

What Is Physically Wrong with the Description of Odd-Electron Bonding by Hartree–Fock Theory? A Simple Nonempirical Remedy

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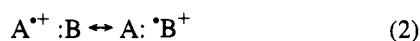
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Abstract: The odd-electron (one and three) bond involves resonance between two charge-shift related structures, in both MO and VB theory. A physically correct description of odd-electron bonding should reflect the instantaneous response of the orbital size and shape to the charge fluctuation inherent in the odd-electron bonding. VB theory contains this response and involves charge-fluctuation-adapted orbitals in the resonance structures, resulting in reliable bond energies. In contrast, due to its constraints, the Hartree–Fock theory fails to represent this crucial feature of the odd-electron bond and generates thereby poor bond energies. A nonempirical remedy for this Hartree–Fock bias is proposed. This is the “Uniform Mean-Field Hartree–Fock” (UMHF) procedure which is based on the simple unrestricted Hartree–Fock method, but involves orbital occupancy constraints and correction of the resonance energies by non-empirical factors. The UMHF approach is tested on three-electron- and one-electron-bonded molecules and is shown to yield bonding energies in satisfactory agreement with more sophisticated calculations (up to and beyond fourth order of Moller–Plesset perturbation theory). The UMHF procedure is offered as a routine inexpensive tool for obtaining odd-electron bond energies for large molecules.

Introduction

Odd-electron bonds are now recognized to play an important role in radical and electron transfer chemistry. First described by Pauling in 1931,¹ these bonds owe their stability to a resonance between two Lewis structures that are mutually related by charge transfer, as shown in (1) for one-electron bonds and in (2) and (3) for typical three-electron bonds:



It has been pointed out that a significant resonance energy requires a similar stability of the two resonating Lewis structures.^{2,3} Clark³ has shown that the odd-electron bond energy decreases exponentially with ΔIP , the difference between the ionization potentials of A and B. Consequently, many of the known odd-electron bonds are homonuclear, or at least involve two atoms of similar IP. Moreover, odd-electron bonds are seldom observed in neutral species, because the charge transfer in (4) is generally strongly endothermic, especially in the gas phase.



In MO theory the stability of one- and three-electron bonds can be shown^{4,5} to arise from the fact that they possess one net bonding electron in the MO's generated by the $(AB)^{\cdot}$ species.

Experimentally, one-electron⁶ and especially three-electron bonds^{7–38} are abundant and well-characterized. Numerous

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$(R_2S \cdot SR_2)^+$ radical cations,^{8,13} $(RS \cdot SR)^-$ radical anions,^{14–17} and $R_2S \cdot SR$ neutral radicals^{15,18–20} have been identified, as well as $N \cdot N$,^{21–25} $P \cdot P$,^{26,27} $As \cdot As$,^{26,28} $Se \cdot Se$,²⁹ $I \cdot I$,^{30,31} and more generally all kinds of $X \cdot Y$ ($X, Y = N, S, P$, halogen, etc.) two-center-three-electron (2c,3e) bonds.^{32–38} Despite the ample observations of these species, very little experimental data exists for the strengths of their odd-electron bonds, and thermodynamic data are remarkably sparse. Apart from some recent accurate gas-phase determinations of (2c,3e) binding energies,^{12,31} the majority of measurements have been indirect, involving estimations of energy gaps between σ -bonding and σ^* -antibonding levels. This situation makes theoretical calculations particularly useful, and indeed, apart from a few cases of diatomic ions, most of the information about odd-electron bonding energies in chemistry comes from ab initio theoretical studies.^{3,5,12,13,39–45} High-level computations are restricted to small to medium size species, while size limitation makes Hartree–Fock (HF) theory as the only feasible level to obtain odd-electron bond energies for experimentally occurring odd-electron bonds.²⁴ It would have been desirable, therefore, to have a reliable HF method for odd-electron bonding. However, at present the standard HF levels do not seem to be such reliable tools.

Clark³ and Radom⁵ have carried out systematic calculations on series of cation radicals involving odd-electron bonds between atoms of the first and second rows of the periodic table, with hydrogen atoms as substituents. These calculations, performed at both unrestricted Hartree–Fock (UHF) and Moller–Plesset perturbation (MP) levels, exhibit a number of important and sometimes intriguing features:

(i) The inclusion of electron correlation is essential for the calculation of three-electron bonding energies. The Hartree–Fock error is nonsystematic and always large, sometimes of the

same order of magnitude as the bonding energy itself (see later Table 1), or even slightly larger than the bonding energy as in the case of the F_2^- anion radical.⁴⁶ The error is smaller in the case of one-electron bonds,³ yet it may be as large as 13 kcal/mol as in the $CH_3CH_3^+$ cation (see Table 2). In all cases, the lack of electron correlation leads to an underestimation of the bonding energy. In contrast, for the isomeric species that are devoid of odd-electron bonding, e.g., the hydrogen-bonded complexes between cation radicals and their neutral molecules, the UHF bonding energies are quite good—close to accurate values calculated at the MP4 level.⁵

(ii) Paradoxically, the UHF optimized geometries of odd-electron-bonded species are correct. Considering that bond energies are poorly reproduced at this level, one would have expected the optimized odd-electron bond lengths to be too long. Nevertheless, the distance between the odd-electron bonded atoms is well reproduced at the UHF level. In some cases,⁵ the Hartree–Fock-optimized structure with correct geometric parameters is incorrectly found to be a transition state rather than a true minimum. There is therefore a disparity in the descriptions of the bond length and bond energy of three-electron bonds in UHF theory.

(iii) The MP2 level is satisfactory and provides geometries and bonding energies in good agreement with higher orders of perturbation theory.^{5,47}

(iv) Curiously, the Hartree–Fock error seems to disappear if a minimal basis set is used,⁵ and the resulting three-electron bonding energies are, if not accurate, at least of the right order of magnitude. We will see below that this point is not fortuitous but can be rationalized based on the physical description of the odd-electron bond.

Another problematic aspect of calculations is that some but not all of the odd-electron bond dissociation energies are quite sensitive to substituent effects,^{5,12,48} so that no standard bonding energies can be defined. This, and the findings of Clark³ and Radom⁵ that the accurate calculation of odd-electron bonding energies requires moderate to large basis sets, restricts the computations by necessity to small model systems whose relevance to larger molecules is limited. What we are after, then, is a reliable computational method that emerges from the correct physical description of the odd-electron bond and is economical and useful as a routine computational tool to obtain odd-electron bond energies.

