not a contradiction, but only a reflection of the difference between the approximations employed; it is not surprising that the valence orbitals of atoms in compounds will become largely different from those of free atoms when, as has been done by Craig and Zauli, a higher approximation is taken. The problem is whether the higher approximation is necessary or not in order to interpret electronic structures of molecules. It is, therefore, a happy finding for those who desire matters to be as simple as possible that our ylides I and II can be adequately treated by the ordinary procedure using the free 3d orbitals of the sulfur of phosphorus atom, which predicts their energies semiquantitatively.

Acknowledgments. We wish to thank Dr. Tsunetoshi Kobayashi for useful discussions on the estimation of the resonance integrals. One of us (K. I.) wishes to thank Professor Michio Kurata for his kind hospitality during the course of this work.

A Generalized Orbital Description of the Reactions of Small Molecules[1]

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Abstract: The usual Hartree–Fock method leads to an improper description of the breaking of a bond, a problem that is overcome by the generalized valence-bond method. This method uses one orbital per electron as in the valence-bond method, but solves for the orbitals self-consistently as in the Hartree–Fock method. In this paper we consider the changes in the orbitals as the H_2 and LiH bonds are broken and we consider the orbital description of the $H_2 + D \rightleftharpoons H + HD$ and $LiH + H \rightleftharpoons Li + H_2$ exchange reactions. We find that this orbital description leads to simple concepts in terms of which the changes in the system during reaction can be understood. It is expected that these concepts will apply to a large number of reactions.

A primary goal of chemistry is to elucidate the details of the processes occurring during chemical reactions. Thus, one wants to understand how all the bonds distort, form, and break in the transition region and why some reactions have high activation energies while others have low ones. Unfortunately, the intermediate states in such reactions are quite ephemeral, leading to difficulties in experimentally establishing an unambiguous description of the states in the transition region. Theoretical studies of such states, however, can be quite informative, since we can choose the nuclear configuration and reaction path and can examine in detail the changes in the bonding for each likely course of the reaction. Even so, not every theoretical approach is equally useful. It is not only necessary that the theoretical method lead to an accurate description of the potential surface or interaction energy, but it is also important that the resulting wave functions lead to concepts useful in understanding the relationships between whole classes of reactions.

The most generally used theoretical approach for *a priori* calculations of the wave functions of molecules has been the Hartree–Fock method or approximations thereto. Despite many successes in describing the ground states of molecules, this method has a key deficiency in its inability to describe properly the processes of breaking a bond.[4] We have found that an alternative approach, the generalized valence-bond (GVB) method, leads to a proper description of bond breaking and yet retains the useful orbital interpretation. This method has been far less extensively developed than the Hartree–Fock method; however, calculations on some simple reactions have now been carried out and lead to some concepts that are expected to be of rather general applicability.

We will concentrate here on the description of the $H_2 + D \rightleftharpoons H + HD$ and $LiH + H \rightleftharpoons Li + H_2$ exchange reactions with an emphasis on the orbital description of these systems in the transition region.

The Theoretical Methods for the Calculation of Molecular Wave Functions

First, some comparison between the Hartree–Fock and GVB methods will be appropriate.

The Hartree–Fock Method. A common approach for electronic wave functions of molecules has been the Hartree–Fock method,[5] in which the wave function is taken as an antisymmetrized product (determinant) of spatial and spin functions; the antisymmetrization ensures that Pauli's principle is satisfied. Thus, for H_2 the Hartree–Fock wave function is

$$\mathcal{A}[\phi(1)\alpha(1)\phi(2)\beta(2)] = \phi(1)\phi(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrizer (determinant operator), ϕ is the best possible doubly occupied spatial orbital,

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(1) Partially supported by a grant (No. GP-15423) from the National Science Foundation.

(2) Alfred P. Sloan Fellow.

(3) NSF Predoctoral Fellow.

(4) *E.g.*, R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).

(5) D. R. Hartree, "The Calculation of Atomic Structures," Wiley, New York, N. Y., 1957.

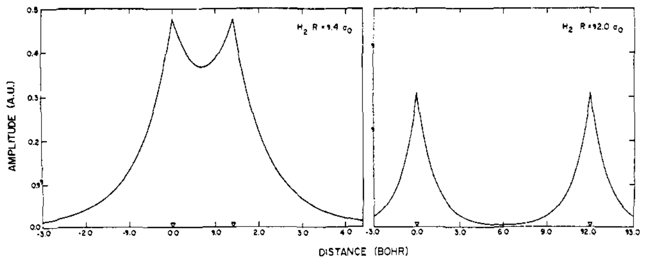

Figure 1. The Hartree–Fock orbital of H_2 for (a) $R = 1.4\ a_0 = 0.741$ Å and (b) $R = 12.0\ a_0 = 6.35$ Å.

and α and β are spin functions. For H_2 the optimum ϕ is *gerade* as shown[6,7] in Figure 1 and can be expanded as

$$\phi = \chi_l + \chi_r$$

where χ_l is a function localized near the left proton and χ_r is localized near the right one. In this expansion the spatial part of the total wave function is

$$\phi(1)\phi(2) = (\chi_r\chi_r + \chi_l\chi_l) + (\chi_r\chi_l + \chi_l\chi_r) \qquad (2)$$

(where we have omitted the electron numbers from the products on the right; the first term in each product depends on the corrdinates of electron 1 and the second on those of electron 2). This form (2) applies to all internuclear distances R, whereas for large internuclear distances the wave function should be of the form

$$(\chi_r\chi_l + \chi_l\chi_r) \qquad (3)$$

i.e., there should be nearly zero probability of both electrons being simultaneously near the same nucleus (here χ is essentially a hydrogen 1s orbital). Because of the spurious ionic terms in (2), the Hartree–Fock wave function behaves incorrectly at large R, as indicated in Figure 2, which compares the Hartree–Fock and exact energies.[8] Such a poor description of the breaking or formation of a bond is intolerable in studies of chemical reactions.

