Compact valence bond functions with breathing orbitals: Application to the bond dissociation energies of \( \text{F}_2 \) and \( \text{FH} \)

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An original computational method of \textit{ab initio} valence bond type is proposed, aiming at yielding accurate dissociation energy curves, while dealing with wave functions being very compact and clearly interpretable in terms of Lewis structures. The basic principle is that the wave function is allowed to have different orbitals for different valence bond structures. Thus, throughout the dissociation process, the so-called “breathing orbitals” follow the instantaneous charge fluctuations of the bond being broken by undergoing changes in size, hybridization, and polarization. The method is applied to the dissociation of \( \text{F}_2 \) and \( \text{FH} \). For each molecule, a wave function involving only three valence bond configurations yields equilibrium bond lengths within 0.01 Å, and dissociation energies within about 2 kcal/mol of the results of estimated or true full configuration interaction in the same basis sets. The effect of dynamical electron correlation on calculated dissociation energies is analyzed. It is shown that restricting the correlation to its nondynamical part results in an improper treatment of ionic terms due to a mean-field compromise in the optimization of the orbitals.

I. INTRODUCTION

It is well established that diabatic states are a much better basis than adiabatic ones for the treatment of dynamical problems in situations where the Born-Oppenheimer approximation breaks down. Considerable efforts have been devoted to the calculation of such states, which are not eigenfunctions of the Hamiltonian, but display some electronic characteristics that vary slowly with the internuclear coordinates. The most natural way of calculating diabatic states is to use valence bond (VB) theory, which has the advantage of yielding wave functions having a clear relationship to Lewis structures, but methods of this type have been far, up to now, from reaching the accuracy of methods based on the molecular orbital concept and using multiconfiguration self-consistent field (MCSCF) and/or large configuration interaction (CI) techniques. The latter methods, however, only yield adiabatic functions, so that one has to transform the adiabatic functions into diabatic states which are not uniquely defined. VB wave functions, on the other hand, are not only useful for dynamic purposes but also for the construction of the VB curve-crossing diagrams of Shaik and Pross, which have been successfully applied to chemical reactivity. In both cases, what is needed is an accurate diabatic wave function having a clear physical content, as compact as possible so that the physical interpretation is not scattered over a large number of determinants, and accurate. In that latter respect, it is clear that we are not interested in very low absolute energies, but rather in reliable relative energies throughout a potential surface. In particular, an accurate method should be able to account for the major events that occur in a chemical reaction, i.e., bond breaking and bond making, and thus to yield dissociation energies with an error not exceeding about 5 kcal/mol.

There are some VB methods available yielding compact VB functions: the generalized valence bond method (GVB) of Goddard, or the spin-coupled valence bond method (SCVB) of Gerratt and Cooper. The methane molecule, for example, is described by a single configuration by such methods, which allow to visualize the local bonds of the ground state, and provide in addition good starting points for further CI. The GRVB method of Voter and Goddard can even deal with several resonating sub-GVB functions, whose shape and coefficients are optimized simultaneously. But such methods do not fit our purposes, for two reasons: (i) they allow for the delocalization of the orbitals, and consequently the relationship of the wave functions to Lewis structures depends on the degree of delocalization; (ii) their description of the two-electron bond is not better than that of a complete active space self-consistent field (CASSCF) wave function. Better accuracy is obtained by further CI, but the compactness is lost. On the other hand, the classical VB method, dealing with purely local orbitals, offers the best relationship with Lewis structures, but the difficulty lies in the optimization of the orbitals. If they are optimized in the free atoms, the molecular wave functions are exceedingly inaccurate. Better accuracy is obtained if one optimizes the atomic orbitals (AOs) of a multistructure molecular VB function, in which the VB structures differ from each other by the occupancies of a common set of AOs. But such a method, that we will refer to as classical VB, is not more accurate than CASSCF, unless a sizeable number of VB structures is involved, and once again the compactness is lost. The dilemma is thus clear: the classical VB method yields wave functions with a clear physical
content in terms of Lewis structures and is suitable for calculations of diabatic states, but the wave functions are either not accurate or not compact. Methods of other types can be accurate, but they are not compact either and they are hardly interpretable.