In this line, the first general aim of the present study is to establish the physical basis for the failure of the Hartree–Fock procedure for odd-electron bonds. This will be done by answering the following questions: (i) Why are correlation effects so important in three-electron bonds, despite the fact (shown later) that the Hartree–Fock wave function for odd-electron bonds is qualitatively correct? (ii) Why does the Hartree–Fock method yield correct geometries for odd-electron bonded species, while the bonding energies are exceedingly underestimated? (iii) Why does the Hartree–Fock error disappear in a minimal basis set?

The second aim of this study is to propose a nonempirical remedy for the Hartree–Fock method, dubbed Uniform Mean-

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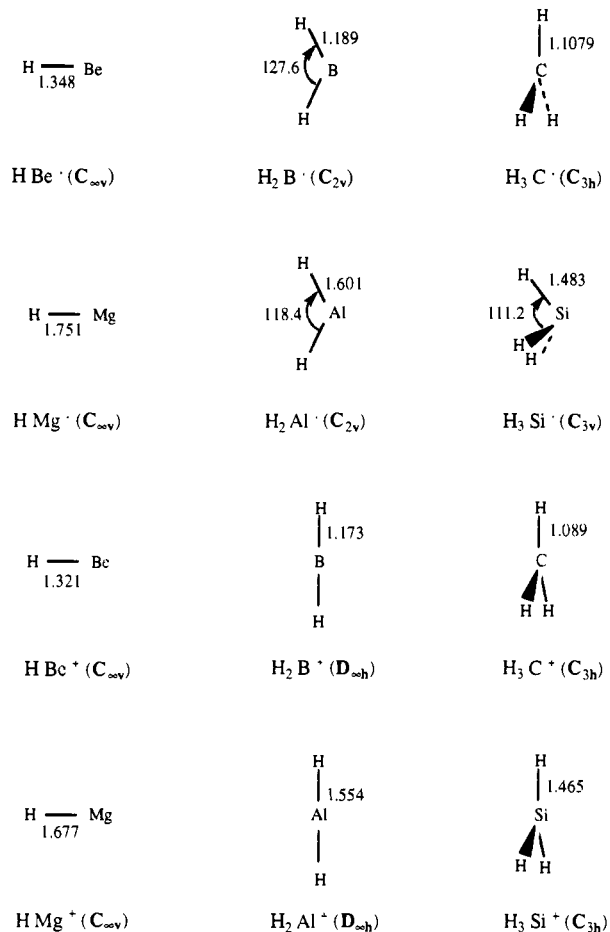
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Chart 1. MP2-Optimized Structures for Fragments



Field HF (UMHF), that would take advantage of the correct qualitative form of the wave function and allow good bond energies to be obtained without resort to electron correlation.

Theoretical Methods

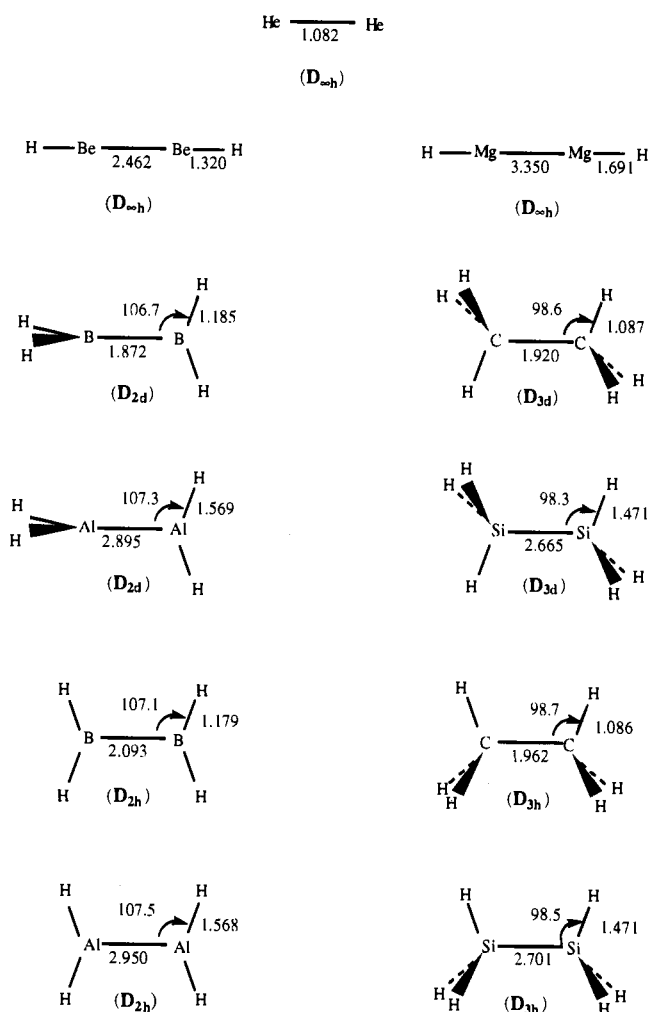
Standard unrestricted Hartree–Fock (UHF) calculations were performed with the GAMESS and GAUSSIAN-92 suites of programs.⁴⁹ All the computational results displayed in the tables, including those quoted from other sources, were performed with the 6-31G* basis set,⁵⁰ with the exception of the He₂⁺ species that was calculated with the 6-31G** basis set that contains p-type polarization functions for the helium atoms.⁵⁰

The Moller–Plesset (MP) perturbation theory⁵⁰ was used in its unrestricted formalism throughout this study. The MP dissociation energies were calculated at the MP2//MP2 and MP4//MP2 level, i.e. the geometries of the molecules and separated fragments have been optimized at the second order of perturbation (MP2), while the final energies were calculated at the second (MP2) and fourth (MP4) orders; the frozen-core approximation is applied in this latter case. The MP4//MP2 and MP2//MP2 results are quoted from ref 5 for the three-electron bonds (Table 1) while those for the one-electron bonds were calculated in this work (Table 2). The MP2-optimized geometries of the one-electron bonded species and their separated fragments are displayed in Charts 1 and 2 (bond lengths in Å, angles in deg).

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Chart 2. MP2-Optimized Structures for One-Electron-Bonded Radical Cations



For the sake of consistency, the geometries employed to calculate odd-electron UMHF bonding energies were those optimized at the UHF level, and quoted from refs 3 and 5, since the UMHF and UHF methods are equivalent in the vicinity of the local minima of the odd-electron-bonded species.

