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Electronic Densities & Valence Bond wave functions

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Abstract

Valence bond wave functions are studied from the density point of view. The density is plotted as a difference with the quasi state built on the same orbitals. The densities of the components of the VB wave function are also shown. The breathing orbital effect leads to small modifications of the density. It is shown that while the densities of ionic and covalent components are the same, their coupling ends-up in modifications of the electronic density.

Introduction

The bond between atoms is a key concept in chemistry, and over decades Klaus Ruedenberg has played a significant role in defining and understanding how concepts in quantum chemistry (physics) can be used to describe bonds.¹⁻⁷ The analysis he, and co-workers made, provide a complete, yet clear picture of what occurs when two atoms share their electrons. Among other results, it is notably shown that the electron cloud repolarizes and screens the nucleus/nucleus electrostatic repulsion, hence a bonding situation occurs. This picture is explained in text books.⁸

Numerous studies have been performed to describe bonding by various analyses, such as energy decomposition schemes,⁹⁻¹³ Atoms In Molecules (AIM),¹⁴ Natural Bond Orbital (NBO),¹⁵ Electron Localization Function (ELF),¹⁶ among others, and more generally density analysis can lead to topological approaches that are of major interest in the chemistry community.^{17,18} The electron cloud is describe by a density obtained by some quantum chemistry calculation, usually based on Molecular Orbital (MO) approaches, including (or not) a part of the electronic correlation (Hartree-Fock, Complete Active Space Self-Consistent Field, Density Functional Theory, etc ..). This density is analyzed, usually, through electronic density derivatives. However, the bonding density can also be compared to that of an unbounded situation.

Valence Bond approaches

In this contribution, we particularly focused on the densities obtained from Valence Bond (VB)^{19,20} wave functions in a few exemplary cases of σ and π bonds for simple and emblematic systems (H_2 , F_2 and C_2H_4). Moreover, we focused on the non-orthogonal version of VB methods.²¹

We shall recall here the basis of the two VB levels that we use in the present paper on the basis of a symmetric two-center two-electron system, say H_2 , in the H_a-H_b system. In the following we call $\{a,b\}$ the basis of two orbitals centered of each atom H_a and H_b . It is noteworthy that the two orbitals are similar to the 1s atomic orbitals, although we can consider that they are variationally optimized to minimize the energy of the corresponding wave function. This is called the VB Self Consistent Field level (VBSCF). Yet they remain strictly localized on their

atom, without any delocalization tails. Finally, for a symmetrical case the VBSCF wave function writes:

$$\Psi_{\text{VBSCF}} = C_{\text{cov}}(|a\bar{b}| + |b\bar{a}|) + C_{\text{ion}}(|a\bar{a}| + |b\bar{b}|) \quad (1)$$

Both the orbitals and the coefficients are optimized, so the covalent part of the bond $|a\bar{b}| + |b\bar{a}|$ is balanced with that of the ionic part $(|a\bar{a}| + |b\bar{b}|)$. As in MO approaches, several fragments of VB wave functions have been proposed, and they include a variable part of the electronic correlation. As far as a unique pair of electrons is concerned, and in minimal basis set, the VB and the CAS wave function are equal, and they both include the non-dynamical correlation of that electron pair. Extended gaussian basis set in Valence Bond like wave functions²² lead to orbitals that somehow lose their local character, so we restricted the computations to triple zeta basis set.

In the mid 1990's Hiberty and co-workers significantly upgraded the VBSCF wave function by introducing the breathing orbital effect,^{23,24} which allows the orbitals of the VB wave function to adapt to the charge fluctuation. For instance, the doubly occupied a orbital in the ionic structure can get some diffuseness and polarization. We shall label it a'' when it is doubly occupied as in $(-)\text{H}_a \dots \text{H}_b(+)$. Similarly, the a orbital in the covalent configuration $(\bullet)\text{H}_a \dots \text{H}_b(\bullet)$, can be labelled a' , as it is different from a'' , and different from the averaged a orbital of the VBSCF wave function (See Figure 1). These a'' and b'' orbitals are allowed to polarize toward the positive $\text{H}(+)$ neighbor, and allowed to gain some diffuseness due to the charge fluctuation. Such a VB wave function is called a “Breathing Orbitals Valence Bond” (BOVB) wave function.

$$\Psi_{\text{BOVB}} = C'_{\text{cov}}(|a'\bar{b}'| + |b'\bar{a}'|) + C''_{\text{ion}}(|a''\bar{a}''| + |b''\bar{b}''|) \quad (2)$$

Because such a BOVB wave function extends the VBSCF level, it includes a part of the dynamical correlation. However, at the bond dissociation, the ionic terms vanish, and the BOVB wave function only retains the covalent terms. Thus, BOVB dissociates to ROHF fragments (in the case of H_2 , F_2 for instance). We must finally consider that BOVB incorporates a variable part of the dynamical correlation. It was shown that the dissociation energies obtained at the BOVB level were of remarkable accuracy because it includes this useful part of the dynamical correlation.²⁵ The breathing orbital effect includes a good part of what we called the differential dynamical correlation, the one that varies when a bond is formed.