The aim of this paper is to present an ab initio computational method of VB type, suitable for the calculation of diabatic states and reconciling the properties of compactness and interpretability with an energetically accurate description of the chemical bond, so as to give correct potential energy curves. In other words, we are trying to make the classical VB functions compact and accurate.

Obtaining accurate dissociation energies from simple wave functions has been the subject of many studies in quantum chemistry. To mention but a few strict ab initio theories: the optimized valence configuration of Wahl and Das has been pioneering, later followed by the dissociation-consistent-CI (DCCI) and correlation-consistent-CI (CCCI) methods of Carter and Goddard, based on the GVB theory, and its CIPS/DCCI derivative. The aim of these methods is to correct for the deficiency of the CASSCF method, which only yields the nondynamical correlation energy, so as to correctly account for the differential correlation energy between the separated fragments and the molecule at equilibrium geometry. Thus, an important problem to solve is to understand the reason behind the CASSCF error, i.e., the nature of the differential correlation energy.

II. THE NATURE OF THE CASSCF DIFFERENTIAL CORRELATION ENERGY

A CASSCF calculation is a special case of MCSCF calculation, involving the configurations corresponding to all the possible occupations of a given set of orbitals, called the active set. In what follows we will only consider valence-CASSCF calculations, in which the active set is composed of the valence orbitals. In the F₂ case, the valence set involves eight orbitals (six lone pairs, one bonding and one antibonding MOs) for 14 electrons, and the main configurations are those in which the lone pairs remain doubly occupied. Thus, a CASSCF calculation on F₂ is practically equivalent to a GVB(1/2) calculation, and both terms will be used interchangeably in the following.

While the Hartree–Fock method is known to overestimate the ionic components of a two-electron bond at any distance, the CASSCF method is in principle correct in that respect. Taking the F₂ single bond as an example, a GVB or CASSCF wave function is nearly similar to a classical VB function in which both the coefficients and the orbitals of the three VB structures 1–3 would be optimized simultaneously. Yet, CASSCF provides much too long a bond length, and a dissociation energy about half the full CI value in the same basis set (Table I).

To understand the reason for this failure one has to note that the CASSCF wave function is constructed out of a unique set of MOs, while the best orbitals for 1 are expected to be different from those of 2 and 3. Similarly, the local lone pairs of, e.g., the left fluorine, feels the field of a neutral atom in 1, that of an F⁻ anion in 2, and that of an F⁺ cation in 3. The CASSCF method does not take into account the dynamical changes the orbitals should undergo to follow the charge fluctuations, as its orbitals are optimized in an averaged field corresponding to a neutral situation, and are thus well adapted to 1, but not to 2 and 3. Therefore, one can anticipate an unbalanced CASSCF description of the covalent and ionic structures, the latter being disfavored. This must result in dissociation energies being too small, as the two-electron bond is partly ionic at short distance, but becomes purely covalent at large separation. In that spirit, Cloet et al. and Malrieu have shown, on the basis of an orthogonal valence bond analysis, the impact of dynamical correlation effects on the ionic structures.

Our basic hypothesis is that the CASSCF error essentially comes from this mean-field orbital optimization. It implies that an improved VB description, in which each of the structures 1–3 would have its own set of independently optimized orbitals, should be able to yield correct equilibrium bond lengths and dissociation curves. It should be noted that our hypothesis bears some relation with that of Goodgame and Goddard, who also ascribed the poor GVB dissociation energies to an improper treatment of ionic situations, as will be discussed below.

The remedy for the above CASSCF error can be of two kinds: direct or indirect. The indirect way consists of simulating an independent optimization of the orbitals of 1–3 by adding further structures, of the single excitation type, to the CI. This can be done in the framework of classical VB, but also in that of the orthogonal VB or the GVB method. This is the spirit of the DCCI and CCCI methods, although in these cases the CI involves excitations higher than singles. However, several points are noteworthy: (i) methods based on CASSCF plus single excitations alone systematically overestimate potential wells, although in these cases the CI involves excitations higher than singles. However, several points are noteworthy: (i) methods based on CASSCF plus single excitations alone systematically overestimate potential wells, although in these cases the CI involves excitations higher than singles. However, several points are noteworthy: (i) methods based on CASSCF plus single excitations alone systematically overestimate potential wells; (ii) singly excited VB structures are not always easy to connect to a particular Lewis structure, as a given single excitation may in some cases be generated by more than one parent VB structure; (iii) although the CI involving parent structures and their monoeexcitations may not be very large, it clearly does not satisfy our condition of compactness.

