom H, whereas the Ob orbital is effectively concentrated in the single lobe which lies near the hydrogen.

c. Changes in the interatomic quasiclassical interactions due to charge transfer in $H_2O$ The changes in the interatomic quasiclassical interactions, due to charge transfer, are given in the second column of Figure 5.

The SNA terms on the right side of the column represent the shielded nuclear attractions of the hydrogen atom for the electronic charges transferred to the oxygen atom, i.e., the $q^T(Oa)Oa^2$'s (see Eq. II-2-8 and Figure 1). These terms are all negative since, as mentioned in Sec. II-B, the hydrogen atom has a net quasiclassical attraction for electronic charge. The only large terms are for the bonding orbitals, since in these cases the $q^T(Oa)Oa^2$'s are much closer to the hydrogen atom, and also the $q^T(Oa)$'s are larger.

The SNA terms on the left side of the column represent the shielded nuclear attractions of the neutral "orbital atom-fragments", of the oxygen atom, for the positive resultant charge on the hydrogen atom, i.e., $q^T(H)Hh^2$. The "orbital-fragment" of a spherically symmetric orbital on the oxygen atom would slightly repel $q^T(H)Hh^2$, since it would have a slight net attraction for electronic charge. Thus the HhOi interaction is very slightly repulsive. The $O\ell$ atomic-fragment has a strong repulsion for $q^T(H)Hh^2$, since the nuclear charge fraction is much closer to the hydrogen atom than the electronic charge cloud of the $O\ell$ orbital. Conversely for the Ob orbital-fragment there exists a small attraction for $q^T(H)Hh^2$; it is not nearly as large as the repulsion of the $O\ell$ atomic-fragment, since in this case the interacting electronic charge distributions overlap considerably, weakening their attractive interaction. In the case of Oy, we see a slight repulsion, no doubt due to the fact that only one lobe of the Oy orbital acts to shield the corresponding fractional nuclear charge.

The OEI terms in the center of the column represent the quasiclassical interactions of the $q^T(Oa)Oa^2$'s, i.e., the electronic charges transferred to the oxygen orbitals, with $q^T(H)Hh^2$, i.e., the charge density of the positive "hole" left on the hydrogen atom. These are, of course, all attractive, with the greatest attractions coming when the corresponding charge distributions are closest, such as with the bonding orbitals.

### d. Intra-atomic quasiclassical effects of charge transfer in $H_2O$

The changes in the intra-atomic quasiclassical interaction, due to charge transfer, are given in the second column of Figure 4, according to orbitals.

In Sec. II-B it was observed that it is reasonable to include the kinetic energies of the $\rho^T(Aa)$'s along with these intra-atomic quasiclassical energies, since the totals which then result can be interpreted as being close in principle to the electronegatives of the atoms.

The kinetic energies (KIE) of the electronic charges transferred to the oxygen atom are all seen to be positive, as they must be. The

| Orbital | | Promotion | | | | | |
|---|---|---|---|---|---|---|---|
| | | k | s | z | y | x | Total |
| O k | KIN | -.57 | 6.24 | - | - | - | -.55 |
| | NA | 1.17 | -6.49 | - | - | - | 1.16 |
| | EI | -.66 | -13.11 | 28.23 | -13.78 | -.04 | -.79 |
| | TOT | -.06 | -13.36 | 28.23 | -13.78 | -.04 | -.18 |
| O s | KIN | 6.24 | -19.69 | - | - | - | -13.46 |
| | NA | -6.49 | 64.41 | - | - | - | 57.94 |
| | EI | -13.11 | -4.67 | 9.17 | -14.02 | -9.67 | -36.50 |
| | TOT | -13.36 | 40.05 | 9.17 | -14.02 | -9.67 | -7.98 |
| O z | KIN | - | - | 32.62 | - | - | 32.62 |
| | NA | - | - | -114.70 | - | - | -114.70 |
| | EI | 28.23 | 9.17 | 12.15 | -.62 | 19.50 | 71.62 |
| | TOT | 28.23 | 9.17 | -69.93 | -.62 | 19.50 | -10.46 |
| O y | KIN | - | - | - | -16.08 | - | -16.08 |
| | NA | - | - | - | 56.55 | - | 56.55 |
| | EI | -13.78 | -14.02 | -.62 | 1.35 | -9.34 | -29.85 |
| | TOT | -13.78 | -14.02 | -.62 | 41.82 | -9.34 | 10.62 |
| O x | KIN | - | - | - | - | - | - |
| | NA | - | - | - | - | - | - |
| | EI | -.04 | -9.67 | 19.50 | -9.34 | - | - |
| | TOT | -.04 | -9.67 | 19.50 | -9.34 | - | - |
| Total | | | | | | | |
| O | KIN | | | | | | 2.53 |
| | NA | | | | | | .94 |
| | EI | | | | | | 4.49 |
| | TOT | | | | | | 7.95 |

Figure 4. Intra-atomic energy contributions for $H_2O$

| | | Quasi-classical | Sharing Penetration | | SP+QC |
|---|---|---|---|---|---|
| Orbital | | QCT | SPN | SPT | Total |
| O i | KIN | .00 | | | .00 |
| | SNA | .00 | | | .00 |
| | OEI | .00 | .00 | .00 | .00 |
| | TOT | .00 | .00 | .00 | .00 |
| O ℓ | KIN | 2.69 | | | 2.69 |
| | SNA | -2.88 | | | -2.88 |
| | OEI | .24 | .71 | -2.35 | -1.40 |
| | TOT | .05 | .71 | -2.35 | -1.59 |
| O b | KIN | 9.44 | | | 9.44 |
| | SNA | -8.11 | | | -8.11 |
| | OEI | .58 | 6.97 | -3.45 | 4.10 |
| | TOT | 1.91 | 6.97 | -3.45 | 5.43 |
| O y | KIN | 10.31 | | | 10.31 |
| | SNA | -7.83 | | | -7.83 |
| | OEI | 0.59 | 6.49 | -2.60 | 4.48 |
| | TOT | 3.07 | 6.49 | -2.60 | 6.02 |
| O x | KIN | .00 | | | .00 |
| | SNA | .00 | | | .00 |
| | OEI | .00 | .00 | .00 | .00 |
| | TOT | .00 | .00 | .00 | .00 |
| Total O | KIN | 22.44 | | | 22.44 |
| | SNA | -18.82 | | | -18.82 |
| | OEI | 1.41 | 14.18 | -8.40 | 7.19 |
| | TOT | 5.03 | 14.18 | -8.40 | 10.81 |
| Total H | KIN | -2.39 | | | -2.39 |
| | SNA | 1.79 | | | 1.79 |
| | OEI | 0.26 | 4.71 | .12 | 5.09 |
| | TOT | -0.34 | 4.71 | .12 | 4.49 |
| Total $H_2O$ | KIN | 17.66 | | | 17.66 |
| | SNA | -15.23 | | | -15.23 |
| | OEI | 1.93 | 23.61 | -8.17 | 17.37 |
| | TOT | 4.35 | 23.61 | -8.17 | 19.80 |

Figure 4 (Continued)

| Orbital Pair | | Quasiclassical Electrostatic | | | Sharing | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Penetration | | | Interference | | | | | |
| | | | | | | | | Intra-bond | | | Inter-bond | | |
| | | QCN | QCT | QC(N+T) | SPN | SPT | SP(N+T) | SIN | SIT | SI(N+T) | SIN | SIT | SI(N+T) |
| O H | | | | | | | | | | | | | |
| i h | KIN | | | | | | | .00 | | .00 | .00 | | |
| | SNA | -.06 | .02 .00 | -.04 | | | | .11 .00 | .00 .00 | .11 | .06 .00 | .00 | .00 |
| | OEI | | .00 | .00 | .00 | .00 | .00 | -.10 | | -.10 | .06 | | .06 |
| | TOT | -.06 | .02 | -.04 | .00 | .00 | .00 | .00 | .00 .00 | .00 | | .00 | .06 |
| l h | KIN | | | | | | | 3.60 | | 3.60 | | | |
| | SNA | .94 | .87 -.04 | 1.77 | | | | .26 -.26 | -.11 -.02 | -.13 | -.01 | -.03 | -.04 |
| | OEI | | -.13 | -.13 | -.18 | .66 | .48 | -.19 | | -.19 | -.02 .12 | | .11 |
| | TOT | .94 | .70 | 1.64 | -.18 | .66 | .48 | 3.41 | -.11 -.02 | 3.28 | .09 | -.03 | .07 |
| b h | KIN | | | | | | | -9.04 | | -9.04 | | | |
| | SNA | -2.25 | -.18 -.42 | -2.85 | | | | 2.73 -.85 | .09 -.08 | 1.89 | .30 | -.12 | .18 |
| | OEI | | -.37 | -.37 | -4.41 | .85 | -3.56 | -.01 | | -.01 | .08 .01 | | .09 |
| | TOT | -2.25 | -.97 | -3.22 | -4.41 | .85 | -3.56 | -7.16 | .09 -.08 | -7.15 | .39 | -.12 | .27 |
| y h | KIN | | | | | | | -7.70 | | -7.70 | | | |
| | SNA | -.98 | .06 -.35 | -1.27 | | | | 3.72 -2.45 | -.09 -.30 | .89 | .79 | .25 | 1.04 |
| | OEI | | -.35 | -.35 | -4.16 | .46 | -3.70 | .34 | | .34 | -.19 -.03 | | -.22 |
| | TOT | -.98 | -.63 | -1.61 | -4.16 | .46 | -3.70 | -6.09 | -.09 -.30 | -6.48 | .57 | .25 | .81 |
| x h | KIN | | | | | | | .00 | | .00 | | | |
| | SNA | .17 | .43 .00 | .60 | | | | -.38 .00 | .00 .00 | -.38 | .00 | .00 | .00 |
| | OEI | | .00 | .00 | .00 | .00 | .00 | -.58 | | -.58 | .23 .00 | | .23 |
| | TOT | .17 | .43 | .60 | | .00 | .00 | -.96 | .00 .00 | -.96 | .23 | .00 | .23 |
| Bond Total O H | KIN | | | | | | | -13.14 | | -13.14 | | | |
| | SNA | -2.17 | 1.20 -.81 | -1.79 | | | | 6.45 -3.56 | -.12 -.40 | 2.38 | 1.07 | .10 | 1.17 |
| | OEI | | -.84 | -.84 | -8.75 | 1.97 | -6.78 | -.54 | | -.54 | .16 .10 | | .26 |
| | TOT | -2.17 | -.46 | -2.63 | -8.75 | 1.97 | -6.78 | -10.79 | -.12 -.40 | -11.30 | 1.33 | .10 | 1.44 |
| Bond Total H H' | KIN | | | | | | | 3.88 | | 3.88 | | | |
| | SNA | -.22 | .06 .06 | -.10 | | | | -.76 -.76 | -.02 -.02 | -1.54 | .16 | -.24 | -.09 |
| | OEI | | .28 | .28 | .18 | .11 | .30 | .01 | | .01 | .10 .10 | | .21 |
| | TOT | -.22 | .40 | .18 | .18 | .11 | .30 | 2.37 | -.02 -.02 | 2.34 | .36 | -.24 | .12 |
| Total $H_2O$ | KIN | | | | | | | -22.41 | | -22.41 | | | |
| | SNA | -4.57 | 2.46 -1.57 | -3.68 | | | | 12.14 -7.87 | -.25 -.80 | 3.22 | 2.30 | -.04 | 2.26 |
| | OEI | | -1.40 | -1.40 | -17.31 | 4.05 | -13.27 | -1.07 | | -1.07 | .42 .31 | | .73 |
| | TOT | -4.57 | -.52 | -5.08 | -17.31 | 4.05 | -13.27 | -19.21 | -.25 -.80 | -20.26 | 3.03 | -.04 | 2.99 |

Figure 5. Interatomic energy contributions for $H_2O$

| Orbital Pair | | Totals | | |
|---|---|---|---|---|
| | | N | T | N+T |
| O H | | | | |
| i h | KIN | .00 | .00 | .00 |
| | SNA | .05 | .02 | .07 |
| | OEI | -.04 | .00 | -.04 |
| | TOT | .01 | .02 | .02 |
| ℓ h | KIN | 3.60 | .00 | 3.60 |
| | SNA | .94 | .67 | 1.60 |
| | OEI | -.26 | .53 | .27 |
| | TOT | 4.28 | 1.20 | 5.47 |
| b h | KIN | -9.04 | .00 | -9.04 |
| | SNA | -.07 | -.72 | -.78 |
| | OEI | -4.22 | .48 | -3.74 |
| | TOT | -13.43 | -.23 | -13.66 |
| y h | KIN | -7.70 | .00 | -7.70 |
| | SNA | 1.08 | -.42 | .66 |
| | OEI | -4.04 | .11 | -3.93 |
| | TOT | -10.67 | -.31 | -10.98 |
| x h | KIN | .00 | .00 | -.00 |
| | SNA | -.21 | .43 | .22 |
| | OEI | -.35 | .00 | -.35 |
| | TOT | -.57 | .43 | -.14 |
| Bond Total O H | KIN | -13.14 | .00 | -13.14 |
| | SNA | 1.79 | -.03 | 1.76 |
| | OEI | -9.02 | 1.13 | -7.90 |
| | TOT | -20.38 | 1.10 | -19.28 |
| Bond Total H H' | KIN | 3.88 | .00 | 3.88 |
| | SNA | -1.58 | -.15 | -1.73 |
| | OEI | .39 | .39 | .79 |
| | TOT | 2.69 | .24 | 2.93 |
| Total $H_2O$ | KIN | -22.41 | .00 | -22.41 |
| | SNA | 2.00 | .21 | 1.79 |
| | OEI | -17.65 | 2.65 | -15.01 |
| | TOT | -38.06 | 2.44 | -35.62 |

Figure 5 (Continued)

largest ones are seen to be for the orbitals which receive the most transferred charge, since there are only very minor differences between the kinetic energies of the various orbitals (except for the Oi orbital, which receives no transferred charge).

The shielded nuclear attractions (SNA) are seen to be of about the same magnitude as the kinetic energies, but opposite in sign. The reasons that the shielded nuclear attractions are of about the same magnitude, but somewhat less than the kinetic energy terms, were discussed in Sec. II-B-4.

The quasiclassical interactions between the various charges transferred to the oxygen atom (OEI) were partitioned among the various orbitals by dividing each interaction energy equally between the two orbitals involved. It is seen that they are, of course, all positive, and their magnitudes small, as would be expected since they represent the interactions of relatively small charges which are widely distributed in space. Their magnitudes are seen to reflect generally the amounts of charge transferred to each orbital.

### 4. Interference II

a. Interference partitioning of the pair density Orbital expansion for the pair density: The electronic pair density resulting from a calculation based on atomic orbitals has a unique expansion in terms of them, viz.,

$$\pi(1,2) = \sum_{\mathrm{Aa,Bb}} \sum_{\overline{\mathrm{Aa}},\overline{\mathrm{Bb}}} p(\mathrm{AaBb}|\overline{\mathrm{AaBb}})[\mathrm{Aa}(1)\,\mathrm{Bb}(1)][\overline{\mathrm{Aa}}(2)\overline{\mathrm{Bb}}(2)] \quad . \qquad \text{(II-2-15)}$$

Here the first orbital product AaBb refers to the first electron of the interacting electron pair, and the second orbital product $\overline{AaBb}$ to the second electron. From a physical point of view, the form of Eq. II-2-15 can be understood by remembering that $\pi$ is related to the electrostatic interactions between electron densities. The $p(AaBb/\overline{AaBb})$'s will sometimes be referred to as "pair bond-orders".

It is often instructive to consider $\pi$ as composed of two components $\pi_c$ and $\pi_x$ as given in the equation

$$\pi(1,2) = \pi_c - \pi_x = \rho(1)\rho(2) - \pi_x(1,2) \ . \qquad \text{(II-2-16)}$$

Here $\pi_c$ represents the pair density for the classical electrostatic interaction of the molecular charge density $\rho$ with itself, and hence has the form $\rho(1)\rho(2)$. The generally much smaller component $\pi_x$ represents the correction to $\pi_c$ which is necessary to obtain the true pair density $\pi$. For a SCF type wave function, $\pi_x$ is everywhere positive, and can be interpreted as corresponding to the self-repulsions of electrons. These self-interactions are erroneously included in $\pi_c$ and must be taken out in order to get the true interelectronic interactions (24).

Interference related pair densities: The terms constituting the partitioning of $\pi$, as given in Eq. II-1-18, can be grouped into interference and non-interference related terms. The definition of the interference related terms ($\pi^{IP}$, $\pi^{IT}$, and $\pi^{II}$) is chosen in a manner very much analogous to that used in obtaining $\rho^I$, i.e., by assuming that each interatomic orbital pair generates certain characteristic interference terms independently of the other pairs, and that the pair bond-orders act merely as weighting factors. This partitioning is carried out by expressing the orbital products of Eq. II-2-15 in terms of $\langle AaBb \rangle$ and $(Aa^2+Bb^2)$ according to Eq. II-2-8. For the coulombic part, $\pi_c$, this procedure is equivalent to substituting the partitioning of $\rho$ (into $\rho^I$ and $\rho^P+\rho^T$) in $\rho(1)\rho(2)$.

The above described procedure yields two types of interference related terms, viz., those proportional to $\langle AaBb \rangle \cdot \overline{Aa}^2$,[1] and others proportional to $\langle AaBb \rangle \cdot \overline{\langle AaBb \rangle}$.

The terms proportional to $\langle AaBb \rangle \cdot \overline{Aa}^2$ constitute $\pi^{IP}+\pi^{IT}$, and their form is seen to agree with their conceptual interpretation as corresponding to the electronic interaction between $\rho^P(Aa) + \rho^T(Aa)$ and $\rho^I(AaBb)$. For this reason, the energies arising from them, after being summed over the orbitals **Aa** of atom A, are combined with the nuclear attraction energy of $\rho^I(AaBb)$ in the field of the nucleus of A, to give a shielded nuclear attraction energy for the interference density $\rho^I(AaBb)$ with respect to atom A.

In order to keep the transfer and nontransfer energy terms separated, the shielding electronic interactions between the $\rho^T(Aa)$'s and $\rho^I(AaBb)$'s were taken out of the above terms and tabulated separately as charge transfer contributions to the interference energies.[2] Both the shielded

[1] The partitioning also results in terms proportional to $\langle AaBb|\overline{AaAa'}\rangle$, but these are so small that they will not be elaborated further here.

[2] In separating out these interactions, it was assumed that they are completely of a coulombic quasiclassical nature and therefore have pair density terms of the form $\rho^T(Aa)\rho^I(AaBb)$. This assumption is not completely justified, but the smallness of the terms involved, coupled with the fact that total electronic interactions are usually about 90 percent coulombic, suggests that the error so introduced should be relatively small.

nuclear attraction energies for the neutral atoms, and those due to the changes in the shielding because of charge transfer, are listed in Figure 5 in the row SNA.

The second type of interference terms, i.e., those proportional to $\langle AaBb\rangle \cdot \overline{\langle AaBb\rangle}$, constitute $\pi^{II}$ of Eq. II-1-18, and are interpreted conceptually as corresponding to electronic interactions between $\rho^I(AaBb)$ and $\rho^I(\overline{AaBb})$. These interactions are summed up according to orbital products on the basis of dividing the interaction energy equally between the two orbital products involved.

### b. Potential contributions to the interference energy in $H_2O$

The shielded nuclear attractions (SNA) of the promoted oxygen and hydrogen atoms for the interference densities $\rho^I(HhOa)$ are given in the left and right sides respectively of the seventh column of Figure 5. The changes in these terms due to charge transfer are given in the left and right sides respectively of the eighth column. The shielded nuclear attractions (SNA) of the opposite H' atom for the $\rho^I(HhOa)$'s are given in the tenth column of Figure 5, with the corresponding changes due to charge transfer being given in the eleventh column.

From the neutral shielded nuclear attractions of the seventh column, it is seen that the two bonding-orbital pairs HhOb and HhOy follow the total effects for the OH bond, which were discussed in Sec. II-1-3, and in fact determine the nature of the total effects. Thus the central negatively charged regions of the interference density $\rho^I(HhOb)$ and $\rho^I(HhOv)$ are shifted very close to the H atom, so that their interactions with that atom become attractive instead of repulsive as in a homonuclear situation.

The shielded nuclear attractions for $\rho^I(\mathrm{HhO}\ell)$, although similar in sign to those for the bonding orbital pairs, have a different origin. First, the central region of $\rho^I(\mathrm{HhO}\ell)$ is positive in charge, since $\rho^I(\mathrm{HhO}\ell)$ is an antibonding interference density. Secondly, since the $\mathrm{O}\ell$ orbital lies toward the "back" of the oxygen atom, this central region of $\rho^I(\mathrm{HhO}\ell)$ lies close to the oxygen atom as was the case with the bonding orbitals. This results in $\rho^I(\mathrm{HhO}\ell)$ being attracted by the H atom, as it would be in a homonuclear case, and being repelled by the O atom (which is opposite to the homonuclear case), due to the predominance of the repulsion of the O atom for the large central positive region of $\rho^I(\mathrm{HhO}\ell)$ close to it. Another situation which no doubt contributes to the repulsion of $\rho^I(\mathrm{HhO}\ell)$ by the oxygen atom is the fact that this atom has its greatest affinity for negative charge on the side towards the hydrogen atoms, and therefore has its greatest repulsion for positive charge just where the large positive region of $\rho^I(\mathrm{HhO}\ell)$ is located. In comparison with the shielded nuclear attraction terms for the bonding orbital pairs, those for $\rho^I(\mathrm{HhO}\ell)$ are weak. This again indicates a weaker interference, which is due to the small overlap between the $\mathrm{O}\ell$ and Hh orbitals.

The negative potential energy of $\rho^I(\mathrm{HhOx})$ with respect to the shielded oxygen atom (-.38 ev) occurs because the electronic interactions, which we interpret as being between $\rho^I(\mathrm{HhOx})$ and the promoted oxygen electrons, are of an attractive character instead of being repulsive. This is because these interactions are of the same sort which led to the negative energy arising from $\pi^{II}(OH|OH)$, which was pointed out in Sec. II-B. Since this latter effect will be discussed in detail a little further on, the present effect will not be further elaborated on here.

The energies of the $\rho^{I}(HhOa)$'s with respect to the shielded (opposite) H' atom are seen to follow the general trend except for that of $\rho^{I}(HhO\ell)$, which is essentially zero. This latter is again due to the close proximity of the central positively charged region of $\rho^{I}(HhO\ell)$ to the oxygen atom, so that the interactions of the H atom with both the positively and negatively charged regions of $\rho^{I}(HhO\ell)$ are about equal.

As mentioned earlier, the terms representing the electronic interactions which arise between the $\rho^{I}(HhOa)$'s are divided up and summed according to the orbital products HhOa. For the various orbital products of the OH bond, these sums are given in the seventh column of Figure 5 in the row labeled OEI.

For the HhOy orbital pair there is the expected repulsion (.34 ev), which is actually considerable considering the diffuse and overlapping natures of the interacting charge distributions, i.e., $\rho^{I}(HhOy)$ with the various $\rho^{I}(HhOa)$'s. With the HhOi, HhO$\ell$, and particularly the HhOx orbital pairs, negative rather than positive contributions are found, and they lead to the over-all attractive interaction arising from $\pi^{II}(OH|OH)$, which was noted in Sec. II-B-3. The origin of these contributions is best seen from a consideration of the HhOx orbital pair. As noted earlier, $\rho^{I}(HhOx)$ is identically zero because the bond-order p(HhOx) is zero for symmetry reasons. However the orbital product HhOx is not identically zero, and hence there exist contributions to $\pi$ of the form p(HhOx/HhOx) (HhOx)(HhOx) which give rise to electronic interaction energies. (Pair density contributions of the form p(HhOx/HhOa)(HhOx)(HhOa), with Oa≠Ox, lead to vanishing energy integrals because of symmetry.) These contributions to $\pi$ actually arise from the exchange term $\pi_X$, since the coulomb term $\pi_C$ vanishes on account of $\rho^I$(HhOx) being identically zero. Similar markedly negative energy contributions were observed earlier which were interpreted as interactions between $\rho^I$(HhOx) and $\rho^P$(O).

In view of the significance of $\pi_X$ discussed earlier, these contributions must be considered as self-repulsions of electrons which are shared by the Ox and Hh orbitals.[1] As pointed out in Sec. II-B, these energy contributions appear to be related in character to those terms which give rise to Hund's rule for energy levels of different multiplicity.