The Orbital Response to Charge-Fluctuation

Three-Electron Bonds. Why does the Hartree–Fock level underestimate bonding energies so much? In the case of homonuclear two-electron bonds, the explanation is simple: the Hartree–Fock wave function incorrectly describes the bond as 50% covalent and 50% ionic, while the covalent component should be largely preponderant. However, there is nothing as such in homonuclear odd-electron bonds. Consider Ψ_{HF} , the Hartree–Fock wave function of a three-electron bond modeled by the He₂⁺ radical cation:

$$\Psi_{\text{HF}} = |\sigma_g \bar{\sigma}_g \sigma_u| \quad (5)$$

The orbitals σ_g and σ_u in the determinant in eq 5 are respectively bonding and antibonding molecular orbitals:

$$\sigma_g = \chi_l + \chi_r \quad (6)$$

$$\sigma_u = \chi_l - \chi_r \quad (7)$$

where the normalization factors have been dropped (as well as in all subsequent formulas in this paper), and the atomic orbitals χ_l and χ_r are assumed to be the same in (6) and (7).

More insight into the physical meaning of the single determinant in eq 5 can be gained by substituting (6) and (7) into (5), and transforming Ψ_{HF} into a function of valence bond type:

$$\Psi_{\text{HF}} = |\overline{\chi_1 \chi_1 \chi_r}| + |\overline{\chi_1 \chi_r \chi_r}| \quad (8)$$

Actually the physical picture involved in eq 8 corresponds to the familiar description (eq 2) of three-electron bonds in terms of two resonance structures $\mathbf{1} \leftrightarrow \mathbf{2}$. Thus,



a fundamental feature of odd-electron bonding is charge fluctuation which is described formally the same by both VB and MO methods. Here lays an apparent paradox: despite its formally correct description, the UHF (or ROHF) method does not produce meaningful bonding energies, not even orders of magnitude.

A subtle inadequacy is revealed however if eq 8 and resonance structures ($\mathbf{1} \leftrightarrow \mathbf{2}$) are considered in detail. For symmetry reasons inherent to the Hartree–Fock method, the χ_1 and χ_r atomic orbitals are the same in both determinants, which means that the doubly occupied and the singly occupied orbitals of the left and right atoms in $\mathbf{1}$ have exactly the same shape and size, and are optimized for an average occupation of 3/2 electrons. It follows that neither one of the resonating structures $\mathbf{1}$ or $\mathbf{2}$ are correctly described at this level, and that an appropriate function should correspond to $\mathbf{3} \leftrightarrow \mathbf{4}$, in which the doubly occupied orbitals χ_1^n and χ_r^n are different, and in particular larger, than the singly occupied ones χ_1^i and χ_r^i .



These orbitals, which are charge-fluctuation-adapted, have been called “breathing orbitals” in a recent work,⁵¹ by reference to their change in size to match the charge fluctuation.

This extra flexibility is not possible in the Hartree–Fock framework but is possible in valence bond (VB) theory, which allows a wave function, Ψ_{VB} , to be defined completely analogous to Ψ_{HF} in eq 8, except that the orbitals χ_1^n and χ_r^n are different from χ_1^i and χ_r^i , so that the orbitals can now adapt their shape to their actual occupancy in $\mathbf{3}$ and $\mathbf{4}$

$$\Psi_{\text{VB}} = |\overline{\chi_1^n \chi_r^n}| + |\overline{\chi_1^i \chi_r^i}| \quad (9)$$

$$\chi_1^n \neq \chi_1^i \quad (10)$$

$$\chi_r^n \neq \chi_r^i \quad (11)$$

where the superscripts *i* and *n* indicate that the orbitals belong either to the ionic fragment or to the neutral one.

Up to now we have considered only “active” orbitals, i.e. those orbitals that are directly involved in the three-electron bonds. But molecules larger than He_2^+ also involve “inactive” orbitals, alongside the three-electron bond. Such orbitals maintain constant occupation but still respond to the charge fluctuation, and to the instantaneous changes of the fragment on which they reside. Thus, the inactive orbitals would also

fluctuate in size and shape in response to the charge fluctuation between the fragments. Once again though, this flexibility that exists in VB is prohibited in Hartree–Fock, due to its builtin symmetry constraints. The corresponding expressions for Ψ_{HF} and Ψ_{VB} with inclusion of inactive orbitals become therefore eqs 12 and 13:

$$\Psi_{\text{HF}}(3\text{-e}) = |\dots\phi_1\dots\phi_r\dots\overline{\chi_1\chi_1\chi_r}| + |\dots\phi_1\dots\phi_r\dots\overline{\chi_1\chi_r\chi_r}| \quad (12)$$

$$\Psi_{\text{VB}}(3\text{-e}) = |\dots\phi_1^n\dots\phi_r^i\dots\overline{\chi_1^n\chi_1^n\chi_r^i}| + |\dots\phi_1^i\dots\phi_r^n\dots\overline{\chi_1^i\chi_r^n\chi_r^n}| \quad (13)$$

Here the orbitals of types ϕ_1 and ϕ_r represent some inactive orbitals of the left and right fragments, respectively, and the *i*-superscribed orbitals are all different from their *n*-superscribed analogs in eq 13.

In accord with their above difference, Ψ_{HF} and Ψ_{VB} differ drastically in their performances. Indeed, F_2^- is found to be *higher* in energy, by 4 kcal/mol, than the separated F and F^- fragments at the ROHF level⁴⁷ in the 6+31G* basis set, while Ψ_{VB} yields a bonding energy, in the same basis set, of 29.7 kcal/mol,⁵¹ close to the experimental value of 30.2 kcal/mol. Thus, a simple description of the three-electron bond in terms of two resonance structures is quantitatively correct if the orbitals are allowed to follow the instantaneous charge fluctuation, by rearranging in size and shape. This effect, that we have called “breathing orbital effect”,⁵¹ is not taken into account by the Hartree–Fock method, that generates orbitals which are not adapted to the instantaneous electronic population of the fragments at bonding distances. In contrast, at large distances, the charge fluctuation vanishes: one fragment has one electron more than the other and both of them have orbitals adapted to their specific number of electrons. As a consequence, the Hartree–Fock method describes the separated fragments better than the bonded molecule, and provides binding energies which are too small.

One-Electron Bonds. The single determinantal Hartree–Fock wave function for a one-electron bond involves a singly occupied σ_g orbital and can be expanded, as above, into its VB components:

$$\Psi_{\text{HF}}(1\text{-e}) = |\dots\phi_1\dots\phi_r\dots\chi_1| + |\dots\phi_1\dots\phi_r\dots\chi_r| \quad (14)$$

where χ_1 and χ_r are the active fragment orbitals of the left- and right-hand side fragments.