A direct way to correct for the CASSCF error is the method that we propose in this work. It consists of expressing the wave function in terms of classical VB structures 1–3, and effectively performing the independent orbital optimizations so as to minimize the overall energy. As a result, each VB structure has its specific set of orbitals, different from one structure to the other. This way, each atomic orbital follows the fluctuation of bonding electrons by undergoing polarization, rehybridization and size changes. As this last change is intuitively expected to be the major one, such orbitals have been called “breathing orbitals,” in analogy with vibrational breathing modes.
III. BREATHING ORBITALS

A. Historical background

Weinbaum has been first to use different orbitals for different structures in a valence bond calculation of the H₂ ground state.¹⁵ The basis set was of single-zeta type, but the orbital exponents of each of the three VB structures H–H, H⁺H⁺ and H⁺H⁻ were independently optimized so as to minimize the energy of the adiabatic root. Interestingly, the exponents were not found to be so different from each other, so that the technique was not considered as worthwhile. This simple calculation suggests that the major breathing orbital effect, if significant, should not generally lie in active orbitals, but rather in inactive ones, which are absent in the H₂ case. Other calculations have been performed later on H₂ and LiH by Yokohama,¹⁶ and on CH by Raimondi et al.,¹⁷ in which the orbitals adjacent to the bond were either absent or left out of the independent orbital optimization process, with the same disappointing results. For systems involving adjacent orbitals, Murrel et al.¹⁸ have calculated the F₂ ground state by using a simplified optimization technique consisting of optimizing the breathing orbitals by Hartree–Fock calculations on atoms bearing the same charge as in the relevant VB structures. But isolated ions and ion pairs have very different orbitals and once again the technique did not lead to a reasonable potential well. A more elaborate technique consisted of minimizing the energies of single VB structures in turn, and to use these orbitals in the complete wave function. This technique has been successful for long-range¹⁹ or weak interactions,²⁰ but failed to give a reasonable two-electron bonding energy for F₂.²¹ An extension of this approach has been recently proposed by Hollauer and Nascimento,²² with the generalized multistructural method, on the example of He⁺.²³ However, neither of these methods reoptimize the orbitals for the final multiconfigurational wave function, which is important to minimize the individual energies of the VB structures and to maximize the resonance energy at the same time. This is the object of the breathing orbital valence bond method (BOVB) that we present in this article. In a preliminary report of this work,²⁴ we have applied the method to the F₂ molecule, at fixed geometry, at a basic level of approximation (level I below). The method has later been applied by Langenberg and Ruttkin²⁴ on the HI system of glyoxal. In the present paper, we push the method to higher levels and compare the equilibrium bond lengths and bonding energies of F₂ and FH with available full CI estimations.

B. The breathing orbital valence bond method

The breathing orbital valence bond method (BOVB) rests on the assumption that an electronic system should be well described by a VB wave function involving all relevant VB structures, if the latter are represented in a balanced way by configuration state functions (CSFs) having fully adapted orbitals, optimized without any mean-field restrictions.

The first step is to define the active system of orbitals and electrons. The active orbitals are those that are involved in bond-breaking or bond-making processes in a reaction, while the inactive ones keep the same occupancy throughout (note the difference with the active set of a valence CASCI calculation). Then a set of Lewis structures is defined, corresponding to all the covalent or ionic bonds within the active orbitals and electrons, and the corresponding CSFs of VB type are constructed. Last, all the orbitals, active or inactive, and the coefficients of the various CSFs are optimized simultaneously, by any nonorthogonal MCSCF technique, with full allowance for the orbitals to be different from one CSF to the other.

