Correlation-consistent valence bond method with purely local orbitals: application to hydrogen, lithium dimer, hydrogen fluoride, fluorine and collinear hydrogen (H3) and lithium (...

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obtained for *rac-* and *meso-*2DPP. In *meso-*1DPP and *meso-*2DPP the excimer-like ground-state dimer (TT) leads to a value smaller than unity for the excimer amplitude ratio $R = -A(-)/A(+)$ in time-resolved fluorescence measurements. With both racemic, 2,4-dipyrenylpentanes, sandwich dimers are not observed. However, in *rac-*1DPP, contrary to *rac-*2DPP, a conformer partially overlapping at the protons H9 and H10 is present. This partial-overlap dimer undergoes rapid excimer formation, leading again to a value smaller than unity for the ratio *R*.

From an analysis of the NMR spectra, completely overlapping ground-state dimers are not detected in the two series of dipyrenylalkanes, 2Py(*n*)2Py and 1Py(*n*)1Py. This is in contrast to what has been observed with the bis(pyrenylcarboxy)alkanes 2PC(*n*)2PC and 1PC(*n*)1PC as well as with the *meso-*2,4-di-pyrenylpentanes. Instead, a conformer is detected in which the pyrenyls only overlap at the edges, as in *rac-*1DPP. This is the case with 1Py(0)1Py, 1Py(3)1Py, and 1Py(6)1Py, in which the partial overlap occurs at H9 and H10. In time-resolved fluorescence measurements with 2Py(3)2Py, 2Py(14)2Py, 1Py-(3)1Py, and 1Py(13)1Py, it is seen that the excimer amplitudes practically sum to zero, confirming the conclusions based on the NMR experiments.

Correlation-Consistent Valence Bond Method with Purely Local Orbitals. Application to H₂, Li₂, FH, F₂, and Collinear H₃ and Li₃

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We propose a general method for constructing ab initio valence bond wave functions. The emphasis is put on building compact wave functions designed to be as close as possible to the concept of chemical bonding schemes. This is achieved through the use of strictly local fragment orbitals, leading to nonorthogonal configuration interaction. A set of rules is proposed for selecting the configuration list such that correlation consistency is enforced over the potential surface. The compactness of the wave function is ensured by correlating only the electrons occupying active orbitals, defined as the orbitals directly involved in bond breaking or bond making. The method is applied to the dissociation of H₂, Li₂, FH, and F₂, and to the collinear exchange reactions X + X₂ → X₂ + X (X = H, Li). The dimensions of the corresponding valence bond CIs are respectively 6, 12, 31, and 24 symmetry-adapted configurations for the dimers, and 26 and 60 for the trimers. All calculated equilibrium bond lengths, dissociation energies, and reaction barriers are found to agree, within 0.02 Å and 3 kcal/mol, with best reference calculations in the same basis set. The method appears to be well suited for the calculation of diabatic curve crossing diagrams as introduced by Shaik and Pross.

The valence bond (VB) theory of electronic structure has recently regained acceptance in the world of chemistry,[1-3] from both the qualitative and quantitative points of view. On the qualitative side, the discussion of molecular structure and reactivity in terms of atomic properties has been developed by Goddard et al.[4] More recently, the study of chemical reactions by VB diagrams has been introduced by Shaik and Pross.[2] Such diagrams have already been widely used and proved to be helpful for understanding and predicting the size of the reaction barriers in reactions like S$_N$2 substitution[3] or radical exchange,[5] and have also been used to understand electron delocalization in π systems.[5,6] This model considers the energy barrier of a reaction as a consequence of the avoided crossing of two VB diabatic curves: one representing the bonding scheme of the reactants, the other that of the products (see the following paper for more details). Shaik and Pross[2,3] have shown that it is possible to relate the energetic behavior of these VB structures to simple thermodynamic quantities, and, by means of simple approximations, to order the size of the energy barrier in some families of reactions. These applications of the VB diagrams are still qualitative in nature, and to our knowledge no quantitative calculations have yet been performed to confirm or falsify their validity. It is thus essential to develop a reliable computational method of the VB type, which on the one hand provides energies of adiabatic states with good accuracy and on the other hand allows one to follow the energetic behavior of the various VB structures involved in the qualitative theory of curve crossing VB diagrams.

On the quantitative side, ab initio VB methods have become practical for generating potential energy surfaces and are referred to as generalized valence bond (GVB),[7] resonating GVB (R-GVB),[8] spin-coupled valence bond (SCVB)[9] and so on. They provide wave functions having nearly the quality of multiconfigurational SCF (e.g., CASSCF[10]), with the extra advantage of compactness. As with CASSCF, quantitative accuracy further requires extensive configuration interaction (CI). Such calcula-

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tions quickly become untractable for systems of chemical interest, and this situation calls for the development of simpler methods designed to mimic the results of larger calculations at much lower cost. This is the philosophy of the correlation-consistent CI method recently proposed by Goddard et al.[11] However, such methods provide wave functions that are not so easy to interpret as chemical bonding schemes. The reason is that each orbital is not constrained to be localized on a unique center or fragment; if they are strongly delocalized, a pair of singlet-coupled orbitals can no longer be interpreted as a bond between two fragments.

On the contrary, the method we develop in this paper can be defined as a nonorthogonal CI between determinants built from orbitals each purely localized on a single fragment, hereafter called fragment orbitals (FO's). Thus, the VB structures which are composed of such determinants are readily interpreted and constitute the wave functions closest to the concept of chemical bonding scheme. This brand of VB method is in fact the oldest and most simple one, from the conceptual point of view, and is the one to use if energetics have to be associated unambiguously with chemical bonding schemes, as for example in the curve-crossing diagrams of Shaik and Pross.[2] This method is fairly general and flexible, since a large freedom is granted to the user in the choice of the configurations to include in the CI, and in the definition of the orbitals within each fragment.

It is the aim of this first paper to propose well-defined principles to choose the FO's and select the configurations in the latter VB method, so as to get quantitative or semiquantitative potential energy surfaces. These principles will be tested with the calculations of equilibrium geometries and dissociation energies for various diatomic molecules, selected so as to exhibit a spectrum of properties: H_2 and Li_2 as representing strong and weak covalent bonds between light atoms, F_2 as a covalent bond with lone pairs facing each other, and FH as a strongly heteropolar bond. The ground-state potential energy surfaces for two radical exchange reactions $(X + X_2 \rightarrow X_2 + X, X = H, Li)$ will also be investigated.

In the following paper, the principles defined here will be applied to the calculation of complete VB diagrams for the two above-mentioned exchange reactions, and the basic hypotheses of Shaik and Pross[2] will be discussed.

Technical Details

As the purely local FO's are necessarily nonorthogonal, the computation of the Hamiltonian matrix elements is complicated by the well-known $(n!)$ problem and requires the calculation of the minors of the overlap matrix. We have used the Prosser and Hagstrom[12] transformation, which results in important savings in computer time.[13] The nonorthogonal CI program has been written by Flament[14] and Lefour. The SCF calculations have been performed with the MONSTERGAUSS program,[15] and we have used the RHF Davidson Hamiltonian[16] for open shell cases.