What is the problem here? It is just that the Hartree–Fock method *forces* both electrons to be in one orbital, whereas, for large separations, we must have two singly occupied orbitals [as in (3)]. An obvious solution to this problem is to go back to (1) and allow the orbital to be different for the spin-up and spin-down electrons

$$\mathcal{A}[\phi_a(1)\alpha(1)\phi_b(2)\beta(2)] = \phi_a\phi_b\alpha\beta - \phi_b\phi_a\beta\alpha \qquad (4)$$

(where in each term on the right the first orbital is for electron 1 and the second is for electron 2; similarly, the first spin function is for electron 1 and the second is for electron 2). Variationally optimizing ϕ_a and ϕ_b in (4), one obtains the *unrestricted Hartree–Fock* (UHF) wave function.[9] In this case at large R, ϕ_a concentrates on the left nucleus and ϕ_b concentrates on the right nucleus so that the wave function dissociates correctly. We know that the ground state of H_2 is a singlet state; however, we can rewrite (4) as

$$^1/_2[(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha) + (\phi_a\phi_b - \phi_b\phi_a)(\alpha\beta + \beta\alpha)] \qquad (4')$$

where the first term in (4′) corresponds to a singlet spin state and the second term corresponds to a triplet spin state. Thus, unless

$$\phi_a = \phi_b$$

(which makes the second term zero), the wave function has both singlet and triplet components. We are on the horns of a dilemma: to obtain the correct spin symmetry, we must doubly occupy the orbitals, resulting in improper dissociation; to obtain the correct dissociation, we must singly occupy the oribitals, resulting in the wrong spin symmetry. Since for studying chemical reactions we want both the correct dissociation and the correct spin symmetry, we *must* go beyond the Hartree–Fock approximation. Yet the interpretation of the many-electron wave function in terms of one-particle orbitals has been of great use in forming a conceptually useful description of the states of atoms and molecules; we certainly want to retain this interpretability in any improvement upon Hartree–Fock.

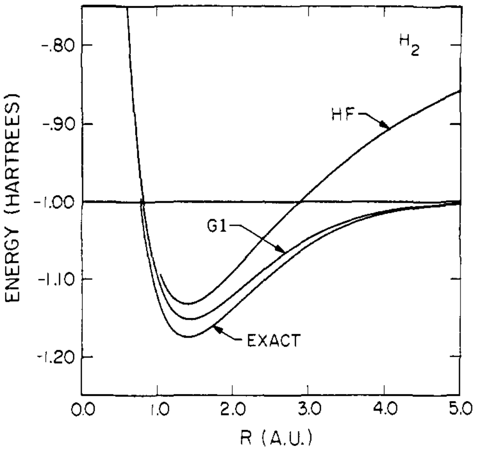

Figure 2. The energy of H_2 as obtained fom Hartree–Fock (HF) and SOGI calculations, compared with the exact nonrelativistic energies.

Many workers have contributed to the development of methods designed to remove these problems with spin symmetry and dissociation while retaining the conceptual advantages associated with an orbital-type wave function. We will present here only a short sketch of these developments while describing the theoretical methods used herein.

The Generalized Valence-Bond Method. In the Hartree–Fock method the antisymmetrizer, $\mathcal{A}$, took care of the Pauli principle but not the spin symmetry (*i.e.*, $\mathcal{A}\Phi$ satisfies Pauli's principle for an arbitrary many-electron wave function Φ but has a correct spin symmetry only for specific choices of Φ). Now we will replace $\mathcal{A}$ by the group operator[10] G_i^γ, which *simultaneously* takes care of *both* the spin symmetry *and* the Pauli principle (*i.e.*, $G_i^\gamma\Phi$ satisfies Pauli's principle and has the correct spin symmetry for arbitrary Φ). For a

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(6) S. Fraga and B. J. Ransil, *J. Chem. Phys.*, **35**, 1967 (1961).

(7) Most figures are in terms of hartree atomic units, which are defined such that $\hbar = 1$, $|e| = 1$, $m_e = 1$. In these units the unit of energy is the hartree (1 hartree = 27.2117 eV = 627.526 kcal) and the unit of length is the bohr (1 bohr = 1 a_0 = 0.529177 Å). For the most recent conversion factors, see B. N. Taylor, W. H. Parker, and D. N. Langenberg, *Rev. Mod. Phys.*, **41**, 375 (1969).

(8) In Figure 2 the HF energy is from ref 6 and the exact (nonrelativistic) energy is from W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **41**, 3663 (1964).

(9) J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 471 (1954); J. C. Slater, *Phys. Rev.*, **82**, 538 (1951); G. W. Pratt Jr., *ibid.*, **102**, 1303 (1956); R. K. Nesbet, *Proc. Roy. Soc., Ser. A*, **230**, 312 (1955).

(10) W. A. Goddard III, *Phys. Rev.*, **157**, 81 (1967).