An important feature of the method is that the active orbitals are defined as purely localized on a single atom or fragment. The reason for this choice is twofold: (i) dealing with local orbitals is important for the wave function to be interpretable. As a Lewis structure is characterized by a specific occupancy of AOs, we keep a maximum correspondence between the Lewis structures and the mathematical form of our CSFs. (ii) The breathing orbital effect looses its meaning if the ionic structures are contaminated by covalent ones, as happens when the CSFs are composed of delocalized orbitals. In such a case, the wave function would display little or no charge fluctuation, and the orbital breathing would be inefficient.²⁵(a) On the other hand, inactive orbitals may or may not be delocalized, as this alters neither the efficiency of the breathing orbital effect, nor the relevance of the CSFs to specific Lewis structures. Both possibilities will be investigated below.

The balanced description of each Lewis structure allows each of them to be represented by a single CSF, resulting in a very compact wave function. If the active system is reduced to a two-electron bond, the set of Lewis structures is composed of one covalent and two ionic structures, as in 1–3 above. For more complex reactions like nucleophilic or radi cal attacks, the number of CSF would remain under ten. So only the active part of the molecule is treated at the VB level, the inactive orbitals being treated at a level of Hartree–Fock type. This ensures the correlation of the active electrons, while the inactive electrons are left “uncorrelated,” the corresponding error being expected to remain constant throughout a potential surface. The breathing orbital effect corresponds to a correlation between active and inactive electrons, which we have supposed to be that part of the correlation energy that varies along the reaction process. So we directly calculate the differential correlation energy, and no other component of electron correlation. Accordingly, in a dissociation reaction the BOVB asymptotic energy is exactly the sum of the energies of the separated fragments calculated at the restricted open-shell Hartree–Fock (ROHF) level.

IV. COMPUTATIONAL PROGRAMS AND BASIS SETS

All calculations have been performed with the TURTLE program, written by Verbeek, Langenberg, and two of us (CPB and JHvL)²⁵,²⁶ on the basis of the VBSCF method of Balint-Kurti and van Lenthe.²⁷ This is a very general multi configuration method that allows for the use of nonorthogonal orbitals, which can be restricted to be fully localized. Both the coefficients of the CSFs and their orbitals are optimized simultaneously, and different CSFs may be allowed to have different orbitals. Two algorithms—approximate Newton–Raphson²⁸ and super-CI,²⁹—are available for the orbital optimization process. Here we have used the latter
TABLE I. Dissociation energies and optimized equilibrium bond lengths for the $F_2$ molecule.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_e$ (Å)</th>
<th>$D_e$ (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6-31+G^*$ basis set</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GVB</td>
<td>1.506</td>
<td>14.0</td>
<td>This work</td>
</tr>
<tr>
<td>CASSCF</td>
<td>1.495</td>
<td>16.4</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level I</td>
<td>1.485</td>
<td>27.9</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level II</td>
<td>1.473</td>
<td>31.4</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level III</td>
<td>1.449</td>
<td>33.9</td>
<td>This work</td>
</tr>
<tr>
<td>MP4</td>
<td>1.453</td>
<td>...</td>
<td>33</td>
</tr>
<tr>
<td>Estimated full CI</td>
<td>...</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td><strong>LSB Basis Set</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOVB level III</td>
<td>1.443</td>
<td>31.6</td>
<td>This work</td>
</tr>
<tr>
<td>Estimated full CI</td>
<td>1.44±0.005</td>
<td>28–31</td>
<td>32 and 38</td>
</tr>
<tr>
<td>Experimental</td>
<td>1.412</td>
<td>38.3</td>
<td>39</td>
</tr>
</tbody>
</table>

A. Level I

The first level is similar to that reported in our preliminary letter. All orbitals, active and inactive, are purely local, and the ionic structures 2 and 3 are of closed shell type, i.e., in each of these structures the two active electrons are located in a unique doubly occupied orbital. At this level, the breathing orbital effect already results in a dramatic improvement of the wave function relative to CASSCF. At an interatomic distance of 1.485 Å, $F_2$ is found to be bound by 27.9 kcal/mol, to be compared with the CASSCF and GVB(1/2) values of 16.4 and 14.0 kcal/mol, respectively.

As the breathing orbital effect is expected to stabilize the ionic structures much more than the covalent ones, it is of interest to examine its effect on the energies of structures 1, 2, and 3 separately, i.e., on the diagonal elements of the $3 \times 3$ CI matrix. In agreement with physical intuition, breathing orbitals lower the energy gap between covalent and ionic structures by 115 kcal/mol, relative to a wave function in which 1, 2, and 3 are restricted to share the same set of orbitals.