### 5. Sharing penetration

a. Partitioning of the interference free density The interference free terms occurring in the general partitioning of $\pi$, given in Eq. II-1-18, are obtained by subtracting from $\pi$ the interference related terms discussed in the preceding section. Thus they are found to be

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[1] It is seen from this that the sharing of electrons between two orbitals does not necessarily lead to an interference term for the electron density. This arises from the fact that it is not justified to identify the electrons with the molecular orbitals of an SCF wave function.

$$\pi^{P} + \pi^{SP} + \pi^{QCT} + \pi^{SPT} = \pi - (\pi^{IP} + \pi^{IT} + \pi^{II})$$

$$= \sum_{Aa} \sum_{Bb} q(Aa|Bb)Aa^2(1)Bb^2(2)$$

$$+ \sum_{A} \sum_{\substack{a,\bar{a}\\ a\ \bar{a}}} \sum_{B} \sum_{b} q(AaA\bar{a}|Bb)Aa(1)A\bar{a}(1)Bb^2(2)$$

$$+ \sum_{A} \sum_{\substack{a,\bar{a}\\ a\ \bar{a}}} p(AaA\bar{a}|AaA\bar{a})Aa(1)A\bar{a}(1)Aa(2)A\bar{a}(2) \ . \tag{II-2-17}$$

The first summation on the right hand side of this equation is by far the most important. The second summation gives rise to an entirely negligible energy, since both the $q(AaA\bar{a}|Bb)$'s as well as the corresponding electronic interaction integrals are very small. The last summation is small, though not negligible, since the $p(AaA\bar{a}|AaA\bar{a})$'s are not small, but the corresponding integrals are.[1]

Since different atomic orbitals of the same atom are orthogonal, the last two summations of the right side of Eq. II-2-17 vanish when the pair density of that equation is integrated over pair density space. Furthermore, since the atomic orbitals are normalized, and this

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[1] There are no contributions to the pair density of Eq. II-2-14 of the form $(AaA\bar{a}|Aa'A\bar{a}')$, where $a \neq a'$ and $\bar{a} \neq \bar{a}'$, since the original $\pi$ of Eq. II-2-12 contained no such terms, and the interference partitioning resulted in none. The original $\pi$ did not contain these terms because, for the valence atomic orbitals, the intra-atomic parts of $\rho$ are diagonal, and this results in the intra-atomic parts of $\pi$ being diagonal for a SCF wave function where $\pi$ is constructed from $\rho$ by a given relation.

integration[1] gives the total number of electron pairs, viz., N(N-1)/2, we have

$$1/2\iint(\pi^P + \pi^{SP} + \pi^{QCT} + \pi^{SPT})dV_1dV_2 = 1/2 \sum_{Aa}\sum_{Bb} q(Aa|Bb) = N(N-1)/2 \quad . \tag{II-2-18}$$

Hence, q(Aa|Bb) is called the pair population for the orbital pair AaBb, i.e., the probability of finding an electron in orbital Aa simultaneously with another one in orbital Bb, times the number of electron pairs. The non-negligible first and last summations of Eq. II-2-17 are given in terms of contributions of orbital pairs, with the major contributions having the coefficients q(Aa|Bb). This is quite analogous to $\rho^P + \rho^T$ being given as a sum of orbital contributions with populations q(Aa).

As a consequence of the decomposition of Eq. II-2-16 of the original pair density $\pi$, the interference free pair density of Eq. II-2-17 consists of a coulombic part and an exchange or self-pair-density part. Since the interference partitioning of $\pi$ is such that the decomposition of $\pi_c = \rho(1)\rho(2)$ is just that resulting from substituting the partitioning of $\rho$ in $\rho(1)\rho(2)$, the coulombic parts of the pair density of Eq. II-2-17 are of the form $q(Aa)q(Bb)Aa^2(1)Bb^2(2)$, and hence belong to the first summation. Thus we have

$$q(Aa|Bb) = q(Aa)q(Bb) - q_x(Aa|Bb) \tag{II-2-19}$$

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[1] The integration in question is understood to be $1/2\iint dv_1dv_2$ so that each pair of volume elements is only counted once. This must be since, by definition, $\pi(x_1,x_2)$ gives the total number of pairs between the points $x_1$ and $x_2$. The same integration convention applies also to the calculation of the electronic interaction energies.

where the $q_x(Aa|Bb)$'s arise from the interference free part of the exchange pair density $\pi_x$. It follows furthermore that the last two summations of the right side of Eq. II-2-17 arise entirely from the interference free part of $\pi_x$, which in part accounts for their smallness.

If, now, the partitioning of q(Aa) in terms of $q^P(Aa)$ and $q^T(Aa)$, as given in Eq. II-2-12, is substituted into the coulombic terms of Eq. II-2-19, then those terms yield the following contributions to Eq. II-2-17: the coulombic intra-atomic parts of $\pi^P$, all the interatomic parts of $\pi^P$, and all parts of $\pi^{QCT}$. The latter two have already been discussed in the previous section in connection with the neutral quasiclassical interactions of the promoted atoms, and the quasiclassical effects of charge transfer respectively.

It remains therefore to find the intra-atomic exchange terms of the promotion state pair density $\pi^P$, and also the terms $\pi^{SP}$ and $\pi^{SPT}$ of Eq. II-2-17 which describe the sharing penetration due to electronic sharing before charge transfer, and due to charge transfer, respectively. The latter two terms must be entirely exchange in character, since the coulombic pair density of Eq. II-2-17 has been exhausted by its contributions to $\pi^P$ and $\pi^{QCT}$. This is in agreement with our earlier interpretation of no electronic density changes being associated with $\pi^{SP}$ and $\pi^{SPT}$.

Since the contributions of the third sum of the right side of Eq. II-2-17 are completely intra-atomic in character, and furthermore are of a sort which we know the promoted states must contain, they are considered to comprise part of the intra-atomic $\pi^P$. The contributions to the second sum are considered to constitute part of $\pi^{SP}$, since the conservation relation between the electron density and pair density is immediately satisfied if this is assumed. Actually these latter terms are so small that their interpretation is of no consequence whatsoever.

The contributions of the $q_x(Aa|Bb)$'s to $\pi^P$, $\pi^{SP}$, and $\pi^{SPT}$, will be examined in the sections to follow. They are given by the quantities $q_x^P(Aa|Bb)$'s, $q_x^{SP}(Aa|Bb)$, and $q_x^{SPT}(Aa|Bb)$'s, respectively, which satisfy the relation

$$q_x(Aa|Bb) = q_x^{SPT}(Aa|Bb) + q_x^{SP}(Aa|Bb) + q_x^P(Aa|Bb) \ . \qquad \text{(II-2-20)}$$

Additional definitions are required in order to obtain values for the individual components in Eq. II-2-20. The definitions adopted here lead to the following scheme: the $q_x^{SPT}(Aa|Bb)$'s, and thereafter the $q_x^{SP}(Aa|Bb)$'s, are calculated separately. Then the $q_x^P(Aa|Bb)$'s are obtained by subtracting the $q_x^{SPT}(Aa|Bb)$'s and $q^{SP}(Aa|Bb)$'s from the corresponding $q_x(Aa|Bb)$'s. In view of the above, then, the four components of Eq. II-2-17 are given by expressions of the form

$$\begin{aligned}\pi^P = {} & \sum_{Aa}\sum_{Bb} q^P(Aa)q^P(Bb)Aa^2(1)Bb^2(2) \\ & - \sum_{A}\sum_{a,\bar{a}} q_x^P(Aa|A\bar{a})Aa^2(1)A\bar{a}^2(2) \\ & + \sum_{A}\sum_{a,\bar{a}} p(AaA\bar{a}|AaA\bar{a})Aa(1)A\bar{a}(1)Aa(2)A\bar{a}(2) \qquad \text{(II-2-21)}\end{aligned}$$

$$\pi^{SP} = \sum_{Aa} \sum_{Bb} q_x(Aa|Bb)Aa^2(1)Bb^2(2)$$

$$+ \sum_{A} \sum_{a,\bar{a}} \sum_{Bb} q(AaA\bar{a}|Bb)Aa(1)A\bar{a}(1)Bb^2(2) \qquad \text{(II-2-22)}$$

$$\pi^{SPT} = - \sum_{Aa} \sum_{Bb} q_x^{SPT}(Aa|Bb)Aa^2(1)Bb^2(2) \qquad \text{(II-2-23)}$$

$$\pi^{QCT} = \sum_{Aa} \sum_{Bb} q^P(Aa)q^T(Bb)Aa^2(1)Bb^2(2)$$

$$+ 1/2 \sum_{\substack{Aa \\ Aa \neq Bb}} \sum_{Bb} q^T(Aa)q^T(Bb)Aa^2(1)Bb^2(2) \qquad \text{(II-2-24)}$$

*b. Charge transfer effects on the sharing penetration* The non-coulombic effects on the pair density due to charge transfer, given by Eq. II-2-23, are found by an argument which is similar to that used in finding $\rho^T$. We set (24)

$$q_x^{SPT}(Aa|Bb) = [q^T(Aa)\lambda(Bb)+\lambda(Aa)q^T(Bb)]|V_x(Aa|Bb)| \qquad \text{(II-2-25)}$$

where $\lambda(Aa)$ and $\lambda(Bb)$ are parameters which are determined by the following conservation relation between the transfer parts of the electron density and pair density.[1]

$$\sum_{Bb} q_x^{SPT}(Aa|Bb) = q^T(Aa) \qquad \text{(II-2-26)}$$

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[1] This equation results from the conservation relation $\iint dv_1 \pi_x(1,2) = \rho(2)$ which establishes a generally valid connection between the density and pair density of any system.

The $V_x(Aa|Bb)$'s are pair density quantities analogous to the $v(Aa)$'s, and are given by

$$V_x(Aa/Bb) = q_x(Aa|Bb) - p_x(Aa^2|Bb^2) \qquad \text{(II-2-27)}$$

where the $p_x(Aa^2|Bb^2)$'s are the exchange parts of the $p(Aa^2|Bb^2)$'s of Eq. II-2-15.

c. Neutral sharing penetration effects The effect on the pair density arising from sharing penetration between the neutral promoted atoms constitutes $\pi^{SP} = -\pi_x^{SP}$, given in Eq. II-2-22.

Since there are no exchange, i.e., self-repulsion, pair density terms between the promoted atoms before electron sharing and penetration is allowed, any parts of the interatomic $q_x(Aa|Bb)$'s which remain after the subtraction of the $q_x^{SPT}(Aa|Bb)$'s from the $q_x(Aa|Bb)$'s must be considered to arise from sharing penetration. Hence they are identified as the interatomic parts of $\pi_x^{SP}$.

The intra-atomic parts of $\pi^{SP}$ cannot be obtained in this way, since the intra-atomic parts of $\pi_x^P$ are not necessarily zero. These intra-atomic parts of $\pi^{SP}$ are found by the following reasoning. We use the interatomic contributions to $\pi^{SP}$ as a measure of the amount of electron sharing penetration for the various orbitals and consider

$$q^{SP}(Aa) = \sum_{Bb}{}' q_x^{SP}(Aa|Bb) \quad A \neq B \qquad \text{(II-2-28)}$$

as a measure of the total interatomic electron sharing of the orbital (Aa). The intra-atomic terms of $\pi^{SP}$ are then defined by

$$q_x^{SP}(Aa|A\bar{a}) = -q^{SP}(Aa)q^{SP}(A\bar{a})/\sum_a q^{SP}(Aa) \quad . \qquad \text{(II-2-29)}$$

The choice of the numerator in Eq. II-2-29 is based on the following arguments. Since the intra-atomic terms of $\pi_x^{SP}$ referring to two orbitals Aa and A$\bar{a}$ describe self-repulsions of certain electrons which are shared between them, these terms are affected by interatomic sharing only to the degree that these same electrons are being shared with the other atoms, i.e., to the degree that both orbitals Aa and A$\bar{a}$ are acquiring interatomic sharing contributions. Thus, if an electron is not involved in interatomic sharing, there is no reason why its sharing within the atom should be affected when other electrons change their internal sharing situations due to external sharing. These other electrons merely substitute for each other in their interactions with the first electron.

The denominator of Eq. II-2-29 is a consequence of the choice of the numerator and the conservation relation

$$\sum_{Bb} q_x^{SP}(Aa|Bb) = 0 \qquad \text{(II-2-30)}$$

where the sum runs over both inter- and intra-atomic terms. This condition expresses the fact that sharing penetration is considered to change the pair density without any change in the electron density.

d. Sharing penetration effects in $H_2O$ The values of the $q_x^{SP}(Aa|Bb)$'s and $q_x^{SPT}(Aa|Bb)$'s in the case of $H_2O$, obtained from Eqs. II-2-29 and II-2-25 respectively, are given in Figure 3.

The pair populations describing the "neutral" (i.e. before charge transfer) sharing penetration for the Ob and Oy orbitals are seen to be quite large, whereas those involving the Oℓ orbital are comparatively small. This reflects the fact that the Ob and Oy orbitals strongly share electrons with the hydrogens, while the Oℓ orbital does so much less.

The almost negligible smallness of the terms involving the Oℓ orbital is however peculiar, since the interference terms, which were discussed earlier, indicated small but not negligible sharing for this orbital, although in an antibonding manner. It may be that this result is similar to the negative sharing penetration between the two hydrogen atoms, noted in Sec. II-B-4; for in both instances, there are antibonding interactions involved. Furthermore, negative sharing penetration terms have been observed in a number of other molecules in connection with antibonding interactions (23, 12). These results seem to indicate a possible conflict between the *concept* of sharing penetration and the *method* we have used to obtain a quantitative measure of it. It appears however that there is at least a consistency in the way in which the negative terms arise. While it is possible that they come about because of limitations in the wave functions being analyzed, it seems more likely to us[1] that

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[1] It may be noted that the negative sharing penetration energy which arises between the two hydrogen atoms is a direct result of the sign of $q_x(Hh|Hh')$, and that the latter arises directly from the interference partitioning. It does not arise from any arbitrariness in the definition of the interference density $\rho^I(Hh|Hh')$, which is uniquely determined in this case. It may arise from our particular way of extending the interference partitioning to the pair density, though this seems unlikely. Also it may arise from inaccuracies in the present wave function, which are known to be serious in the region between the two hydrogen atoms, due to the general breakdown of the MO method for large internuclear distances, and perhaps to inaccurate three-center integrals. This possibility too seems somewhat unlikely, since large negative sharing penetration terms have been observed even in diatomic molecules.

the physical picture may involve a fundamental conceptual omission.

The pair populations describing charge transfer sharing-penetration do not differ greatly for the orbitals involved. According to our picture, they represent changes in penetration arising from the slight shift in the probability densities of the shared electrons, attending charge transfer. In view of the very small sharing penetration for the $O\ell$ orbital before charge transfer, the change in this penetration due to charge transfer would seem unduly large. However, it is in line with the sharing indicated by the interference terms.

For both the neutral and the transfer penetration, the energies arising from the *intra*-atomic pair populations have been divided up equally between the two orbitals involved, and then summed for each orbital. The resulting sums are given in Figure 4, under neutral and transfer sharing penetration interactions. As would be expected in view of our method of dividing and then summing, the energy contributions for the orbitals follow the trend of the pair populations discussed above.

The energies from the *intera*tomic pair populations of the neutral and transfer penetration are given in Figure 5 in the fourth and fifth columns respectively. These energies too are seen to reflect their corresponding pair populations. No dividing and summing by orbital pairs was necessary in this case, since the hydrogen atom has only one orbital so that there is a one to one correspondence between the orbital pairs and the interatomic pair populations.

### 6. Promotion

a. Promotion densities    From Eqs. II-1-16 and II-1-18, the electron density of the promoted state of an atom A is given by

$$\rho^P(A) = \sum_a q^P(Aa)Aa^2 \qquad \text{(II-2-31)}$$

and from Eq. II-2-18, the corresponding pair density by

$$\pi^P(A) = \sum_{a,\bar{a}} q^P(Aa)q^P(A\bar{a}) - q_x^P(Aa|A\bar{a}) \quad Aa^2(1)A\bar{a}^2(2)$$

$$+ \sum_{a,\bar{a}} p(AaA\bar{a}|AaA\bar{a})Aa(1)A\bar{a}(1)Aa(2)A\bar{a}(2) \qquad \text{(II-2-32)}$$

where $q^P(Aa)$ is the orbital population of the orbital Aa of the promoted atom A, and the $q_x^P(Aa|A\bar{a})$'s are those parts of the $q_x(Aa|A\bar{a})$'s which remain after the $q_x^{SP}(Aa|A\bar{a})$'s and $q_x^{SPT}(Aa|A\bar{a})$'s have been subtracted.

The density effects of promotion are defined as the difference between the densities of Eqs. II-2-31 and II-2-32 and the corresponding densities for the ground state of the atom. For the hydrogen atoms the choice of the ground state densities is unique. However for the oxygen atom any of a number of ground state densities could have been chosen, each corresponding to a different orientation of that atom. Of these, that orientation was selected in which the 2px orbital is doubly occupied, and the 2py and 2pz orbitals each singly occupied. (The 1s and 2s orbitals are of course doubly occupied.) This is a natural choice since then the promotion effects do not involve the 2px orbital, which has already been seen to be largely inactive in the chemical binding due to its being a molecular orbital in itself. The electron density of the ground state of an atom A is given by

$$\rho^G(A) = \sum_a q^G(Aa)Aa^2 \qquad \text{(II-2-33)}$$

where $q^G(Aa)$ is the number of electrons in the orbital Aa. The corresponding pair density is given by

$$\begin{aligned}\pi^G(A) &= \rho^G(A)\rho^G(A) - \pi_x^G(A) \\ &= \sum_{a,\bar{a}} q^G(Aa)q^G(A\bar{a})Aa^2(1)A\bar{a}^2(2) - \sum_{a,\bar{a}} q_x^G(Aa|A\bar{a})Aa^2(1)A\bar{a}^2(2)\end{aligned}$$

$$\text{(II-2-34)}$$

where the $q_x^G(Aa|A\bar{a})$'s are the exchange pair density elements of the ground state.

In general, promotion contains two kinds of effects, viz., contractive (or expansive) promotion which is reflected by an increase (or decrease) in the orbital exponents, and hybridization promotion which results in the formation of the valence orbitals by the hybridization of the spherical orbitals. There are no promotion effects for the hydrogen atoms, since the wave function does not allow mixing with higher hydrogen orbitals, nor variation of the orbital exponents of the 1s basis orbitals. Also, since the orbital exponents of the basis orbitals of the oxygen atom were not varied, we have to deal only with hybridization promotion there.

The electron densities of Eqs. II-2-33 and II-2-34 are given in terms of the original spherical Slater type orbitals, since these orbitals are the appropriate ones for the description of the free atom. (If other orbitals were used, the expression for $\rho^G(A)$ would contain cross terms between the orbitals.) Since promotion involves a distortion of the densities of the free atoms in their ground states, which are most simply represented in terms of Slater type orbitals, it seems more significant to investigate the effects of promotion in terms of these. We therefore transform the electron densities of the promoted atoms, given by Eqs. II-2-31 and II-2-32, back to the original Slater type orbitals, before subtracting out the ground state densities.

When the electron density $\rho^P(A)$ of the promoted atom is transformed from the valence hybrid orbitals to the Slater orbitals, it is no longer a simple sum of orbital contributions as in Eq. II-2-31, but comes to contain contributions from cross terms between the Slater orbitals. Furthermore, the pair density of the promoted state comes to have terms of the form $(AaA\bar{a}|Aa'A\bar{a}')$ and $(AaA\bar{a}|Aa'^2)$. Consequently, the promotion densities, and therefore the promotion energy, contain such cross terms.

In the subsequent sections we will attempt a decomposition of the promotion energy into a sum of orbital contributions. From the foregoing it is clear that such a partitioning requires considerable, if somewhat arbitrary, partitioning of cross terms among the orbitals involved.

*b. One-electron energies* As was mentioned in the previous section, the difference $\rho^P(0)-\rho^G(0)$ contains cross terms, when expressed in terms of the original spherical orbitals. Thus, the kinetic and nuclear attraction promotion energies also contain contributions from orbital pairs, which are given in Figure 4. In the present case such cross terms occur only between the 1s and 2s orbitals, a result which is due partly to the vanishing of the kinetic and nuclear attraction integrals between p-type and s-type orbitals, and partly to the fact that $\rho^P(0)$ contains no cross terms between orbitals of different molecular symmetry.

If

$$\gamma(Aa) = q^P(Aa) - q^G(Aa) \qquad \text{(II-2-35)}$$

denotes the change in population of orbital (Aa) as a result of promotion, it seems reasonable to divide up the cross terms among the two orbitals in proportion to their $\gamma(Aa)$'s. Thus if the $\gamma(Aa)$ of an orbital vanishes, it would not be reasonable to attribute any kinetic or nuclear attraction promotion energy to it.

The kinetic and nuclear attraction promotion effects for the individual orbitals, resulting from this partitioning, are given in Figure 4.

Both the 2s and 2py orbitals suffer decreases in kinetic energy and increases in potential energy, because they lose electronic charge to the 2pz orbital. Concomitantly the opposite effects are observed for the latter. Both the kinetic and potential energies of the 2s orbital are somewhat greater than those of the 2p orbitals. Therefore the almost complete cancellation of the kinetic and potential energy effects for the 2s, 2py, and 2pz orbitals occurs only because the 2s orbital receives a substantial promotion contribution from its cross term with the 1s orbital. The potential and kinetic energy contributions of this cross term are therefore of considerable importance in understanding the overall kinetic and potential energy effects of hybridization promotion. The exact significance of this electron density cross term is clear, but it may represent to some extent an attempt at contraction promotion, which was not allowed through variable orbital exponents.

c. Electronic interaction energy The transformation of $\pi^P(0)$ to the original spherical orbitals results in three types of terms in the electronic interaction promotion energy, viz., terms of the types $(Aa^2|A\bar{a}^2)$ and $(AaA\bar{a}|AaA\bar{a})$, and terms involving more than two orbitals. The terms which contain more than two orbitals are very small, and are divided up among the various orbital-pairs which they contain on the basis of how many times the orbital-pairs occur in the term, with one orbital of the pair being associated with one electron, and the other with the other electron. Thus a term of the form $(ab|cd)$ is divided equally among the four pairs ac, ad, bc, and bd. This is a somewhat arbitrary division, but in view of the extreme smallness of the terms involved, it cannot cause any misinterpretation. Thus the electronic interaction promotion energy is reduced to contributions from orbital-pairs only, which are given for the oxygen atom in Figure 4.

As with the kinetic and nuclear attraction terms, we now proceed to divide these orbital-pair contributions among the orbitals. Consider first their coulombic parts. Since $\gamma(Aa)$ is the change in population of the orbital Aa during promotion, the coulombic promotion pair density for the $AaA\bar{a}$ orbital pair is

$$q^P(Aa)q^P(A\bar{a}) - q^G(Aa)q^G(A\bar{a}) = \gamma(Aa)\bar{q}(A\bar{a}) + \gamma(A\bar{a})\bar{q}(Aa) \qquad (II\text{-}2\text{-}36)$$

where $q^G(Aa)$ is the initial population of orbital Aa, and $\bar{q}(Aa)$ is $1/2[q^G(Aa) + q^P(Aa)]$. Now if the $\gamma(Aa)$ of an orbital is zero, it would be unreasonable to attribute any of the coulombic promotion to it. More generally, it would appear sensible to attribute to orbital Aa the fraction $\gamma(Aa)\bar{q}(A\bar{a})/[\gamma(Aa)\bar{q}(A\bar{a}) + \gamma(A\bar{a})\bar{q}(Aa)]$ of the coulombic promotion energy between orbitals Aa and $A\bar{a}$.

Since the exchange part of the electronic interactions can be viewed as subtracting out the self-repulsions of the electrons, we partition it exactly like the coulombic part. Thus, we partition the total orbital-pair contributions by means of Eq. II-2-36. The resulting orbital promotion effects are given in Figure 4. Both the 2s and 2py orbitals suffer a decrease in electronic interaction energy during promotion, no doubt due to the fact that they both lose electrons thereby decreasing greatly their external and internal electronic interactions. For the same reason the 2pz orbital shows an even stronger rise in electronic interaction energy, in that it accepts the promoted electrons from the 2s and 2py orbitals. The 1s orbital also suffers a slight decrease in electronic interaction energy due to the loss of a very small fraction of its electronic population during promotion. The net result of hybridization promotion on the electronic interactions then is to increase them somewhat (4.5 ev), due to the shift of electrons into the 2pz orbital from the 2s and 2py orbitals. In a more general way the increase in energy may be viewed as resulting from the greater concentration of electronic charge along the z axis, as compared to the ground state in which the charge is symmetrically distributed in the y-z plane. This greater concentration results from the greater accumulation of charge in the 0$\ell$ and 0b orbitals, both of which have greater "internal" electronic interactions (which are the strongest type) than the 2s and 2p orbitals.

The essential conclusion to be drawn from the discussion of promotion is not the picture in terms of particular atomic orbitals, but the result that the promotion energy has two components: a small increase in the one-electron energy, seemingly connected with a pseudo-contractive effect, and a somewhat larger increase in the electronic repulsion energy, due to the slight compression of the valence electrons around the z-axis. It should be kept in mind that the numerical results may change considerably when contractive promotion is taken into account by the variation of the orbital exponents.