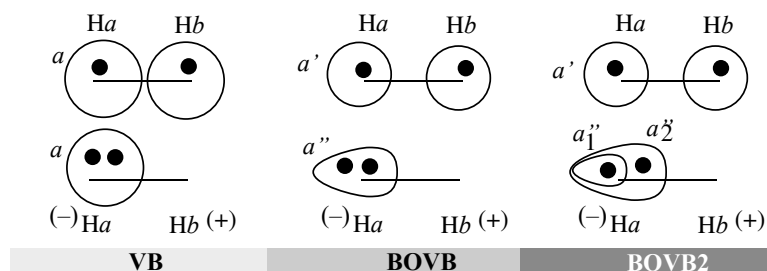


Figure 1: Schematic representation of the covalent component (top) of VB wave functions (left), and one of the two ionic (bottom). In this ionic the electron of H_b has jumped to H_a , leaving an empty orbital on B, not represented. In the breathing Orbital framework (BOVB and BOVB2,

right), the orbitals adapt to the charge fluctuation, although they remain localized on their center (non-orthogonal and strictly local). In the standard VB approach (left) the orbitals are optimized for an averaged occupation.

It shall be noted that at the BOVB level, the breathing orbital effect applies not only to the active orbitals, but also to inactive ones, that is, to those that have a fixed number of electrons across the different components (configurations). Remarkable examples where studied with F_2 and its anion $F_2(-)$ where the breathing of the fluorine lone pairs has a clear and significant effect.^{23,24,26} The method applied to a variety of systems.^{27–30} It provides a compact yet quite accurate wave functions that dissociates to the ROHF fragments, with bond dissociation energies comparable to more correlated methods (Coupled Cluster, large CI) (see Figure 2).

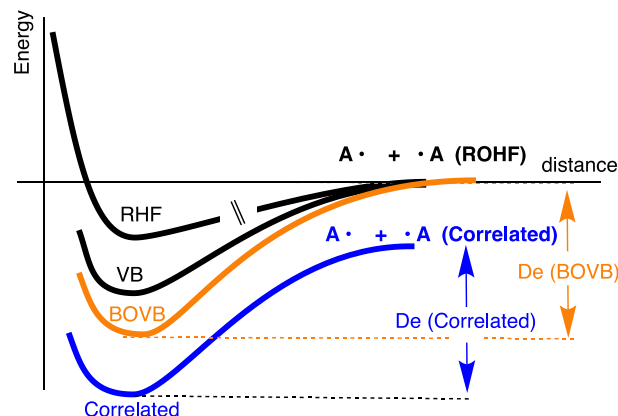


Figure 2: Schematic homolytic dissociation curves for a two-electron two-center bond (A-A); the VB methods all dissociate to the ROHF fragment.

Different strategies can be used to improve the BOVB wave function,²⁵ in the current contribution we simply use the one where the doubly occupied active orbitals of the ionic structures are split, which provides something that could be related to a part of the radial correlation to these electrons. This level is labelled BOVB2. It keeps the compactness of BOVB, and still dissociates to the ROHF fragments because it only modifies the ionics, that vanish at the dissociation. However, in some cases (like H_2) the calculation of the bond dissociation energy needs additional terms brought by π excitations, which are not included in the VB wave functions.²⁸ In the present paper we shall use electronic density differences to visualize the components of the Valence Bond wave function. It is organized as follows: after specifying the computational details, a brief discussion of the energetics of the three systems H_2 , F_2 and C_2H_4 will follow and the link to density differences will be presented and discussed.