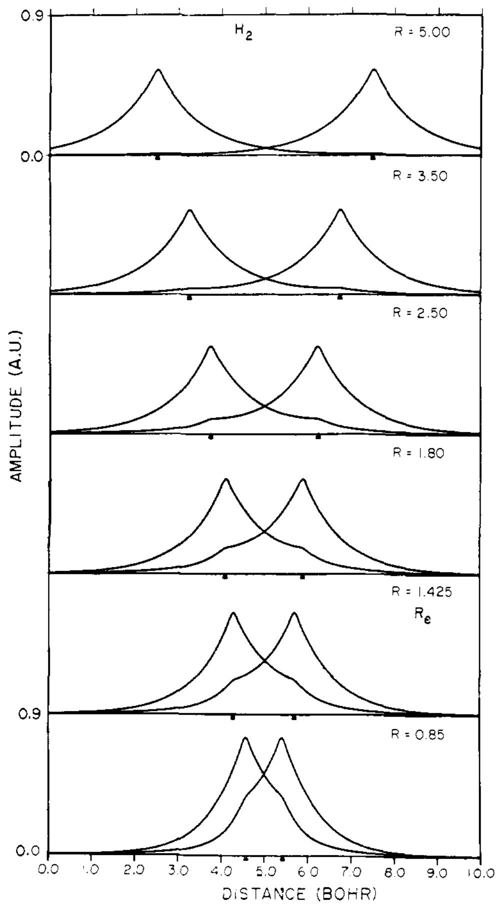

Figure 3. The SOGI orbitals of H_2 as a function of internuclear distance. Atomic units are used (ref 7).

two-electron singlet state, this wave function is

$$G_1^{\gamma}[\phi_a(1)\phi_b(2)\alpha(1)\beta(2)] = \frac{1}{4}(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha) \quad (5)$$

Since (5) has the correct spin symmetry regardless of the form of ϕ_a and ϕ_b, we need not make any restrictions (*e.g.*, double occupation) on these orbitals. We now require that the orbitals be self-consistently optimized. This leads to a set of *two* one-particle equations to be solved rather than one as in Hartree–Fock. The resulting self-consistent orbitals are called the generalized valence-bond (GVB) orbitals (previously such wave functions have also been referred to as G1 or GI wave functions).[10]

The GVB orbitals for the ground state of H_2 are shown[11] in Figure 3. Here we see that as R decreases from infinity, the orbitals gradually and smoothly change from atomic functions to the correct molecular functions at equilibrium, R_e. Comparing the GVB orbitals for R_e (1.4 a_0) with the atomic function, we find that the amplitude of the orbital has increased throughout the bonding region and has decreased in the nonbonding regions.[10] As a result, the overlap S_{ab} of the GVB molecular orbitals ϕ_a and ϕ_b is larger than would be the overlap of the atomic functions at the same distance. A comparison between Figures 1 and 3 shows a characteristic difference between Hartree–Fock and GVB orbitals. Hartree–Fock orbitals can generally be taken as symmetry functions for the total molecular symmetry group, whereas the GVB orbitals may have lower symmetry.

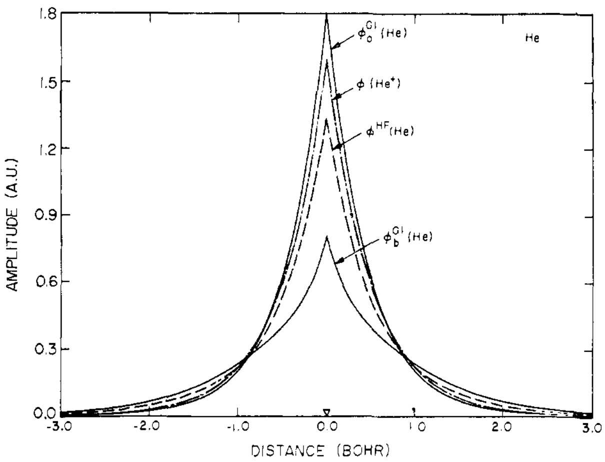

Figure 4. The SOGI orbitals of He compared with the orbital of He^+ and the HF orbital of He.

If ϕ_a and ϕ_b of (5) are taken to be H 1s orbitals (χ_a and χ_b) on two protons

$$(\chi_a\chi_b + \chi_b\chi_a)(\alpha\beta - \beta\alpha) \quad (6)$$

then (6) is just the simple Heitler–London or valence-bond wave function. This wave function can be improved by adding in ionic components

$$(\chi_a\chi_b + \chi_b\chi_a) + c(\chi_a\chi_a + \chi_b\chi_b) \quad (7)$$

and optimizing the mixing coefficient c (and the orbital exponents of the exponential basis functions, χ) to obtain the Weinbaum–Pauling wave function.[12] The interpretation of wave function 7 seems more complicated than for the simple wave functions 5 or 6, but Coulson and Fischer[13] showed that (7) could be written in the form (5) if

$$\phi_a = \chi_a + c'\chi_b$$

$$\phi_b = \chi_b + c'\chi_a$$

Thus the GVB wave function of H_2 can be considered as a generalization of the Coulson–Fischer form of the Weinbaum–Pauling wave function in which we now variationally solve for the best possible orbitals for (5), rather than restricting the orbitals to be expressible in terms of an H 1s function on each center.