# III. IS THE SHIFT OF CHARGE INTO A BOND RESPONSIBLE FOR THE POTENTIAL ENERGY LOWERING DURING MOLECULE FORMATION?

## A. Introduction

The application of the analysis of binding energies, developed by Ruedenberg (24), to a number of molecules has led that author to suspect that the shift of electronic charge into the bond region, which is known to accompany chemical binding, may not be the principle factor in the lowering of potential energy during molecule formation. Here this analysis (24) is given for the binding energy of $H_2^+$. This is followed by a thorough examination of the potential energy effects of "the shift of charge into the bond region" in the case of $H_2^+$. The results indicate that, in this molecule at least, the lowering of potential energy upon bond formation is in fact caused primarily by a contraction of the electronic charge cloud around each of the two nuclei, and not by the shift of additional charge into the so-called "low potential" region between the nuclei.

The above investigations were carried out on the Dickenson wave function (8) for $H_2^+$. By allowing for polarization of the 1s orbitals through the admixture of 2pσ-type orbitals, this function is very nearly exact, giving a binding energy of 2.73 ev as compared to the exact value of 2.79 ev. It was decided to carry out the examination of "the potential energy effects of charge shifts" on this function, so as to avoid as much as possible any wrong interpretations which might result from a more approximate function.

## B. Analysis of the Binding Energy and the Shift of Charge into the Bond Due to Overlap

The analysis (24) begins by assuming hypothetically that the separated $H^{+\frac{1}{2}}$ ions (or the H atom, if the system is considered as $H + H^+$)[1] are promoted to certain "promoted states".[2] These are unique in that they represent as far as one can go in describing the actual condition of the $H^{+\frac{1}{2}}$ ions in the final molecule, without interatomic terms becoming involved. One then imagines that the two promoted $H^{+\frac{1}{2}}$ ions are brought together to the equilibrium internuclear separation, where they interact in a coulombic quasiclassical fashion, i.e., we compute their classical electrostatic interactions at this distance, considering that their charge distributions remain fixed at what they were when the ions were promoted, but separated. Finally, we imagine that the promoted $H^{+\frac{1}{2}}$ wave functions "interfere" to give the resultant molecular wave function. This interference is exactly analogous to that of classical waves, except that the requirement for a normalized resultant function results in an overall scaling down of the interfering functions when constructive interference occurs, and a similar scaling up when destructive interference occurs.

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[1] At large internuclear distances the wave function of the ground state of $H_2^+$ approaches that of a hydrogen atom 1s function on either of the two centers or any normalized linear combination of these. Since the symmetric linear combination corresponds most closely to the molecule, this is the limiting function which will be referred to here.

[2] These energy changes are just those of a singly occupied 1s orbital when its orbital exponent (effective nuclear charge) changes from unity to that of the 1s orbital of the Dickenson function.

The Dickenson function is the simple normalized sum of two normalized hybrid orbitals

$$\chi_A = N(1s_A + c2p\sigma_A), \text{ and } \chi_B = N(1s_B + c2p\sigma_B) \qquad \text{(III-1-1)}$$

on the two centers A and B respectively. Here N is their normalization constant. The polarization parameter (c) and the effective nuclear charges of the 1s and $2p\sigma$ orbitals are taken so as to give the best total molecular energy. The $2p\sigma$ orbital on each center is directed towards the other center.

The scheme of the above described analysis is seen to be immediately satisfied if we consider the $\chi_i$'s, each "occupied" with 1/2 electron, to represent the promoted $H^{+\frac{1}{2}}$ wave functions (or for the $H + H^+$ system, the promoted H atom represented by the singly occupied $\chi$). The orbital $\chi_i$ represents, i.e. is "occupied" by, 1/2 electronic charge if it is multiplied by $1/\sqrt{2}$, since then its square, which is its charge density, integrated over all space is 1/2.

For the $H_2^+$ molecule the electronic charge distribution is given by

$$\rho = |\psi|^2 = N^2\{\chi_A^2 + \chi_B^2 + 2\chi_A\chi_B\} \quad \text{with } N = \frac{1}{\sqrt{2(1 + S)}}$$

We have in effect partitioned $\rho$ into two parts:

$$\rho^P = \tfrac{1}{2}\chi_A^2 + \tfrac{1}{2}\chi_B^2$$

and

$$\rho^I = \rho - \rho^P = \frac{1}{1+S}\langle\chi_A\chi_B\rangle = \frac{1}{1+S}\{\chi_A\chi_B - \frac{S}{2}[\chi_A^2 + \chi_B^2]\}$$

The energies arising from the above described effects are given in Figure 6. It is seen that contractive promotion, computed by excluding the 2p orbital from the promoted state, results in a very strong rise in kinetic energy and a very strong drop in potential energy. This is as expected (24). The electronic charge is brought nearer the nuclei, and the curvature of the wave function also increases.

The deformation promotion, which reflects the effect of bringing the 2p function into the promoted state, is seen to give a very slight rise in kinetic energy and a small rise in potential energy. Since both the kinetic and nuclear attraction energy integrals between 1s and 2p orbitals on the same center vanish, these effects represent the changes in energy of the small amount of charge which is transferred into the 2p orbital during deformation. Thus the kinetic energies of both orbitals are nearly the same, (no doubt due to the fact that the two orbitals have about the same "size" and overall curvature) but the nuclear attraction energy of the 1s orbital is greater (as might be expected because the 2p orbital has a node at the nucleus).

The quasiclassical interactions give a small drop in potential energy, in contrast to the situation with a wave function made for s-type orbitals only (25). This is due to the polarizing effect of the 2p orbital on the promoted state charge density. Thus, the interaction of the nucleus of one center with the 1s2p dipole charge distribution of the other center is seen to be the attractive effect. The interactions with the 1s1s monopole and 2p2p quadrupole charge distributions (which, because their orbital parts contain nonvanishing electronic charge, include in both cases enough of the nuclear charge to form a neutral unit) are seen to be slightly repulsive.

The interference is seen to lower the kinetic energy strongly, and raise the potential energy somewhat. This is again as expected, since the constructive interference and its associated renormalization effect on the total wave function results in a shift of electronic charge from the regions near the nuclei to the central bond region. Thus electronic charge is moved to regions of higher potential energy, and lower kinetic energy. The kinetic energy contribution from a given point in space is proportional to the square of the gradient of the wave function, and this is very high near the nuclei as seen from Figure 7.

Thus, the present analysis fully confirms the findings and conclusions of Ruedenberg (24), namely that, in terms of atomic orbitals, the essential aspects of chemical binding must be described as an interplay between interference (lowering kinetic and raising potential energy) and contractive promotion (raising kinetic and lowering potential energy). This situation is not changed by the admixture of p-orbitals, i.e., when allowance is made for polarization of the atomic orbitals. Even though such polarization, predictably, leads to an attractive, i.e., negative, quasiclassical contribution to the bonding energy, these quasiclassical effects cannot replace the dominant effects of interference and contractive promotion.

Now, since the so-called overlap effects are associated with interference and not with promotion, it follows that the accumulation of charge in the bond due to overlap not only does not lower the potential energy but, in fact, is associated with an increase in potential energy. In view of this result, one may raise the question whether it would be possible to define the "accumulation of charge in the bond" in a different way and without reference to overlap, and whether any such definition could possibly lead to a lowering of the potential energy. This question will be considered in the subsequent section.

## C. Other Definitions of "Charge Shifted into the Bond" and Their Energy Effects

### 1. Partitioning of charge density based on symmetry

Three methods were tried for separating the effects of the two charge shifts, i.e. charge shifted into the bond and charge shifted toward the nuclei. The first starts with the statement that none of the charge lying along the internuclear axis, on the sides of the nuclei away from the center of the molecule, can possibly be considered to have been shifted there by a shift of charge into the bond region. In other words, while a considerable amount of charge may have been shifted from these "outside regions" into the bond, we do not expect that any appreciable charge has been shifted into them by any charge shift that can reasonably be called "a shift of charge into the bond region". It should be noted that this is a very generous definition of "charge shifted into the bond", since many more restrictive definitions could be made. On the other hand, to include any of the charge in these outside regions as "charge in the bond", would be almost tantamount to referring to the entire charge density of the molecule as "charge in the bond".

In view of the above, we therefore assume that any of the charge density along the "outside axes" must be charge which was there originally, or was shifted there by the clustering shift about the nuclei. Since the clustering charge shift by definition is spherically symmetric about each nucleus, we can now quantitatively separate the two charge shifts.[1]

When the potential energy effects associated with these two charge shifts are evaluated, it is found that the potential energy is lowered ~5.36 ev due to the clustering shift, while the shift of the charge into the bond lowers the potential energy only .63 ev. The interaction energy of a proton with an unperturbed hydrogen atom at the equilibrium internuclear distance is .75 ev.

Thus, we can hypothetically consider the formation of $H_2^+$ in terms of the following three steps:

(1) The $H^{+\frac{1}{2}}$ ions, each having one half electron in a hydrogen 1s orbital, approach each other unperturbed to the equilibrium internuclear separation. There is associated with this step an increase of .75 ev in potential energy. (This step can equally well be thought of, energy wise, as the approach of a proton to an unperturbed hydrogen atom.)

(2) There is a clustering of part of the charge density of each of the ions more closely about its nucleus. There is a drop in potential energy of 5.36 ev due to this process.

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[1] Mathematically, this partitioning is carried out by constructing a hypothetical electron density on each nucleus which is spherically symmetric and varies radially according to the charge density of the molecule along the "outside axes". Each of these "atomic" densities is the square of a hypothetical wave function composed of a linear combination of two 1s orbitals and a 2s orbital, all of the Slater type.

(3) There is a shift of another part of the charge into the bond regions, and away from the outlying regions of the molecule. The potential energy is lowered .63 ev due to this shift.

Steps (2) and (3) can be considered in either order, since they involve shifts of different parts of the charge density.

It is seen that the three changes in the potential energy sum to a lowering of 5.24 ev, which for the Dickenson function (8), is the total drop in potential energy on molecule formation.

It is of interest to consider also the kinetic energy changes associated with the three above steps. There is of course no kinetic energy change in step (1), due to the fact that the wave function remains that of a hydrogenic 1s orbital. Step (2) raises the kinetic energy 5.59 ev. Step (3) lowers the kinetic energy 3.07 ev.

## 2. A geometrical partitioning of the charge density

The second partitioning of the charge density was carried out in an attempt to analyze the situation from a somewhat different viewpoint. Here, the charge density of the final molecule was partitioned into two halves by a plane passing through the center of the molecule and perpendicular to the internuclear axis. The potential energy of each of the two halves in the field of its own nucleus, and also that of the other nucleus, were computed. It was found that the potential energy of each half was -16.31 ev in the field of its own nucleus, and -6.72 ev in the field of the other nucleus. Therefore the sum of the attractions of the nuclei for the electronic "half charges" opposite them is .17 ev less than the nuclear repulsion energy, which is $e^2/R_{AB} = e^2/2a_o = 13.60$ ev.

The meaning of the above partitioning can best be understood by hypothetically considering the charge density about each of the separated $H^{+\frac{1}{2}}$ ions to become distorted into the shape of the "half charge". This leads to a drop of 5.42 ev in potential energy. If the nuclei are now brought to their equilibrium position, the potential energy rises $\sim$.17 ev. If the charge distributions of the separated $H^{+\frac{1}{2}}$ ions had not been distorted, and the nuclei brought to the equilibrium position, the rise in potential energy would have been $\sim$.75 ev, as was mentioned above. We see then that the distortion of the charge distributions gives a much larger drop in "intra-atomic" potential energy than "interatomic".

It is interesting that in both the foregoing charge density partitionings, the lowering of the potential energy due to "intra-atomic" effects is$\sim$5.4 ev and that due to "interatomic" effects is$\sim$.6 ev.

### 3. Partitionings based on hypothetical wave functions

A still different approach can be taken by constructing a hypothetical normalized wave function of the Dickenson type which has the value of the Dickenson function at the midpoint between the nuclei, but the values of the $H^{+\frac{1}{2}}$ 1s wave functions at each nucleus. This wave function gives rise to an electronic charge density which resembles closely that of the molecule in the bond region, but near the nuclei resembles that of the separated ions. The potential energy corresponding to this wave function should therefore, by its difference from that of the true function, tell us something about the potential energy lowering due to the build up of the charge in the bond.

It is found that the potential energy for this hypothetical wave function is -29.16 ev, i.e., 1.95 ev less than that of a hydrogen atom. Since the rise in potential energy due to bringing the two $H^{+\frac{1}{2}}$ unperturbed ions to the molecular internuclear distance is .75 ev, we see that the lowering of potential energy due to the shift of charge into the bond (as defined by this method) is 2.70 ev. This is about half the total drop in potential energy on molecule formation, and is therefore considerably higher than the estimates of the previous two definitions.

The underlying reason for this large estimate is no doubt due to the fact that, by building up the charge in the center between the nuclei to what it would be in the final molecule, we have also included some charge which is shifted there by the radial shift toward the nuclei. This is due to the fact that even in an isolated H atom, if we increase the effective nuclear charge so as to "pull in" the charge cloud, we will build up the charge density for some distance out from the nucleus. Actually in this case the clustering shift itself builds up the charge density somewhat in the center of the bond. Also the charge shift into the bond would no doubt take some charge from the very low potential regions near the nuclei, which we have not allowed for here. Thus, this definition of "the charge shifted into the bond" probably does not include all the "charge shifted into the bond", and definitely includes "charge shifted toward the nuclei", which it should not.

Benjamin Gimarc of John Hopkins University suggested to the author that the opposite situation also be examined. Here a wave function was constructed such that it had the electronic charge density of the molecule at the nuclei. At the midpoint of the bond it had the value of the super-

Figure 6. Quantitative partitioning of the binding energy of $H_2^+$ (Dickinson Calculation)

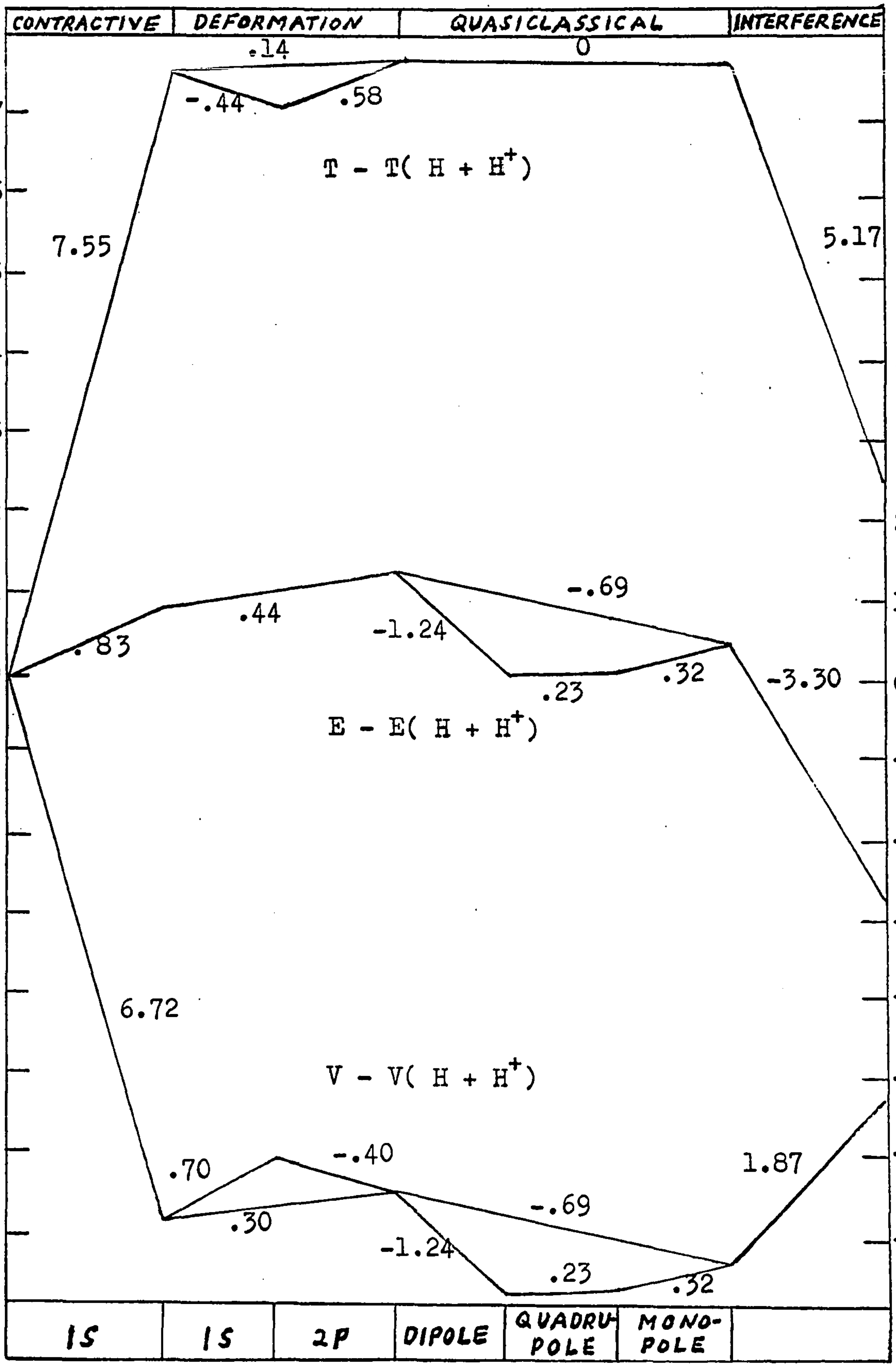
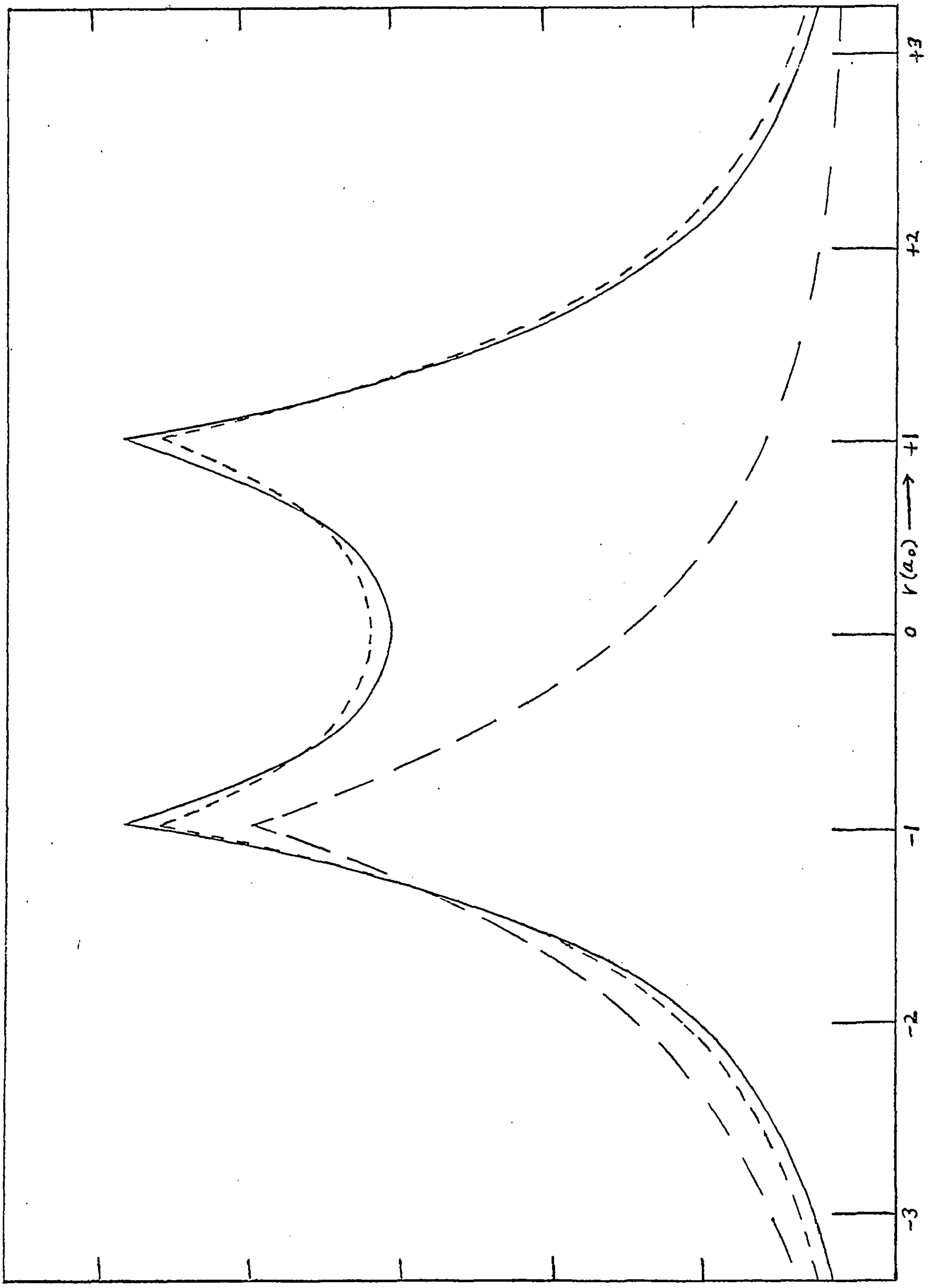

CONTRACTIVE
DEFORMATION
QUASICLASSICAL
INTERFERENCE
.14
0
-.44
.58
T - T( H + H$^+$)
7.55
5.17
-.69
.44
-1.24
.83
.32
.23
-3.30
E - E( H + H$^+$)
6.72
V - V( H + H$^+$)
.70
-.40
1.87
-.69
.30
-1.24
.23
.32
1S
1S
2P
DIPOLE
QUADRUPOLE
MONOPOLE
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7

Figure 7. Graphs of the Dickinson function for $H_2^+$ (———), the exact function for $H_2^+$ (-----), and the $1/\sqrt{2}\cdot 1s$ function for the H atom (— — —).


0.5
0.4
0.3
0.2
0.1
$\psi \cdot a_0^{3/2}$
-3
-2
-1
0
$r(a_0)$
+1
+2
+3

position of two $H^{+\frac{1}{2}}$ charge densities. This function was found to have a potential energy 2.67 ev lower than that of the hydrogen atom, so that this charge shift results in a total lowering in potential energy of 2.67 + .75 = 3.42 ev.

## 4. Conclusions

If the orbital exponent (i.e., the effective nuclear charge in the case of n=1 orbitals) of a hydrogen 1s orbital is increased from 1 to 1.25, the potential energy drops 6.8 ev, due to the closer clustering of the electronic charge about the nucleus. In the approximate wave functions for $H_2^+$ (in particular for the very accurate Dickenson function used here) built from atomic orbitals, the orbital exponents are around 1.25. In view then of the fact that one does not expect too different a behavior of the potential energy of $H_2^+$, as compared to that of a H atom, when the orbital exponents increase from 1 to 1.25, it should not be surprising that 5 to 6 ev of the lowering of the potential energy must be attributed to clustering.

# IV. LOCALIZED ATOMIC AND MOLECULAR ORBITALS

## A. Introduction

V. Fock (10) pointed out that a one-determinant many-electron wave function is invariant with respect to unitary transformations among its molecular orbitals. It is completely determined by the finite-dimensional function space spanned by these orbitals and does not depend on the basis chosen within this space. In particular, the orbitals resulting from the Hartree-Fock equations represent only one of the many possible unitary bases in the self-consistent-field space, defined by the minimization of the energy integral. While they seem to be convenient for describing spectral transitions and ionization potentials, it appears likely that for an analysis of the intrinsic properties of a particular state, for example the ground state, another unitary basis in the self-consistent-field space may be more effective.

This fact was used by C. A. Coulson (7) who, in discussing the dipole moment of the C-H bond, transformed the symmetry molecular orbitals of methane into localized molecular orbitals along the four bonds, which he called equivalent molecular orbitals. Later, the possibility of constructing equivalent orbitals in the presence of a general symmetry group was systematically analyzed by J. E. Lennard-Jones (13, 14 and 15). Whereas the Hartree-Fock orbitals belong to irreducible representations (as long as the Hartree-Fock operator is invariant), the equivalent orbitals span reducible representations: certain symmetry operations transform one equivalent orbital into another.