Computational details

Our VB computations were all done with the XMVB program embedded in Gamess.^{31,32} Coupled Cluster reference values were done with Gaussian 09.³³ The geometry we used are the following: $r_e(H_2)=0.741 \text{ \AA}$; $r_e(F_2)=1.410 \text{ \AA}$; $C_2H_4 (D_{2h})$: $d_{CC}=1.339 \text{ \AA}$, $d_{CH}=1.086 \text{ \AA}$ $\angle CCH=121.2^\circ$.³⁴ The computations were all done with the 6-311+G(d,p) Pople's basis set^{35,36} as defined in these programs, with 6D primitives. The densities were obtained via wfn files as produced by Gamess. Cube files were obtained with Cheesman's program of AIM2000³⁷ 'cubev', and density differences were visualized as isosurfaces in VMD.³⁸ The VB wave functions are described in the introduction and related references. We frequently refer to the

computed density of Quasi-Classical States (QS).²⁰ It is defined as $\Psi_{QS} = |\bar{a}\bar{b}|$, and it corresponds to one of the determinants of the covalent structure (Ψ_{cov}) in the VB wave function ($\Psi_{VB} = c_{cov}\Psi_{cov} + c_{ion}\Psi_{ion}$). As such it uses the orbitals of Ψ_{VB} , without further re-optimization. The QS state is not an eigenfunction of the \widehat{S}^2 operator, but its density is useful here as an unbounded reference to visualize the densities of bounding wave functions. We shall thus, for instance, see the effect of the singlet coupling in the covalent structure. Similarly, the density of Ψ_{cov} and Ψ_{ion} are done with the Ψ_{VB} orbitals, without further re-optimization. Of course, the other densities involve optimized orbitals (Ψ_{HF} , Ψ_{VB} , Ψ_{BOVB} , Ψ_{BOVB2} and $\Psi_{CAS(2,2)}$).

Results and discussion

Energetics

The two first systems we present are H_2 and F_2 . They have been the subject of countless publications. We shall discuss rapidly the results for the energies, and focus on the isosurfaces of the density differences. The energies for H_2 and F_2 are presented in Table 1. The QS entry stands for the Quasi-Classical State as described in the computational details, i.e with the orbitals of Ψ_{VB} . The relative energies (ΔE , in kJ.mol^{-1}) are binding energies, relative to the neutral infinitely separated fragments ($2 \times H\bullet$). The positive value shows an unbounded situation: the energy of the QS state for H_2 is only 10 kJ.mol^{-1} above $2 \times H\bullet$. The covalent structure already brings most of the binding energy (380 kJ.mol^{-1}), a value quite comparable to CCSD (443 kJ.mol^{-1}) in the same basis set. The HF level of calculation, which suffers from the well-known default to surestimate the ionic contribution, accounts for 348 kJ.mol^{-1} for the binding energy, 50 kJ.mol^{-1} is brought by the non-dynamical correlation (CAS(2,2) or VB), and CCSD calculation grabs about 46 kJ.mol^{-1} of dynamic correlation. The Breathing Orbital Effect (BOE) catches 20 kJ.mol^{-1} of this dynamic correlation.

The energies for F_2 show that this system is an interesting test case for correlated methods. The HF level is largely unbounded (by almost $+159 \text{ kJ.mol}^{-1}$ here). Non dynamic correlation brought by the CAS(2,2) catches about half of the binding energy and the rest corresponds to the so called dynamical correlation, obtained at the CCSD(T) level. Interestingly, the BOVB2 method ends up having a dissociation energy comparable to the CCSD(T) value, although it dissociates to the ROHF fragments. It shall be noted that the BOE can be as large as 100 kJ.mol^{-1} (which corresponds to the difference between Ψ_{BOVB2} and Ψ_{VB}). Hence, a large part of the binding energy is brought by this effect. The QS state in F_2 is much higher than the separated fragments, and so is the covalent structure. F_2 is a typical example of a “charge shift” bond, and the binding energy comes from the resonance between the structures.³⁹

Table 1: Energy values for H_2 and F_2 in the 6-311++G(d,p) basis set: absolute (E in Hartree) and binding energies (ΔE in kJ/mol).

System	Method	E (Hartree)	$\Delta E (\text{kJ.mol}^{-1})$
H_2	QS	-0.995792	+10.1
	COV	-1.144389	-380.1
	HF	-1.132485	-348.8
	CAS(2,2)	-1.150941	-397.3
	VB	-1.150412	-395.9

	BOVB	-1.150809	-396.9
	BOVB2	-1.158111	-416.1
	CCSD	-1.168372	-443.0
F₂	QS	-198.621762	+448.9
	COV	-198.714132	+206.4
	HF	-198.732098	+159.2
	CAS(2,2)	-198.808662	-41.8
	VB	-198.797809	-13.3
	BOVB	-198.830760	-99.8
	BOVB2	-198.835164	-111.4
	CCSD(T)	-199.194248	-106.3
H• E _{ROHF} = E _{CCSD} = -0.49982 Hartree			
F• E _{ROHF} = -99.39637 H; E _{CCSD(T)} = -99.57688 Hartree			

Table 2: Energetics for C₂H₄ in the 6-311++G(d,p) basis set. ΔE values are relative to the QS state.