Choice of Atomic Orbitals and Selection of Valence Bond Functions. Basic Principles

A. Active Orbitals. A reaction is considered here as a group of fragments between which some bonds are broken while others are created. Therefore, a fragment is simply defined as an atom, or a group of atoms which remain bonded together throughout the reaction process. For instance in the S_N2 reaction: $N^- + CH_3X \rightarrow NCH_3 + X^-$, N, CH_3 and X would constitute the three fragments. For each fragment, one then distinguishes the "active"

FO's, which are involved in bond making or bond breaking, from the other orbitals which are called "inactive" hereafter. These latter orbitals can be either lone pairs, or bonding orbitals linking together the constituents of a fragment, as, e.g., the C–H bond in CH_3.

The partition into active and inactive orbitals is meaningful provided that their mixing remains small. The easiest way to minimize this mixing is by performing a separate SCF calculation for each fragment, followed by Boys' localization.[17] In the cases considered in the present paper, all fragments are single atoms, so that no localization is necessary.

B. Multistructure Description of the Chemical Bonding Schemes. Having defined, for each fragment, the active and inactive orbitals, one can generate the bonding schemes to be included in the wave function. This is done by linking together the active orbitals, through covalent and ionic bonds, in all chemically significant ways. The CI space is then constituted of several sets of determinants, each set exhibiting a particular occupation and spin coupling of the active orbitals so as to correspond to a given bonding scheme. These sets form the analogues of configurations in MO-CI theory and will be called valence bond functions (VBFs) hereafter. Now if one uses a nonminimal basis set, the SCF-occupied active and inactive orbitals of each fragment have their virtual counterparts, so that a large number of VBFs may correspond to the same bonding scheme. Including the VBFs corresponding to all possible bonding schemes in the nonorthogonal VB CI would lead to the same result as a complete CI in the MO space of configurations, but in such a case the computation of the very numerous matrix elements of the VB Hamiltonian would be extremely time consuming. However, one is generally interested in bond energies, reaction enthalpies, activation barriers, etc., that is, energy differences rather than absolute values. We can then aim at quantitative accuracy within the active space only. In this space, the complete set of excited VBFs is not necessary either. Thus, each bonding scheme can be described by a limited number of VBFs, which can be generated in a systematic way, as shown below.

C. Selection of the Valence Bond Functions. Let us first specify the type of results we are searching for. Extreme accuracy is not being sought here; rather, we want to be able to get relative energies for potential energy surfaces, with an error not greater than typically 4–5 kcal/mol with respect to the best MO-CI methods using the same basis set. This accuracy is normally sufficient to provide a safe basis for discussing reaction mechanisms. In this line, the principles which will guide our selection of VBFs are as follows:

(i) The electron pairs which are correlated are only the "active" ones, those which are broken or created in the reaction. The other, "inactive", electron pairs are left uncorrelated. This amounts to assuming that this lack of electron correlation introduces an error which, while being large, remains constant over the potential surface. This idea is in fact not new and underlies other methods like that of Das and Wahl for diatomics,[18] or the correlation-consistent CI recently developed by Goddard et al.,[11] both of which have proved to be successful.

(ii) The most compact wave function would be such that each bonding structure is described by a single VBF. However, this would require each VBF to have its own set of optimal orbitals, for reliable energetics to be obtained. No method has yet been developed for obtaining self-consistent orbitals for such (nonadiabatic) VB functions, and such a method would imply the serious drawback of having to deal with a very large number of orbitals. Yet an equivalent wave function can be obtained, through singles CI (generalized Brillouin's theorem), by the following method. A set of VBFs, hereafter called elementary VBFs, is built out of occupied Hartree–Fock orbitals of the neutral fragments. Then, each elementary VBF is complemented with a series of additional

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VBFs, hereafter called complementary, whose role is equivalent to optimizing the orbitals in the elementary ones. These complementary VBFs are deduced from the elementary by monoexcitations to Hartree–Fock virtual fragment orbitals and can be divided into three categories, according as they play the role of rehybridization, polarization, or optimization of orbital size. We illustrate below, in the latter case, the equivalence of orbital optimization and singles CI.

Optimization of the Orbital Size. Let us consider a covalent bond between two AO's χ_a and χ_b, belonging respectively to atoms A and B, and suppose that χ_a and χ_b are the best possible orbitals for such a bond, within a given basis set that is chosen here to be split valence. This means that χ_a (χ_b) has an optimal size, or in other words is an optimal combination of two basis functions, one being tighter and the other more diffuse. The corresponding VBF, of Heitler–London type, reads

$$\psi = |...\chi_a\bar{\chi}_b...| + |...\chi_b\bar{\chi}_a...| \quad (1)$$

Now χ_a and χ_b can be expressed as linear combinations of the SCF-optimized orbitals, χ_a^0 and χ_b^0 and their virtual counterparts, χ_a^1 and χ_b^1, arising from the SCF calculations of the separate fragments A and B in their ground states:

$$\chi_a = \lambda\chi_a^0 + \mu\chi_a^1 \quad (2a)$$

$$\chi_b = \lambda\chi_b^0 + \mu\chi_b^1 \quad (2b)$$

and ψ can be expressed in terms of these latter orbitals:

$$\psi = \lambda^2(|...\chi_a^0\bar{\chi}_b^0...| + |...\chi_b^0\bar{\chi}_a^0...|) + \lambda\mu(|...\chi_a^0\bar{\chi}_b^1...| + |...\chi_b^1\bar{\chi}_a^0...| + |...\chi_a^1\bar{\chi}_b^0...| + |...\chi_b^0\bar{\chi}_a^1...|) + \mu^2(|...\chi_a^1\bar{\chi}_b^1...| + |...\chi_b^1\bar{\chi}_a^1...|) \quad (3)$$

If we now make the assumption that χ_a^0 is not too different from χ_a, i.e., that the choice of the FO's χ_a^0 and χ_b^0 is nearly adequate for the elementary VBF, then μ is small in (2a) and (2b) and μ^2 can be neglected relative to λ^2, and the third term in (3) which is a diexcitation with respect to the elementary structure cancels out. The first remaining term is called an elementary VBF, and the other two VBFs, which constitute the second term in (3), are the complementary VBFs, deduced from the elementary one by monoexcitations. Therefore, adding complementary VBFs to the elementary ones (eq 3) is equivalent to optimizing a singly occupied orbital in a unique VBF. The same reasoning holds true if the orbital to be optimized is doubly occupied, as in the case of lone pairs or inactive bonds:

$$|\chi_a\bar{\chi}_a| = \lambda^2(|...\chi_a^0\bar{\chi}_a^0...|) + \lambda\mu(|...\chi_a^0\bar{\chi}_a^1...| + |...\chi_a^1\bar{\chi}_a^0...|) + \mu^2(|...\chi_a^1\bar{\chi}_a^1...|) \quad (4)$$

Here again, the third term in μ^2 is small in the expansion of the optimal VBF which can be mimicked by the expansion in (4), limited to the two first terms in λ^2 and $\lambda\mu$.