J. E. Lennard-Jones and J. A. Pople (14) pointed out that the equivalent orbitals presumably maximize the sum of the orbital self-repulsion terms in the electronic interaction energy and therefore minimize the "non-classical" off-diagonal exchange terms. Because of this property they can be considered as that unitary orbital basis in the self-consistent-field space which exhibits maximum "localization". This characterization is of interest, because it furnishes a criterion which is applicable beyond the scope of the equivalent orbitals, namely within one symmetry species as well as in the absence of any symmetry.[1]

Finally J. E. Lennard-Jones and J. A. Pople (15) also suggested that such localized orbitals might be the most suitable ones for extending the wave function to take into account correlation. For, it seems reasonable to expect that they would exhibit a minimum of interorbital correlation, so that intra-orbital correlation would remain the essential correction (20). Thus A. Hurley, J. E. Lennard-Jones, and J. A. Pople (11) proposed to replace each doubly filled localized molecular orbital by a pair function.

In view of this interest in localized orbitals it is remarkable that no attempts have been made to develop a method for finding them without the help of symmetry. There seems to prevail an opinion that considerable difficulties stand in the way. S. F. Boys (3) has suggested to approximate such orbitals by what he terms "exclusive orbitals". They are

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[1] That maximum localization might be an appropriate criterion in these cases, was first conjectured by J. E. Lennard-Jones and J. A. Pople (14). Thereafter the idea seems to have gained more and more ground.

obtained by maximizing the product of the distances between the centroids of charge of all molecular orbitals, a non-linear process carried out by consecutive iterations. There are cases however where the procedure is impossible as, for example, between various s-orbitals on one atom. Another kind of localized molecular orbital was considered by Ruedenberg (24) who defined "valence molecular orbitals" by extremizing the total overlap population of the individual molecular orbitals. The method, which involves solution of an eigenvalue problem, is again not completely general, inasmuch as it does not apply within an isolated atom.

Here we describe an exact method for finding those molecular orbitals which maximize the sum of the orbital self-repulsion energies. While the process is iterative, its execution is very similar, in method as well as complexity, to the solution of an eigenvalue problem by Jacobi's method. We propose that the name "localized molecular orbitals (LMO's)" be used for these orbitals. Only in the presence of a symmetry group can they acquire properties which, under certain conditions, cause them to become equivalent orbitals.

## B. Definition of Localized Orbitals

We consider the case of a determinantal wave function of 2N electrons with N doubly occupied orthonormal orbitals $\psi_1 \psi_2 \ldots \psi_N$, viz.,

$$\Phi = \mathcal{A} \left\{ (\psi_1 \alpha)^{(1)} \; (\psi_1 \beta)^{(2)} \ldots . \; (\psi_N \alpha)^{(2N-1)} \; (\psi_N \beta)^{(2N)} \right\}$$

(IV-2-1)

as determined by a self-consistent-field calculation. Actually, the orbitals are not uniquely determined by $\Phi$; any unitary transformation between them will leave the wave function invariant and we must say that $\Phi$ is associated with the N-dimensional linear space subtended by $\psi_1 \ldots \psi_N$.

The electron interaction energy of $\Phi$ can be written

$$EI = (\Phi | \sum_{i<j} r_{ij}^{-1} | \Phi) = C - X \quad , \tag{IV-2-2}$$

$$C = \frac{1}{2}\int dV_1 \int dV_2 r_{12}^{-1} \rho(1) \rho(2) \quad ,$$

$$= 2\sum_n \sum_m [\psi_n^2 | \psi_m^2] \quad , \tag{IV-2-3}$$

$$X = \frac{1}{4}\int dV_1 \int dV_2 \, r_{12}^{-1} \rho^2(1|2) \quad ,$$

$$= \sum_n \sum_m [\psi_n \psi_m | \psi_n \psi_m] \quad , \tag{IV-2-4}$$

where

$$\rho(1|2) = \sum_n \psi_n(1) \psi_n^*(2) \quad , \tag{IV-2-5}$$

$$\rho(1) = \rho(1|1) \quad , \tag{IV-2-6}$$

$$[f|g] = \int dV_1 \int dV_2 \, f(1) \, g(2)/r_{12} \quad . \tag{IV-2-7}$$

Since EI depends only upon $\Phi$, it is of course invariant against unitary transformations among the $\psi$'s. More specifically, however, the density kernel $\rho(1|2)$ is invariant under such transformations, and so are therefore the "Coulomb term" C and the "Exchange term" X, separately.

Such is not the case however for the sum of the diagonal terms

$$D(\psi) = \sum_n [\psi_n^2|\psi_n^2] \quad , \tag{IV-2-8}$$

which occurs in C as well as in X. It is therefore a meaningful question to ask for that orthonormal basis $\lambda_1\lambda_2\ldots\lambda_N$ in the space spanned by $\psi_1\psi_2\cdots\psi_N$ which maximizes $D(\psi)$ i.e., given the basis $\psi_1\ldots\psi_N$, find a unitary transformation

$$\lambda_\nu(x) = \sum_n \psi_n(x)\, T_{n\nu} \quad , \tag{IV-2-9}$$

such that

$$D(\lambda) = \sum_\nu [\lambda_\nu^{\;2}|\lambda_\nu^{\;2}] \tag{IV-2-10}$$

is maximum.

The following remarks can be made regarding the orbitals $\lambda_1\ldots\lambda_N$.

Since $D(\psi)$ can obviously be considered as a measure of the "overall localization" of the basis set $\psi_1\ldots\psi_N$, the $\lambda_1\ldots\lambda_N$ represent, in the given linear space, that orthonormal basis which exhibits "maximum localization". They will be called localized orbitals.

Because of the invariance of C and X under unitary transformations, maximization of D implies minimization of

$$C' = \sum_{\nu\neq\mu} [\lambda_\nu^2|\lambda_\mu^2] \quad , \tag{IV-2-11}$$

and

$$X' = \sum_{\nu \neq \mu} [\lambda_\nu \lambda_\mu | \lambda_\nu \lambda_\mu] \quad . \qquad \text{(IV-2-12)}$$

The expression C' represents the total of all inter-orbital repulsions, and the quantity X' can be considered as the total of the self-energies of all overlap-charge-distributions $(\psi_i \psi_j)$. These minimum properties indicate that, in going beyond the SCF approximations, one is likely to find the smallest correlation correction between different orbitals, if one chooses the $(\lambda_1 \lambda_2 \ldots \lambda_N)$as starting point.

If it should happen that the minimum X' vanishes identically, then this would mean that these localized orbitals have the properties of orthogonal Hartree orbitals (as opposed to Hartree-Fock orbitals).[1,2] Thus, the localized orbitals $\lambda_1 \lambda_2 \ldots \lambda_N$ are those basis orbitals in the self-consistent- field space which approach most closely the behavior postulated for the Hartree orbitals.

The localized orbitals provide a quantitative basis for the qualita-

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[1] As "orthogonal Hartree orbitals" we define those orbitals which minimize the energy of a Hartree product of orthogonal orbitals. The resulting equations differ from the Hartree equations by having off-diagonal Lagrangian multipliers $\lambda_{ij}$. It can be shown that orbitals which satisfy these modified Hartree equations also satisfy the condition of Eq. IV-3-14, and hence represent the localized orbital basis in their function space (which is of course not identical with the Hartree-Fock space).

[2] Hartree's functions satisfy the equations which result by discarding the off-diagonal $\lambda_{ij}$ mentioned in the previous footnote. This introduces some non-orthogonality. But frequently, the Hartree functions and the orthogonal Hartree functions are not too different. Both exhibit localized character. This localized character is entirely lost however, if one introduces into the Hartree equations the common additional averaging process over the electron-interaction potential. Under these conditions, one obtains nonlocalized symmetry orbitals.

tive chemical concepts of "localized electrons" and "delocalized electrons". Since it is always possible to construct a delocalized orbital basis from a localized orbital basis by a unitary transformation, it is obviously easy to choose many delocalized bases in a given SCF space. In order to see to which degree electrons act as localized units, one has to determine to which degree the SCF orbitals of maximal localization are restricted to certain parts of space.

## C. Determination of the Localized Orbitals

### 1. Orbital pair case

For a pair of orbitals it is not difficult to find the proper localization transformation. Thus, letting

$$\begin{aligned} u_1(x) &= \cos\gamma\,\psi_1(x) + \sin\gamma\,\psi_2(x) \\ u_2(x) &= -\sin\gamma\,\psi_1(x) + \cos\gamma\,\psi_2(x) \end{aligned} \qquad \text{(IV-3-1)}$$

we have a general orthogonal transformation of $\psi_1(x)$ and $\psi_2(x)$ into $u_1(x)$ and $u_2(x)$. Then

$$\begin{aligned} (u_1u_2|u_1u_2) &= 1/4\ \sin^2 2\gamma(A_{12}) + 1/2\ \sin 4\gamma(B_{12}) \\ &\quad + \cos^2 2\ (\psi_1\psi_2|\psi_1\psi_2)\ , \end{aligned} \qquad \text{(IV-3-2)}$$

where

$$\begin{aligned} A_{12} &= (\psi_1\psi_2|\psi_1\psi_2) - 1/4\ ((\psi_1^2|\psi_1^2) \\ &\quad + (\psi_2^2|\psi_2^2) - 2(\psi_1^2|\psi_2^2)) \end{aligned} \qquad \text{(IV-3-3)}$$

and

$$B_{12} = (\Psi_1^2|\Psi_1\Psi_2) - (\Psi_2^2|\Psi_1\Psi_2) \quad . \tag{IV-3-4}$$

However, because the exchange energy is invariant,

$$(u_1^2u_1^2) + (u_2^2u_2^2) + 2(u_1u_2\ u_1u_2) = (\Psi_1^2|\Psi_1^2) + (\Psi_2^2|\Psi_2^2) + 2(\Psi_1\Psi_2|\Psi_1\Psi_2) \quad . \tag{IV-3-5}$$

This relation holds also for any two orbitals of a set of N orbitals (see footnote in next section). Thus,

$$D(u) = D(\Psi) + A_{12} - A_{12}\cos 4\gamma + B_{12}\sin 4\gamma \quad , \tag{IV-3-6}$$

where

$$D(u) = (u_1^2|u_1^2) + (u_2^2|u_2^2) \tag{IV-3-7}$$

and

$$D(\Psi) = (\Psi_1^2|\Psi_1^2) + (\Psi_2^2|\Psi_2^2) \tag{IV-3-8}$$

Thus, if we define some angle $\alpha$ by

$$\sin 4\alpha = B_{12}/\sqrt{A_{12}^2 + B_{12}^2} \tag{IV-3-9}$$

$$\cos 4\alpha = -A_{12}/\sqrt{A_{12}^2 + B_{12}^2} \quad , \tag{IV-3-10}$$

we have

$$D(u) = D(\Psi) + A_{12} + \sqrt{A_{12}^2 + B_{12}^2}\cos 4(\gamma - \alpha) \quad . \tag{IV-3-11}$$

Further, using Eq. IV-3-5 again, we have

$$(u_1u_2|u_1u_2) = (\Psi_1\Psi_2|\Psi_1\Psi_2) - (1/2)\,A_{12} - (1/2)\sqrt{A_{12}^2 + B_{12}^2}\ .$$

(IV-3-13)

From Eqs. IV-3-9 and IV-3-10 we have

$$\tan 4\alpha = -B_{12}/A_{12}\ ,$$

a result which can also be obtained by differentiating Eq. IV-3-2, setting the result equal to zero, and $\gamma$ equal to $\alpha$.

When $\gamma = \alpha + \pi n/2$ for n = 0,1,2,3, etc., it is seen that D(u) is maximum and $(u_1u_2|u_1u_2)$ is minimum. Also when $\gamma = \alpha + \pi\ n/4$ for n = 1,3,5, etc., D(u) is minimum and $(u_1u_2|u_1u_2)$ is maximum.

One can take the transformation to the localized orbitals to be $\gamma = \alpha$, the other angles, for D(u) a maximum, differing from it by corresponding to a change in sign of $u_1$ and/or $u_2$.

It should be noted that $\tan 4\alpha$ is zero for $\alpha = 0, \pi/4$, etc., so that if we take $\alpha = 0°$, then $B_{12}$ is zero and D(u) is at an extrema. Thus for the extrema

$$(u_1u_2|u_1^2) - (u_1u_2|u_2^2) = 0 \qquad \text{(IV-3-14)}$$

## 2. N-orbitals case

For the case of three or more orbitals, the use of an analytic technique, similar to that used in the preceding section, appears to be too complex. Therefore, some iterative technique is implied. One might attempt various types of steepest descent methods to "feel" the way to that transformation which minimizes the exchange integrals between orbitals. The method which is used here consists of successively applying the above described pair transformation to the various pairs of orbitals. This iterative procedure is very similar to Jacobi's diagonalization procedure, which is known to be one of the fastest methods for diagonalization.

Each stage of the iteration method consists of the following two steps.

Find that pair $\psi_i, \psi_j$ (among all pairs of $\psi_n \psi_m$) which, upon 2x2 maximization of D will yield the greatest increase in D. According to Eq. IV-3-6, this is that pair $\psi_i \psi_j$ for which

$$D_{max}(u_i u_j) - D(\psi_i \psi_j) = A_{ij} + \sqrt{A_{ij}^2 + B_{ij}^2} \qquad \text{(IV-3-15)}$$

is the largest, $A_{ij}$ and $B_{ij}$ being defined by Eqs. IV-3-3 and IV-3-4.

Find the corresponding transformation IV-3-1, and thus two new orbitals $\psi_i', \psi_j'$ which now replace the previous orbitals $\psi_i \psi_j$.

Writing the total sum in the form

$$D(\psi) = \sum_{n \neq i,j} [\psi_n^2 | \psi_n^2] + [\psi_i^2 | \psi_i^2] + [\psi_j^2 | \psi_j^2] \quad , \qquad \text{(IV-3-16)}$$

one recognizes that replacing $\psi_i, \psi_j$ by $\psi_i', \psi_j'$ will increase the last two terms, but leave the first (N - 2) terms unchanged.[1] Thus, each iteration consists of performing that 2x2 orthogonal transformation which guarantees the maximum increase in the total D($\psi$). Convergence is achieved, when all $\frac{1}{2}N(N - 1)$ quantities of Eq. IV-3-15 are smaller than the prescribed convergence criterion, e.g., the numerical accuracy of the calculation.

## D. Localization between 1s and 2s Orbitals

As illustration we apply the procedure to a case which has been unaccessible to previous approximate methods, namely the construction of localized orbitals from the 1s Slater orbital and the 2s Slater orbital in oxygen.

These Slater orbitals are

$$(1s) = \sqrt{(\zeta^3/\pi)}\; e^{-\zeta_1 r} \;, \quad \zeta_1 = 7.7 \;, \qquad \text{(IV-4-1)}$$

$$(2s) = \sqrt{(\zeta_2^5/3\pi)}\; r e^{-\zeta_2 r} \;, \quad \zeta_2 = 2.275 \;.$$

The conventional orthogonal orbitals are those obtained by Schmidt

---

[1] It is also easily seen that the sums

$$\sum_{\substack{n<m \\ n,m\neq ij}} [\psi_n \psi_m | \psi_n \psi_m]$$

and

$$\sum_{n\neq i,j} [\psi_n \psi_i | \psi_n \psi_i] + [\psi_n \psi_j | \psi_n \psi_j]$$

remain invariant. Hence, the change in the sum of all exchange integrals is equal to the change in $[\psi_i \psi_j | \psi_i \psi_j]$ alone.

orthogonalization, viz.,

$$(1s^o) = 1s \quad ,$$
$$(2s^o) = [(2s) - S\,(1s)]/\sqrt{1-S^2} \quad ,$$
$$(2s^o) = -0.24008(1s) + 1.02842(2s) \quad . \qquad \text{(IV-4-2)}$$

They give rise to the exchange integral

$$[1s^o2s^o|1s^o2s^o] = 0.0703(e^2/a) = 1.91 \text{ ev.} \qquad \text{(IV-4-3)}$$

If they are chosen as the basis orbitals ($\psi_1, \psi_2$) for the construction of an arbitrary orthogonal basis ($u_1, u_2$) according to Eq. IV-3-1, then the variation of the exchange integral with the transformation angle $\gamma$, as given by Eq. IV-3-12, becomes (in atomic units, $e^2/a$)

$$[u_1u_2|u_1u_2] = 0.4539 - 0.4401 \cos 4(\gamma + 7^o20.5') \quad . \qquad \text{(IV-4-4)}$$

From this equation follows that the localized orbitals result for $\gamma = -7^o20.5'$. Expressed in terms of the original Slater orbitals, they become

$$\text{Inner orbital} = is = \lambda_1 = 1.02248(1s) - 0.13142(2s) \quad ,$$
$$\text{Outer orbital} = os = \lambda_2 = -0.110322(1s) + 1.01998(2s) \quad . \qquad \text{(IV-4-5)}$$

Their exchange integral is

$$[is\ os|is\ os] = 0.0138(e^2/a) = 0.376 \text{ ev.} \qquad \text{(IV-4-6)}$$

so that localization has reduced the exchange integral by more than a factor 5.

It is of interest that those orthogonal orbitals which result from "symmetric orthogonalization", as proposed by P. O. Lowdin (16), are very close to the localized orbitals. In terms of the original Slater orbitals, they are

$$\begin{aligned} (1s^L) &= a(1s) + b(2s) \quad , \\ (2s^L) &= b(1s) + a(2s) \quad , \\ 2a &= (1 + S)^{-\frac{1}{2}} + (1 - S)^{-\frac{1}{2}} \quad , \\ 2b &= (1 + S)^{-\frac{1}{2}} - (1 - S)^{-\frac{1}{2}} \quad . \end{aligned}$$

Hence

$$\begin{aligned} (1s^L) &= 1.02129(1s) - 0.12088(2s) \quad , \\ (2s^L) &= -0.12088(1s) + 1.02129(2s) \quad , \qquad \text{(IV-4-7)} \end{aligned}$$

which corresponds to a value of $\gamma = -6^{\circ}45'$ in terms of Eq. IV-4-4. Their exchange integral

$$[1s^L 2s^L | 1s^L 2s^L] = 0.0141(e^2/a) = 0.384 \text{ ev} \quad , \qquad \text{(IV-4-8)}$$

is only 0.008 ev larger than that of the localized orbitals. Since the Lowdin orbitals represent that set of orbitals which "differs least", in the sense defined by Carlson and Keller (4), from the non-orthogonal Slater orbitals (Eq. IV-4-1), it is remarkable that the latter have a considerably larger exchange integral, namely

$$[1s2s | 1s2s] = 0.1246(e^2/a) = 3.39 \text{ ev.} \qquad \text{(IV-4-9)}$$

Finally, Eq. IV-4-4 shows that minimal localization (maximal delocalization) is reached for $\gamma = 37^{\circ}39.5'$, at which point the exchange integral assumes the maximal value

$$[u_1u_2|u_1u_2]_{max} = 0.8940(e^2/a) = 24.3 \text{ ev} \quad . \qquad \text{(IV-4-10)}$$

## E. Discussion

It can be seen that the low exchange integral for the localized orbitals (is), (os) comes about because the 1s orbital is somewhat contracted towards the nucleus and, more important, because the inner loop of the 2s orbital is concomitantly attenuated. In view of this observation one is led to expect that, in case of sp, $sp^2$ or $sp^3$ hybridization, the exchange integral between different (2s-2p) hybrid orbitals will be further reduced if the (1s) orbital is also included in the localization process. For, in that case the (2s-2p) hybrids would get some 1s admixture which would attenuate all of them in the region where they overlap each other.

As mentioned before, the localized orbitals are those for which inter-orbital correlation is expected to be smallest. That it is possible to reduce the inter-orbital correlation to a small value is made likely by the results found by Allen and Shull in Be (2). Their results suggest that Watson's very accurate configuration interaction function can be closely reproduced from two separate pair functions. The relation to localized orbitals is being investigated at present.

These results have some bearing on the concept of "inner shells" in a many-electron atom, where a unitary transformation between the orbitals is arbitrary. There is no reason why Schmidt orthogonalization should define the various "shells". It seems to us that, within one symmetry, the localized orbitals correspond much more closely to the concept of inner and outer shells.

This definition of inner shells finds further support in the observation that there seems to be evidence that the localized inner shell orbitals (is) of an atom may mix very little with the valence orbitals in the molecule. Thus, in an analysis of the $H_2O$ calculation of Ellison and Shull (9) we were led to define certain "valence atomic orbitals"

$$
\begin{aligned}
(is^{v}) &= 1.02265(1s) - 0.14809(2s) + \sim 0.05(2p\sigma) \quad , \\
(os^{v}) &= -0.0469143(1s) + 0.843313(2s) + \sim 0.5(2p\sigma) \quad , \qquad \text{(IV-5-1)}
\end{aligned}
$$

from the molecular wave function. The inner valence atomic $is^{v}$, which is seen to be very similar to the inner localized atomic orbital (is) of Eq. IV-4-5, was found to mix very little into the valence molecular orbitals. This behavior is in strong contrast to that of the Schmidt-orthogonalized inner shell, i.e. the Slater 1s orbital. [The exchange integral between $1s^{v}$ and $os^{v}$ is $0.0219(e^2/a) = 0.595$ ev.]

While the foregoing conclusions have been made on the basis of the oxygen Slater orbitals, we believe that similar results will emerge when the Hartree-Fock orbitals are considered. This conjecture is based on a comparison of the electron interaction integrals in the two cases. One finds (26) (in atomic units, $e^2/a$)

| | Hartree-Fock | Slater |
|---|---|---|
| $[1s1s\|1s1s]$ | 4.7421 | 4.8125 |
| $[1s1s\|2s2s]$ | 1.1331 | 1.1334 |
| $[2s2s\|2s2s]$ | 0.7974 | 0.8039 |
| $[1s2s\|1s2s]$ | 0.0767 | 0.0703 |

In particular the similarity in the value of the exchange integrals [1s2s|1s2s] makes it likely, that localization of the Hartree-Fock orbitals would yield a lowering of the exchange integral similar to that found for the Slater orbitals.

The localization transformation has been applied also to the 1s and 2s (orthogonal) Slater orbitals of Be. This involves a rotation of about 5°, and the resulting localized 2s orbital is graphed in Figure 9. There we have also graphed the Slater and SCF 2s orbitals for Be.

## F. Localization between 2s, 2px, 2py Orbitals

From Eq. IV-3-14 it is clear that localization of the atomic orbitals 2s, 2px, and 2py will lead to the trigonal hybrids t1, t2, and t3

$$tk = (1/3)^{\frac{1}{2}}\ 2s + (2/3)^{\frac{1}{2}}\ pk, \qquad \text{(IV-6-1)}$$

where p1, p2, p3 are the three 2p orbitals yielding pairwise the inner product

$$\int pj(x)\ pk(x)\ dV = -1/2 \quad , (j \neq k) \qquad \text{(IV-6-2)}$$

for example

$$\begin{aligned} p1 &= 2px, \\ p2 &= -1/2\ (2px) + \quad 3/2\ (2py) \quad , \\ p3 &= -1/2\ (2px) - \quad 3/2\ (2py) \quad . \end{aligned} \qquad \text{(IV-6-3)}$$

The orbital triple (2s), (2px), and (2py) presents therefore a convenient case with known solutions, where our iteration procedure can be tested.

A machine program was applied to the orthogonal Slater orbitals of oxygen and the results are exhibited in Figure 8. The following observations are of interest:

Although the increasing error in the invariant total exchange energy X indicates that, after about fifteen iterations, the calculation is becoming unreliable in the sixth decimal, the individual integrals as well as the localized orbitals themselves nevertheless improve consistently up to the thirty-first iteration;

The improvement in $D(\lambda)$ due to the last pair transformation is always smaller than the total defect in $D(\lambda)$;

The total defect in $D(\lambda)$ is always considerably smaller than the maximal absolute deviations in the individual integrals;

The deviations in the individual integrals are always smaller than the maximal deviation in the localization criterion $B_{12}$.