Now the ionic structures still need improvement, as the closed-shell structures of 2 and 3, with doubly occupied active orbitals, miss some radial correlation of the active electrons. As a consequence, the dissociation energy, as calculated at this level, is somewhat smaller than the value of 33 kcal/mol estimated by Lepetit et al. as an upper bound for the full CI limit in the same basis set, while the calculated equilibrium distance is rather long.

B. Level II

The defect of level I can be cured without increasing the number of VB structures, just by allowing the two active electrons of the ionic structures to occupy different orbitals. Accordingly, in our level II, the active orbitals of 2 and 3 are split, much like lone pairs would be split in a GVB calculation, leading to structures 4 and 5. As a result, the ionic structures are further lowered by 4.5 kcal/mol, while the energy of the covalent structure is unchanged. As a consequence, the dissociation energy is lowered by 3.5 kcal/mol relative to level I, and the equilibrium bond length is shortened, however, still not enough to reach the fourth-order Möller–Plesset (MP4)-optimized value in the same basis set. This time the treatment of active electrons cannot be questioned, so one must examine the interactions between inactive electrons.

A drawback of the purely local description of lone pairs, that characterizes levels I and II of our method, is that it yields an entirely repulsive interaction between two lone pairs facing each other, thus neglecting some attractive charge-transfer terms which should contribute to diminish the four-electron repulsions. Among these terms, the $n$ charge transfers in the ionic structures can be expected to be
most important, as they correspond to $\pi$ backdonation of $F^-$ towards $F^+$. On the other hand, in a MO description, two lone pairs facing each other are represented by one bonding and one antibonding orbitals, both doubly occupied. In a minimal basis set, the AO and MO descriptions are strictly equivalent, but in an extended basis set, the MO description has one additional degree of freedom because the AOs forming the bonding and antibonding MOs may have different shape, and one can show that this just corresponds to the charge-transfer VB structures that are missing in levels I and II.  

C. Level III

There are two ways to account better for the interactions between $\pi$ lone pairs, and specifically to include the stabilizing charge transfers. One can either introduce some additional VB structures, or describe the $\pi$ lone pairs as delocalized orbitals. We have chosen this latter solution in our level III, because it has the important advantage of keeping the simple expression of the wave function, with the same number of CSFs as in levels I and II, while the interpretation of the VB functions in terms of covalent or ionic Lewis structures is unchanged. As a result of this improvement, the calculated equilibrium bond length is now close to the MP4-optimized value, and the dissociation energy is lowered by 2.5 kcal/mol, thus reaching the value 33.9 kcal/mol, close to the estimation of Lepetit et al. Counterpoise calculations, using the covalent structure only, show that this energy lowering is really due to charge transfer; the basis set superposition error (BSSE) calculated at equilibrium distance in the 6-31+G** basis set was only 0.04 kcal/mol for $F_2$, and 0.03 kcal/mol for $FH$.

D. Comparison with full CI estimations in LSB basis set

In order to better calibrate our method, we have repeated our estimations of $R_e$ and $D_e$, in the basis set used by Laidig, Saxe, and Bartlett in their series of calculations aimed at estimating the bond length and dissociation energy of $F_2$ at the full CI level. Using various high quality methods, these authors estimated their basis set limit to 1.44±0.005 Å for $R_e$ and 1.26±0.05 eV for $D_e$, but these calculations have been reexamined by Daudey et al., who estimated $D_e$ to be close to 1.30 eV (30 kcal/mol). Close to these estimations is also the value of 1.24 eV reported by Daudey et al., using a size-consistent truncated CI method in the same LSB basis set. Our calculated values in the same basis set and with the level III of our method are 1.443 Å for $R_e$ and 1.37 eV (31.6 kcal/mol) for $D_e$, thus quite close to the 1.21–1.35 eV bracket of full CI estimations.

E. CPU considerations

As an order of magnitude, a single-point energy calculation on $F_2$, at level III and in 6-31+G* basis set, requires about 2.5 min of CPU time per iteration, on a RS 6000/550 work station. The number of iterations crucially depends on the appropriate choice of the guess orbitals. It can vary from 4–5, e.g., in a potential surface scan where the orbitals of one point are used as a guess for the next point, to 20–30 or more in a single-point calculation using guess orbitals taken, e.g., from fragments calculated at the Hartree–Fock level. In this latter case, convergence would certainly be improved with the help of an orbital optimization algorithm specific to the BOVB method, which will be the object of future developments.