Following the above-defined principle that the only electrons to be correlated (through an adequate generation of elementary VBFs) are those in active orbitals only, the diexcited VBF in (4) (third term in μ^2) is not included in the CI if the orbital χ_a is inactive.

It is important to note that the complementary VBFs are chosen so as to have the *unique* role of mimicking the orbital optimization of the elementary VBFs, and as such obey the following restrictions: (i) the monoexcitations are intrafragment; (ii) they are restricted to pairs of FO's (χ_a^0,χ_b^0) sharing the same local symmetry properties and localized in the same region of the space, which requires the virtual orbitals to be localized. In addition, to ensure the coherence of the wave function (balanced description of bonded fragments with respect to separated ones), these restrictions have the useful effect of limiting the number of VBFs and keeping their correspondence to chemical bonding schemes.

Rehybridization. The orbitals arising from the SCF calculations of the fragments usually involve some hybridization, which is in general not optimal for describing the active FO's that are involved in covalent or ionic bonds. In that case, too, complementary VBFs can be added to remedy this inadequacy. For example, if a

fragment has an electron occupancy of the type s^2p, then optimizing the s/p character of the singly and doubly occupied orbitals is equivalent to adding, in the CI space, a complementary VBF in which the fragment has the p^2s occupancy. The same reasoning holds true if s and p are not pure spectroscopic AO's but some particular hybrids, as will happen most of the time in fragments composed of more than one atom.

Polarization. Orbital polarization is another feature that the FO's have to optimize to minimize the energy of the wave function. Again, this can be done by adding, in the CI space, some complementary VBFs. These are deduced from the elementary ones by monoexcitations to FO's of the type 2p for hydrogens, 3d for first-row atoms, and so on. If the orbital to polarize is an inactive bonding type orbital, some complementary VBFs involving a monoexcitation from this orbital to the corresponding antibonding one must also be added.

Expected Reliability. As the complementary VBFs play the role of optimizing the active or inactive orbitals, the energy of the wave function should be independent, to first order, of the choice of the elementary FO's, provided this choice is not too far from optimal. Otherwise, the second-order terms (e.g., third term in μ^2 in eq 4) would become nonnegligible and the quality of the results would be seriously affected by the neglect of these terms. However, the adequacy of the FO's can be easily controlled by the coefficients of the complementary VBFs which must remain small relative to those of the elementary ones. An SCF optimization of the FO's is in general satisfactory, but if not, one may directly use the coefficients of the complementary and elementary VBFs to define new, and better adapted, FO's for the new elementary VBFs. Indeed, optimizing the orbitals on neutral fragments leads to some bias against ionic VBFs. Our experience with the method indicates that even the heteropolar bonds (e.g., C–H in methane) are satisfactorily described. However, some problems arise for highly polar molecules, and the above-discussed principle may be used to improve the orbitals, as exemplified below for the FH molecule.

The above method defines a coherent CI space, designed to reproduce the results of the mixing of a small number of carefully chosen VBFs, each one having its own set of optimized orbitals. Thus, the truncation of the CI is guided by well-defined principles, such that no further CI is necessary, unlike limited MCSCF calculations. The weaknesses of the latter methods will be illustrated, in VB terms, with the example of F_2.

Results

A. H_2. We have used the split-valence plus polarization 6-31G** basis set,[19] which includes a set of 2p orbitals (hereafter called x_a, y_a, z_a and x_b, y_b, z_b respectively for each hydrogen atom H_a and H_b). The 1s type AO's arise from an SCF calculation which provides the s_a and s_a' occupied and virtual orbitals for H_a, and similarly s_b and s_b' for H_b.

As is well-known, the bond between the hydrogen atoms in the H_2 molecule is an unequal mixture of covalent and ionic structures, so that there are three elementary VBFs, **1–3**, where circles

covalent H_a–H_b ionic $H_a^-H_b^+$ ionic $H_a^+H_b^-$
    1   2   3
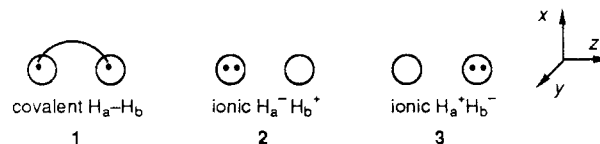
represent the s_a and s_b AO's and dots represent the electrons. The corresponding wave functions are respectively ($|s_a\bar{s}_b| + |s_b\bar{s}_a|$), $|s_a\bar{s}_a|$ and $|s_b\bar{s}_b|$.

According to the principles described above, four complementary VBFs are necessary to account for the optimization of the orbital size in **1–3**, and four additional ones play the role of polarizing the covalent and ionic bonds. The resulting VBF list, which includes six symmetry-adapted combinations, is displayed in Table I together with the variational coefficients at the equi-

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**TABLE I: Types of VBFs Used in the Valence Bond Calculation of H_2**[a]

VBF	type of bonding	excitation	coeff
elementary	H_a–H_b		0.761
	$H_a^-H_b^+$		0.142
optimization of	H_a–H_b	$s_a \rightarrow s_a'$	0.099
orbital size	$H_a^-H_b^+$	$s_a \rightarrow s_a'$	0.025
polarization	H_a–H_b	$s_a \rightarrow z_a$	0.003
	$H_a^-H_b^+$	$s_a \rightarrow z_a$	0.023

[a] The excitations are defined with respect to the following orbital occupations: $s_a s_b$ for H_a–H_b and s_a^2 for $H_a^-H_b^+$.

librium geometry. It appears that the coefficients of the elementary VBFs are much larger than those of the complementary ones, which ensures a priori the quality of the wave function. Indeed, the H–H bond length, as calculated by this method, is 0.74 Å, the same value as that obtained by Kolos and Wolniewicz[20] in a most sophisticated calculation.

On the other hand, our calculated dissociation energy, 98.3 kcal/mol, is in moderate agreement with the result of complete CI in the same basis set, 105.9 kcal/mol. However, this discrepancy comes from our neglect of π structures and not from the VB method itself. Indeed, including π structures in the VB calculation leads to a potential well of 103.2 kcal/mol, now in excellent agreement with the full CI result. Thus, π structures account for less than 5% of the potential well and do not appear to be a must for a semiquantitative description of the H–H bond. Moreover, an underestimation of the potential well is not likely to have important consequences on the energetics of the H_3 potential surface, for throughout the $(H + H_2)$ reaction the number of bonds, or more specifically the total bond order, is nearly constant. Accordingly, π structures have been discarded in our studies of H_3, in both this paper (see below) and the following one. The computed vibrational frequency, 4369 cm^{-1}, is in reasonable agreement with the value 4398 cm^{-1} as computed by Das and Wahl[18d] and with the experimental value[21] of 4401 cm^{-1}.