The last observation is particularly gratifying, if it can be assumed to hold generally true. For, in problems where the answer is unknown, the quantities $B_{ij}$ are the only ones which can be calculated to test the quality of the localization. It is encouraging that they seem to provide an upper bound for the deviations of the individual integrals. It is questionable whether the number of iterations found necessary here is typical. Our particular case possibly shows a slower than average convergence, since the indeterminacy in the p-orbitals may favor evasive oscillations from iteration to iteration.

| Number of Iterations | n = ∞ | n = 0 | n = 3 | n = 8 | n = 13 | n = 18 | n = 24 | n = 31 |
|---|---|---|---|---|---|---|---|---|
| | Exact Value | Deviations from Exact Value after n Pair Transformations | | | | | | |
| $[\lambda_1\lambda_2\|\lambda_1\lambda_2]$ | 0.062323 | .112615 | .001792 | .000227 | .000055 | .000014 | .000014 | .000003 |
| $[\lambda_1\lambda_3\|\lambda_1\lambda_3]$ | 0.062323 | .112615 | .001792 | .000227 | -.000110 | -.000027 | -.000007 | -.000007 |
| $[\lambda_2\lambda_3\|\lambda_2\lambda_3]$ | 0.062323 | -.014335 | .009597 | -.000442 | .000055 | .000014 | -.000007 | .000003 |
| $[\lambda_1\lambda_1\|\lambda_1\lambda_1]$ | 1.002199 | -.198288 | .003152 | -.000665 | .000080 | .000020 | -.000011 | .000004 |
| $[\lambda_2\lambda_2\|\lambda_2\lambda_2]$ | 1.002199 | -.111750 | -.014757 | .000319 | -.000163 | -.000041 | -.000011 | -.000011 |
| $[\lambda_3\lambda_3\|\lambda_3\lambda_3]$ | 1.002199 | -.111750 | -.014757 | .000319 | .000080 | .000020 | .000020 | .000004 |
| $B_{12}$ | 0 | 0 | -.055922 | .001641 | -.000411 | .000103 | .000000 | .000026 |
| $B_{13}$ | 0 | 0 | -.055922 | .001641 | -.000000 | .000000 | .000051 | .000000 |
| $B_{23}$ | 0 | 0 | .000000 | .000000 | .000411 | .000103 | .000051 | -.000026 |
| $D(\lambda)$ | 3.006597 | -.421789 | -.026362 | -.000027 | -.000003 | -.000002 | -.000003 | -.000003 |
| X | 3.380538 | 0 | 0 | .000001 | .000002 | .000002 | .000003 | .000004 |

Figure 8. Results for the trigonal hybridization of the 2s, 2px and 2py Slater orbitals of the Oxygen atom.

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| $(\lambda_1 \vert 2s)$ [a] | 0.57735 | .42265 | .12976 | -.00453 | +.00056 | .00014 | -.00007 | .00004 |
| $(\lambda_2 \vert 2s)$ | 0.57735 | -.57735 | .27735 | .00225 | -.00113 | -.00028 | -.00007 | -.00007 |
| $(\lambda_3 \vert 2s)$ | 0.57735 | -.57735 | .27735 | .00225 | .00056 | .00014 | .00014 | .00004 |
|  | Improvement in D(λ) due to Last Pair Transformation [b] |  |  |  |  |  |  |  |
| $\Delta^n D(\lambda)$ | ——— | ——— | .03954271 | .00000965 | .00000060 | .00000003 | .00000001 | .00000000 |

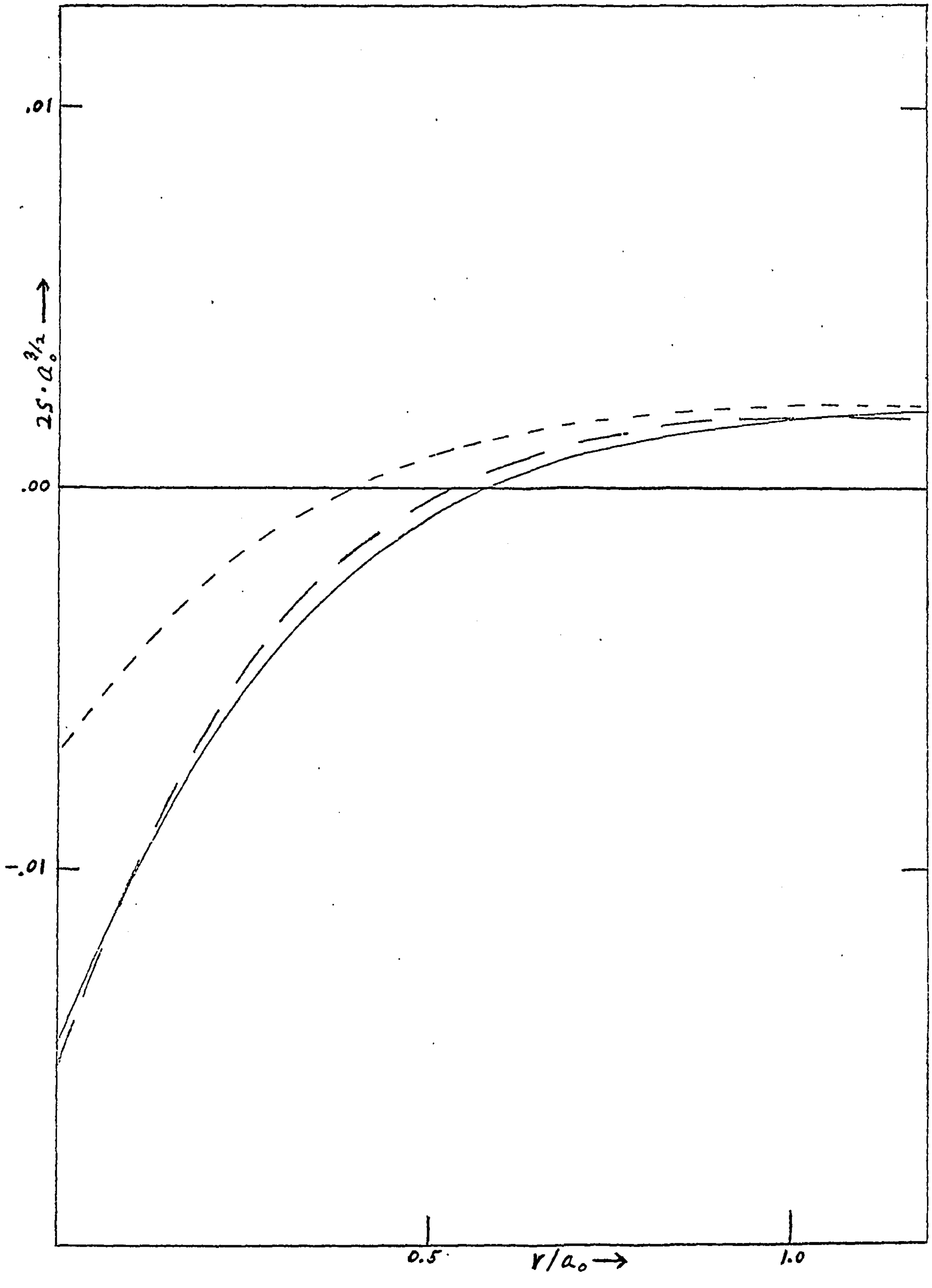
---

[a] Overlap integrals indicating the amount of s-character in the trigonal hybrids and, hence, characterizing the basis transformation.

[b] Test parameter determining the interruption of the iterative cycle.

Figure 8 (Continued)

Figure 9. Graphs, along a radial vector, of the best-atom (———), SCF (— — —), and best-atom localized (-----) 2s orbitals for the Be atom.


.01
.00
-.01
$2S \cdot a_0^{3/2} \longrightarrow$
0.5
$r/a_0 \longrightarrow$
1.0

## G. Localized Molecular Orbitals

### 1. Introduction

Optimally localized molecular orbitals (LMO's) have been found for a number of small diatomic molecules using the method outlined in the preceding sections. All these molecules contain only atoms from the first two rows of the periodic table. The SCF wave functions used were found by Ransil (21). They are of the LCAO-MO (linear combinations of atomic orbitals-molecular orbitals) type (22), and minimal basis set functions; i.e., usually only enough Slater atomic orbitals from each atom have been used as are necessary to describe these atoms in the free state. This restriction results in less than exact SCF molecular orbitals, but the deviation is not too great as can be seen from Figures 10, 11, and 12, in the case of the HF molecule. The basis atomic orbitals are the much used Slater 1s, 2s', and 2p orbitals (26). We have Schmidt orthogonalized the Slater 2s' orbital to the 1s orbital (which results in no real change in the basis set, since the new 2s orbital equals $(2s' - S\ 1s)/\sqrt{(1-S^2)}$, where S is the overlap integral $\int 1s\ 2s'\ d\tau$ between the Slater orbitals). The 2s orbital is quite similar to the SCF atomic orbitals of the free atom, as can be seen from Figure 9 for the Be atom.

The localized molecular orbitals were obtained using a machine program on the IBM 7094 digital computer. The criteria used to terminate the binary transformations was that, if an improvement of more than $10^{-8}$ in the sum of the diagonal exchange integrals could not be obtained by any binary transformation, then the program was terminated for that molecule. This leads to an error in the LCAO coefficients for the LMO's of about $10^{-4}$ for most of the molecules, but the error can become as big as $10^{-2}$ for some of the large heteronuclear molecules such as LiF. An indication of the accuracy of the LCAO coefficients is given by their deviations from agreement in the case of, in principle, equal contributions to equivalent orbitals.

Generally speaking, the LMO's turn out to be pretty much as anticipated qualitatively by earlier authors. One invariably obtains 1s type LMO's on second row atoms, but not with hydrogen atoms. Also, in single bonded molecules (with the exception of the excited state of NH), there results a single bond orbital between the two atoms, and various lone pair orbitals on them. In multiple bonded molecules (such as $N_2$) one obtains "banana" type equivalent bond orbitals. Also if there is more than one lone pair orbital on a given atom, they turn out to be equivalent. Finally, the orbitals which are of lone pair or inner shell type usually have small "negative" contributions from the other atom, i.e., they have a node in the bond region.

With the exception only of Li it is found that the localized 1s type inner shell orbital is localized from the 2s atomic orbital (which enters the various valence LMO's) in about the same manner as it was found to be in the oxygen and beryllium atoms in a preceding section. The inner shell orbitals, for a given atom, are found to be remarkably similar as one goes from molecule to molecule. In some cases this is true also for the lone pair orbitals. (It should, of course, be kept in mind that the sign of a particular orbital is of no consequence, so that in comparing orbitals one may mentally change the sign of all the expansion coefficients for a given orbital.)

In some cases, however, the calculations yield quite interesting results which could not be anticipated without actually carrying out the localization process, e.g., the proper distribution between lone pair orbitals and bonding orbitals in BF.

In the following we will first pass briefly through the different types of molecules, describing their LMO's and commenting on their exchange integrals. (Usually various cases of orbital exponents will not be discussed separately, since the results are all very similar.) We will then discuss the relation of these orbitals to the valence molecular orbitals defined by Ruedenberg (24), and compare the two sets of orbitals for the various molecules.

## 2. Calculations and discussions of SCF-LCAO-LMO's

The Figures 14 to 24 list the pertinent numerical results, of the localization process, for the various molecules. The exchange integrals for both the original SCF MO's and LMO's are given first. They are of interest because, in contrast to the coulombic integrals, the off-diagonal exchange integrals (which will sometimes be referred to as the exchange integrals per se) suffer large relative changes due to localization. The transformation matrices connecting the two sets of molecular orbitals are given next, which reflect the extent of difference between the two sets of MO's. It can be expected that the transformation to localized MO's will be achieved by almost the same transformation for the exact SCF MO's.

Finally, there are given the LCAO expansions for the LMO's in terms of the orthogonalized Slater atomic orbitals. They give an idea of the forms of the LMO's in space. This conceptual advantage of the minimal basis set is largely lost in the case of the longer expensions required for the exact SCF orbitals.

For all the small molecules, the above information is given for three sets of Slater orbital exponents: values obtained from Slater's rules[1]; values which minimize the energy of the separated atoms; and values which minimize the energy of the particular molecule. The atomic orbitals having these values are referred to respectively as Slater atomic orbitals (SAO), best-atom atomic orbitals (BAO), and best-molecule atomic orbitals (BMO). For some of the larger molecules, tables for all three cases are not given. Actually very little difference of a qualitative nature exists between the various sets, and, whenever it is available, the BMO set is of course the most valuable and correct.

In the figures the original SCF MO's are denoted by their conventional symbols, which are given also in Ransil's tables (21). The LMO's are denoted by the following symbols:

iA = LMO which is chiefly an inner shell on atom A;

$\sigma$A = LMO which is chiefly a $\sigma$-type lone pair on atom A;

$\ell$t1A
$\ell$t2A = LMO's which are chiefly trigonal equivalent lone pairs on
$\ell$t3A atom A;

b$\sigma$AB = LMO which is a $\sigma$-type bonding orbital between atoms A and B;

---

[1] See, for example, p. 368 of Reference 26.

bt1AB
bt2AB = LMO's which are chiefly trigonal bonding equivalent orbitals
bt3AB between atoms A and B (In general polarized "banana bonds").

The Slater atomic orbitals on the other hand are denoted by:

Ao = 1s orbital on atom A;

As = orthogonal 2s orbital on atom A;

Ap$\sigma$ = 2p$\sigma$ orbital on atom A;

Ap$\pi$ = 2px orbital on atom A;

Ap$\overline{\pi}$ = 2py orbital on atom A.

The LiH molecule has a localized 1s type orbital on the Li atom, and a bond orbital extending over both atoms but lying predominantly on the H atom. The SCF MO's do not differ greatly from these orbitals, so that the molecular orbital transformation is almost an identity transformation. Nevertheless, the exchange integral between the two orbitals has been reduced by a factor of about four. This is very similar to the situation encountered in atoms with the Be $1s^2 2s^2$ structure.

The BH molecule is seen to have a 1s type orbital and a lone pair type orbital on the B atom. Also there is a bond orbital extending about equally over both atoms. The transformation between the MO's sets is still close to an identity one, but not nearly so much as in LiH. The exchange integrals have been reduced, on the whole, by a factor of about five.

The NH molecule does not have a singlet ground state. Therefore the excited state $1\sigma^2 2\sigma^2 1\pi^4$ was calculated by Ransil, and is investigated here. This leads to a 1s type orbital on the nitrogen atom, and three equivalent bond orbitals pointing from the N atom toward a circle around the H atom. This occurs because the N atom does not have a $\sigma$-type lone pair for hybridization with the $\pi$ orbitals, and serves to emphasize that the usual situation of lone pairs and bonding orbitals between atoms may be greatly disrupted in going to excited states. The exchange integrals are reduced by about a factor of two.

The HF molecule has a 1s and three equivalent lone pair orbitals on the F atom. Also there is a bond orbital lying slightly more on the fluorine than the hydrogen. The exchange integrals have been reduced, on the whole, by a factor of about two. The transformation matrix between the two sets of MO's still has somewhat the character of an identity transformation, although much less so than in LiH or BH. In Figures 12 and 13, the values of the HF LMO's, along the bond axis, have been graphed.

Turning now to some homonuclear molecules, we see that for the $Li_2$ molecule we have a localized 1s orbital on each of the Li atoms, and a bond orbital extending equally over both atoms. It should be noted that the 1s orbital is quite similar in composition to the 1s orbital in LiH. The MO transformation is seen to be essentially an identity one for the bonding orbital, and a symmetry ($45^\circ$ rotation) one for the 1s orbitals. The exchange integrals are reduced, on the whole, by a very large factor, because this reduction is almost entirely due to the reduction in the exchange integral due to the symmetry transformation. This is very large because we go from two orbitals $1\sigma_g$ and $1\sigma_u$ which have very large differential overlap (overlap of the absolute values), to two orbitals iLi and iLi$'$, which have almost no differential overlap.

For the $Be_2$ molecule, which is not bound and is therefore a hypothetical molecule taken with an internuclear distance of 2 Å, we have essentially a 1s and a 2s orbital on each of the atoms. Thus the MO transformation matrix is essentially a product of two symmetry transformations, and the reduction in the exchange integrals is again very large. The 1s orbitals are of a localized character, and the 2s orbitals are beginning to develop a surprising amount of contribution from the other atom.

The $N_2$ molecule is seen to have a 1s type orbital and a lone pair orbital on each of the atoms. Between the two atoms there are three equivalent "banana" bond orbitals. The 1s orbitals are seen to be of localized character, and the lone pair orbitals mainly of 2s atomic orbital composition, with enough $2p\sigma$ composition to direct them well toward the "back" of the N atom. The exchange integrals have been reduced, on the whole, by about 85 percent, but a fair amount of this is due to symmetry transformations of the $1\sigma_g$ and $1\sigma_u$ orbitals into the iN and iN' orbitals, the $2\sigma_g$ and $2\sigma_u$ orbitals into the $\ell\sigma N$ and $\ell\sigma N'$ orbitals, and the $3\sigma_g$, $1\pi_u$ and $1\bar{\pi}_u$ orbitals into the "banana" bond orbitals.

For the $F_2$ molecule, we find three equivalent lone pairs on each of the F atoms, and a bond orbital between the two atoms. There are also the localized inner shell 1s type orbitals on each atom and these are extremely similar to the corresponding ones in HF, BF, and LiF. Also the lone pairs of the F atom are quite similar to those in HF, but are slightly less directed toward the rear of the F atom, in that the $p\sigma$ contribution to these lone pairs ((BMO) case) is -.1243 as compared to

-.1982 for the (BMO) case of the HF molecule. The exchange integrals have been reduced, on the whole, by about 85 percent, but as with the $N_2$ molecule a large share of this is no doubt due to symmetry transformations.

The inner shell for the F atom in the (SAO) case is

$$1s_{LMO} = .9915\ 1s - .1303\ 2s \quad . \qquad \text{(IV-7-1)}$$

It is evident that this inner shell is almost the same in the HF, $F_2$, BF, and LiF molecules as it is here.

The results for the (SAO) case of the BF molecule are particularly interesting since they yield a somewhat unexpected result. The usual picture would be that of a single bond between the two atoms and three lone pairs on the F atom. However, one could also conceive the structure to be somewhat similar to that of $N_2$, since the two molecules are isoelectronic. The actual structure turns out to be intermediate between these two extremes, but, somewhat surprisingly, it seems to be considerably closer to the $N_2$ structure. Thus, we have a localized 1s type orbital on both atoms, and three equivalent, but somewhat distorted, "banana" bond orbitals. Also while the lone pair orbital on the B atom appears to be quite normal, the one on the F atom is seen to have become somewhat bonding in character. It appears that the bonding is still mainly due to the weakened "banana" bonds, but the F lone pair seems to be coming into the bonding to a slight extent.

This observed intermediate character agrees with the binding energy value of 8.5 ± .5 ev, which is low compared to the values 9.9 ev for $N_2$

and 11.24 ev for CO, but is high for a single bond value, e.g., 6.0 ± .5 ev for LiF.

It should be noted that the lone pair orbital on the B atom is similar to the lone pair for the (SAO) case in BH. If we neglect the small contributions to these lone pairs from the other atom, and consider only their contributions from the B atom, we find that these contributions (when each is normalized) have an overlap of .99963. The sum of the contributions from the F atom (as measured by the sum of the LCAO coefficients) is seen to be close to the contribution from the hydrogen atom.

It should also be noted that the inner shell on the F atom is very similar to that on the F atom in the (SAO) case of HF. If we again consider only the (normalized) contributions from the F atom, which are the only contributions of consequence in this case, we find that they have an overlap of .99994.

The lone pair orbitals on the F atom are not too similar to those for the (SAO) case of HF, and the overlap of their normalized components from the F atom are only .8589. This no doubt is due to the triple bond character of the BF molecule.

In the (SAO) case of the LiF molecule we have a localized 1s type orbital on each of the atoms, a $\sigma$-type lone pair on the F atom, and three equivalent "banana" type bonding orbitals between the atoms. The "banana" bonding orbitals are strongly polarized toward the F atom. This result is somewhat striking, in that one would usually picture the F atom as having three equivalent lone pair orbitals pointing toward the back, and a single bonding orbital connecting it with the Li atom. However, $\pi$-bonding is apparently quite important in this molecule, at least in terms of the present approximate wave function. It is seen that the inner shells of both the Li and F atoms are quite similar to those of the same atoms in the LiH, $Li_2$, HF, $F_2$, and BF molecules.

For the (SAO) case of the CO molecule we have a localized inner shell on each of the atoms, and a lone pair on each. Also we have three "banana" bond orbitals between the two atoms, which are slightly polarized toward the O atom. This structure is seen to be about intermediate between those of $N_2$ and BF, with which it is isoelectronic. The inner shell of the O atom is very similar to that for the isolated O atom obtained earlier, which, when expressed in terms of the orthogonal Slater orbitals, is

$$1s_{LMO} = .9918\ 1s - .1278\ 2s \quad . \qquad \text{(IV-7-2)}$$

### 3. Comparison of valence molecular orbitals with localized molecular orbitals

The fact that the LMO's usually turn out to be inner shell, lone pair, and bond type orbitals, leads one to suspect that they may be quite similar to certain valence molecular orbitals proposed by Ruedenberg (24), after the latter are transformed to equivalent orbitals where possible.

The valence molecular orbitals are SCF orbitals defined so as to have successively maximum overlap populations (19). Thus, that orbital is found which has the maximum overlap population, then an orbital orthogonal to the first is found which has the next greatest overlap population, and so on. This determines a unique set of SCF orbitals. These orbitals are still symmetry orbitals (belong to irreducible representations of the symmetry group of the molecule). They are found by diagonalization of the matrix whose elements are

$$p_{nm} = 2 \sum_k c_{k,n}\, c_{k,m} \quad , \qquad \text{(IV-7-3)}$$

where $c_{k,n}$ is the LCAO coefficient of atomic orbital $\underline{k}$ in molecular orbital $\underline{n}$. This is because the non-overlap populations of the MO's are defined by

$$p_{nn} = 2 \sum_k c_{k,n}\, c_{k,n} = 2(1-2 \sum_j{}' c_{k,n} c_{j,n}) \qquad \text{(IV-7-4)}$$

and the extremization of these quantities results from the diagonalization of the matrix whose elements are given by Eq. IV-7-3. This explains why the valence molecular orbitals are symmetry orbitals, since atomic orbitals do not simultaneously enter molecular orbitals of different irreducible representation, so that the total matrix of the $p_{nm}$'s reduces to several submatrices corresponding to the different irreducible representations.

In order to compare the VMO's with the LMO's we must hybridize the former to equivalent orbitals, wherever the LMO's are equivalent orbitals. In Figures 25 and 26 we give these "equivalent VMO's" for a number of the molecules discussed in the previous section. Only one case of orbital exponents (usually (BMO)) is given for each molecule. This is sufficient for the qualitative comparisons which we wish to make with the LMO's of Figures 14 to 24.

In the HF molecule, one obtains an inner shell VMO, a lone pair VMO, and a bonding VMO, due to the successive-extremizations of overlap. If one now hybridizes the lone pair VMO with the two 2pπ orbitals on the F atom, one should obtain orbitals roughly similar to the LMO's for this molecule. In Figures 12 and 13 we have graphed the values, along the bond axis, of the VMO's and corresponding LMO's for this molecule. The two sets of orbitals are seen to correspond fairly well. The inner shell orbitals of the two types have an overlap of 1.0000, the lone pair orbitals an overlap of .9872, and the bond orbitals an overlap of .9693. This is to be compared with the overlap of the inner shell LMO with the canonical 1$\sigma$ orbital, which is .9872, the overlap of the lone pair LMO with the canonical 2$\sigma$ orbital, which is .8069, and the overlap of the bonding LMO with the canonical 3$\sigma$ orbital, which is .8156.

For the LiH molecule there is found an inner shell VMO on the Li atom and a bond orbital lying mainly on the H atom. This situation is similar to the LMO's, but it must be remembered that it is also quite similar to that of the original SCF MO's. The overlap of the inner shell localized orbitals is .9927, and that of the bond orbitals is .9927. This is to be compared with the overlap of the i LMO with the canonical 1$\sigma$ orbital which is .9975, and the overlap of the b LMO with the canonical 2$\sigma$ orbital which is .9975.

The BH molecule has an inner shell VMO, a lone pair VMO, and a bonding VMO, as was the case with the LMO's. However it is seen that the two sets of localized orbitals here correspond fairly closely, and they have overlap integrals of .9925 for the inner shell orbitals, .9831 for the lone pair orbitals, and .9937 for the bond orbitals.

In the NH molecule we have hybridized the bonding VMO with the 2p$\pi$ orbitals, so as to have orbitals which correspond to the LMO's. It is seen that, as with the HF and BH molecules, the correspondence between the two sets of orbitals is not too bad.

The corresponding valence molecular orbitals for $Li_2$ are obtained by applying a symmetry transformation to the $1\sigma_g$ and $1\sigma_u$ orbitals obtained from the successive-extremization of overlap populations. The correspondence of the inner shells to the LMO ones is not particularly striking, but the correspondence of the bonding orbital is not bad. In this case the correspondence may be only because these orbitals, in either case, do not differ appreciably from the canonical SCF orbitals after the $1\sigma_g$ and $1\sigma_u$ orbitals of the latter have been transformed into equivalent orbitals.

For the $N_2$ molecule we obtain orbitals corresponding to the LMO's after carrying out the proper symmetry transformations on the valence molecular orbitals. The correspondence of the two sets of localized orbitals is seen to be fairly good, but not complete, especially for the inner shells.

In heteronuclear diatomic molecules (other than the hybrids) we cannot use an equivalence transformation to bring the VMO's closer to the LMO's. It is therefore difficult to recognize a correspondence between the two sets of molecular orbitals. This circumstance illustrates the difference in significance of the two types of orbitals.

Figure 10. Minimal basis set SCF $2\sigma$ orbital (————), and exact SCF $2\sigma$ orbital (------), for HF, along the bond axis.