VI. RESULTS AND DISCUSSION FOR FH

We now turn to a different type of single bond, that of hydrogen fluoride. This is a typical polar bond, in which the ionic component $F^-H^+$ is expected to be almost as much important as the covalent one. Another difference with the preceding case is that the bond is now quite strong, with an experimental dissociation energy of 141.1 kcal/mol. The single bond is now described by the three VB structures 6–8, among which the last one, of the type $F^+H^-$, is expected to be very minor. As in the $F_2$ case, we have used the levels I, II, and III of the theory to calculate the spectroscopic constants. However, the very polar nature of the molecule may be expected to rise a specific problem, due to the special importance of the ionic structure 7. Indeed, a key approximation of the method at levels up to and including III is that the correlation of the inactive electrons is not explicitly taken into account, as being supposed to remain constant throughout the dissociation process. Now, as the inactive electrons of, e.g., a $\pi$ lone pair in structure 7 feel a different electric field than the same electrons in structure 6, one may expect the intrapair correlation energy of this lone pair to be different from 6 to 7, and the neglect of this correlation energy might have some consequences when the ionic structure gets important. To check this possible source of error, we have pushed the VB model to a further level, in which the orbitals of the $\pi$ lone pairs are split in structures 6 and 7, just as the active $\pi$ orbitals of structures 4 and 5. This way the radial correlation energy of the lone pair is introduced in both the molecule and the separated fragments, and allowed to be different from 6 to 7. Calculations at this level IV have been performed in a 6-31+G** basis set first, in order to compare levels III and IV, then in DZP and DZP+ basis sets, to compare our spectroscopic constants and dissociation curves with those calculated at the full CI level by Bauschlicher.

A. 6-31+G** results at levels I, II, III, and IV

The calculated bond lengths and dissociation energies, at various levels, are displayed in Table II. At the crudest level, with a closed shell constraint for the ionic structure 7 and all orbitals being constrained to remain purely local, the dissociation energy is significantly too small. One may wonder why level I is so poor, in absolute terms, in the FH case, while it was not so bad in $F_2$. The reason lies in the different importance of ionic structures in $F_2$ and $FH$. In the former...
TABLE II. Dissociation energies and optimized equilibrium bond lengths for the FH molecule.

<table>
<thead>
<tr>
<th>Method</th>
<th>Re (Å)</th>
<th>De (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31+G** basis set</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GVB(1/2)</td>
<td>0.920</td>
<td>113.4</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level I</td>
<td>0.918</td>
<td>121.4</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level II</td>
<td>0.911</td>
<td>133.5</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level III</td>
<td>0.906</td>
<td>136.3</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level IV</td>
<td>0.916</td>
<td>137.4</td>
<td>This work</td>
</tr>
<tr>
<td>DZP+ basis set</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOVB level III</td>
<td>0.906</td>
<td>136.5</td>
<td>This work</td>
</tr>
<tr>
<td>BOVB level IV</td>
<td>0.912</td>
<td>138.2</td>
<td>This work</td>
</tr>
<tr>
<td>Full CI</td>
<td>0.917</td>
<td>141.1</td>
<td>31</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.917</td>
<td>141.1</td>
<td>39</td>
</tr>
</tbody>
</table>

*The 2s orbitals are not included in the CI.

As a result, the bond dissociation energy case, ionic structures 2 and 3 are relatively minor and their closed shell structure does not affect the overall bonding too much. This does not hold in the FH case, where the F−H+ structure 7 is expected to have a weight close to 50%, so that the lack of correlation of the active electrons in 7 now has a major effect on the bonding energy. Accordingly, the calculations at level II, obtained by replacing structure 7 by 9, in which the active orbital has been split, result in a lowering of 12.1 kcal/mol of the dissociation energy.