B. Li_2. The 1s electron pair of each lithium atom is considered inactive and therefore has been frozen in a doubly occupied core orbital. The description of the σ bond involves the same CI as that for H_2. But unlike the case of H_2, the π structures cannot be neglected in Li_2, as it is well-known[22] that they account for about one-third of the potential well. Thus three elementary structures of π type, **4–6**, are generated, using the 2p AO's x_a and

covalent π Li_a–Li_b ionic π $Li_a^-Li_b^+$ ionic π $Li_a^+Li_b^-$
          4   **5**   **6**
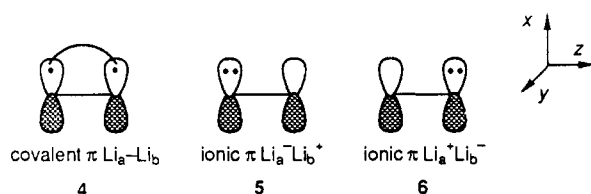
x_b, plus three identical structures using the 2p AO's lying in the *zy* plane. As the set of 2p AO's is split in the 6-31G basis set[19a] that we have used, the optimized x_i, y_i, z_i 2p AO's and their x_i', y_i', z_i' counterparts (i = a, b) correspond respectively to the occupied and virtual 2p AO's arising from an SCF calculation of the lithium atom in its ^2P excited state. On the other hand, the s_i and s_i' valence AO's of each lithium atom (Li_a and Li_b) have been determined, as for H_2, through an SCF calculation of the atom in its ground ^2S state.

A total of 29 VBFs (12 symmetry-adapted combinations) is thus generated for Li_2; their optimized coefficients, displayed in Table II, show that both the π structures and the p components of the σ bonds are indeed not negligible; they have therefore been included in the set of elementary structures for the generation of complementary VBFs. The higher p involvement in Li_2 than in

**TABLE II: Types of VBFs Used in the Valence Bond Calculation of Li_2**[a]

VBF	type of bonding	excitation	coeff
elementary	Li_a–Li_b		0.792
	$Li_a^-Li_b^+$		0.075
	π Li_a–Li_b		0.092
	π $Li_a^-Li_b^+$		0.056
optimization of	Li_a–Li_b	$s_a \rightarrow s_a'$	0.029
orbital size	$Li_a^-Li_b^+$	$s_a \rightarrow s_a'$	0.014
	π Li_a–Li_b	$x_a \rightarrow x_a', y_a \rightarrow y_a'$	0.018
	π $Li_a^-Li_b^+$	$x_a \rightarrow x_a', y_a \rightarrow y_a'$	0.023
polarization	Li_a–Li_b	$s_a \rightarrow z_a$	0.106
	Li_a–Li_b	$s_a \rightarrow z_a'$	0.033
	$Li_a^-Li_b^+$	$s_a \rightarrow z_a$	0.020
	$Li_a^-Li_b^+$	$s_a \rightarrow z_a'$	0.024

[a] The excitations are defined with respect to the following valence orbital occupations: $s_a s_b$ for Li_a–Li_b and s_a^2 for $Li_a^-Li_b^+$, $x_a x_b$ and $y_a y_b$ for π Li_a–Li_b, x_a^2 and y_a^2 for π $Li_a^-Li_b^+$.

H_2 is not surprising, given the low ^2S–^2P splitting in Li. Comparison of Tables I and II also shows that the Li–Li bond has less ionic character than the H–H bond. This is at first glance paradoxical given the fact that the covalent-ionic energy difference at infinite interatomic distance is much smaller in Li_2 (110 kcal/mol) than it is in H_2 (296.3 kcal/mol). We have checked that this difference is still significantly larger in H_2 than it is in Li_2 when both molecules are at their equilibrium geometries. The reason for the different ionicities of the ground states of these dimers lies in the Hamiltonian matrix element coupling the covalent and ionic wave functions. This element is high in H_2 because the bond is exceptionally short, and very small in Li_2 because, in return, the Li–Li bond is exceptionally long.

Extensive calculations on various alkali-metal clusters[23] have shown that, if accurate results do necessitate extended basis sets and CIs, the main features of the potential surfaces can be satisfactorily reproduced with a limited s,p basis set, the lack of d orbitals leading to a systematic underestimation of potential wells and overestimation of bond lengths, without introducing qualitative biases. In accord, the Li–Li bond length, as calculated with our wave function, is 2.76 Å, in good agreement with the value 2.74 Å obtained by Kendrick and Hillier[24] in a CI calculation using a larger s,p basis set (triple-ζ for p orbitals), but somewhat longer than the experimental value,[25] 2.67 Å. Our calculated dissociation energy is 17.2 kcal/mol, in satisfactory agreement with the value 19.2 kcal/mol obtained by full CI in the same basis set and with the value 20.2 kcal/mol of Kendrick and Hillier. These values are, however, somewhat far from the experimental dissociation energy, 24.2 kcal/mol, which reflects the importance of d orbitals in the description of the Li–Li bond. Indeed the OVC value of Das and Wahl, calculated with polarization functions, is 22.8 kcal/mol. Our computed frequency, 353 cm^{-1}, compares well with theirs (345 cm^{-1}) and with experiment[26] (351 cm^{-1}).

C. FH. We turn now to a very polar molecule, hydrogen fluoride. For making easier the comparison with other works, we have used the DZ + P basis set of Huzinaga and Dunning.[27] Four elementary structures, **7–10**, have been considered, the last one

covalent F–H   ionic F$^-$H$^+$ ionic F$^+$H$^-$ covalent F–H
      7   **8**   **9**   **10**
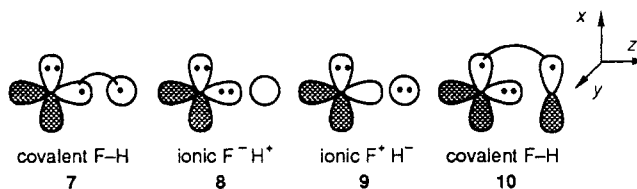
(20) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1965**, *43*, 2429.
(21) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
(22) See e.g.: Das, G. *J. Chem. Phys.* **1967**, *46*, 1568.

(23) Koutecky, J.; Fantucci, P. *Chem. Rev.* **1986**, *86*, 539.
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(25) *International Tables of Selected Constants, Vol. 17, Spectroscopic Data Relative to Diatomic Molecules*; Rosen, E., Ed.; Pergamon: Oxford, 1970.
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(27) Dunning, T. H.; Hay, P. J. Gaussian Basis Sets for Molecular Calculations. In *Methods in Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977; p 1.