As in the three-electron case, here too the expansion shows that the Hartree–Fock description for one-electron-bonded systems is formally correct, corresponding to the resonating picture of eq 1, but again lacking the instantaneous adaptation of the orbitals to the charge fluctuation. However, the Hartree–Fock underestimation of bonding energies is now much less severe than in three-electron bonds, and this can be understood by considering the VB analog of eq 14, with charge-fluctuation-adapted orbitals, superscribed by *i* and *n*:

$$\Psi_{\text{VB}}(1\text{-e}) = |\dots\phi_1^n\dots\phi_r^i\dots\chi_1^i| + |\dots\phi_1^i\dots\phi_r^n\dots\chi_r^n| \quad (15)$$

Comparison of eqs 14 and 15 shows that the breathing orbital effect is now restricted to the set of inactive orbitals, unlike the three-electron bond where the effect is expressed in active as well as in inactive orbitals. It is expected, therefore, that the Hartree–Fock bias in one-electron bonds will be less pro-

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nounced than in three-electron-bonded species, resulting in a smaller Hartree–Fock error.

The Uniform Mean-Field Hartree–Fock (UMHF)

Procedure: A Remedy

Since the Hartree–Fock wave function has a formally correct blend of the resonating charge shift structures, it may be reasonable to seek a way to rectify the bias of the method. Such a remedy to the Hartree–Fock error need not necessarily involve an improvement of the *absolute* energies; but in keeping with the nature of the problem, the remedy should lead to a consistent description of both the molecule and the separated fragments. In this sense, the consistency of the dissociation energy profile for an odd-electron bond rests on two conditions: (i) a consistent description of the individual resonance structures at all distances, and (ii) a satisfactory estimate of the resonance energy due to mixing of these resonance structures. These two aspects are considered below in turn.

A Consistent Description of the Individual Resonance Structures. It follows from the preceding discussion that an obvious defect of the Hartree–Fock method is an improper description of the individual resonance structures at *bonding distances*, as compared to a much better description at large distances. The VB method with charge-fluctuation-adapted orbitals⁵¹ cures this defect by improving the description of the bonded species, but this VB method has the drawback of being CPU consuming. An alternative economical solution consists of removing the imbalance by *extending the Hartree–Fock mean-field defect to any distances up to that of separated fragments*. This can be done by freezing the mean-field orbital occupancy of the bonded molecule (e.g., 3/2 and 1/2 for three-electron and one-electron homonuclear bonds) at any distance between the fragments. Thus, the absolute error that is so introduced with respect to the physically correct VB solutions (eqs 13 and 15) would become precisely of the same nature at a short distance and all the way to infinite distance, resulting thereby in a balanced and consistent dissociation curve. This is the main principle of the “Uniform Mean-Field Hartree–Fock (UMHF) procedure” we propose in this work. In the case of symmetrical molecules, the procedure is particularly simple and consists of maintaining the symmetry of the wave function all the way to the limit of separated fragments which are considered as a symmetrical supersystem in a mean field. More generally, the method can easily be extended to molecules having no particular symmetry, as will be discussed in the Appendix.

Figure 1 displays schematic dissociation curves which compare the UMHF method to the VB and UHF methods, for a three-electron bonded system of the type X_2^+ . At the UHF level, the wave function is symmetric at bonding distances but symmetry-broken at long distances. Somewhere in-between these two distances, the dissociation curve displays a singularity due to sudden symmetry breaking. On the other hand, the VB wave function which, at large distances, approximately coincides with the UHF curve, gradually deviates from this curve and becomes smoothly a linear combination of two symmetry-broken VB structures with charge-fluctuation-adapted orbitals at bonding distances. The UMHF curve, which keeps its symmetry at all distances, coincides with the UHF curve at bonding distances but departs from it at the limit of separated fragments.

The above basic UMHF procedure was applied to all the homonuclear three-electron and one-electron bonds, of the $H_nX \cdot :XH_n^+$ and $H_nX \cdot XH_n^+$ types, that have been considered by Clark³ and Radom.⁵ The unrestricted (UHF) method was preferred over the restricted (ROHF) method because of greater

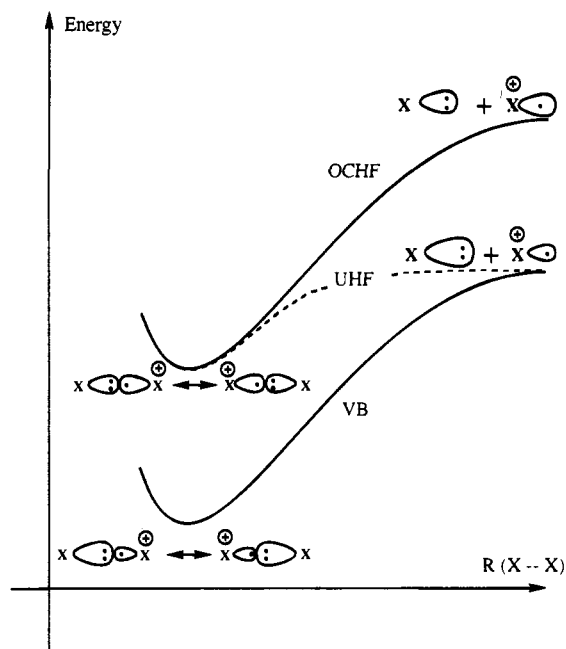


Figure 1. Schematic dissociation profiles as calculated by the VB, UHF, and UMHF methods. The R coordinate is the interatomic distance between the odd-electron-bonded atoms. The UHF curve, dotted line, merges into the UMHF one at short distances and into the VB one at infinite distance. In-between, it displays a discontinuity due to sudden symmetry breaking.

flexibility of the former. For the diatomic cation radicals, the UMHF calculations are carried out with left-right symmetry imposition on the wave function. For polyatomic species, the fragments undergo geometry reorganization during the dissociation, and therefore the UMHF calculation requires two steps. First, the molecule and the wave function keep their left-right symmetry, and only the distance between the odd-electron-bonded atoms is gradually elongated. Second, the geometries of the fragments (one neutral molecule and one radical cation) are optimized at the UHF level. The ensuing reorganization energy (a negative quantity) is added to the dissociation energy calculated in the first step, to get the final dissociation energy.