The dissociation energy is further improved by allowing the π orbitals to be delocalized, as in level III. It should be noted that this delocalization is now associated to physical effects different from those of the F2 case, as FH has only two electrons in each of the π planes instead of four. Thus, π delocalization now takes into account: (i) the contribution of π two-electron bonds to the overall bonding of FH, and (ii) some π backdonation, from fluorine to hydrogen, in the F−H+ VB structure. As a result, the bond dissociation energy is further lowered by some 3 kcal/mol and reaches 136.3 kcal/mol, a very reasonable value taking into account the lack of polarization functions higher than d in our basis set.

We now examine the possible problem of the nonconstancy of the correlation among inactive electrons, throughout the dissociation, by pushing the VB model to level IV. This consists of replacing structures 6 and 9 by 10 and 11, in which all orbitals are singly occupied and coupled in a singlet way. The number of VB structures is unchanged from level III to level IV, but the latter level is of course more costly as the number of orbitals and determinants is larger. The results, displayed in Table II, yield a bond length practically similar to the experimental value, and a dissociation energy of 137.4 kcal/mol, lowered by only 1.1 kcal/mol relative to level III. This indicates that the further complexity reached in level IV is definitely not worthwhile, and confirms the validity of the simpler model.

### Table III. Energies of the FH molecule at three interatomic distances. Re is the experimental equilibrium distance of 0.917 Å. Both the full CI and the BOVB calculations use the same DZP basis set.

<table>
<thead>
<tr>
<th>Distance</th>
<th>E(hartrees)</th>
<th>ΔE(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full CI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>-100.250</td>
<td>56.84</td>
</tr>
<tr>
<td>1.5 Re</td>
<td>-100.160</td>
<td>49.75</td>
</tr>
<tr>
<td>2 Re</td>
<td>-100.081</td>
<td>49.83</td>
</tr>
</tbody>
</table>

BOVB calculations use the same DZP basis set.

**B. A comparison with full CI results in DZP and DZP+ basis sets**

It is difficult to estimate the quality of our bond lengths and dissociation energies by comparing them to experimental values, as it is known that very large basis sets are needed to accurately reproduce any spectroscopic constants of diatomics involving fluorine. Fortunately, some full CI calculations are available in the case of FH, with the DZP and DZP+ basis sets, thus allowing some comparison between full CI and our method.

A calculation of the dissociation energy and equilibrium bond length has been performed by Bauschlicher and Taylor, using the DZP+ basis set, yielding the values 136.3 kcal/mol and 0.921 Å, respectively. Using the same basis set, we found the values 136.5 kcal/mol and 0.906 Å, respectively, at level III, and 138.2 kcal/mol and 0.912 Å at level IV, both levels being in agreement with Bauschlicher's value within 2 kcal/mol. It should be noted, however, that Bauschlicher's calculation is not a true full CI, as the 2s orbital has been excluded from the CI. Now a true full CI calculation has been performed in a smaller basis set (DZP), which does not report a dissociation energy but, perhaps even more interestingly, some points of the dissociation curve. The three calculated points correspond to Re, the experimental bond length, 1.5 and 2 Re. Using the same DZP basis set, we have calculated the energies of FH at the same geometries, at the level IV of our VB method, and compared our energy profile with the full CI one. The results, displayed in Table III, show very small differences between the two energy profiles. Indeed, from Re to 1.5 Re, the VB energy increases by 57.67 kcal/mol, only 0.83 kcal/mol in error relative to the full CI energy increment of 56.84 kcal/mol. The error is ten times smaller from 1.5 to 2 Re, and can be expected to become insignificant from 2 Re to infinite distance. This shows that, at least in this basis set, the VB and full CI dissociation curves are extremely similar as far as relative energies are concerned, and that the VB error on the dissociation energy is about 1 kcal/mol.

VII. CONCLUSIONS

The BOVB method aims at reconciling compactness and accuracy, by yielding very simple wave functions that dissociate well. Applied to the dissociation of F₂ and FH, two rather difficult test cases, the method shows a good agreement with full CI, both in terms of dissociation energies and of shape of the dissociation curve, while dealing with three configurations only. For comparison, the smallest MCSCF wave function for F₂ necessary to get the same agreement with estimated full CI involves 968 CSFs in a basis set of about the same type as ours (5s5p3d). This compactness, and the purely local nature of the active orbitals, makes the wave functions clearly interpretable in terms of Lewis structures, and thus suitable for calculating diabatic potential energy surfaces.