Note that if in (5) we set $\phi_a = \phi_b = \phi_{HF}$, we obtain the Hartree–Fock wave function (1), and if we set ϕ_a and ϕ_b to be atomic functions centered on each proton, we obtain the Heitler–London or valence-bond (VB) wave function. Thus the GVB method can be considered as a generalization and synthesis of the Hartree–Fock and VB methods.

For a two-electron atom such as H^-, He, or Li^+, the GVB orbitals split radially so that one of the orbitals is more concentrated near the nucleus than the other orbital,[14] as shown for He in Figure 4. The tighter

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[11] Based on GVB (or G1) calculations using a basis of six 1s Gaussian functions and two 2p Gaussians contracted to three 1s and one 2p functions on each proton.

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

[13] C. A. Coulson and I. Fischer, *Phil. Mag.*, 40, 386 (1949).

[14] W. A. Goddard III, *J. Chem. Phys.*, **48**, 1008 (1968); note that for two electrons the wave functions variously referred to as GF, G1, GI, and SOGI are all identical.

orbital ϕ_a is typically similar to the orbital for the one-electron ion as shown in Figure 4, while the other orbital ϕ_b is more diffuse, something like the state of an electron moving in a shielded nuclear potential.[15] Wave functions of the form (5) for two-electron atoms were investigated by Shull and Löwdin,[16] who discussed the interpretation in terms of radical correlation.

For a four-electron singlet state, the simple valence-bond wave function is taken to have the form

$$\psi_1 = \mathcal{A}[(\phi_a\phi_b + \phi_b\phi_a)(\phi_c\phi_d + \phi_d\phi_a)\alpha\beta\alpha\beta] \quad (8a)$$

But for more than two electrons one can generally construct several independent many-electron wave functions from the same set of orbitals. For example, if

$$\psi_2 = \mathcal{A}[(\phi_a\phi_d + \phi_d\phi_a)(\phi_c\phi_b + \phi_b\phi_c)\alpha\beta\alpha\beta] \quad (8b)$$

then

$$\Psi = C_1\psi_1 + C_2\psi_2 \quad (8c)$$

is the most general wave function for a four-electron singlet state that uses each of four orbitals $\{\phi_a, \phi_b, \phi_c, \phi_d\}$ in each term. For the ground state of a molecule, a single coupling scheme as in (8a) often leads to a good description and we will refer to such a wave function as the valence-bond (VB) wave function.

An important step forward was made by Hurley, Lennard-Jones, and Pople[17a] (HLJP) and by Parks and Parr,[17b] who discussed wave functions of the form (8a) and suggested using a simple constraint to simplify calculations; namely, that the orbitals of each pair [*e.g.*, (ϕ_a, ϕ_b)] be required to be orthogonal to all other pairs [in this case (ϕ_c, ϕ_d)]. This restriction is called the strong orthogonality (SO) restriction and greatly simplified the calculations (although leading to a somewhat worse energy). HLJP also suggested the use of variational calculations to determine the best orbitals for each pair and considered more general expansions for each pair function.

Other more general formulations of the problem of forming spin eigenfunctions (eigenstates of $\hat{S}^2$) that satisfy Pauli's principle were developed by Yamanouchi and Kotani,[18] Matsen,[19] Löwdin,[20] and others.[21] Here we will concentrate on one particular approach that makes use of the group operators,[22] G_i^{γ}, which *simultaneously* take care of *both* the spin symmetry *and* the Pauli principle. That is, $G_i^{\gamma}\Phi$ satisfies Pauli's principle and has the correct spin symmetry for arbitrary Φ.

For a four-electron singlet state, there are two different group operators, G_1 and $G_2 \equiv G_f$, corresponding to the two ways of coupling the spins of four electrons into a singlet state. For the convenience of those unfamiliar with the Wigner projection operators, the wave functions $G_i\Phi\chi$ are expanded in terms of valence-bond-type configurations

$$G_1\Phi\chi = \mathcal{A}[(\phi_a\phi_b + \phi_b\phi_a)(\phi_c\phi_d + \phi_d\phi_c)\alpha\beta\alpha\beta] \quad (9a)$$

$$\begin{aligned} G_f\Phi\chi = \mathcal{A}\{[\phi_a\phi_b + \phi_b\phi_a)(\phi_c\phi_d + \phi_d\phi_c) - \\ (\phi_a\phi_d + \phi_d\phi_a)(\phi_b\phi_c + \phi_c\phi_b)]\alpha\beta\alpha\beta\} \quad (9b) \end{aligned}$$

where $\Phi = \phi_a\phi_b\phi_c\phi_d$ and $\chi = \alpha\beta\alpha\beta$ [in (9) multiplicative constants have been deleted].

In the GI-type methods the variational principle is applied to obtain the best possible orbitals for wave functions of the type in (9) but with no orthogonality restrictions placed upon the orbitals (the best wave function of the form (9a) is called the G1 wave function; the best of the form (9b) is called the GF wave function). The variational equations (self-consistent-field equations) for the orbitals have the form

$$H_k\phi_k = \epsilon_k\phi_k \quad (10)$$

where the operator H_k contains the average effective fields due to electrons in the other orbitals of the system. Thus each orbital can be considered as the eigenstate of an electron moving in the average field due to electrons in the other orbitals.