The results for three-electron bonds are displayed in the third column of Table 1, entitled “UMHF uncorrected”, together with the dissociation energies calculated by Radom at the UHF, MP2, and MP4 levels⁵ with the same basis set. It is apparent that our procedure, already at this simple stage, yields much improved dissociation energies relative to UHF results. In all cases the orders of magnitude are correct, and the errors relative to MP4 results never exceed 7 kcal/mol.⁵²

The breathing orbital effect can roughly be estimated at this point as the corresponding difference between dissociation energies calculated at the UMHF and UHF methods. This difference is seen to display regular tendencies. First, the effect gradually increases as the bonded atoms are varied from left to right of the periodic table, ranging from 22 kcal/mol in $NH_3-NH_3^+$ to 32 kcal/mol in Ne_2^+ , and from 11 to 15 kcal/mol in the corresponding second-row species. Second, the breathing orbital effect is consistently smaller for the second-row species in comparison with their first-row counterparts. These tendencies reflect nicely the dependence of the effect on the intrinsic size of the orbitals, and on the nature of the adjacent inactive

(52) We have checked, on the example of Ne_2^+ , that the UMHF method still behaves well when the basis set is increased. In the 6-31G(2d,f) basis set, the MP4 and uncorrected UMHF methods provide bonding distances of 1.698 and 1.718 Å, respectively, and bonding energies of 38.2 and 41.5 kcal/mol.

Table 1. Calculated Dissociation Energies, in kcal/mol, of Some Three-Electron-Bonded Radical Cations^a

	symmetry	UHF//UHF ^b	UMHF ^b uncorrected	β	S	UMHF ^{b,c} corrected	MP2//MP2 ^d	MP4//MP2 ^d
HeHe ⁺	<i>D_{∞h}</i>	43.2	58.1	0.901	0.973	49.6	49.9	53.2
NeNe ⁺	<i>D_{∞h}</i>	9.1	40.7	0.997	0.971	39.4	38.8	37.0
ArAr ⁺	<i>D_{∞h}</i>	11.2	26.2	0.988	0.969	25.0	24.2	23.7
HFFH ⁺	<i>C_{2h}</i>	19.8	51.9	0.985	0.952	48.5	48.2	45.4
HClClH ⁺	<i>C₂</i>	17.4	31.9	0.978	0.960	29.9	29.5	28.9
H ₂ OOH ₂ ⁺	<i>C_{2h}</i>	22.9	51.1	0.975	0.946	47.0	46.5	44.0
H ₂ SSH ₂ ⁺	<i>C_{2h}</i>	19.8	32.6	0.961	0.956	30.0	30.1	29.6
H ₃ NNH ₃ ⁺	<i>D_{3d}</i>	24.1	46.2	0.948	0.942	40.2	40.3	39.2
H ₃ PPH ₃ ⁺	<i>C_{2h}</i>	19.4	30.1	0.990	0.937	27.3	27.3	26.8
Me ₂ OOME ₂ ⁺	<i>C_{2h}</i>	1.3	33.1	—	—	30.7	31.9	—

^a Except for He₂⁺, all calculations use the 6-31G* basis set. The 6-31G** basis set has been used for He₂⁺. ^b UHF-optimized structures from ref 5 except for He₂⁺ and Me₂OOME₂⁺ (this work). He—He and O—O bond lengths are 1.078 and 2.084 Å at this level for the latter species. ^c Dissociation energy corrected for resonance energy (see eq 26). ^d MP2-optimized structures from ref 5, except for He₂⁺ (this work) and Me₂OOME₂⁺. For the latter the UHF geometry has been used. For He₂⁺ the MP2-optimized bond length is 1.0815 Å.

Table 2. Calculated Dissociation Energies, in kcal/mol, of Some One-Electron-Bonded Radical Cations^a

	symmetry	UHF//UHF ^b	UMHF ^b uncorrected	S	UMHF ^{b,c} corrected	MP2//MP2 ^d	MP4//MP2 ^d
HBeBeH ⁺	<i>D_{∞h}</i>	48.1	51.3	0.991	50.4	49.4	49.7
HMgMgH ⁺	<i>D_{∞h}</i>	31.4	33.7	0.989	32.9	31.8	32.1
H ₂ BBH ₂ ⁺	<i>D_{2d}</i>	45.6	54.4	0.982	52.1	54.6	56.0
H ₂ BBH ₂ ⁺	<i>D_{2h}</i>	39.3	48.2	0.982	46.1	46.1	47.1
H ₂ AlAlH ₂ ⁺	<i>D_{2d}</i>	28.5	32.9	0.987	31.7	31.3	32.0
H ₂ AlAlH ₂ ⁺	<i>D_{2h}</i>	26.7	31.0	0.987	29.8	29.4	30.1
H ₃ CCH ₃ ⁺	<i>D_{3d}</i>	38.2	54.4	0.977	51.7	51.4	51.0
H ₃ CCH ₃ ⁺	<i>D_{3h}</i>	36.7	52.8	0.977	50.1	49.6	49.2
H ₃ SiSiH ₃ ⁺	<i>D_{3d}</i>	30.4	37.2	0.985	35.8	36.0	36.7
H ₃ SiSiH ₃ ⁺	<i>D_{3h}</i>	29.5	36.3	0.985	35.0	35.0	35.6

^a All calculations use the 6-31G* basis set. ^b UHF-optimized structures, taken from ref 3. ^c Dissociation energy corrected for resonance energy (see eq 26, with $\beta = 1$). ^d MP2-optimized structures (this work, Chart 2).

orbitals. Accordingly, the tendencies in the breathing orbital effect observed in Table 1 may be explained as follows: (i) As the atom X varies from left to right of the periodic table, the orbitals of X become gradually more compact, and one can expect that the smaller the orbitals, the more sensitive they become to the freedom to respond to the charge fluctuation. (ii) In the same series, the three-electron-bonded X atoms bear gradually fewer substituents and more lone pairs. The latter electrons are closer to nuclei, and therefore more sensitive to the charge fluctuation, in comparison with electron pairs in X—H bonds.

These two factors combine to increase the breathing orbital effect from left to right along a row of the periodic table. Similarly, one may note that the breathing orbital effect is consistently smaller in the second row than in the first, in agreement with the increased diffuseness of the valence orbitals from top to bottom of the periodic table.

The UMHF procedure was applied also to the series of one-electron bonds previously studied by Clark.³ As has been discussed above, the breathing orbital effect in one-electron bonds involves only the inactive orbitals. The effect can therefore be expected to be smaller than in three-electron bonds, and directly proportional to the number of inactive electron pairs, i.e. more and more important from lithium to carbon and from sodium to silicon. Finally, for the same reasons as those discussed for the three-electron bonds, the effect should be smaller in the second-row species in comparison with their first-row counterparts. Our results, displayed in the third column of Table 2, confirm these predictions and yield once again dissociation energies of the right order of magnitude, and significantly better than the UHF values.