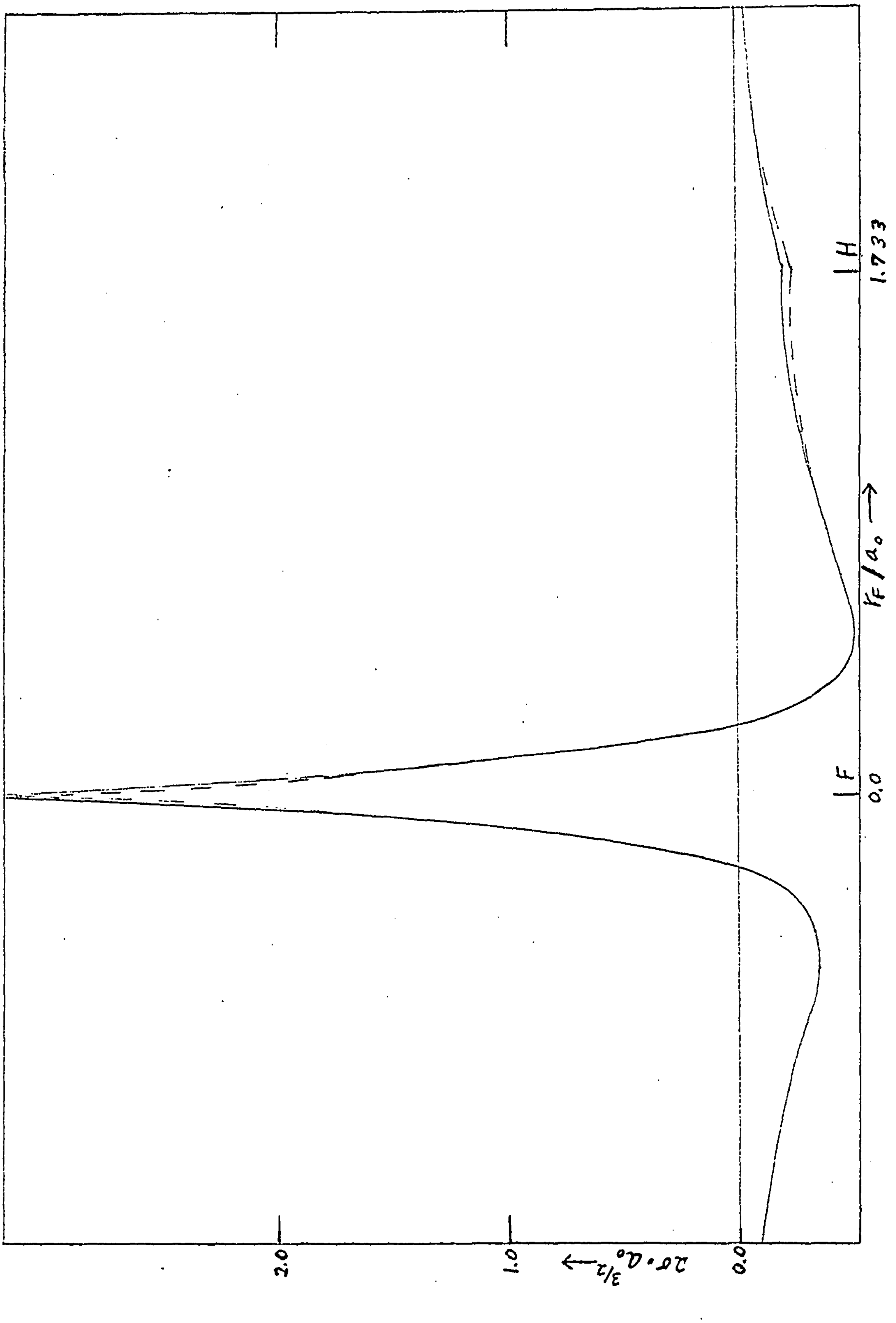

2.0
1.0
0.0
2σ·a₀^3/2 →
F
0.0
r_F/a₀ →
H
1.733

Figure 11. Minimal basis set SCF $3\sigma$ orbital (————), and exact SCF $3\sigma$ orbital (------) (from References 6 and 20), for HF, along the bond axis.

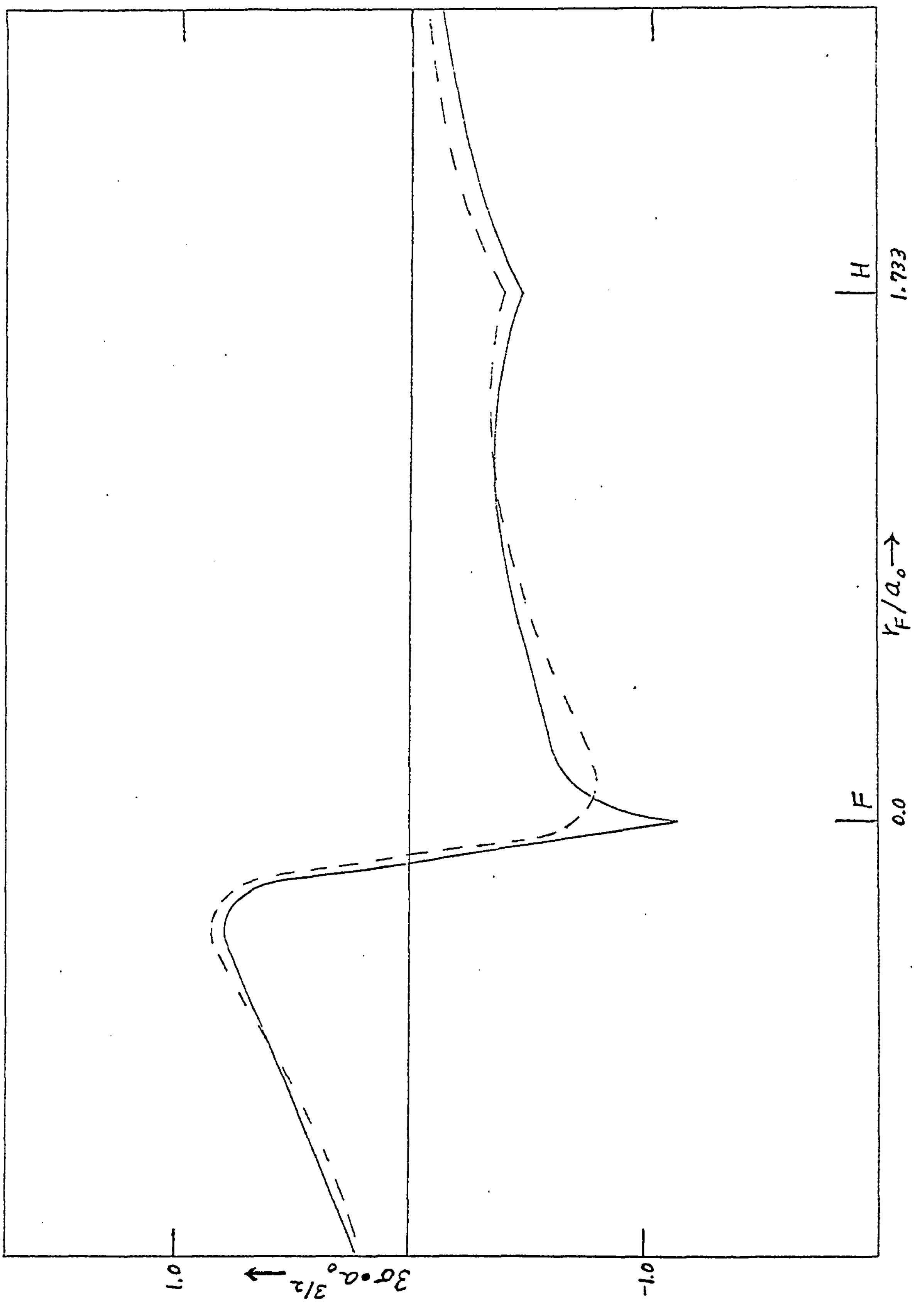

1.0
$3\sigma \cdot a_0^{3/2}$ ←
-1.0
F
0.0
H
1.733
$r_F/a_0$ →

Figure 12. Minimal basis set SCF $1\sigma$ orbital (———), exact SCF $1\sigma$ orbital (—-—-) (from References 6 and 20), LMO inner shell (------), and VMO inner shell (—— ——), for HF, along bond axis.

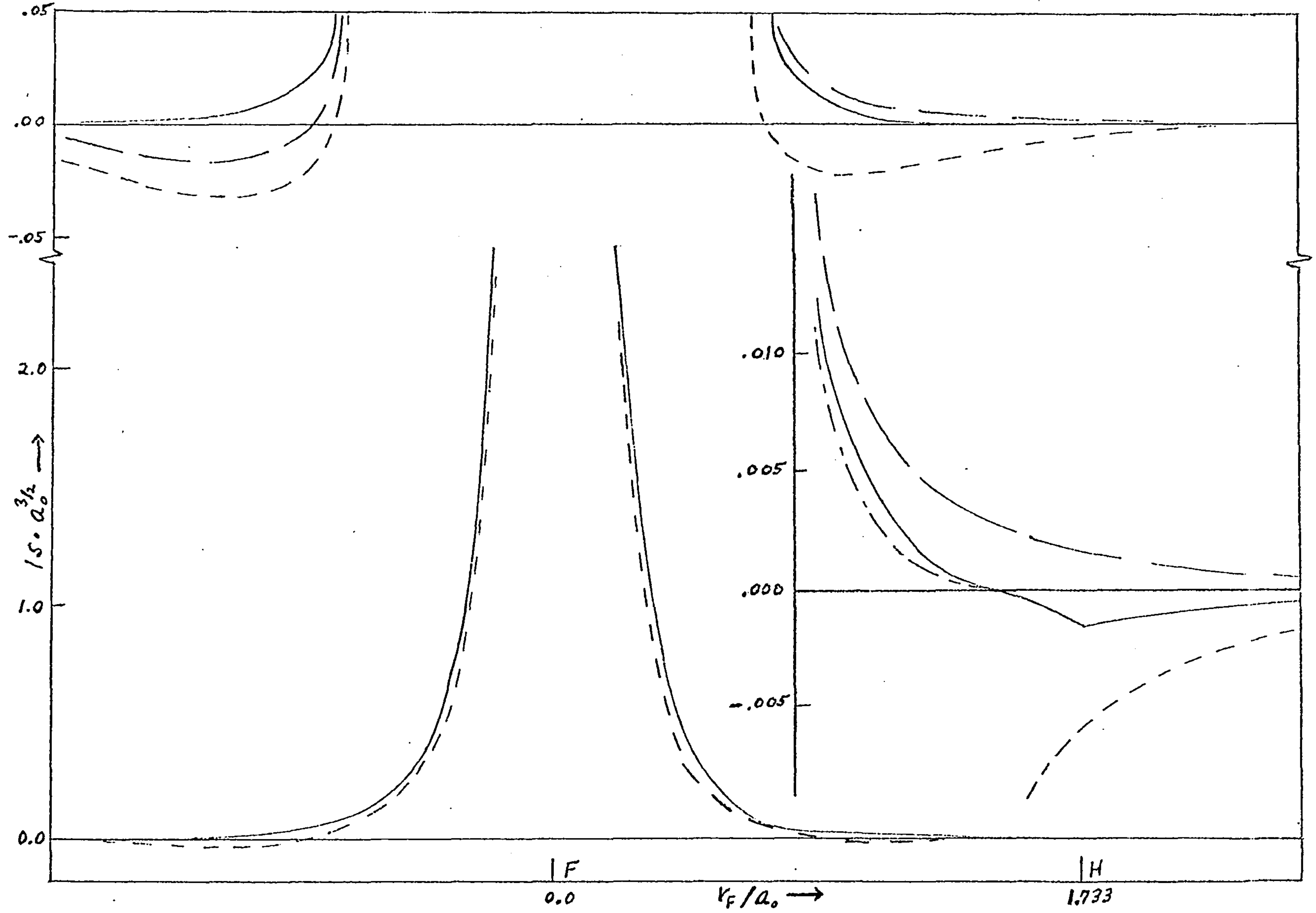
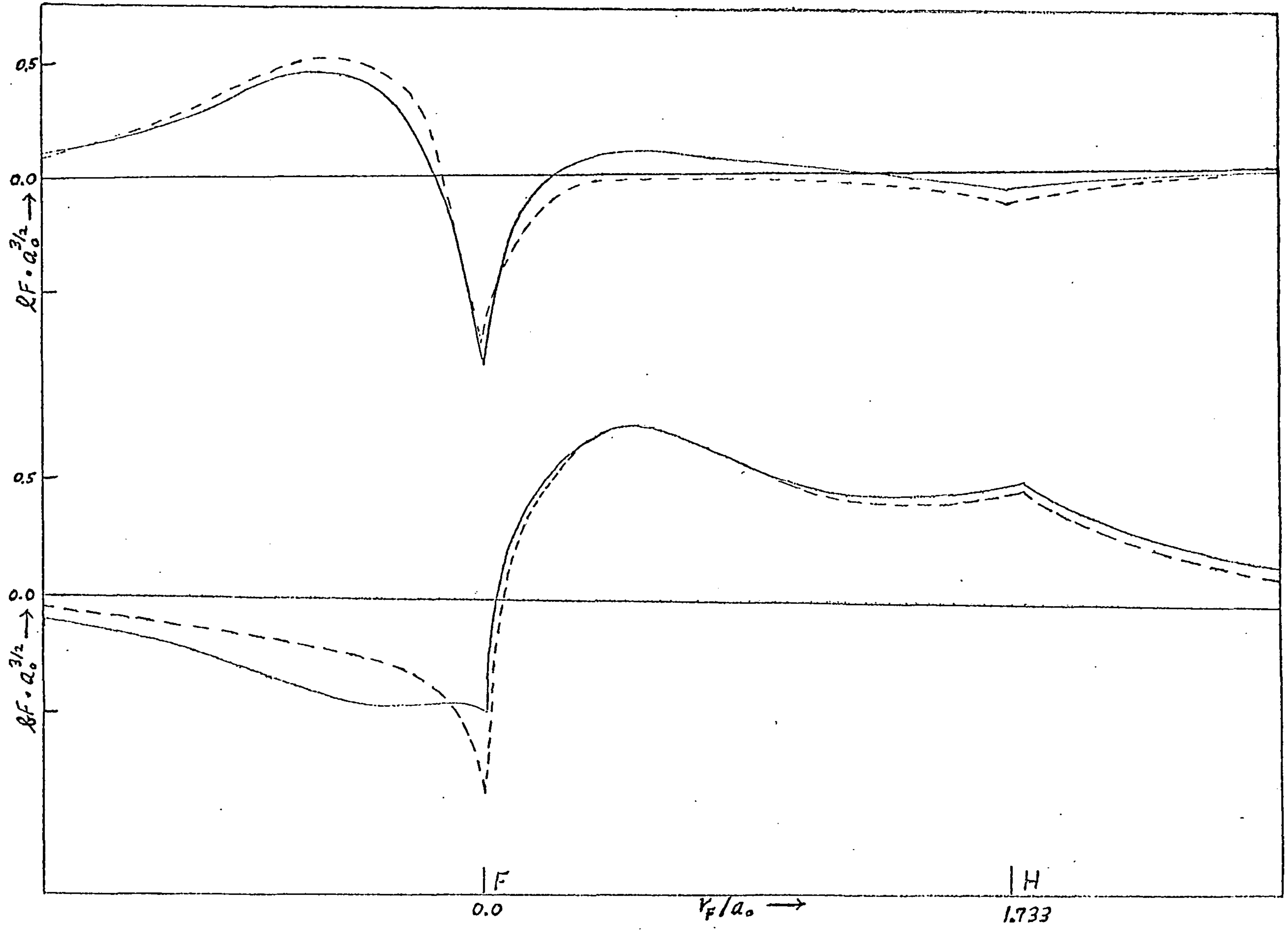

.05
.00
-.05
2.0
1.0
0.0
IS · a₀^{3/2} →
.010
.005
.000
-.005
F
0.0
r_F/a₀ →
H
1.733

Figure 13. LMO lone pair orbital (————), VMO lone pair orbital (------), LMO bonding orbital (————), and VMO bonding orbital (------), for HF, along bond axis.


0.5
0.0
$\rho_F \cdot a_0^{3/2} \rightarrow$
0.5
0.0
$\rho_F \cdot a_0^{3/2} \rightarrow$
F
H
0.0
$r_F/a_0 \rightarrow$
1.733

LiH(BMO)

| | 1σ | 2σ |
|---|---|---|
| 1σ | 1.67016 | 0.01013 |
| 2σ | 0.01013 | 0.48114 |

| | iLi | bσLiH |
|---|---|---|
| iLi | 1.68464 | 0.00268 |
| bσLiH | 0.00268 | 0.48157 |

| | 1σ | 2σ |
|---|---|---|
| iLi | 0.99746 | 0.07121 |
| bσLiH | -0.07121 | 0.99746 |

| | oLi | sLi | pσLi | oH |
|---|---|---|---|---|
| iLi | 1.00241 | -0.00449 | -0.02233 | -0.04386 |
| bσLiH | 0.00979 | -0.30243 | -0.21039 | -0.70254 |

LiH(SAO)

| | 1σ | 2σ |
|---|---|---|
| 1σ | 1.67777 | 0.00871 |
| 2σ | 0.00871 | 0.46787 |

| | iLi | bσLiH |
|---|---|---|
| iLi | 1.69066 | 0.00213 |
| bσLiH | 0.00213 | 0.46814 |

| | 1σ | 2σ |
|---|---|---|
| iLi | 0.99779 | 0.06644 |
| bσLiH | -0.06644 | 0.99779 |

| | oLi | sLi | pσLi | oH |
|---|---|---|---|---|
| iLi | 1.00217 | -0.00539 | -0.02048 | -0.03955 |
| bσLiH | 0.01065 | -0.31920 | -0.23021 | -0.68415 |

LiH(BAO)

| | 1σ | 2σ |
|---|---|---|
| 1σ | 1.67068 | 0.00835 |
| 2σ0. | 0.00835 | 0.46668 |

| | iLi | bσLiH |
|---|---|---|
| iLi | 1.68296 | 0.00207 |
| bσLiH | 0.00207 | 0.46696 |

| | 1σ | 2σ |
|---|---|---|
| iLi | 0.99788 | 0.06501 |
| bσLiH | -0.06501 | 0.99788 |

| | oLi | sLi | pσLi | oH |
|---|---|---|---|---|
| iLi | 1.00215 | -0.00709 | -0.01997 | -0.03857 |
| bσLiH | 0.01161 | -0.31892 | -0.22870 | -0.68652 |

Figure 14. Data for LMO's of LiH: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

BH(BMO)

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| 1σ | 2.91124 | 0.02286 | 0.02234 |
| 2σ | 0.02286 | 0.53855 | 0.06011 |
| 3σ | 0.02234 | 0,06011 | 0.50444 |

| – | bσBH | iB | ℓσB |
|---|---|---|---|
| iB | 0.00435 | 2.97315 | 0.00756 |
| ℓσB | 0.01030 | 0.00756 | 0.53801 |
| bσBH | 0.60929 | 0.00435 | 0.01030 |

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| iB | 0.99260 | -0.08955 | -0.08199 |
| ℓσB | 0.10882 | 0.35659 | 0.92790 |
| bσBH | -0.05386 | -0.92996 | 0.36370 |

|  | oB | sB | pσB | oH |
|---|---|---|---|---|
| iB | 0.99491 | -0.09958 | 0.03124 | -0.01494 |
| ℓσB | 0.11176 | 0.90638 | -0.46229 | -0.18413 |
| bσBH | -0.00972 | -0.27730 | -0.44348 | -0.55833 |

BH(SAO)

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| 1σ | 2.92115 | 0.02269 | 0.02261 |
| 2σ | 0.02269 | 0.50966 | 0.06080 |
| 3σ | 0.02261 | 0.06080 | 0.49033 |

|  | iB | bσBH | ℓσB |
|---|---|---|---|
| iB | 2.98515 | 0.00377 | 0.00742 |
| ℓσB | 0.00742 | 0.01063 | 0.53281 |
| bσBH | 0.00377 | 0.57174 | 0.01063 |

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| iB | 0.99242 | -0.08954 | -0.08416 |
| ℓσB | -0.11184 | -0.37434 | -0.92052 |
| bσBH | -0.05092 | -0.92296 | 0.38152 |

|  | oB | sB | pσB | oH |
|---|---|---|---|---|
| iB | 0.99489 | -0.09960 | 0.03305 | -0.01297 |
| ℓσB | -0.11892 | -0.94686 | 0.42748 | 0.23005 |
| bσBH | 0.00371 | -0.21053 | -0.41255 | -0.61387 |

BH(BAO)

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| 1σ | 2.90932 | 0.02429 | 0.02224 |
| 2σ | 0.02429 | 0.50672 | 0.06493 |
| 3σ | 0.02224 | 0.06493 | 0.48012 |

|  | bσBH | iB | ℓσB |
|---|---|---|---|
| iB | 0.00337 | 2.97664 | 0.00757 |
| ℓσB | 0.01082 | 0.00757 | 0.53462 |
| bσBH | 0.56429 | 0.00337 | 0.01082 |

|  | 1σ | 2σ | 3σ |
|---|---|---|---|
| iB | 0.99202 | -0.09316 | -0.08496 |
| ℓσB | 0.11502 | 0.39260 | 0.91249 |
| bσBH | -0.05165 | -0.91498 | 0.40018 |

|  | oB | sB | pσB | oH |
|---|---|---|---|---|
| iB | 0.99458 | -0.10267 | 0.03549 | -0.01557 |
| ℓσB | 0.12077 | 0.92804 | -0.44343 | -0.19610 |
| bσBH | 0.00167 | -0.21601 | -0.41649 | -0.60253 |

Figure 15. Data for LMO's of BH: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

NH(BMO)

|  | $1\sigma$ | $2\sigma$ | $1\pi$ | $1\bar{\pi}$ |
|---|---|---|---|---|
| $1\sigma$ | 4.14963 | 0.05182 | 0.01604 | 0.01604 |
| $2\sigma$ | 0.05182 | 0.65260 | 0.11802 | 0.11802 |
| $1\pi$ | 0.01604 | 0.11802 | 0.68884 | 0.03712 |
| $1\bar{\pi}$ | 0.01604 | 0.11802 | 0.03712 | 0.68884 |

|  | bt1NH | iN | bt2NH | bt3NH |
|---|---|---|---|---|
| bt1NH | 0.76279 | 0.01159 | 0.05100 | 0.05099 |
| iN | 0.01159 | 4.23015 | 0.01159 | 0.01159 |
| bt2NH | 0.05100 | 0.01159 | 0.76279 | 0.05100 |
| bt3NH | 0.05099 | 0.01159 | 0.05100 | 0.76280 |

|  | $1\sigma$ | $2\sigma$ | $1\pi$ | $1\bar{\pi}$ |
|---|---|---|---|---|
| bt1NH | 0.06945 | -0.57318 | -0.57985 | -0.57482 |
| iN | -0.99274 | -0.12031 | 0.00001 | 0.00001 |
| bt2NH | -0.06947 | 0.57311 | 0.20792 | -0.78961 |
| bt3NH | -0.06947 | 0.57318 | -0.78775 | 0.21471 |

|  | oN | sN | $p\sigma$N | $p\pi$N | $p\bar{\pi}$N | oH |
|---|---|---|---|---|---|---|
| bt1NH | 0.05720 | 0.48057 | 0.08061 | -0.57985 | -0.57482 | 0.15260 |
| iN | -0.99536 | 0.08794 | 0.01621 | 0.00001 | 0.00001 | 0.03509 |
| bt2NH | -0.05722 | -0.48052 | -0.08060 | 0.20792 | -0.78961 | -0.15258 |
| bt3NH | -0.05722 | -0.48057 | -0.08061 | -0.78775 | 0.21471 | -0.15260 |

Figure 16. Data for LMO's of NH: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