The solutions of (10) depend upon the coupling used [*e.g.*, (9a) or (9b)] and hence the interpretation of the orbitals might depend upon the coupling. In fact, the best wave function that can be expressed in terms of products of the orbitals

$$\phi_a\phi_b\phi_c\phi_d$$

will in general be a mixture of the two couplings of (9). This leads us to the spin-coupling-optimized GI (or SOGI) method,[23,24] in which the orbitals and spin coupling are simultaneously optimized. This again leads to orbital variational equations just as in (10). In the following discussions the completely optimized SOGI wave functions will be used for all systems. The term generalized valence bond (GVB) is also used to refer to SOGI wave functions but is a somewhat broader term and is also used to refer to G1 wave functions when the spin coupling differences are not great.

For an atom such as Li we find two tight core-like functions very similar to the orbitals of Li^+ and one much more diffuse valence function.[23] As shown in Figure 5 this valence orbital is similar to the Hartree–Fock valence orbital in the valence region, but differs markedly in the core region in that the SOGI valence orbital *has no node*. This illustrates another difference between SOGI and Hartree–Fock: orthogonalizing the Hartree–Fock orbitals does not change the energy but, because of the less restrictive form of the SOGI wave function, orthogonalizing the SOGI orbitals generally raises the energy. It is possible to modify greatly the shape of the Hartree–Fock valence orbital in the region close to the nucleus (while not changing the total energy) by mixing in various amounts of core character

$$\phi_{val}' = \phi_{val} - c\phi_{core}$$

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(15) For H^- the ϕ_b GVB orbital is quite diffuse, as expected, since the nuclear potential is nearly completely shielded. The Hartree–Fock wave function does rather poorly for H^-, not even accounting for the stability of the system. [See W. A. Goddard III, *Phys. Rev.*, 172, 7 (1968).]

(16) H. Shull and P.-O. Löwdin, *J. Chem. Phys.*, 30, 617 (1959).

(17) (a) A. C. Hurley, J. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc., Ser. A*, 220, 446 (1953); (b) J. M. Parks and R. G. Parr, *J. Chem. Phys.*, **28**, 335 (1958).

(18) T. Yamanouchi, *Proc. Phys.-Math. Soc. Jap.*, **18**, 623 (1936); M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Tables of Molecular Integrals," Maruzen Co., Tokyo, 1963.

(19) F. A. Matsen, *Advan. Quantum Chem.*, 1, 59 (1964).

(20) P. O. Löwdin, *Phys. Rev.*, **97**, 1509 (1955).

(21) For a brief review of these developments, see W. A. Goddard III, *Int. Quantum Chem. Suppl.*, 3, 593 (1969).

(22) W. A. Goddard III, *Phys. Rev.*, 157, 73 (1967).

(23) R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, 51, 1073 (1969).

(24) See also related work by U. Kaldor and F. E. Harris, *Phys. Rev.*, **183**, 1 (1969); S. Lunell, *ibid.*, 173, 85 (1968); S. Hameed, S.S. Hui, J. I. Musher, and J. M. Schulman, *J. Chem. Phys.*, 51, 502 (1969).

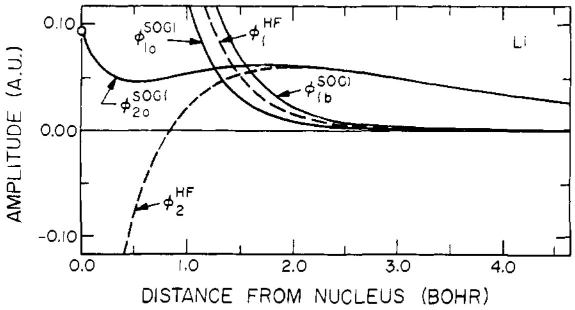

Figure 5. The valence orbital of Li as obtained from SOGI and HF calculations.

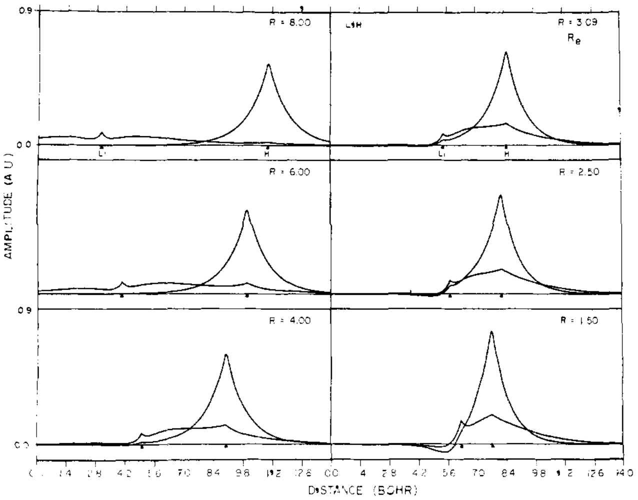

Figure 6. The SOGI valence orbitals of LiH as a function of internuclear distance. Atomic units are used (ref 7).

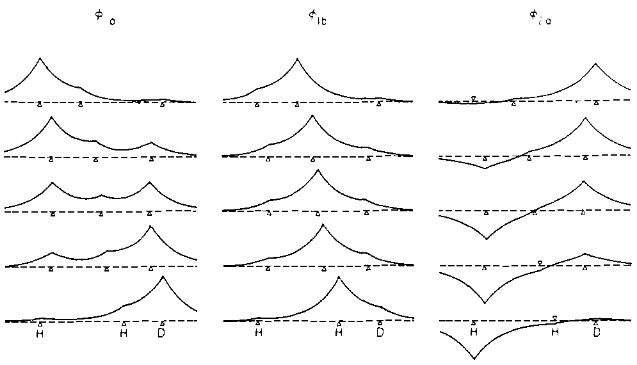

Figure 7. The SOGI orbitals for the $H_2 + D \rightarrow H + HD$ exchange reaction. Each column corresponds to a different orbital and each row to a different nuclear configuration. The middle row is at the saddle point.