The Influence of Breathing Orbitals on the Resonance Energy. It is noteworthy that our procedure, as used at the above simple stage (third columns of Tables 1 and 2), yields dissociation energies which are systematically overestimated relative to MP2 and MP4 results. This suggests that the

systematic error might originate in a well-defined physical reason rather than in a mere inaccuracy. As the energies of the individual VB structures are in principle calculated in a balanced way throughout the dissociation curve, a possible source of error lies in the calculation of the resonance energy (RE), i.e. the stabilization associated with the mixing of the two VB structures. This hypothesis is conceptualized and generalized in the discussion that follows.

In qualitative VB theory (as in qualitative MO theory), the exact polyelectronic hamiltonian is replaced by a sum of effective mono-electronic hamiltonians **h**, so that the effective polyelectronic hamiltonian, **H**, reads:

$$\mathbf{H} = \mathbf{h}(1) + \mathbf{h}(2) \dots + \mathbf{h}(i) + \dots \quad (16)$$

Some simple rules allow the calculation of the matrix elements of **H** between determinants.^{53,54} In the case where two determinants are related by a charge transfer from one spin orbital to the other, all other orbitals being equal, the off-diagonal matrix element is simply the resonance integral between the two orbitals that participate in the charge transfer. Thus, for the three-electron bond with the mean-field orbital description in eq 12 (charge transfer: $\chi_1 \rightarrow \chi_r$), the leading term of the off-diagonal matrix element in eq 17 will take the simple form in eq 18:

$$\mathbf{H}_{\text{off}}^a(3-e) = \langle \dots \phi_1 \dots \phi_r \dots \chi_1 \chi_r | \mathbf{H} | \dots \phi_1 \dots \phi_r \dots \chi_1 \chi_r \rangle \quad (17)$$

$$\mathbf{H}_{\text{off}}^a(3-e) \approx \langle \chi_1 | \mathbf{h} | \chi_r \rangle \quad (18)$$

where the superscript a indicates that we are dealing with averaged AOs that do not follow the charge fluctuation.

(53) Shaik, S. In *New Concepts for Understanding Organic Reactions*; Bertran, J., Csizmadia, I. G., Eds.; Kluwer: Dordrecht, 1989; NATO ASI Ser. Vol. C267.

(54) Shaik, S. S.; Duzzy, E.; Bartov, A. *J. Phys. Chem.* **1990**, *94*, 6574.

Consider now the matrix element in eq 19, for the case where breathing (charge-fluctuation-adapted) orbitals are used as in eq 13. Here the ϕ_1^n , ϕ_r^n , χ_1^n , and χ_r^n orbitals of the first determinant are slightly different from ϕ_1^i , ϕ_r^i , χ_1^i , and χ_r^i in the second. This will introduce a product of overlaps $\mathbf{S}(3-e)$ preceding the resonance integral, as expressed in eqs 20 and 21.

$$\mathbf{H}_{\text{off}}^b(3-e) = \langle |\dots\phi_1^n\dots\phi_r^n\dots\chi_1^n\chi_r^n|\mathbf{H}|\dots\phi_1^i\dots\phi_r^i\dots\chi_1^i\chi_r^i\rangle \quad (19)$$

$$\mathbf{H}_{\text{off}}^b(3-e) = \mathbf{S}(3-e) \langle \chi_1^n | \mathbf{h} | \chi_r^n \rangle \quad (20)$$

$$\mathbf{S}(3-e) = \dots\langle \phi_1^n | \phi_1^i \rangle \dots \langle \phi_r^n | \phi_r^i \rangle \dots \langle \chi_1^n | \chi_1^i \rangle \langle \chi_r^n | \chi_r^i \rangle \quad (21)$$

where the superscript b in eq 19 stands for breathing orbitals. The $\mathbf{S}(3-e)$ term is a product of pairwise overlaps between the orbitals of the first determinant and their analogs of the second determinant, eq 21.

Note also that the resonance integral in eq 18 is taken with respect to the averaged orbitals (χ_1, χ_r), while the resonance integral in eq 20 is taken with respect to the more diffuse counterpart of the charge-fluctuation-adapted orbitals (χ_1^n, χ_r^n). It is clear, therefore, from eqs 18 and 20 that the use of charge-fluctuation-adapted vs mean-field orbitals leads to different off-diagonal matrix elements, and therefore to different resonance energies whose ratio can be expressed as follows:

$$\frac{\text{RE}^b}{\text{RE}^a} = \frac{\mathbf{H}_{\text{off}}^b(3-e)}{\mathbf{H}_{\text{off}}^a(3-e)} = \beta \mathbf{S}(3-e) \quad (22)$$

where β is the ratio of the resonance integrals:

$$\beta = \frac{\langle \chi_1^n | \mathbf{h} | \chi_r^n \rangle}{\langle \chi_1 | \mathbf{h} | \chi_r \rangle} \quad (23)$$

Since we understand the nonempirical basis for the overestimated UMHF bond energies, we are in a position to remedy this problem and obtain thereby accurate dissociation energies within the UMHF procedure. This can be done by extracting the nonempirical value of the $\beta\mathbf{S}$ factor. Indeed, since dissociation energies are proportional to REs, then multiplying the uncorrected dissociation energies by the factor $\beta\mathbf{S}$ would lead to accurate dissociation energies.

Computing the β and \mathbf{S} factors requires an easy access to charge-fluctuation-adapted orbitals without having to actually compute them within the resonating VB wave function. It has been shown recently⁵¹ that the charge-fluctuation-adapted orbitals of a three-electron-bonded species are very close to the orbitals arising from Hartree-Fock calculations on the separate fragments. Thus, the i-superscribed orbitals can be taken as the UHF orbitals of an ionic fragment, while the n-superscribed ones can be taken as the UHF orbitals of the same fragment but with a neutral electronic occupancy. The averaged orbitals are simply calculated as arithmetic means of i- and n-superscribed breathing orbitals.

Once the orbitals have been determined, the \mathbf{S} term, which is a simple product of overlaps, is readily calculated. The calculation of the β term is achieved by utilizing options which exist in most quantum chemical software⁴⁹ and which allow the computation of energy expectation values of guess functions composed of input orbitals at will. The option is the zero SCF iteration that orthogonalizes the orbitals without changing the guess determinant, and provides its expectation energy, outputted as the energy at zero iteration.