TABLE III: Types of VBFs Used in the Valence Bond Calculation of FH[a]

VBF	type of bonding	excitation	coeff
elementary	F–H		0.574
	F⁻H⁺		0.440
	F⁺H⁻		0.050
	π F–H		0.040
optimization of orbital size	F–H	$z_f \to z_f'$	0.012
		$s_h \to s_h'$	0.001
		$x_f \to x_f', y_f \to y_f'$	0.013, 0.017[b]
		$s_f \to s_f'$	0.015, 0.025[b]
	F⁻H⁺	$z_f \to z_f'$	0.009
		$x_f \to x_f', y_f \to y_f'$	0.081
		$s_f \to s_f'$	0.046
		$z_f^2 \to z_f'^2$	0.030
	F⁺H⁻	$s_h \to s_h'$	0.006
		$x_f \to x_f', y_f \to y_f'$	0.026
		$s_f \to s_f'$	0.001
rehybridization	F–H	$s_f \to z_f$	0.015
		$z_f \to s_f'$	0.017
	F⁻H⁺	$z_f \to s_f'$	0.049
	F⁺H⁻	$s_f \to z_f$	0.010
charge delocalization in F⁺	F⁺H⁻	$x_f^2 \to z_f^2, y_f^2 \to z_f^2$	0.013
polarization[c]	F–H	$z_f \to zz_f$	0.025
		$s_h \to z_h$	0.047
		$x_f \to xz_f, y_f \to yz_f$	0.008, 0.010[b]
	F⁻H⁺	$z_f \to zz_f$	0.020
		$x_f \to xz_f, y_f \to yz_f$	0.031
		$z_f^2 \to zz_f^2$	0.019
	F⁺H⁻	$s_h \to z_h$	0.006
		$x_f \to xz_f, y_f \to yz_f$	0.006

[a] The excitations are defined with respect to the following valence orbital occupations: $s_f^2 x_f^2 y_f^2 z_f s_h$ for F–H, $s_f^2 x_f^2 y_f^2 z_f^2$ for F⁻H⁺, and $s_f^2 y_f^2 z_f^2 x_f x_h$ and $s_f^2 x_f^2 z_f^2 y_f y_h$ for π F–H. [b] The two possible spin couplings between the four singly occupied AO's have been allowed. [c] The notations zz, xz, and yz stand, respectively, for the $(2zz - xx - yy)$, xz and yz Gaussian d-type functions of the five-dimensional set of polarization orbitals in the DZ + P basis set.

being a structure of π type (the additional lone pair on F being omitted for clarity). From this set, the complementary structures displayed in Table III have been generated, plus the additional structure **11** (and its symmetrical analogue in the zy plane)

ionic F⁺ H⁻
11
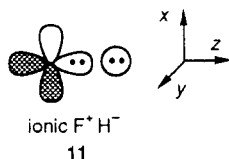
corresponding to the delocalization of the positive charge over the x_f and y_f AO's of fluorine in F⁺H⁻. Note also that due to the small coefficients of π structures, we have not judged it necessary to generate complementary structures out of them. In a first calculation, the AO's have been routinely optimized by means of atomic SCF calculations. It turned out, however, that this choice was far from optimal, as the coefficient of one complementary VBF ($s_h \to s_h'$ in F–H) had the exceedingly large value 0.193.[28] The root cause is that the SCF AO of the hydrogen atom is rather different from that best adapted to form a covalent bond with fluorine. The answer is to redefine s_h and s_h' AO's for hydrogen, and also z_f and z_f' 2p AO's for fluorine, from the relative coefficients of elementary and complementary covalent structures. It should also be noted that the diexcited VBF ($z_f^2 \to z_f'^2$ in F⁻H⁺) has been included in the CI, according to the above-defined principles, because the z_f orbital is active and the F⁻H⁺ ionic structure is very important in the ground state of hydrogen fluoride. In less polar molecules, such a structure may or may

not be added but should generally have a negligible coefficient. Therefore, it has been discarded in the homopolar molecules treated in this work.

The list of VBFs is displayed in Table III, with the coefficients calculated with the newly defined AO's for F and H. It can be seen that now all the complementary VBFs have small coefficients, which should in principle make the VB wave function reliable. Indeed, the F–H bond length that we obtained is quite satisfactory, 0.935 Å vs 0.917 Å experimentally[21] and, more meaningfully, 0.915 Å in a GVB + CI calculation by Hay, Wadt, and Kahn (HWK)[29] using the same basis set. Our computed vibrational frequency, 4077 cm⁻¹, is also in good agreement with the experimental value[30] of 3962 cm⁻¹. Our dissociation energy is 130.1 kcal/mol, vs 141 kcal/mol experimentally, but in excellent agreement with the value 130.3 kcal/mol reported by HWK, thus emphasizing once again that the limitations of our calculations lie in the basis set rather than in the VB method itself. This latter point is confirmed by a recent study of the basis set dependence of the dissociation energy of hydrogen fluoride by Binkley and Frisch,[31] who showed that the use of multiple sets of d functions on fluorine and p functions on hydrogen increases binding by 4 kcal/mol, and that adding higher polarization functions in the basis set further brings 3 kcal/mol.

D. F₂. While being homopolar, this molecule is quite different in nature from H_2 and Li_2 because of its six lone pairs facing each other. Calculating its dissociation energy is a challenge for any computational method and is one of the classical problem cases of quantum chemistry. Indeed, while the molecule is experimentally known[32] to be bound by 38.5 kcal/mol, the molecule is calculated to be unstable by almost the same quantity, at the Hartree–Fock limit.[33] Moreover, this poor performance of the Hartree–Fock wave function is not only due to the lack of correlation of the bonding electrons, since a two-configuration MCSCF (TCSCF) calculation yields a potential well of only 12.9 kcal/mol in DZ + P basis set,[34] and 15–16 kcal/mol with basis sets involving up to f polarization functions.[35,36] We shall see that the VB method not only provides satisfactory results, but also illustrates the problem encountered with other methods.

The list of VBFs is displayed in Table IV. In addition to VBFs similar to those of the other diatomic molecules, some terms, which display a charge transfer between two lone pairs facing each other, have been added (see the entry "pair–pair interactions" in Table IV). Indeed, preliminary calculations on the repulsive interaction between two helium atoms[28] have shown that such charge-transfer VBFs are necessary to properly describe the interaction between two overlapping doubly occupied AO's. On the other hand, the elementary structures of π type have been discarded after preliminary tests showing their ineffectiveness, as well as some complementary structures which proved to be very minor in a former calculation in DZ basis set (see Table IV). This led to a total of 24 symmetry-adapted VBFs in the final wave function, as shown in Table IV.