Indeed, there is a whole range of values of *c* for which the new valence orbital would be nodeless. Thus the shape of the Hartree–Fock valence orbital in the core region can have no special physical significance. On the other hand, the SOGI orbitals of Li are *completely* specified by minimizing the energy and the shape of the orbital even in the core region could have some significance.

Now consider the LiH molecule; there are four electrons and four orbitals

$$\phi_{1a}, \phi_{1b}, \phi_{2a}, \phi_{2b}$$

Two orbitals, ϕ_{1a} and ϕ_{1b}, are essentially the same as the core orbitals of Li and Li^+ and we will not discuss them further (they are, of course, solved for self-consistently in the calculations). The remaining orbitals (called the valence orbitals) are responsible for the bond. As can be seen from Figure 6, ϕ_{2a} becomes an Li valence orbital for large *R*, while ϕ_{2b} becomes an H 1s atomic orbital.[25] As *R* is decreased, ϕ_{2b} changes very little but ϕ_{2a} changes a great deal, increasing substantially throughout the bonding region. Since ϕ_{2b} changes only slightly from the form of an H orbital, one might consider ϕ_{2a} as primarily responsible for the bond in LiH.[26,27] In this case one would expect LiH^+ to be only very weakly bound (which it is).

For larger atoms there are additional changes from Hartree–Fock because nonbonding pairs of orbitals also split in SOGI. However, rather than discussing the SOGI orbital picture for larger molecules, we will now consider some simple H-exchange reactions involving the H_2 and LiH molecules.

Results

Some Simple Exchange Reactions. First we will consider the $H_2 + D \rightleftharpoons H + HD$ exchange reaction. There are three electrons and three orbitals. Two of these orbitals (call them ϕ_{1a} and ϕ_{1b}) start out as the bonding orbitals for the reactant molecule H_2 and the other orbital (call it ϕ_{2a}) starts out as a nonbonding orbital on the D. As H_2 and D approach each other, the three orbitals delocalize over the three centers in the transition region and then relocalize again as the products move apart. The changes in the orbitals along the reaction path are shown in Figure 7, where each column corresponds to one of the three orbitals and each row corresponds to a specific nuclear configuration (the positions of the nuclei are indicated by the triangles). The first row corresponds to a point where the interaction between the H_2 and D is just starting to be significant, the third row corresponds to the transition state, and the second row is an intermediate point. Rows four and five are analogous to rows two and one but on the product side of the reaction.

We see that the orbitals change continuously and that the bonding pair [ϕ_{1a}, ϕ_{1b}] of the reactants remains nodeless and highly overlapping during the reaction and becomes the bonding pair of the products. On the other hand, the free D orbital (ϕ_{2a}) builds in a node in the region of the pair [ϕ_{1a}, ϕ_{1b}] and retains low overlap with this bonding pair during the reaction, becoming the free orbital of the products. Thus in this exchange reaction, the orbitals also exchange.

In Figure 8 we show a similar plot of the orbitals for the $LiH + H \rightleftharpoons Li + H_2$ reaction (we do not discuss the two Li core orbitals since they are essentially unchanged during the reaction; they are of course solved for self-consistently along with the other orbitals). The orbitals ϕ_{2a} and ϕ_{2b} start off as the bonding pair on LiH,

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[25] All of the LiH and LiH_2 calculations reported here are based on SOGI calculations using a basis of 13 1s Gaussian functions and 3 2p Gaussians contracted to 5 1s and 1 2p functions on the Li plus the basis of ref 11 on the H.

[26] F. E. Harris and H. S. Taylor, *Physica*, 30, 105 (1964).

[27] W. E. Palke and W. A. Goddard III, *J. Chem. Phys.*, 50, 4524 (1969).

become delocalized in the transition region (row C is at the saddle point or transition state of the reaction), and then become localized as an H_2 bonding pair in the product region. At the same time, the free H orbital (ϕ_{3a}) of the reactants delocalizes over the three centers in the transition region and relocalizes onto the Li in the product region. Thus just as in the $H_2 + D$ reaction, the orbitals exchange during the reaction.

Discussion

First we consider the exchange of orbitals that occurs in these reactions. We know that these reactions have low activation energies, in both cases about one-tenth of the energy to break the bond of the reactant molecule. Therefore, we must preserve the bond for all points on the reaction path. What is often stated is that the bond of the reactant gradually weakens while the bond of the product gets stronger, with the whole system retaining essentially one full bond.[28] However, Figures 7 and 8 allow a somewhat more complete interpretation. Here we see that there is one pair of orbitals describing the bond of the reactants and one pair describing the bond of the products. Thus in each case one might identify the bond with the pair of orbitals in the same regions. But from Figures 7 and 8 we see that *the bonding pair of orbitals of the reactant changes continuously during the reaction to become the bonding pair of the products.* That is, one might view such a concerted reaction as the shifting of the bonding pair of orbitals from one pair of centers to a new pair rather than as the breaking of one bond and simultaneous formation of a new one. Of course, while the bonding pairs are shifting the other orbitals of the system must also readjust.