Using this technique, the resonance integral between charge-fluctuation-adapted AO's χ_1^n and χ_r^n can be expressed as proportional to the energy difference between two determinants, as in eq 24 (dropping the normalization factors):

$$\langle \chi_1^n | \mathbf{h} | \chi_r^n \rangle \propto \langle |\dots\phi_1\dots\phi_r\dots\chi_1(\chi_1^n + \chi_r^n)\chi_r|\mathbf{H}|\dots\phi_1\dots\phi_r\dots\chi_1(\chi_1^n + \chi_r^n)\chi_r\rangle - \langle |\dots\phi_1\dots\phi_r\dots\chi_1\chi_r^n|\mathbf{H}|\dots\phi_1\dots\phi_r\dots\chi_1\chi_r^n\rangle \quad (24)$$

where the two determinants only differ by one spin orbital, which is a pure fragment orbital in the second determinant and a bonding combination in the first.⁵⁵

A similar procedure can be used for the matrix element corresponding to averaged orbitals:

$$\langle \chi_1 | \mathbf{h} | \chi_r \rangle \propto \langle |\dots\phi_1\dots\phi_r\dots\chi_1(\chi_1 + \chi_r)\chi_r|\mathbf{H}|\dots\phi_1\dots\phi_r\dots\chi_1(\chi_1 + \chi_r)\chi_r\rangle - \langle |\dots\phi_1\dots\phi_r\dots\chi_1\chi_r|\mathbf{H}|\dots\phi_1\dots\phi_r\dots\chi_1\chi_r\rangle \quad (25)$$

Then the β factor is obtained by means of eq 23.

As a systematic test of the above procedure, we applied it to all the three-electron-bonded species of Table 1 and calculated the final dissociation energies $\text{De}(\text{RE-corrected})$ by multiplying the uncorrected values by the $\beta\mathbf{S}$ factor:

$$\text{De}(\text{RE-corrected}) = \beta\mathbf{S}\text{De}(\text{uncorrected}) \quad (26)$$

Note that in the case of polyatomic species, the corrective factor applies to the dissociation energy of the symmetrical fragments, calculated before the symmetry of the supersystem is broken upon geometry relaxation of the fragments to their charge-specific geometry (see discussion above).

The results, displayed in the sixth column of Table 1, show that in accord with our qualitative analysis all the β and \mathbf{S} factors are smaller than unity, and therefore the $\beta\mathbf{S}$ terms lower the uncorrected UMHF bond energies. As a result, the final UMHF dissociation energies, displayed in the sixth column, are extremely close, within <1 kcal/mol, to the MP2/MP2 values as computed in the same basis set, themselves in good agreement with MP4 calculations. Moreover, the errors are not systematic but can be positive or negative—an indication that they do not reflect a physically based inadequacy of the method.

The corrective factors for the one-electron bond dissociation energies are even easier to calculate than in the three-electron case. Indeed, as discussed above, there is no breathing orbital effect in the orbitals that are directly involved in the bond, i.e. χ_1 and χ_r . As a consequence, these orbitals are the same irrespective of the other orbitals in the system. Thus, the two different off-diagonal matrix elements now share a common mono-electronic \mathbf{h} integral and differ only in the overlap terms, $\mathbf{S}(1-e)$ of the inactive orbitals:

$$\mathbf{H}_{\text{off}}^a(1-e) = \langle \chi_1 | \mathbf{h} | \chi_r \rangle \quad (27)$$

$$\mathbf{H}_{\text{off}}^b(1-e) = \mathbf{S}(1-e) \langle \chi_1 | \mathbf{h} | \chi_r \rangle \quad (28)$$

(55) Applying the rules of qualitative VB theory, the energy difference between the two different determinants in eq 24 is nothing but the energy difference between two orbitals: the pure AO χ_1^n and the bonding MO ($\chi_1^n + \chi_r^n$). This energy difference is well-known from qualitative MO theory to be proportional to the reduced resonance integral, $\langle \chi_1^n | \mathbf{h} | \chi_r^n \rangle$.

$$S(1-e) = \dots \langle \phi_l^n | \phi_l^n \rangle \dots \langle \phi_r^n | \phi_r^n \rangle \dots \quad (29)$$

Therefore, the ratio of the two matrix elements depends now only on the overlap factor $S(1-e)$, so that the corrected dissociation energies for one-electron bonds can be calculated through eq 26 by setting β to unity. Note that the overlap product in eq 29 does not contain active orbitals, unlike the case of three-electron bonds. This and the fact that the corrective factor involves no β term in one-electron bonds implies that the REs are less overestimated, at the Hartree–Fock level, in one-electron than in three-electron bonds.

The S factors and final UMHF dissociation energies for one-electron bonds are displayed in the fourth and fifth columns of Table 2. The corrected bond energies are once again in excellent agreement with the dissociation energies calculated at the MP2 and MP4 levels in the same basis set, with a maximum deviation of nearly 1 kcal/mol. The only exception is $B_2H_4^+$ in its D_{2d} conformation: here the UMHF bonding energy amounts to 52.1 kcal/mol, vs 54.6 and 56.0 kcal/mol at the MP2 and MP4 levels, respectively. However, the error does not lie in the description of the odd-electron bond, as indicated by the good UMHF value for the D_{2h} conformation. Rather, it lies in the incorrect description, at the Hartree–Fock and MP2 levels, of the interaction between the empty orbital of one boron atom and the hydrogens of the other, in the twisted D_{2d} conformation, a hyperconjugative phenomenon that falls outside the scope of the present method.

Having shown in great detail that the resonance energies can be scaled nonempirically, we may tentatively point out the possibility of using an average of the individual βS terms, as a uniform scaling factor for all bonds, in the following form:

$$\begin{aligned} \text{De(RE-corrected)} &= \eta \text{De(uncorrected)}; \\ \eta(3-e) &= 0.926; \quad \eta(1-e) = 0.985 \quad (30) \end{aligned}$$

These average scaling factors lead to bond energies in excellent agreement with the accurate values in Tables 1 and 2. However, only future applications will reveal the feasibility of having average scaling factors which can be used across the board.

Application: A Prediction of Substituent Effect. The question of substituent effect on three-electron bond strength is an important and still unsettled question. It has recently been addressed by Asmus⁴⁸ and by Illies et al.⁴⁷ by reference to the bond energies of $R_2S \cdot SR_2^+$ species. The results of Illies et al.⁴⁷ clearly show that the bond strength is almost constant in the series with $R = H, Me, \text{ and } Et$. In contrast, preliminary calculations of $R_2O \cdot OR_2^+$ by Radom et al.,⁵ on a crude UHF/3-21G level, indicate that this latter series is expected to exhibit significant substituent effect. To make a definitive prediction, we applied the UMHF method to calculate the bond energy of the $Me_2O \cdot OMe_2^+$ radical cation, and to compare it with the energy of the water dimer cation. Using the average η scaling factor above, the resulting UMHF bond energy amounts to 30.7 kcal/mol, in close agreement with the MP2 result of 31.9 kcal/mol (Table 1, last entry). Furthermore, a comparison of this value with the bond energy of the water dimer cation radical (Table 1, entry 6) shows that the CH_3 substituents exert a weakening of ca. 15 kcal/mol. Thus, the UMHF predicts that the $O \cdot O^+$ bond strength should exhibit a significant substituent effect unlike the $S \cdot S^+$ bond. This application projects the utility of the UMHF approach to provide an easy access to experimentally interesting three-electron-bonded species, and for making predictions of yet unknown trends.