Using the same DZ + P basis set as for hydrogen fluoride, we find a dissociation energy of 39.7 kcal/mol, in good agreement with the experimental value (38.5 kcal/mol), and with the GVB + CI value of 42.7 kcal/mol reported by Cartwright and Hay[34] using the same basis set. The computed frequency, 925 cm⁻¹, is close to the experimental value[32] 924 cm⁻¹ and to the value 946

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TABLE IV: Types of VBFs Used in the Valence Bond Calculation of F_2; Missing Coefficients Corespond to VBFs Which Proved To Be Negligible in Preliminary Calculations without Polarization VBFs[a]

VBF	type of bonding	excitation	coeff
elementary	F_a-F_b		0.725
	$F_a^-F_b^+$		0.255
optimization of orbital size	F_a-F_b	$z_a \to z_a'$	0.025
		$s_a \to s_a'$	
		$x_a \to x_a', y_a \to y_a'$	
	$F_a^-F_b^+$	$z_a \to z_a'$	0.013
		$s_a \to s_a'$	0.026
		$s_b \to s_b'$	0.017
		$x_a \to x_a', y_a \to y_a'$	0.044
		$x_b \to x_b', y_b \to y_b'$	0.038
rehybridization	F_a-F_b	$s_a \to z_a$	0.041
		$z_a \to s_a'$	0.022
	$F_a^-F_b^+$	$s_b \to z_b$	0.040
		$z_a \to z_a'$	0.023
pair–pair interactions	F_a-F_b	$x_a \to x_b', y_a \to y_b'$	0.014
		$s_a \to s_b'$	0.007
	$F_a^-F_b^+$	$x_a \to x_b', y_a \to y_b'$	
		$s_a \to s_b'$	
charge delocalization in F^+	$F_a^-F_b^+$	$x_b^2 \to z_b^2, y_b^2 \to z_b^2$	0.023
polarization[b]	F_a-F_b	$z_a \to zz_a$	0.019
		$x_a \to xz_a, y_a \to yz_a$	0.011
		$x_a \to xz_b, y_a \to yz_b$	0.013
		$s_a \to zz_b$	0.015
	$F_a^-F_b^+$	$z_a \to zz_a$	0.026
		$x_a \to xz_a, y_a \to yz_a$	0.013
		$x_b \to xz_b, y_b \to yz_b$	0.005
		$x_a \to xz_b, y_a \to yz_b$	0.011
		$s_a \to zz_b$	0.014

[a] The excitations are defined with respect to the following valence orbital occupations: $s_a^2 x_a^2 y_a^2 z_a s_b^2 x_b^2 y_b^2 z_b$ for F_a-F_b and $s_a^2 x_a^2 y_a^2 z_a^2 s_b^2 x_b^2 y_b^2$ for $F_a^-F_b^+$. [b] The notations zz, xz, and yz have the same meaning as in Table III.

cm^{-1} of Cartwright and Hay. Our calculated equilibrium bond length, 1.432 Å, is also close to the experimental value,[32] 1.412 Å. The error of 0.02 Å is fully explained by our choice of a rather limited basis set, since Blomberg and Siegbahn have shown that various CI calculations yield an F_2 equilibrium distance too long by 0.02 Å unless f functions are included in the basis set.[35] Given the satisfactory accuracy of the dissociation energy, equilibrium bond length, and vibrational frequency, it is expected that the full energy curve for bond making is well reproduced. The computed curve is displayed in Figure 1 and shows that the energy of the F_2 molecule is smoothly connected to the Hartree–Fock RHF open-shell energy of two isolated F atoms.

It is interesting to examine the coefficients of the VBFs displayed in Table IV. They first show that the nature of the F_2 bond is nearly similar to that of a simple H_2 bond, the former being somewhat more zwitterionic in character. Besides, they provide a clear explanation for the failure of TCSCF (or equivalently GVB(1/PP)) calculations, if not followed by further CI. Indeed the two complementary VBFs $F_a^-F_b^+(x_a \to x_a')$ and $F_a^-F_b^+(x_b \to x_b')$ have rather large coefficients, 0.044 and 0.038, and serve to optimize the size of the lone pairs in the ionic structures of F_2, so as to adapt them to the presence of an electronic charge in the axial z_a or z_b AO. Such terms are implicitly present in the $(1\pi_g 3\sigma_g) \to (3\sigma_u 2\pi_u)$ excitation which has been shown to be of primary importance in any MO-CI calculation of F_2.[18b] They are on the other hand absent in a TCSCF wave function, which is equivalent to a VB wave function in which the covalent and ionic structures would share the same set of lone pair orbitals, optimized so as to accommodate an average single occupation of the axial 2p AO's. As a result, the ionic structures are poorly described in such a calculation, and even though their coefficients are variationally optimized, the resulting total energy is too high. Indeed, the above complementary VBFs have, by themselves, a stabilizing effect of 21 kcal/mol! These terms are also lacking in an SCF calculation, but in addition the wave function is now too ionic. As a result, not only are the ionic terms too high in energy, but their coef-
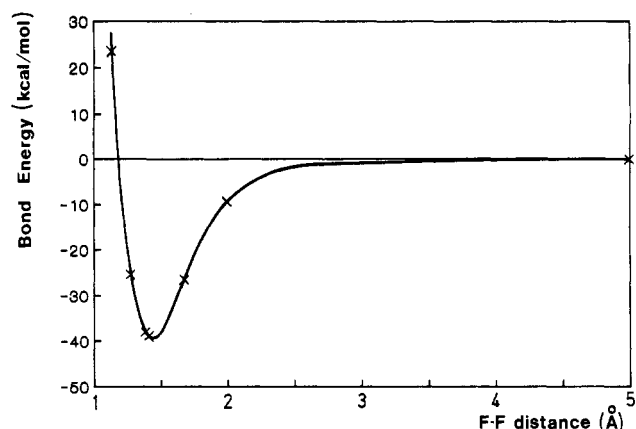

Figure 1. Energy profile for the dissociation of F_2. The VB calculation involves the VBFs displayed in Table IV. Energies are reported in kcal/mol, relative to the energy of two infinitely distant F radicals, each calculated at the RHF Hartree–Fock level.

ficients are also much too large, both effects combining to yield an exceedingly high SCF energy. Therefore, the computational difficulty in F_2 lies in the presence of the numerous lone pairs, but not because of their repulsive interactions. Rather, these lone pairs are very sensitive to the charge fluctuation due to the zwitterionic component of the F_2 bond, and the CI must take this effect into account. Similar problems are, of course, encountered in the description of the O–O bond in O_2, etc, but F_2 is by nature the worst case since it has the highest possible number of lone pairs (the problem is also less dramatic for atoms in other rows down the periodic table). On the other hand, in molecules containing no lone pairs, e.g., ethane, the electrons involved in the C–C bond are rather far from the adjacent ones which are consequently less sensitive to the charge fluctuation, and the TCSCF description of the C–C bond is then reasonably successful.