In Figures 7 and 8 we note that in the transition region, two valence orbitals are nodeless and bonding-like; however, the third valence electron is not bonding-like at all but has nodes that serve to decrease its overlap with the bonding orbitals.

Chemical Bonds and the Permutational Coupling of Orbitals. In order to understand this behavior, consider the singlet state of the H_2 molecule described by the SOGI wave function (5). The optimum orbitals, ϕ_a and ϕ_b, have larger overlap than do atomic orbitals centered on the respective protons. A primary reason for this is that the dominant term in the bonding energy of H_2 is an exchange term

$$-\tau S_{ab}^2/(1 + S_{ab}^2) \qquad (11)$$

where τ is positive and relatively insensitive to both R and optimization of ϕ_a and ϕ_b.[29] By increasing S_{ab} we can decrease (11) (increase the bonding); however, large increases in S_{ab} would increase the other contributions to the total energy. The result is a moderate increase in S_{ab} as R decreases (see Figure 3).

For a two-electron triplet state, the SOGI wave function of H_2 is

$$(\phi_a\phi_b - \phi_b\phi_a)(\alpha\beta + \beta\alpha) \qquad (12)$$

where the orbitals can be taken as localized near the respective protons.[30] In this case the dominant term in the bonding energy is proportional to

$$+\tau S_{ab}^2/(1 - S_{ab}^2) \qquad (13)$$

where τ is the same as in (11). Thus (13) and the total energy are decreased by *decreasing* the overlap.

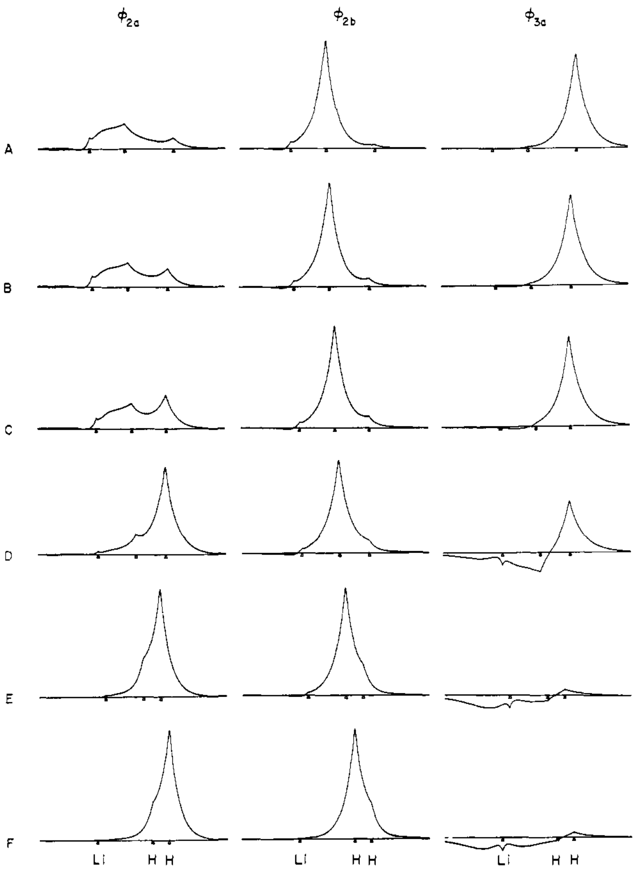

Figure 8. The SOGI orbitals for the LiH + H → Li + H_2 exchange reaction. Each column corresponds to a different orbital and each row to a different nuclear configuration. Row C is for the saddle point geometry.

Orbitals coupled as (5) are said to be *symmetrically coupled* whereas those of (12) are said to be *antisymmetrically coupled.* We see above that symmetric coupling leads to bonding interactions and favors large orbital overlaps, whereas antisymmetric coupling leads to antibonding and favors small orbital overlaps.

For three electrons the totally symmetric combination of three orbitals would be

$$\phi_a\phi_b\phi_c + \phi_b\phi_c\phi_a + \phi_c\phi_a\phi_b + \phi_a\phi_c\phi_b + \phi_b\phi_a\phi_c + \phi_c\phi_b\phi_a \qquad (14)$$

while the totally antisymmetric combination would be

$$\phi_a\phi_b\phi_c + \phi_b\phi_c\phi_a + \phi_c\phi_a\phi_b - \phi_a\phi_c\phi_b - \phi_b\phi_a\phi_c - \phi_c\phi_b\phi_a \qquad (15)$$

For a system such as the ground states of $H_2 + H$ or $He + H$, wave function (14) would lead to bonding just

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[28] For example, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.

[29] (a) C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, 5, 45 (1970); (b) for further discussion of the relation between permutational coupling of orbitals and chemical bonding, see C. W. Wilson Jr., Thesis, California Institute of Technology, 1970.

[30] Expression 13 is the dominant term in the bonding energy if the orbitals of (12) are atomic-like orbitals. The orbitals of (12) can actually be taken as orthogonal to each other and delocalized without changing the total energy; however, this would lead to a change in the form of the terms dominating the bonding energy, which would no longer be so simply related to that of the singlet state.

as did (5), whereas (15) would lead to antibonding. In order to satisfy Pauli's principle, the symmetric spatial function (14) would have to be combined with a totally antisymmetric spin function [analogous to (15)]. However, three spin-one-half particles cannot be combined into a totally antisymmetric spin function (such a spin function would have the form of (15) with $\phi_a = \alpha$, $\phi_b = \alpha$, and $\phi_c = \beta$ and would lead to a zero result). Hence (14) is *not* an allowed wave function for electrons (if it were, H_3 would be strongly bound).