It should be noted that the aim of the BOVB method is not to solve the entire problem of getting diabatic pictures of reactions, but only to calculate diabatic surfaces with the right shapes. There remains to get a correct energy spacing between these surfaces, and one knows that this can be a major difficulty in some cases, especially when an ionic state has to be positioned in energy relative to a neutral one. Consider for example an ionic structure A⁺B⁻ and a covalent one A'B' . At infinite distance, the energy gap between these two asymptotic states is the difference between the ionization potential of A and the electron affinity of B. Unfortunately, electron affinities are extremely difficult to calculate, as they require gigantic CSs as well as very large basis sets. As a result, no ab initio method is able to reproduce the ionic-covalent gap in asymptotic states, and BOVB is not an exception. A classical solution to this dilemma, applied even in large scale CI ab initio calculations, is to use some experimental information. Thus a correct diabatic picture could be obtained by shifting the diabatic curves, just by fitting the asymptotic gaps to experiment. Now one may wonder how a very polar bond, like that of FH, can be correctly described by the BOVB method since the relative positions of ionic and covalent structures is not expected to be exact. The answer is that the ionic structure of the ground state is not quite the same as the diabatic ionic structure, i.e. the ionic structure alone, for two reasons: (i) In the ground state, the breathing orbitals of the ionic structure are optimized not only so as to lower the ionic structure, but also so as to maximize the resonance energy. (ii) Most of the correlation of the ionic structure is brought by the covalent structure in the ground state. As a result, the relative positions of the ionic and covalent structures contributing to the ground state are not to be compared with the positions of diabatic states, and the correlation requirements of the ionic structures are also not the same.

A side conclusion to be drawn from the above results deals with the nature of the error inherent to CASSCF wave functions. Indeed, our level III VB wave functions only differ from GVB (1/2) wave functions, very close to CASSCF, by two features: (i) the breathing orbital effect and (ii) the radial correlation of the active electrons in the ionic structures. These two effects, and especially the former, completely correct for the CASSCF error in dissociation energies and thus constitute the physical nature of the differential dynamical correlation energy. Because CASSCF lacks these two effects, it leads to ionic structures being strongly destabilized relative to the covalent ones, as already noted by Goldgame and Goddard. However, while we agree with these authors that the GVB error lies in the poor description of ionic structures, our explanation is different from theirs. Indeed, they put forward the closed shell nature of the ionic structure [effect (ii) above], whereas we show that the orbital relaxation of the ionic structures relative to the covalent one [the breathing orbital effect (i) above] is the major phenomenon.

The method is of course not restricted to diatomics, and can be extended to larger molecules provided the active system of orbitals and electrons remain of small dimension. As typical examples, we are currently investigating transitions states of S₄2 reactions and reactions of radical attacks. Moreover, the breathing orbital effect does not only apply to two-electron bonds and can be expected to be even more important in three-electron interactions, where the bond is due entirely to the fluctuation of charge and its associated resonance energy. Such calculations are currently in progress in our group, and will be the subject of a forthcoming paper.

1 For reviews, see (a) T. Pacher, L. S. Cederbaum, and H. Köppel, Adv. Chem. Phys. 84, 293 (1992); (b) H. Köppel, W. Domske, and L. S. Cederbaum, ibid., 87, 59 (1994); (c) V. Sidis, ibid., 82, 73 (1992), and references therein. See also, for effective hamiltonian methods (d) F. Spiegelmann and J. P. Malrieu, J. Phys. B 17, 1259 (1984); (e) R. Ciriniglione, J. P. Malrieu, M. Pernisco, and F. Spiegelmann, ibid., 18, 1073 (1985); (f) G. X. Gadadé, and M. Pélissier, J. Chem. Phys. 93, 545 (1990).
11 (a) P. C. Hiberty, 16ème Congrès des Chimistes Théoriciens d’Expression
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34. The delocalization does not need be extended to inactive orbitals because the charge transfers among these orbitals are already taken into account owing to the presence of the ionic structures.

35. Note that the charge transfer terms, when they are introduced explicitly, have coefficients smaller than 0.02 in F₂ [see Refs. 12(b) and 12(c)], so that their presence in level III cannot blur the interpretability of the VB structures.