HF (BMO)

| | $1\sigma$ | $2\sigma$ | $3\sigma$ | $1\pi$ | $1\bar{\pi}$ |
|---|---|---|---|---|---|
| $1\sigma$ | 5.38354 | 0.08022 | 0.02774 | 0.02826 | 0.02826 |
| $2\sigma$ | 0.08022 | 0.86392 | 0.16163 | 0.17928 | 0.17928 |
| $3\sigma$ | 0.02774 | 0.16163 | 0.80921 | 0.04991 | 0.04991 |
| $1\pi$ | 0.02826 | 0.17928 | 0.04991 | 0.97715 | 0.05266 |
| $1\bar{\pi}$ | 0.02826 | 0.17928 | 0.04991 | 0.05266 | 0.97715 |

| | ℓt1F | ℓt2F | iF | bσHF | ℓt3F |
|---|---|---|---|---|---|
| ℓt1F | 1.11470 | 0.07776 | 0.01932 | 0.05534 | 0.07775 |
| ℓt2F | 0.07776 | 1.11468 | 0.01932 | 0.05534 | 0.07776 |
| iF | 0.01932 | 0.01932 | 5.52664 | 0.01286 | 0.01932 |
| bσHF | 0.05534 | 0.05534 | 0.01286 | 0.87429 | 0.05534 |
| ℓt3F | 0.07775 | 0.07776 | 0.01932 | 0.05534 | 1.11472 |

| | $1\sigma$ | $2\sigma$ | $3\sigma$ | $1\pi$ | $1\bar{\pi}$ |
|---|---|---|---|---|---|
| ℓt1F | 0.07903 | −0.46531 | 0.33258 | 0.58925 | −0.56516 |
| ℓt2F | 0.07903 | −0.46525 | 0.33237 | 0.19498 | 0.79298 |
| iF | −0.98981 | −0.13431 | 0.04731 | 0.00001 | 0.00002 |
| bσHF | 0.03923 | −0.57657 | −0.81610 | −0.00006 | −0.00011 |
| ℓt3F | 0.07903 | −0.46535 | 0.33265 | −0.78407 | −0.22754 |

| | oF | sF | pσF | pπF | $p\bar{\pi}F$ | oH |
|---|---|---|---|---|---|---|
| ℓt1F | 0.07826 | 0.56282 | −0.19437 | 0.58925 | −0.56516 | −0.10042 |
| ℓt2F | 0.07825 | 0.56268 | −0.19423 | 0.19498 | 0.79298 | −0.10032 |
| iF | −0.99124 | 0.12993 | −0.02358 | 0.00001 | 0.00002 | −0.00049 |
| bσHF | 0.01025 | 0.19241 | 0.63284 | −0.00006 | −0.00011 | 0.50967 |
| ℓt3F | 0.07826 | 0.56289 | −0.19443 | −0.78407 | −0.22754 | −0.10045 |

Figure 17. Data for LMO's of HF: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

HF (SAO)

| | 1σ | 2σ | 3σ | 1π | 1$\bar{\pi}$ |
|---|---|---|---|---|---|
| 1σ | 5.40509 | 0.08512 | 0.02717 | 0.03226 | 0.03226 |
| 2σ | 0.08512 | 0.86759 | 0.15027 | 0.18316 | 0.18316 |
| 3σ | 0.02717 | 0.15027 | 0.74594 | 0.04921 | 0.04921 |
| 1π | 0.03226 | 0.18316 | 0.04921 | 1.01766 | 0.05484 |
| 1$\bar{\pi}$ | 0.03226 | 0.18316 | 0.04921 | 0.05484 | 1.01766 |

| | bσHF | ℓt1F | ℓt2F | ℓt3F | iF |
|---|---|---|---|---|---|
| bσHF | 0.78102 | 0.05395 | 0.05395 | 0.05395 | 0.01083 |
| ℓt1F | 0.05395 | 1.15260 | 0.07907 | 0.07907 | 0.02122 |
| ℓt2F | 0.05395 | 0.07907 | 1.15259 | 0.07907 | 0.02122 |
| ℓt3F | 0.05395 | 0.07907 | 0.07907 | 1.15262 | 0.02122 |
| iF | 0.01083 | 0.02122 | 0.02122 | 0.02122 | 5.56138 |

| | 1σ | 2σ | 3σ | 1π | 1$\bar{\pi}$ |
|---|---|---|---|---|---|
| bσHF | −0.03324 | 0.55411 | 0.83177 | 0.00002 | −0.00004 |
| ℓt1F | 0.08410 | −0.47380 | 0.31896 | 0.20044 | −0.79153 |
| ℓt2F | −0.08404 | 0.47381 | −0.31902 | 0.78570 | −0.22215 |
| ℓt3F | 0.08408 | −0.47384 | 0.31903 | 0.58525 | 0.56932 |
| iF | 0.98879 | 0.13949 | −0.05342 | −0.00003 | 0.00003 |

| | oF | sF | pσF | pπF | p$\bar{\pi}$F | oH |
|---|---|---|---|---|---|---|
| bσHF | 0.00228 | −0.12132 | −0.62171 | 0.00002 | −0.00004 | −0.56805 |
| ℓt1F | 0.08272 | 0.57642 | −0.17595 | 0.20044 | −0.79153 | −0.10806 |
| ℓt2F | −0.08266 | −0.57645 | 0.17599 | 0.78570 | −0.22215 | 0.10809 |
| ℓt3F | 0.08271 | 0.57648 | −0.17599 | 0.58525 | 0.56932 | −0.10809 |
| iF | 0.99048 | −0.13509 | 0.02645 | −0.00003 | 0.00003 | 0.00382 |

Figure 17 (Continued)

## HF (BAO)

|  | 1σ | 2σ | 3σ | 1π | 1π̄ |
|---|---|---|---|---|---|
| 1σ | 5.38117 | 0.08131 | 0.02566 | 0.03039 | 0.03039 |
| 2σ | 0.08131 | 0.86483 | 0.14964 | 0.18239 | 0.18239 |
| 3σ | 0.02566 | 0.14964 | 0.75034 | 0.04873 | 0.04873 |
| 1π | 0.03039 | 0.18239 | 0.04873 | 0.99801 | 0.05378 |
| 1π̄ | 0.03039 | 0.18239 | 0.04873 | 0.05378 | 0.99801 |

|  | bσHF | iF | ℓt1F | ℓt2F | ℓt3F |
|---|---|---|---|---|---|
| bσHF | 0.79237 | 0.01095 | 0.05543 | 0.05543 | 0.05543 |
| iF | 0.01095 | 5.52754 | 0.02029 | 0.02029 | 0.02029 |
| ℓt1F | 0.05543 | 0.02029 | 1.13193 | 0.07786 | 0.07787 |
| ℓt2F | 0.05543 | 0.02029 | 0.07786 | 1.13193 | 0.07786 |
| ℓt3F | 0.05543 | 0.02029 | 0.07787 | 0.07786 | 1.13193 |

|  | 1σ | 2σ | 3σ | 1π | 1π̄ |
|---|---|---|---|---|---|
| bσHF | 0.03466 | −0.55658 | −0.83007 | −0.00001 | −0.00000 |
| iF | 0.98948 | 0.13585 | −0.04977 | 0.00002 | −0.00002 |
| ℓt1F | −0.08110 | 0.47320 | −0.32067 | −0.40183 | −0.71078 |
| ℓt2F | 0.08108 | −0.47321 | 0.32068 | 0.41463 | −0.70338 |
| ℓt3F | 0.08111 | −0.47320 | 0.32068 | −0.81646 | −0.00738 |

|  | oF | sF | pσF | pπF | pπ̄F |  |
|---|---|---|---|---|---|---|
| bσHF | 0.00125 | 0.14227 | 0.64006 | −0.00001 | −0.00000 | 0.53530 |
| iF | 0.99072 | −0.13380 | 0.02389 | 0.00002 | −0.00002 | 0.00440 |
| ℓt1F | −0.08139 | −0.57584 | 0.17971 | −0.40183 | −0.71078 | 0.10919 |
| ℓt2F | 0.08136 | 0.57586 | −0.17972 | 0.41463 | −0.70338 | −0.10920 |
| ℓt3F | 0.08139 | 0.57585 | −0.17972 | −0.81646 | −0.00738 | −0.10920 |

Figure 17 (Continued)

### $Li_2$(BMO)

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| $1\sigma_g$ | 0.93489 | 0.00960 | 0.73719 |
| $2\sigma_g$ | 0.00960 | 0.22939 | 0.00959 |
| $1\sigma_u$ | 0.73719 | 0.00959 | 0.93547 |

| | iLi | iLi' | bσLiLi' |
|---|---|---|---|
| iLi | 1.68710 | 0.00004 | 0.00205 |
| iLi' | 0.00004 | 1.68710 | 0.00205 |
| bσLiLi' | 0.00205 | 0.00205 | 0.23000 |

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| iLi | -0.70323 | 0.07395 | -0.70711 |
| iLi' | -0.70323 | 0.07398 | 0.70711 |
| bσLiLi' | -0.10461 | -0.99451 | 0.00002 |

| | oLi | sLi | pσLi | oLi' | sLi' | pσLi' |
|---|---|---|---|---|---|---|
| iLi | -1.00225 | 0.01749 | 0.00599 | 0.00013 | 0.04667 | 0.01045 |
| iLi' | 0.00013 | 0.04668 | 0.01046 | -1.00225 | 0.01750 | 0.00600 |
| bσLiLi' | -0.01505 | -0.52106 | -0.11379 | -0.01508 | -0.52106 | -0.11379 |

### $Li_2$(SAO)

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| $1\sigma_g$ | 0.93751 | 0.01028 | 0.73940 |
| $2\sigma_g$ | 0.01028 | 0.23286 | 0.01026 |
| $1\sigma_u$ | 0.73940 | 0.01026 | 0.93738 |

| | iLi | iLi' | bσLiLi' |
|---|---|---|---|
| iLi | 1.69277 | 0.00005 | 0.00216 |
| iLi' | 0.00005 | 1.69277 | 0.00216 |
| bσLiLi' | 0.00216 | 0.00216 | 0.23338 |

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| iLi | -0.70294 | 0.07664 | -0.70711 |
| iLi' | -0.70294 | 0.07668 | 0.70711 |
| bσLiLi' | -0.10842 | -0.99411 | 0.00003 |

| | oLi | sLi | pσLi | oLi' | sLi' | pσLi' |
|---|---|---|---|---|---|---|
| iLi | -1.00353 | 0.00939 | 0.00055 | 0.00128 | 0.05555 | 0.01667 |
| iLi' | 0.00128 | 0.05557 | 0.01668 | -1.00353 | 0.00941 | 0.00056 |
| bσLiLi' | -0.01516 | -0.51672 | -0.11851 | -0.01521 | -0.51672 | -0.11851 |

Figure 18. Data for LMO's of $Li_2$: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

$Li_2$(BAO)

|  | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| $1\sigma_g$ | 0.93401 | 0.00971 | 0.73599 |
| $2\sigma_g$ | 0.00971 | 0.23019 | 0.00969 |
| $1\sigma_u$ | 0.73599 | 0.00969 | 0.93406 |

|  | iLi | iLi' | $b\sigma$LiLi' |
|---|---|---|---|
| iLi | 1.68496 | 0.00004 | 0.00208 |
| iLi' | 0.00004 | 1.68495 | 0.00208 |
| $b\sigma$LiLi' | 0.00208 | 0.00208 | 0.23074 |

|  | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ |
|---|---|---|---|
| iLi | -0.70318 | 0.07441 | -0.70711 |
| iLi' | -0.70318 | 0.07445 | 0.70711 |
| $b\sigma$LiLi' | -0.10526 | -0.99445 | 0.00003 |

|  | oLi | sLi | $p\sigma$Li | oLi' | sLi' | $p\sigma$Li' |
|---|---|---|---|---|---|---|
| iLi | -1.00344 | 0.01098 | 0.00140 | 0.00104 | 0.05285 | 0.01592 |
| iLi' | 0.00104 | 0.05287 | 0.01593 | -1.00344 | 0.01100 | 0.00140 |
| $b\sigma$LiLi' | -0.01317 | -0.51292 | -0.12308 | -0.01321 | -0.51292 | -0.12308 |

Figure 18 (Continued)

Figure 19. Data for LMO's of $Be_2$: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

### $Be_2$(BMO)

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|
| $1\sigma_g$ | 1.27804 | 0.01494 | 1.01334 | 0.01408 |
| $2\sigma_g$ | 0.01494 | 0.35523 | 0.01487 | 0.04318 |
| $1\sigma_u$ | 1.01334 | 0.01487 | 1.27800 | 0.01416 |
| $2\sigma_u$ | 0.01408 | 0.04318 | 0.01416 | 0.27882 |

| | $\ell\sigma$Be' | $\ell\sigma$Be | iBe | iBe' |
|---|---|---|---|---|
| iBe | 0.00097 | 0.00484 | 2.33628 | 0.00003 |
| iBe' | 0.00484 | 0.00097 | 0.00003 | 2.33629 |
| $\ell\sigma$Be | 0.02421 | 0.33747 | 0.00484 | 0.00097 |
| $\ell\sigma$Be' | 0.33747 | 0.02421 | 0.00097 | 0.00484 |

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|
| iBe | 0.70214 | -0.08366 | 0.70258 | 0.07991 |
| iBe' | 0.70214 | -0.08366 | -0.70258 | -0.07991 |
| $\ell\sigma$Be | -0.08366 | -0.70214 | -0.07991 | 0.70258 |
| $\ell\sigma$Be' | 0.08366 | 0.70214 | -0.07991 | 0.70258 |

| | oBe | sBe | p$\sigma$Be | oBe' | sBe' | p$\sigma$Be' |
|---|---|---|---|---|---|---|
| iBe | 0.99573 | -0.09645 | 0.00332 | 0.00539 | 0.02136 | -0.02862 |
| iBe' | 0.00539 | 0.02136 | -0.02862 | 0.99573 | -0.09645 | 0.00332 |
| $\ell\sigma$Be | -0.10165 | -0.99351 | -0.01329 | 0.05976 | 0.26995 | -0.21395 |
| $\ell\sigma$Be' | -0.05976 | -0.26996 | 0.21395 | 0.10165 | 0.99351 | 0.01329 |

### $Be_2$(SAO)

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|
| $1\sigma_g$ | 1.28202 | 0.01562 | 1.01683 | 0.01423 |
| $2\sigma_g$ | 0.01562 | 0.35622 | 0.01554 | 0.04371 |
| $1\sigma_u$ | 1.01683 | 0.01554 | 1.28104 | 0.01429 |
| $2\sigma_u$ | 0.01423 | 0.04371 | 0.01429 | 0.2787 |

| | $\ell\sigma$Be' | $\ell\sigma$Be | iBe' | iBe |
|---|---|---|---|---|
| iBe | 0.00080 | 0.00497 | 0.00003 | 2.34507 |
| iBe' | 0.00497 | 0.00080 | 2.34508 | 0.00003 |
| $\ell\sigma$Be | 0.02456 | 0.33800 | 0.00080 | 0.00497 |
| $\ell\sigma$Be' | 0.33801 | 0.02456 | 0.00497 | 0.00080 |

| | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|
| iBe | 0.70187 | -0.08590 | -0.70250 | 0.08063 |
| iBe' | 0.70187 | -0.08590 | 0.70250 | -0.08062 |
| $\ell\sigma$Be | -0.08590 | -0.70187 | 0.08062 | 0.70250 |
| $\ell\sigma$Be' | 0.08590 | 0.70187 | 0.08063 | 0.70250 |

| | oBe | sBe | p$\sigma$Be | oBe' | sBe' | p$\sigma$Be' |
|---|---|---|---|---|---|---|
| iBe | 0.99756 | -0.08590 | 0.01007 | 0.00382 | 0.01079 | -0.03632 |
| iBe' | 0.00384 | 0.01079 | -0.03632 | 0.99756 | -0.08590 | 0.01007 |
| $\ell\sigma$Be | -0.09186 | -0.93541 | 0.01834 | 0.05112 | 0.21960 | -0.24835 |
| $\ell\sigma$Be' | -0.05112 | -0.21960 | 0.24835 | 0.09186 | 0.93541 | -0.01834 |

$Be_2$(BAO)

|  | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |  | iBe | ℓσBe | ℓσBe' | iBe' |
|---|---|---|---|---|---|---|---|---|---|
| $1\sigma_g$ | 1.27816 | 0.01478 | 1.01312 | 0.01326 | iBe | 2.33450 | 0.00478 | 0.00076 | 0.00002 |
| $2\sigma_g$ | 0.01478 | 0.35299 | 0.01471 | 0.04206 | iBe' | 0.00002 | 0.00076 | 0.00478 | 2.33451 |
| $1\sigma_u$ | 1.01312 | 0.01471 | 1.27747 | 0.01331 | ℓσBe | 0.00478 | 0.33269 | 0.02442 | 0.00076 |
| $2\sigma_u$ | 0.01326 | 0.04206 | 0.01331 | 0.27434 | ℓσBe' | 0.00076 | 0.02442 | 0.33269 | 0.00478 |

|  | $1\sigma_g$ | $2\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|
| iBe | -0.70219 | 0.08328 | -0.70283 | -0.07765 |
| iBe' | 0.70219 | -0.08327 | -0.70283 | -0.07766 |
| ℓBe | -0.08327 | -0.70219 | -0.07766 | 0.70283 |
| ℓBe' | 0.08328 | 0.70219 | -0.07765 | 0.70283 |

|  | oBe | sBe | pσBe | oBe' | sBe' | pσBe' |
|---|---|---|---|---|---|---|
| iBe | -0.99762 | 0.08518 | -0.00840 | -0.00405 | -0.01195 | 0.03463 |
| iBe' | 0.00401 | 0.01195 | -0.03463 | 0.99762 | -0.08518 | 0.00840 |
| ℓBe | -0.09025 | -0.94161 | 0.01021 | 0.05339 | 0.23262 | -0.24765 |
| ℓbe' | -0.05339 | -0.23262 | 0.24765 | 0.09025 | 0.94161 | -0.01021 |

Figure 19 (Continued)

$N_2$(BMO)

| | $1\sigma_g$ | $2\sigma_g$ | $3\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ | $1\pi_u$ | $1\bar{\pi}_u$ |
|---|---|---|---|---|---|---|---|
| $1\sigma_g$ | 2.31485 | 0.03182 | 0.01971 | 1.83095 | 0.03178 | 0.00928 | 0.00928 |
| $2\sigma_g$ | 0.03182 | 0.76061 | 0.05621 | 0.03147 | 0.05145 | 0.10227 | 0.10227 |
| $3\sigma_g$ | 0.01971 | 0.05621 | 0.62251 | 0.01848 | 0.22994 | 0.02918 | 0.02918 |
| $1\sigma_u$ | 1.83095 | 0.03147 | 0.01848 | 2.31480 | 0.03203 | 0.00879 | 0.00879 |
| $2\sigma_u$ | 0.03178 | 0.05145 | 0.22994 | 0.03203 | 0.55583 | 0.05099 | 0.05099 |
| $1\pi_u$ | 0.00928 | 0.10227 | 0.02918 | 0.00879 | 0.05099 | 0.58102 | 0.02390 |
| $1\bar{\pi}_u$ | 0.00928 | 0.10227 | 0.02918 | 0.00879 | 0.05099 | 0.02390 | 0.58102 |

| | iN | bt1NN' | bt2NN' | $\ell\sigma$N' | iN' | $\ell\sigma$N | bt3NN' |
|---|---|---|---|---|---|---|---|
| iN | 4.24785 | 0.00761 | 0.00761 | 0.00153 | 0.00004 | 0.01473 | 0.00761 |
| bt1NN' | 0.00761 | 0.71861 | 0.04817 | 0.03856 | 0.00761 | 0.03856 | 0.04817 |
| bt2NN' | 0.00761 | 0.04817 | 0.71863 | 0.03856 | 0.00761 | 0.03856 | 0.04817 |
| $\ell\sigma$N' | 0.00153 | 0.03856 | 0.03856 | 0.84228 | 0.01473 | 0.00189 | 0.03856 |
| iN' | 0.00004 | 0.00761 | 0.00761 | 0.01473 | 4.24785 | 0.00153 | 0.00761 |
| $\ell\sigma$N | 0.01473 | 0.03856 | 0.03856 | 0.00189 | 0.00153 | 0.84227 | 0.03856 |
| bt3NN' | 0.00761 | 0.04817 | 0.04817 | 0.03856 | 0.00761 | 0.03856 | 0.71863 |

| | $1\sigma_g$ | $2\sigma_g$ | $3\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ | $1\pi_u$ | $1\bar{\pi}_u$ |
|---|---|---|---|---|---|---|---|
| iN | -0.70027 | 0.08794 | 0.04340 | -0.70133 | 0.09020 | 0.00002 | 0.00003 |
| bt1NN' | 0.06015 | 0.55377 | -0.15170 | 0.00002 | 0.00000 | -0.38420 | 0.72049 |
| bt2NN' | -0.06013 | -0.55382 | 0.15173 | -0.00004 | -0.00000 | -0.81602 | 0.02749 |
| $\ell\sigma$N' | 0.06475 | 0.17952 | 0.68086 | -0.09021 | -0.70134 | 0.00000 | -0.00002 |
| iN' | 0.70028 | -0.08790 | -0.04341 | -0.70132 | 0.09022 | 0.00001 | -0.00001 |
| $\ell\sigma$N | 0.06473 | 0.17951 | 0.68088 | 0.09021 | 0.70132 | -0.00000 | -0.00003 |
| bt3NN' | -0.06011 | -0.55382 | 0.15176 | -0.00000 | -0.00000 | 0.43185 | 0.69292 |

Figure 20. Data for LMO's of $N_2$: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

$N_2$(BMO)

| | oN | sN | pσN | pπN | p$\bar{\pi}$N |
|---|---|---|---|---|---|
| iN | -0.99353 | 0.11366 | -0.02993 | 0.00001 | 0.00002 |
| bt1NN' | 0.00987 | 0.20851 | 0.22637 | -0.23874 | 0.44770 |
| bt2NN' | -0.00987 | -0.20852 | -0.22640 | -0.50706 | 0.01708 |
| ℓσN' | -0.02906 | -0.21166 | -0.19128 | 0.00000 | -0.00001 |
| iN' | 0.00371 | 0.00742 | -0.01994 | 0.00001 | -0.00001 |
| ℓσN | 0.12726 | 0.89194 | -0.51631 | -0.00000 | -0.00002 |
| bt3NN' | -0.00982 | -0.20851 | -0.22642 | 0.26835 | 0.43057 |

| | oN' | sN' | pσN' | pπN' | p$\bar{\pi}$N' |
|---|---|---|---|---|---|
| iN | -0.00369 | -0.00739 | 0.01996 | 0.00001 | 0.00002 |
| bt1NN' | 0.00984 | 0.20850 | 0.22637 | -0.23874 | 0.44770 |
| bt2NN' | -0.00982 | -0.20851 | -0.22641 | -0.50706 | 0.01708 |
| ℓσN' | 0.12729 | 0.89195 | -0.51630 | 0.00000 | -0.00001 |
| iN' | 0.99353 | -0.11367 | 0.02996 | 0.00001 | -0.00001 |
| ℓσN | -0.02907 | -0.21164 | -0.19130 | -0.00000 | -0.00002 |
| bt3NN' | -0.00982 | -0.20850 | -0.22642 | 0.26835 | 0.43057 |

Figure 20 (Continued)

$F_2$(BMO)

| | 1σg | 2σg | 3σg | 1σu | 2σu |
|---|---|---|---|---|---|
| ℓt1F | 0.05665 | 0.35529 | -0.19294 | 0.06036 | -0.40376 |
| ℓt1F' | 0.05666 | 0.35529 | -0.19295 | -0.06034 | 0.40375 |
| ℓt2F' | -0.05669 | -0.35534 | 0.19267 | 0.06036 | -0.40381 |
| ℓt3F' | -0.05665 | -0.35530 | 0.19298 | 0.06033 | -0.40377 |
| iF | -0.69984 | 0.09781 | -0.02539 | -0.69936 | -0.10449 |
| ℓt2F | -0.05666 | -0.35528 | 0.19298 | -0.06032 | 0.40378 |
| iF' | -0.69986 | 0.09784 | -0.02537 | 0.69933 | 0.10452 |
| bσFF' | 0.03413 | 0.47268 | 0.88057 | -0.00000 | -0.00012 |
| ℓt3F | -0.05665 | -0.35532 | 0.19298 | -0.06030 | 0.40370 |

| | 1πu | 1π̄u | 1πg | 1π̄g |
|---|---|---|---|---|
| ℓt1F | 0.41464 | -0.40176 | 0.41463 | -0.40176 |
| ℓt1F' | -0.19041 | -0.54506 | 0.19039 | 0.54505 |
| ℓt2F' | -0.56733 | -0.10765 | 0.56715 | 0.10758 |
| ℓt3F' | 0.37681 | -0.43741 | -0.37680 | 0.43742 |
| iF | 0.00003 | -0.00000 | 0.00001 | -0.00001 |
| ℓt2F | -0.14060 | -0.55995 | -0.14061 | -0.55996 |
| iF' | 0.00001 | 0.00001 | -0.00004 | 0.00002 |
| bσFF' | -0.00017 | -0.00000 | 0.00016 | 0.00004 |
| ℓt3F | 0.55515 | 0.15820 | 0.55535 | 0.15824 |

| | oF | sF | pσF | pπF | pπ̄F |
|---|---|---|---|---|---|
| ℓt1F | 0.07776 | 0.56426 | -0.12446 | 0.58693 | -0.56871 |
| ℓt1F' | -0.00426 | -0.03238 | -0.06616 | 0.00670 | 0.01919 |
| ℓt2F' | 0.00425 | 0.03244 | 0.06596 | 0.01986 | 0.00375 |
| ℓt3F' | 0.00426 | 0.03238 | 0.06618 | -0.01327 | 0.01541 |
| iF | -0.99082 | 0.13436 | -0.01673 | 0.00002 | -0.00001 |
| ℓt2F | -0.07774 | -0.56429 | 0.12449 | -0.19903 | -0.79264 |
| iF' | -0.00092 | -0.00791 | 0.00038 | -0.00002 | 0.00002 |
| bσFF' | 0.01401 | 0.15077 | 0.60980 | -0.00001 | 0.00002 |
| ℓt3F | -0.07772 | -0.56426 | 0.12449 | 0.78598 | 0.22397 |

| | oF' | sF' | pσF' | pπF' | pπ̄F' |
|---|---|---|---|---|---|
| ℓt1F | -0.00428 | -0.03239 | -0.06615 | -0.01460 | 0.01415 |
| ℓt1F' | 0.07776 | 0.56426 | -0.12447 | -0.26952 | -0.77154 |
| ℓt2F' | -0.07779 | -0.56429 | 0.12429 | -0.80294 | -0.15233 |
| ℓt3F' | -0.07774 | -0.56429 | 0.12449 | 0.53338 | -0.61918 |
| iF | -0.00088 | -0.00791 | 0.00037 | 0.00001 | 0.00000 |
| ℓt2F | 0.00425 | 0.03240 | 0.06617 | 0.00496 | 0.01973 |
| iF' | -0.99081 | 0.13439 | -0.01672 | 0.00004 | -0.00001 |
| bσFF' | 0.01401 | 0.15060 | 0.60982 | -0.00024 | -0.00003 |
| ℓt3F | 0.00424 | 0.03232 | 0.06618 | -0.01970 | -0.00560 |