E. H_3. We have used this VB method to study the collinear reaction $H + H_2 \to H_2 + H$. The elementary and complementary structures of the H_3 supersystem are logically deduced from those of H_2 if one considers that the central hydrogen is bound to either one of the terminal atoms. Thus, for the description of the $H_a{}^\bullet H_b-H_c$ elementary VBF, we generate the same complementary set in H_b-H_c as for an isolated H_2 molecule, plus single excitations from the $1s_a$ orbital of the remaining hydrogen. In addition to the two covalent and four ionic elementary VBFs, we also include charge-transfer configurations, **12** and **13**. Note that whenever
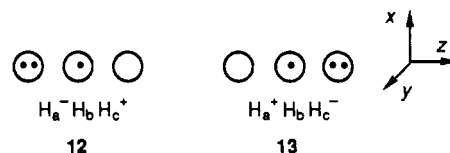
three AO's are singly occupied, there are two linearly independent doublet spin couplings, which have systematically been included. A total of 52 VBFs is generated (generating 26 symmetry-adapted combinations), and their coefficients are displayed in Table V. It appears that the charge-transfer configurations **12** and **13** are very marginal. Our calculated H–H bond lengths are 0.95 Å for the transition state, close to Liu's values, 0.93 Å.[37] Our calculated energy barrier, 15.3 kcal/mol, is also in reasonable agreement with the value 13.0 kcal/mol obtained with full CI in the same basis set (given that we have neglected the π structures) and somewhat higher than Liu's value, 9.6 kcal/mol, computed with a much larger basis set.

F. Li_3. The VBFs used for the collinear $Li + Li_2$ system are the same as those of H_3, augmented with π structures to a total of 166 (64 symmetry-adapted combinations). Their coefficients are displayed in Table VI, and show that once again the charge-transfer structures are unimportant, although their energies,

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TABLE V: Types of VBFs Used in the Valence Bond Calculation of the H_3 Complex[a]

VBF	type of bonding	excitation	coeff
elementary	H_a–$H_b H_c$		0.365
	$H_a^+ H_b^- H_c$		0.129
	$H_a^- H_b^+ H_c$		0.106
	$H_a^- H_b H_c^+$		0.025
optimization of orbital size	H_a–$H_b H_c$	$s_a \to s_a'$	0.068
		$s_b \to s_b'$	0.067
		$s_c \to s_c'$	0.038
	$H_a^+ H_b^- H_c$	$s_b \to s_b'$	0.036
		$s_c \to s_c'$	0.074, 0.001[b]
	$H_a^- H_b^+ H_c$	$s_a \to s_a'$	0.007
		$s_c \to s_c'$	0.034
	$H_a^- H_b H_c^+$	$s_a \to s_a'$	0.026
		$s_b \to s_b'$	0.061, 0.015[b]
polarization	H_a–$H_b H_c$	$s_a \to z_a$	0.007
		$s_b \to z_b$	0.001
		$s_c \to z_c$	0.001
	$H_a^+ H_b^- H_c$	$s_b \to z_b$	0.007, 0.001[b]
		$s_c \to z_c$	0.011
	$H_a^- H_b^+ H_c$	$s_a \to z_a$	0.013
		$s_c \to z_c$	0.011
	$H_a^- H_b H_c^+$	$s_a \to z_a$	0.005, 0.005[b]
		$s_b \to z_b$	0.015

[a] The orbital occupations are defined in the same way as in Table I. [b] The two possible spin couplings between the four singly occupied AO's have been allowed.

at the limits of the diagram, are much lower (5.0 and 4.7 eV) than those of the analogous structures in H_3 (16.6 and 15.1 eV). Thus these structures are in no way responsible for the stability of Li_3 with respect to H_3.

As expected (vide supra), our Li–Li bond lengths in the linear Li_3 trimer are too long (2.965 Å instead of 2.88 Å[38]) due to lack of d orbitals in our basis set. On the other hand, our calculated potential well of 3.8 kcal/mol is close to the full CI value in the same basis set, 4.2 kcal/mol, in good agreement with the value 5.3 kcal/mol obtained with a large s,p basis set by Kendrick and Hillier.[24]

The potential energy surface for linear Li_3 has been previously computed within the VB formalism by Yardley and Balint-Kurti.[39] These authors have however used a rather different method for selecting both the orbitals and the VBFs to be included in the CI. Using a minimal AO basis set, they constructed the polyatomic functions by antisymmetrizing atomic wave functions separately optimized for Li, Li^+, and Li^-. While being of similar dimensions, their CI and ours are in fact significantly different since our truncation method leads us to disregard 86 out of their 148 VBFs, while many of our additional VBFs arise from our use of a split-valence AO basis. Despite these differences, Yardley and Balint-Kurti find collinear Li_3 to be more stable than Li_2 + Li by 4.7 kcal/mol, in good agreement with our value.

The GVB formalism has also been recently applied by Goddard and McAdon[40] to the description of Li_n clusters in terms of interstitial orbitals, centered in the middle of Li_2 bonds rather than atom-centered. Although this picture is not used here, it is not contradictory with our VB model since it derives from the rather large s–p hybridization in Li, an effect taken into account through local s → p excitations and mixing of spin couplings in the present work.

Conclusion

The advantages of the valence bond methodology are known. It provides compact wave functions, expressed in a language useful and familiar to the chemist, which allows a clear understanding of reaction mechanisms in terms of competing bonding schemes whose weights vary throughout the reaction.

These advantages are fully preserved in the VB method that we use here. Dealing with orbitals, each purely localized on a

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(39) Yardley, R. N., Balint-Kurti, G. G. *Chem. Phys.* **1976**, *16*, 287.
(40) McAdon, M. H.; Goddard, W. A., III *J. Phys. Chem.* **1987**, *91*, 2607.

TABLE VI: Types of VBFs Used in the Valence Bond Calculation of the Li_3 Complex[a]