Discussion

It appears from the above study that the Hartree–Fock method is inadequate for portions of the potential surface that

involve charge fluctuation. The reason why UHF geometries for odd-electron-bonded species are nevertheless correct are best discussed in the case of molecules displaying a left-right symmetry, although the reasoning can be made more general. In the vicinity of the local minimum, as energetically high as it may be, the left-right symmetry is generally still intact at the UHF level, and this means that in this portion of the potential surface there is no difference between the UHF method and the UMHF one. Since the latter method is shown to give satisfactory bonding energies, it follows that the UHF potential surface has also a *locally* correct shape resulting therefore in optimized geometries in good agreement with those calculated at the MP2 level, even if the optimized species is at the same time high in energy. Indeed, in some cases,⁵ the odd-electron-bonded species is found, at the UHF level, to be a transition state which by breaking its left-right symmetry rolls down to low-energy hydrogen-bonded species. Clearly, if the geometry optimization were to be carried out within the UMHF framework, the symmetry-breaking mode would have been frozen, resulting *precisely in the UHF geometry*, but now as a real minimum (no imaginary frequency). This implies that all the stationary points calculated at the UHF level should display reasonable geometries, even if they are not found to be of the right nature! Indeed, the geometries of three-electron bonded radicals, as optimized by Radom⁵ at the UHF and MP2 levels, are rather close to each other (compare also our MP2-optimized geometries for one-electron-bonded radicals, in Figure 1, to the geometries optimized by Clark at the UHF level).

Based on the above understanding of the Hartree–Fock error and its link to the breathing orbital effect, we can also account for the surprising performances of the UHF method in minimal basis set.⁵ The adaptation of atomic or fragment orbitals to different electronic charge involves changes in polarization and size. However, these two effects are nonexistent in a minimal basis set which is devoid of polarization functions and where the size of the atomic orbitals is fixed. Therefore, in such a basis set, neither the bonded molecule nor the separated fragments have the freedom to adapt their orbitals to the effective local charge. It follows that the UHF description of the odd-electron bond and its separated fragments is balanced much like in the framework of the UMHF procedure, excluding of course deficiencies inherent to the basis set itself. This explains why Radom⁵ has found surprisingly good orders of magnitudes for three-electron-bonding energies at the simplest of all levels, UHF in STO-3G basis set. Far from being fortuitous, this finding is linked to a general rule—that the Hartree–Fock artefact in charge-fluctuating regions of the potential surfaces vanishes in minimal basis sets. Thus, for very large odd-electron-bonded complexes, optimizing the geometries and calculating the bonding energies at this simple level is not meaningless if only qualitative results are sought.

Conclusion

Charge fluctuation is an inherent physical character of odd-electron bonding, and the electron density should adapt instantaneously to the fluctuating charge. This response of the electron density is reflected through the shape and size of the orbitals. Thus in a resonating picture, each resonance structure is described by charge-fluctuation-adapted orbitals, also called breathing orbitals⁵¹ of the type depicted in 3 and 4. The failure of the Hartree–Fock method to reproduce odd-electron bonding energies originates from an inherent constraint which freezes the orbitals at averaged shapes and sizes and prevents their adaptation to the instantaneous charge fluctuation. While the computational bias affects bond energies, it does not influence

optimized geometries which are found close to being correct at the UHF level; albeit at the same time the UHF stationary point may not be a minimum but a saddle point.

The Hartree–Fock bias results in two different deficiencies: The principal effect is the poor description of the individual resonance structures at bonding distances, while the secondary effect is the overestimation of the resonance energy. Together, these two effects do not compensate each other and consequently the odd-electron-bonded species lies too high in energy relative to the separated fragments. The UMHF procedure that we propose in this work corrects for these two deficiencies, and yields odd-electron dissociation energies in satisfactory agreement with accurate calculations performed in the same basis set. The UMHF procedure is based on the simple UHF method and has the same computational requirements. Further, it can be used by means of standard ab initio programs, without any extra programming effort. The procedure may therefore be used to study large size species and thereby broaden the range of odd-electron-bonded species that can be investigated theoretically.

Appendix: Extension to Unsymmetrical Molecules

The problem at hand is to optimize the orbitals of the separated fragments with the same average occupancy, possibly fractional, as in the bonded molecule. In the UHF framework, one seeks orbitals that minimize the energy of the following functional:

$$\Psi = C_1 |\dots\phi_j\dots\phi_a| + C_2 |\dots\phi_j\dots|; \quad C_1^2 + C_2^2 = 1 \quad (\text{A.1})$$

This is a weighted sum of two determinants, one in which the fragment under scrutiny involves the fluctuating electron in the spin orbital ϕ_a , and one in which the fragment has lost this electron. If the fragment that is considered in eq A.1 is more

electronegative than the other, then the coefficient C_1 will be larger than C_2 , and vice versa.

Applying the traditional Hartree–Fock equations leads to the result that the functional Ψ is minimal in energy if the following \mathbf{F} operator is diagonal in the basis of the optimized orbitals:

$$\mathbf{F} = \mathbf{h} + \sum_j^{\text{occ}} (\mathbf{J}_j - \mathbf{K}_j) + \frac{C_1}{C_1 + C_2} (\mathbf{J}_a - \mathbf{K}_a) \quad (\text{A.2})$$

were the \mathbf{h} , \mathbf{J} , and \mathbf{K} operators have their usual meaning. The orbitals are then determined in the usual way by iteratively diagonalizing the open-shell Fock operator displayed in eq A.2. Note that this operator is of UHF type, but that an ROHF Fock operator with arbitrary fractional occupancies might also be used. The advantage of the second type is that it is already implemented in several standard ab initio Hartree–Fock programs; however, the UHF type may be recommended for its greater flexibility.

The C_1 and C_2 coefficients which must reflect the average electron distribution at the equilibrium geometry must still be determined. This can be done by means of a simple Mulliken population analysis of the bonded molecule, which yields the orbital population C_i^2 for ϕ_a . Note that the inaccuracy which is usually attached to this kind of population analysis does not apply here. Indeed, the Mulliken population of an orbital is inaccurate only when this orbital strongly overlaps with other orbitals, but in the odd-electron species this overlap is always rather weak (about 0.17 as a standard value for three-electron bonds), as has been shown by Radom.⁵

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