Besides (15) (which corresponds to a quartet state), there are other allowed wave functions, corresponding to doublet states. These doublet-state wave functions involve both symmetric and antisymmetric coupling, *e.g.*

$$\begin{aligned}&[\phi_a(1)\phi_c(3) - \phi_c(1)\phi_a(3)]\phi_b(2) + \\ &\quad [\phi_b(1)\phi_c(3) - \phi_c(1)\phi_b(3)]\phi_a(2) + \\ &\quad [\phi_a(2)\phi_c(3) - \phi_c(2)\phi_a(3)]\phi_b(1) + \\ &\qquad [\phi_b(2)\phi_c(3) - \phi_c(2)\phi_b(3)]\phi_a(1) \quad (16)\end{aligned}$$

In (16) ϕ_c occurs only in the antisymmetric combinations (in brackets), whereas the total wave function (16) is unchanged (symmetric) with respect to interchange of orbitals ϕ_a and ϕ_b. The wave function (16) can be viewed as symmetric coupling of ϕ_a and ϕ_b followed by antisymmetric coupling of ϕ_c to the $\phi_a\phi_b$ pair.

For a system such as He + H, the two orbitals on the He are symmetrically coupled and the H orbital must be antisymmetrically coupled to this pair. Thus the interatomic potential terms (those involving coupling of the H orbital with one of the He orbitals) are positive as in (13), resulting in an energy increase as R decreases, leading to an unbound system.[29b] In order to reduce the repulsion energy the H orbital adjusts so as to have a smaller overlap with the He orbitals.

At large R the coupling for H_2 + H is the same as for He + H and the energy again increases as R decreases. As with He + H the free H-atom orbital readjusts to retain a small overlap with the H_2 bonding orbitals. As the distance between the left H's approaches that between the right two, the bonding orbitals become *gerade* and the unpaired orbital becomes *ungerade* so that reactant orbitals change smoothly with the product orbitals.

For LiH + H the orbital coupling of the valence orbitals is the same as for H_2 + H, and we expect similar results, except that the orbitals at the saddle point are not exactly *gerade* or *ungerade* (but have the same nodal character as for H_2 + H).

Reactions. Thus, to form a strong two-electron bond at all points along the reaction path, the first two orbitals retain high overlap and introduce no nodes in the bonding region. Because of Pauli's principle, however, the third orbital must be antisymmetrically coupled to the first pair. For this coupling the energy is minimized by the third orbital obtaining small overlap with the first pair, and it remains nonbonding during the reaction. Since the third orbital cannot be bonding-like simultaneously with the other two being bonding-like, we cannot form a new bond at the same time that we break an old bond (which would require all three orbitals to be partially bonding at some point). Thus we must preserve the bonding character in the present bond and move the bond to the new centers.

In the case of H_3 the bonding orbitals at the transition state (or saddle point) are *gerade* and the nonbonding orbital is *ungerade* (in order to minimize the repulsive interactions with the bonding orbitals). For LiH_2 we have no inversion symmetry at the transition state and the orbitals will not be exactly *ungerade* or *gerade*. Even so, we see in Figure 8 that the bonding orbitals (ϕ_{2a} and ϕ_{2b}) become in a sense spatially symmetric and the nonbonding orbital is in a sense spatially antisymmetric. We might describe ϕ_{2b} as an inner bonding orbital, bonding the central H equally strongly to the outer atoms. Similarly, we might describe ϕ_{2a} as an outer bonding orbital (equally centered in both bonding regions), bonding each outer atom equally strongly to the inner one. Thus these orbitals are symmetric in the sense that they are equally bonding in each of the bond regions. That is, they are symmetric in an energy or bond-strength sense rather than in a group theoretical sense. Similarly, the nonbonding orbital is antisymmetric in the sense that it is equally (but only slightly) deleterious to both bonds; *i.e.*, it is antisymmetric in an energy sense rather than a group theoretical sense.

In order to examine the importance of the nonbonding orbital being *ungerade*, we carried out a calculation (using the geometry of the saddle point) in which the third orbital of H_2D was *forced* to be *gerade*. In this case the energy increased by 6.5 eV.[31] Thus if we do not allow the third orbital to be antisymmetric to the bonding pair, the activation energy would be much greater than the bond energy. That is, the antisymmetric character of the nonbonding orbital is essential to retaining the bond during the concerted reaction. Because of the required antisymmetry for the transition state geometry, the nonbonding orbital changes phase during the reaction.

Summary

In a concerted three-center exchange reaction such as those considered above, the bonding pair of orbitals of the reactants moves to become the bonding pair of orbitals of the products. At the same time, the other orbital in this region readjusts to remain approximately orthogonal to the bonding pair and as a result changes phase as it shifts centers during the reaction. We will show elsewhere[32] that the application of these concepts to larger systems leads to predictions of selection rules for chemical reactions, in general agreement with experiment and with the very successful Woodward–Hoffmann rules.[33]

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(31) The wave function resulting from forcing the outer orbital to be *gerade* just corresponds a state of the $H_2 + D^* \rightleftharpoons H^* + HD$ reaction, where H^* is an $n = 2$ state of the H atom.

(32) W. A. Goddard III, *J. Amer. Chem. Soc.*, **92**, 7520 (1970); *ibid.*, in press.

(33) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).