VBF	type of bonding	excitation	coeff
	σ Bonds		
elementary	Li_a–$Li_b Li_c$		0.362
	$Li_a^+ Li_b^- Li_c$		0.062
	$Li_a^- Li_b^+ Li_c$		0.098
	$Li_a^- Li_b Li_c^+$		0.007
optimization of orbital size	Li_a–$Li_b Li_c$	$s_a \to s_a'$	0.012
		$s_b \to s_b'$	0.024
		$s_c \to s_c'$	0.010
	$Li_a^+ Li_b^- Li_c$	$s_b \to s_b'$	0.030, 0.024[b]
		$s_c \to s_c'$	0.001
	$Li_a^- Li_b^+ Li_c$	$s_a \to s_a'$	0.012
		$s_c \to s_c'$	0.016
	$Li_a^- Li_b Li_c^+$	$s_a \to s_a'$	0.002, 0.018[b]
		$s_b \to s_b'$	0.014
polarization	Li_a–$Li_b Li_c$	$s_a \to z_a$	0.055
		$s_a \to z_a'$	0.014
		$s_b \to z_b$	0.022
		$s_b \to z_b'$	0.010
		$s_c \to z_c$	0.034
		$s_c \to z_c'$	0.014
	$Li_a^+ Li_b^- Li_c$	$s_b \to z_b$	0.031, 0.077[b]
		$s_b \to z_b'$	0.025, 0.026[b]
		$s_c \to z_c$	0.037
		$s_c \to z_c'$	0.001
	$Li_a^- Li_b^+ Li_c$	$s_a \to z_a$	0.019
		$s_a \to z_a'$	0.014
		$s_c \to z_c$	0.041
		$s_c \to z_c'$	0.019
	$Li_a^- Li_b Li_c^+$	$s_a \to z_a$	0.004, 0.002[b]
		$s_a \to z_a'$	0.005, 0.015[b]
		$s_b \to z_b$	0.010
		$s_b \to z_b'$	0.026
	π Bonds[c]		
elementary	$π\ Li_a$–$Li_b Li_c$		0.067
	$π\ Li_a^+ Li_b^- Li_c$		0.062
	$π\ Li_a^- Li_b^+ Li_c$		0.098
	$π\ Li_a^- Li_b Li_c^+$		0.007
optimization of orbital size	$π\ Li_a$–$Li_b Li_c$	$s_c \to s_c'$	0.001
		$x_a \to x_a'$	0.011
		$x_b \to x_b'$	0.010
	$π\ Li_a^+ Li_b^- Li_c$	$s_c \to s_c'$	0.001
		$x_b \to x_b'$	0.016, 0.001[b]
	$π\ Li_a^- Li_b^+ Li_c$	$s_c \to s_c'$	0.004
		$x_a \to x_a'$	0.014
	$π\ Li_a^- Li_b Li_c^+$	$s_b \to s_b'$	0.005
		$x_a \to x_a'$	0.002, 0.003[b]
polarization	$π\ Li_a$–$Li_b Li_c$	$s_c \to z_c$	0.015
		$s_c \to z_c'$	0.002
	$π\ Li_a^+ Li_b^- Li_c$	$s_c \to z_c$	0.005
		$s_c \to z_c'$	0.003
	$π\ Li_a^- Li_b^+ Li_c$	$s_c \to z_c$	0.008
		$s_c \to z_c'$	0.006
	$π\ Li_a^- Li_b Li_c^+$	$s_b \to z_b$	0.009
		$s_b \to z_b'$	0.009

[a] The orbital occupations are defined in the same way as in Table II. [b] The two possible spin couplings between the four singly occupied AO's have been allowed. [c] The π electrons are those involved in a covalent π bond or in a negative charge. The remaining odd electron is in an AO of σ type (s or z).

single fragment, ensures an unambiguous correspondence between VB structures and chemical bonding schemes. The present work shows that such a method may also be quantitative, provided that well-defined principles are used to select the VB structures so as to get a correlation-consistent wave function throughout a reaction process. Indeed, the computation of dissociation energies requires an adequate description of the chemical bond and constitutes a severe test for a computational method. Our VB results proves very satisfactory as compared to full CI results using the same basis sets, according to the three criteria of calculated bond lengths, reaction barriers, and dissociation energies, with energetic errors not exceeding a few kilocalories per mole. Thus the method appears to be very well adapted to the purpose of computing

quantitative diabatic curves of VB type, for thermal as well as photochemical reactions.

Using basis sets larger than DZ + P does not set any conceptual problem; it would simply increase the number of complementary

VBFs and therefore the dimension of the CI. Yet the basis sets used in this work provide reasonably good energetics and have therefore been kept in the following paper in which VB curve-crossing diagrams are calculated.

Quantitative Valence Bond Computations of Curve-Crossing Diagrams for Model Atom Exchange Reactions

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Curve-crossing diagrams are presented and computed for the exchange reactions X$^\bullet$ + X–X → X–X + X$^\bullet$, X = H, Li, by use of a multistructure VB approach. The computations provide the essential diagram quantities G, f, and B. These parameters are 156.8 kcal/mol, 0.37, and 42.4 kcal/mol, respectively, for X = H, and 22.4 kcal/mol, 0.13, and 6.6 kcal/mol for X = Li. The quantitative analyses confirm the qualitative deduction that all these quantities are related to a fundamental property of X, the singlet–triplet splitting ΔE_{st}(X–X) of the dimer. It is possible therefore to predict the height of the barrier and the mechanistic modality of the exchange reaction by reliance on ΔE_{st}; as ΔE_{st} decreases in a series the barrier decreases and eventually the X$_3$ species is converted to a stable intermediate. The B quantity is the quantum mechanical resonance energy (QMRE) of the X$_3$ species. The values of 42.4 kcal/mol for H$_3$ and 6.6 kcal/mol for Li$_3$ are computed as energy differences between a variational bonding scheme and the variational adiabatic and delocalized (X–X–X) state.

I. Introduction

Curve-crossing VB diagrams[1,2] are general models for discussing reactivity patterns. In the two-curve model **1** (state correlation diagram, SCD)[2a,b] the reaction profile arises as a consequence of the avoided crossing of two diabatic (or nearly so) curves, one

1
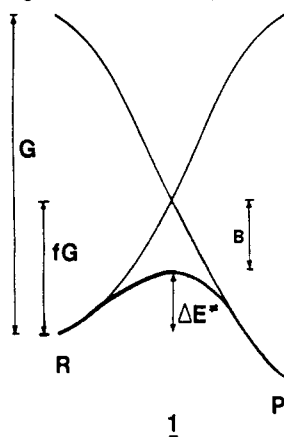
representing the bonding scheme of the reactants, the other that of the products. The barrier of the reaction is given by eq 1 as the difference between the height of the crossing point ΔE_c

$$\Delta E^{\ddagger} = \Delta E_c - B \qquad (1a)$$

$$\Delta E_c = fG \qquad (1b)$$

(relative to the reactants' complex R) and the avoided crossing interaction B. In addition, by appeal to (1), ΔE_c can be expressed as some fraction, f, of the diagram gap, G, at the reactant's extreme.[2a,b]

Knowledge of the f, G, and B quantities is important therefore for predicting and rationalizing trends in the barrier. This approach has proved very useful for the discussion of the barrier problem in S$_N$2, and other electrophile–nucleophile reactions.[2a,b,3] In addition, we have already noted that the stability of X$_n^z$ clusters (n = 3, 4, 6; z = 0, –1; X = monovalent atom or group) correlates with gap size.[4] All of these applications have so far relied on qualitative considerations and it becomes essential to test the ideas by rigorous quantitative means which can generate the diagrams and provide insight into the factors that control the variations of the diagram quantities f, G, and B. As discussed in the preceding paper,[5] the multistructure VB method[6] provides the ideal means toward this goal.

In this paper, the multistructure VB method is used to generate the curve-crossing SCD for two prototypical exchange reactions, **2** and **3**, which represent two mechanistic types of atom exchange

2　　　　　　　　　　　　**3**
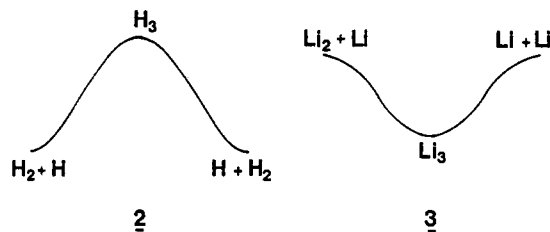
reaction, one passing through a potential barrier and the other

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