Figure 21. Data for LMO's of $F_2$: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

$F_2$(BMO)

| | $1\sigma_g$ | $2\sigma_g$ | $3\sigma_g$ | $1\sigma_u$ | $2\sigma_u$ |
|---|---|---|---|---|---|
| $1\sigma_g$ | 2.87886 | 0.04144 | 0.01440 | 2.50504 | 0.04827 |
| $2\sigma_g$ | 0.04144 | 0.67447 | 0.10895 | 0.04140 | 0.24456 |
| $3\sigma_g$ | 0.01440 | 0.10895 | 0.67341 | 0.01416 | 0.13411 |
| $1\sigma_u$ | 2.50504 | 0.04140 | 0.01416 | 2.87755 | 0.04823 |
| $2\sigma_u$ | 0.04827 | 0.24456 | 0.13411 | 0.04823 | 0.63743 |
| $1\pi_u$ | 0.01494 | 0.10264 | 0.03012 | 0.01484 | 0.09191 |
| $1\bar{\pi}_u$ | 0.01494 | 0.10264 | 0.03012 | 0.01484 | 0.09191 |
| $1\pi_g$ | 0.01616 | 0.08435 | 0.02906 | 0.01638 | 0.10844 |
| $1\pi_g$ | 0.01616 | 0.08435 | 0.02906 | 0.01638 | 0.10844 |

| | $1\pi_u$ | $1\bar{\pi}_u$ | $1\pi_g$ | $1\bar{\pi}_g$ |
|---|---|---|---|---|
| $1\sigma_g$ | 0.01494 | 0.01494 | 0.01616 | 0.01616 |
| $2\sigma_g$ | 0.10264 | 0.10264 | 0.08435 | 0.08435 |
| $3\sigma_g$ | 0.03012 | 0.03012 | 0.02906 | 0.02906 |
| $1\sigma_u$ | 0.01484 | 0.01484 | 0.01638 | 0.01638 |
| $2\sigma_u$ | 0.09191 | 0.09191 | 0.10844 | 0.10844 |
| $1\pi_u$ | 0.67153 | 0.02675 | 0.32717 | 0.02663 |
| $1\bar{\pi}_u$ | 0.02675 | 0.67153 | 0.02663 | 0.32717 |
| $1\pi_g$ | 0.32717 | 0.02663 | 0.68838 | 0.02872 |
| $1\bar{\pi}_g$ | 0.02663 | 0.32717 | 0.02872 | 0.68838 |

| | ℓt1F | ℓt1F' | ℓt2F' | ℓt3F' | iF |
|---|---|---|---|---|---|
| ℓt1F | 1.13968 | 0.00064 | 0.00064 | 0.00096 | 0.02051 |
| ℓt1F' | 0.00064 | 1.13968 | 0.07502 | 0.07502 | 0.00012 |
| ℓt2F' | 0.00064 | 0.07502 | 1.13972 | 0.07502 | 0.00012 |
| ℓt3F' | 0.00096 | 0.07502 | 0.07502 | 1.13968 | 0.00012 |
| iF | 0.02051 | 0.00012 | 0.00012 | 0.00012 | 5.53074 |
| ℓt2F | 0.07502 | 0.00096 | 0.00063 | 0.00064 | 0.02051 |
| iF' | 0.00012 | 0.02051 | 0.02051 | 0.02051 | 0.00000 |
| bσFF' | 0.04512 | 0.04512 | 0.04511 | 0.04512 | 0.00854 |
| ℓt3F | 0.07502 | 0.00064 | 0.00096 | 0.00064 | 0.02051 |

| | ℓt2F | iF' | bσFF' | ℓt3F |
|---|---|---|---|---|
| ℓt1F | 0.07502 | 0.00012 | 0.04512 | 0.07502 |
| ℓt1F' | 0.00096 | 0.02051 | 0.04512 | 0.00064 |
| ℓt2F' | 0.00063 | 0.02051 | 0.04511 | 0.00096 |
| ℓt3F' | 0.00064 | 0.02051 | 0.04512 | 0.00064 |
| iF | 0.02051 | 0.00000 | 0.00854 | 0.02051 |
| ℓt2F | 1.13968 | 0.00012 | 0.04512 | 0.07502 |
| iF' | 0.00012 | 5.53074 | 0.00854 | 0.00012 |
| bσFF' | 0.04512 | 0.00854 | 0.78776 | 0.04511 |
| ℓt3F | 0.07502 | 0.00012 | 0.04511 | 1.13968 |

Figure 21 (Continued)

Figure 22. Data for LMO's of BF: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

BF (SAO)

| | 1σ | 2σ | 3σ | 4σ | 5σ | 1π | 1π̄ |
|---|---|---|---|---|---|---|---|
| 1σ | 5.40393 | 0.00000 | 0.08500 | 0.03101 | 0.00308 | 0.02665 | 0.02665 |
| 2σ | 0.00000 | 2.92115 | 0.00379 | 0.01102 | 0.02962 | 0.00143 | 0.00143 |
| 3σ | 0.08500 | 0.00379 | 0.88095 | 0.15662 | 0.01612 | 0.16722 | 0.16722 |
| 4σ | 0.03101 | 0.01102 | 0.15662 | 0.86718 | 0.03975 | 0.05076 | 0.05076 |
| 5σ | 0.00308 | 0.02962 | 0.01612 | 0.03975 | 0.51067 | 0.01058 | 0.01058 |
| 1π | 0.02665 | 0.00143 | 0.16722 | 0.05076 | 0.01058 | 0.85406 | 0.04240 |
| 1π̄ | 0.02665 | 0.00143 | 0.16722 | 0.05076 | 0.01058 | 0.04240 | 0.85406 |

| | ℓσB | ℓσF | iF | bt1BF | bt2BF | iB | bt3BF |
|---|---|---|---|---|---|---|---|
| ℓσB | 0.52289 | 0.00234 | 0.00032 | 0.00856 | 0.00855 | 0.00740 | 0.00855 |
| ℓσF | 0.00234 | 1.08913 | 0.01904 | 0.07480 | 0.07519 | 0.00110 | 0.07504 |
| iF | 0.00032 | 0.01904 | 5.55578 | 0.01792 | 0.01799 | 0.00002 | 0.01797 |
| bt1BF | 0.00856 | 0.07480 | 0.01792 | 0.97143 | 0.06795 | 0.00134 | 0.06790 |
| bt2BF | 0.00855 | 0.07519 | 0.01799 | 0.06795 | 0.97287 | 0.00128 | 0.06802 |
| iB | 0.00740 | 0.00110 | 0.00002 | 0.00134 | 0.00128 | 2.98574 | 0.00130 |
| bt3BF | 0.00855 | 0.07504 | 0.01797 | 0.06790 | 0.06802 | 0.00130 | 0.97235 |

| | 1σ | 2σ | 3σ | 4σ | 5σ | 1π | 1π̄ |
|---|---|---|---|---|---|---|---|
| ℓσB | 0.00808 | 0.11468 | -0.07184 | -0.22097 | -0.96581 | 0.00020 | -0.00013 |
| ℓσF | -0.09031 | -0.02078 | -0.36423 | 0.90796 | -0.18387 | -0.01999 | 0.01174 |
| iF | 0.98933 | 0.00080 | -0.13840 | 0.04461 | 0.00846 | 0.00006 | -0.00000 |
| bt1BF | -0.06536 | 0.02129 | -0.53285 | -0.22043 | 0.09186 | -0.79833 | 0.13032 |
| bt2BF | 0.06618 | -0.01980 | 0.52713 | 0.18432 | -0.08335 | -0.29281 | 0.76857 |
| iB | 0.00045 | 0.99255 | 0.03358 | 0.05696 | 0.10233 | 0.00007 | -0.00003 |
| bt3BF | -0.06592 | 0.02034 | -0.52923 | -0.19741 | 0.08642 | 0.52586 | 0.62624 |

BF (SAO)

| | oB | sB | pσB | pπB | p$\bar{\pi}$B |
|---|---|---|---|---|---|
| ℓσB | 0.11081 | 0.92966 | −0.38979 | −0.00006 | 0.00004 |
| ℓσF | −0.00071 | −0.12053 | −0.21110 | 0.00590 | −0.00347 |
| iF | −0.00257 | −0.00478 | 0.01379 | −0.00002 | 0.00000 |
| bt1BF | −0.00901 | 0.05186 | 0.13128 | 0.23576 | −0.03848 |
| bt2BF | 0.00888 | −0.04605 | −0.12043 | 0.08647 | −0.22697 |
| iB | 0.99510 | −0.09760 | 0.03712 | −0.00002 | 0.00001 |
| bt3BF | −0.00893 | 0.04817 | 0.12436 | −0.15529 | −0.18494 |

| | oF | sF | pσF | pπF | p$\bar{\pi}$F |
|---|---|---|---|---|---|
| ℓσB | −0.01777 | −0.10908 | −0.08430 | −0.00018 | 0.00012 |
| ℓσF | 0.10113 | 0.67053 | −0.75079 | 0.01804 | −0.01060 |
| iF | −0.99185 | 0.12597 | −0.01993 | −0.00005 | 0.00000 |
| bt1BF | 0.04871 | 0.40239 | 0.27263 | 0.72054 | −0.11762 |
| bt2BF | −0.05041 | −0.41070 | −0.23993 | 0.26428 | −0.69368 |
| iB | 0.00091 | −0.00115 | −0.01982 | −0.00006 | 0.00003 |
| bt3BF | 0.04983 | 0.40771 | 0.25179 | −0.47463 | −0.56522 |

Figure 22 (Continued)

Figure 23. Data for LMO's of LiF: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

LiF (SAO)

| | 1σ | 2σ | 3σ | 4σ | 1π | 1π̄ |
|---|---|---|---|---|---|---|
| 1σ | 5.40531 | 0.00010 | 0.09164 | 0.03181 | 0.02574 | 0.02574 |
| 2σ | 0.00010 | 1.66911 | 0.00624 | 0.00605 | 0.00117 | 0.00117 |
| 3σ | 0.09164 | 0.00624 | 0.88899 | 0.18774 | 0.16435 | 0.16435 |
| 4σ | 0.03181 | 0.00605 | 0.18774 | 0.98702 | 0.04593 | 0.04593 |
| 1π | 0.02574 | 0.00117 | 0.16435 | 0.04593 | 0.78356 | 0.03897 |
| 1π̄ | 0.02574 | 0.00117 | 0.16435 | 0.04593 | 0.03897 | 0.78356 |

| | ℓσF | iF | bt1LiF | iLi | bt2LiF | bt3LiF |
|---|---|---|---|---|---|---|
| ℓσF | 1.14794 | 0.02116 | 0.07117 | 0.00040 | 0.07090 | 0.07089 |
| iF | 0.02116 | 5.55512 | 0.01821 | 0.00004 | 0.01825 | 0.01826 |
| bt1LiF | 0.07117 | 0.01821 | 0.93397 | 0.00094 | 0.06831 | 0.06832 |
| iLi | 0.00040 | 0.00004 | 0.00094 | 1.68609 | 0.00097 | 0.00097 |
| bt2LiF | 0.07090 | 0.01825 | 0.06831 | 0.00097 | 0.93678 | 0.06847 |
| bt3LiF | 0.07089 | 0.01826 | 0.06832 | 0.00097 | 0.06847 | 0.93694 |

| | 1σ | 2σ | 3σ | 4σ | 1π | 1π̄ |
|---|---|---|---|---|---|---|
| ℓσF | 0.08374 | −0.01472 | −0.48072 | 0.87254 | −0.01864 | 0.00259 |
| iF | −0.98935 | 0.00546 | −0.14461 | 0.01537 | −0.00002 | −0.00001 |
| bt1LiF | 0.06878 | 0.04046 | −0.49701 | −0.26200 | 0.80942 | −0.15100 |
| iLi | −0.00192 | 0.99729 | 0.05585 | 0.04778 | 0.00007 | 0.00001 |
| bt2LiF | 0.06866 | 0.04191 | −0.49889 | −0.28867 | −0.26422 | 0.76909 |
| bt3LiF | 0.06867 | 0.04201 | −0.49897 | −0.29013 | −0.52409 | −0.62104 |

LiF (SAO)

| | oLi | sLi | pσLi | pπLi | p$\bar{\pi}$Li |
|---|---|---|---|---|---|
| bσF | 0.01051 | -0.07774 | -0.05498 | 0.00671 | -0.00093 |
| iF | -0.00315 | 0.00801 | 0.01045 | 0.00001 | 0.00000 |
| bt1LiF | -0.01241 | 0.05700 | 0.05486 | -0.29124 | 0.05433 |
| iLi | 1.00172 | 0.00986 | -0.01097 | -0.00002 | -0.00000 |
| bt2LiF | -0.01290 | 0.06024 | 0.05753 | 0.09507 | -0.27673 |
| bt3LiF | -0.01290 | 0.06042 | 0.05767 | 0.18858 | 0.22346 |

| | oF | sF | pσF | pπF | p$\bar{\pi}$F |
|---|---|---|---|---|---|
| bσF | 0.08126 | 0.57000 | -0.83388 | 0.01657 | -0.00231 |
| iF | -0.99192 | 0.12536 | -0.00965 | 0.00002 | 0.00001 |
| bt1LiF | 0.05815 | 0.44664 | 0.27786 | -0.71950 | 0.13423 |
| iLi | -0.00217 | -0.02159 | -0.03180 | -0.00006 | -0.00001 |
| bt2LiF | 0.05781 | 0.44519 | 0.30405 | 0.23487 | -0.68365 |
| bt3LiF | 0.05781 | 0.44509 | 0.30549 | 0.46587 | 0.55205 |

Figure 23 (Continued)

CO(SAO)

| | 1σ | 2σ | 3σ | 4σ | 5σ | 1π | 1$\bar{\pi}$ |
|---|---|---|---|---|---|---|---|
| 1σ | 4.78140 | 0.00000 | 0.05935 | 0.03355 | 0.00550 | 0.01707 | 0.01707 |
| 2σ | 0.00000 | 3.54186 | 0.01344 | 0.02039 | 0.02694 | 0.00461 | 0.00461 |
| 3σ | 0.05935 | 0.01344 | 0.78729 | 0.09608 | 0.03380 | 0.12332 | 0.12332 |
| 4σ | 0.03355 | 0.02039 | 0.09608 | 0.72241 | 0.10878 | 0.05037 | 0.05037 |
| 5σ | 0.00550 | 0.02694 | 0.03380 | 0.10878 | 0.60206 | 0.02188 | 0.02188 |
| 1π | 0.01707 | 0.00461 | 0.12332 | 0.05037 | 0.02188 | 0.65626 | 0.02875 |
| 1$\bar{\pi}$ | 0.01707 | 0.00461 | 0.12332 | 0.05037 | 0.02188 | 0.02875 | 0.65626 |

| | bt1CO | bt2CO | iC | ℓσO | ℓσC | bt3CO | iO |
|---|---|---|---|---|---|---|---|
| bt1CO | 0.78814 | 0.05271 | 0.00370 | 0.05529 | 0.02094 | 0.05271 | 0.01222 |
| bt2CO | 0.05271 | 0.78823 | 0.00370 | 0.05527 | 0.02093 | 0.05271 | 0.01221 |
| iC | 0.00370 | 0.00370 | 3.62662 | 0.00132 | 0.00977 | 0.00370 | 0.00003 |
| ℓσO | 0.05529 | 0.05527 | 0.00132 | 0.96696 | 0.00199 | 0.05527 | 0.01546 |
| ℓσC | 0.02094 | 0.02093 | 0.00977 | 0.00199 | 0.67426 | 0.02093 | 0.00059 |
| bt3CO | 0.05271 | 0.05271 | 0.00370 | 0.05527 | 0.02093 | 0.78823 | 0.01221 |
| iO | 0.01222 | 0.01221 | 0.00003 | 0.01546 | 0.00059 | 0.01221 | 4.90985 |

| | 1σ | 2σ | 3σ | 4σ | 5σ | 1π | 1$\bar{\pi}$ |
|---|---|---|---|---|---|---|---|
| bt1CO | 0.05540 | −0.03233 | −0.54368 | 0.12951 | 0.12813 | 0.55333 | 0.60077 |
| bt2CO | 0.05536 | −0.03249 | −0.54393 | 0.13045 | 0.12858 | 0.24374 | −0.77914 |
| iC | −0.00078 | −0.99182 | 0.06030 | −0.07625 | 0.08273 | −0.00003 | 0.00008 |
| ℓσO | −0.10093 | −0.02192 | 0.28531 | 0.88763 | 0.34647 | 0.00059 | 0.00054 |
| ℓσC | −0.01200 | −0.11254 | −0.11611 | 0.38742 | −0.90753 | 0.00002 | 0.00000 |
| bt3CO | 0.05536 | −0.03239 | −0.54395 | 0.13056 | 0.12860 | −0.79650 | 0.17893 |
| iO | 0.99019 | 0.00106 | 0.11896 | 0.07327 | 0.00283 | 0.00001 | −0.00000 |

Figure 24. Data for LMO's of CO: exchange integrals for SCF MO's and LMO's, transformation matrix from SCF MO's to LMO's, and LCAO expansions of LMO's.

CO(SAO)

|  | oC | sC | pσC | pπC | p$\bar{\pi}$C |
|---|---|---|---|---|---|
| bt1CO | 0.00868 | -0.10075 | -0.17274 | -0.25931 | -0.28154 |
| bt2CO | 0.00858 | -0.10097 | -0.17309 | -0.11423 | 0.36514 |
| iC | -0.99570 | 0.09879 | -0.03737 | 0.00001 | -0.00004 |
| ℓσO | -0.00553 | -0.14415 | -0.20797 | -0.00028 | -0.00025 |
| ℓσC | -0.11880 | -0.90341 | 0.46728 | -0.00001 | -0.00000 |
| bt3CO | 0.00869 | -0.10102 | -0.17311 | 0.37327 | -0.08385 |
| iO | -0.00291 | -0.00180 | 0.01978 | -0.00000 | 0.00000 |

|  | oO | sO | pσO | pπO | p$\bar{\pi}$O |
|---|---|---|---|---|---|
| bt1CO | -0.03016 | -0.31530 | -0.26001 | -0.42676 | -0.46334 |
| bt2CO | -0.03008 | -0.31487 | -0.26086 | -0.18799 | 0.60091 |
| iC | -0.00111 | 0.00426 | 0.02634 | 0.00002 | -0.00006 |
| ℓσO | 0.11723 | 0.78849 | -0.65111 | -0.00045 | -0.00041 |
| ℓσC | 0.01700 | 0.12886 | 0.12563 | -0.00001 | -0.00000 |
| bt3CO | -0.03008 | -0.31481 | -0.26094 | 0.61429 | -0.13800 |
| iO | -0.99346 | 0.11497 | -0.02691 | -0.00001 | 0.00000 |

Figure 24 (Continued)

LiH(BMO)

| | oLi | sLi | pσLi | oH |
|---|---|---|---|---|
| iLi | 0.99625 | -0.04100 | -0.04758 | -0.12843 |
| bσLiH | -0.11140 | -0.29968 | -0.20615 | -0.69209 |

BH(BMO)

| | oB | sB | pσB | oH |
|---|---|---|---|---|
| iB | 0.97372 | -0.21276 | 0.08121 | -0.00002 |
| bσBH | -0.04858 | -0.37169 | -0.39112 | -0.53432 |
| ℓσB | 0.19271 | 0.85142 | -0.50180 | -0.24568 |

NH(BMO)

| | oN | sN | pσN | pπN | $p\bar{\pi}$N | oH |
|---|---|---|---|---|---|---|
| iN | 0.99602 | -0.08260 | -0.01716 | 0.00000 | 0.00000 | -0.03542 |
| bt1NH | 0.05388 | 0.47015 | 0.08801 | -0.57985 | -0.57482 | 0.15747 |
| bt2NH | -0.05388 | -0.47015 | -0.08801 | 0.20792 | -0.78961 | -0.15747 |
| bt3NH | -0.05388 | -0.47015 | -0.08801 | -0.78775 | 0.21471 | -0.15747 |

HF(BMO)

| | oF | sF | pσF | pπF | $p\bar{\pi}$F | oH |
|---|---|---|---|---|---|---|
| iF | 0.99161 | -0.12724 | 0.02268 | 0.00000 | 0.00000 | 0.00004 |
| ℓt1F | 0.07279 | 0.51829 | -0.27840 | -0.15180 | -0.80094 | -0.16979 |
| ℓt2F | 0.07279 | 0.51829 | -0.27840 | 0.77090 | 0.27077 | -0.16979 |
| ℓt3F | 0.07279 | 0.51929 | -0.27840 | -0.61861 | 0.53398 | -0.16979 |
| bσHF | 0.04258 | 0.42672 | 0.53039 | 0.00000 | 0.00000 | 0.45112 |

Figure 25. Data for the VMO's of the diatomic hydrids: LCAO expansions.

Li$_2$(BMO)

| | oLi | sLi | pσLi | oLi | sLi | pσLi |
|---|---|---|---|---|---|---|
| iLi | 1.00057 | 0.06991 | 0.01553 | 0.00181 | -0.04074 | -0.01107 |
| iLi' | 0.00181 | -0.04074 | -0.01107 | 1.00057 | 0.06991 | 0.01553 |
| bσLiLi' | 0.05985 | 0.51715 | 0.11282 | 0.05985 | 0.51715 | 0.11282 |

N$_2$(BMO)

| | oN | sN | pσN | pπN | pπ̄N |
|---|---|---|---|---|---|
| iN | -0.95666 | -0.01595 | 0.15477 | 0.00000 | 0.00000 |
| iN' | 0.03088 | -0.15247 | 0.20921 | 0.00000 | 0.00000 |
| ℓσN | -0.10213 | 0.85949 | -0.49586 | 0.00000 | 0.00000 |
| ℓσN' | -0.27231 | -0.24229 | -0.17158 | 0.00000 | 0.00000 |
| bt1NN' | 0.03467 | 0.23298 | 0.19599 | 0.24826 | -0.44263 |
| bt2NN' | 0.03467 | 0.23298 | 0.19599 | 0.25976 | 0.43607 |
| bt3NN' | 0.03467 | 0.23298 | 0.19599 | -0.50696 | 0.00668 |
| | oN' | sN' | pσN' | pπN' | pπ̄N' |
| iN | 0.03088 | -0.15247 | 0.20921 | 0.00000 | 0.00000 |
| iN' | -0.95666 | -0.01595 | 0.15477 | 0.00000 | 0.00000 |
| ℓσN | -0.27231 | -0.24229 | -0.17158 | 0.00000 | 0.00000 |
| ℓσN' | -0.10213 | 0.85949 | -0.49586 | 0.00000 | 0.00000 |
| bt1NN' | 0.03467 | 0.23298 | 0.19599 | 0.24826 | -0.44263 |
| bt2NN' | 0.03467 | 0.23298 | 0.19599 | 0.25976 | 0.43607 |
| bt3NN' | 0.03467 | 0.23298 | 0.19599 | 0.25976 | 0.43607 |

Figure 26. Data for the VMO's of the homonuclear diatomics: LCAO expansions.

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