	E (Hartree)	ΔE (kJ.mol ⁻¹)
C₂H₄ QS	-77.975842	0.0
COV	-78.047161	-187.2
HF	-78.048410	-190.5
CAS(2,2)	-78.076173	-263.4
VB	-78.075729	-262.3
BOVB	-78.076123	-263.3
BOVB2	-78.078549	-269.7

The energetics for the ethylene molecule are reported in Table 2. All the calculations use a HF frozen skeleton for the σ orbitals. Instead of dissociation energies, the relative energies refer now to Ψ_{QS} , the quasi-classical state, with the orbitals of the corresponding VB wave function. These energies do not really correspond to binding energies, but they show how the correlation energy is distributed. HF is about 190 kJ.mol⁻¹ under the QS state, CAS and VB bring about 60 kJ/mol (non-dynamical correlation), and the BOE is rather small, a few kJ.mol⁻¹. The electronic correlation is thus essentially non-dynamical.

Densities of the wave functions, binding through the electron density difference with the quasi-classical state.

Densities

For standard VB, when the covalent and ionic structures share the same set of orbitals, the wave function is a combination of $\Psi_{\text{cov}}(1,2) = \mathcal{N}(|a\bar{b}| + |b\bar{a}|)$ and $\Psi_{\text{ion}}(1,2) = \mathcal{N}(|a\bar{a}| + |b\bar{b}|)$, with $\mathcal{N}^2 = 1 / 2(1 + S_{ab}^2)$.

The density elements write as follow ⁴⁰: The term $\langle |a\bar{b}| | \hat{\rho}(r) | a\bar{b} \rangle = a(r)^2 + b(r)^2$ is the density considered as the unbounded reference (quasi classic state). The two electrons are on each atom, but there is no singlet coupling. Once the two electrons are singlet coupled, keeping the orbitals fixed, the density is modified; the coupling term brings a density that depends on

the overlap between the $a(r)$ and $b(r)$ orbitals. As a matter of fact, the density brought by the coupling terms in the covalent part is the same as that between the two ionic terms (at fixed orbitals). Both the orbital optimization and the coupling between the components lead to modifications of the density that occur when the level of calculation is increased.

$$\langle |a\bar{b}| | \hat{\rho}(r) | b\bar{a} \rangle = 2 \times S_{ab} a(r)b(r)$$

$$\langle |a\bar{a}| | \hat{\rho}(r) | b\bar{b} \rangle = 2 \times S_{ab} a(r)b(r)$$

$$\rho_{\Psi_{\text{cov}}(1,2)}(r) = 2 \times \mathcal{N}^2 \{a(r)^2 + b(r)^2 + a(r)b(r)S_{ab}\} \quad (1)$$

$$\rho_{\Psi_{\text{ion}}(1,2)}(r) = 2 \times \mathcal{N}^2 \{a(r)^2 + b(r)^2 + a(r)b(r)S_{ab}\} \quad (2)$$

The H₂ case

The density differences displayed in Figure 3 show the most important features of the modification of the electronic density that occurs upon bonding. Compared to the same QS state that is built on the same orbitals, both the covalent, the ionic contributions have the same isosurface pattern. They all show that the electronic density goes between the nucleus to build the bond. The VB density, build on the same orbitals look the same, but there are small differences that shall be discuss later.

The HF-QS density seems to behave the same, although the wave function and the orbitals are different. The impact of the HF error on the electronic density can only be seen when it is compared to either the VB or the CAS density. VB-HF for instance shows a depletion of the electronic density between the nuclei. Such a pattern might look unexpected because we just showed that in the VB framework covalent and ionic contributors both correspond to the same density. However, the correction from HF to CAS (or VB), that is the lowering of the weight of the ionic terms, ends up with this pattern. The two last drawings have a different scale. The isosurface is one order of magnitude smaller. They concern the pattern of the breathing orbital effect, which is very small in H₂ (see discussion on the energetics) and that of the ionic orbital splitting (BOVB2), which has a somehow larger effect on the energetics here. The pattern we obtain apparently re-localizes the electronic density between the atoms, in a less diffuse pattern.

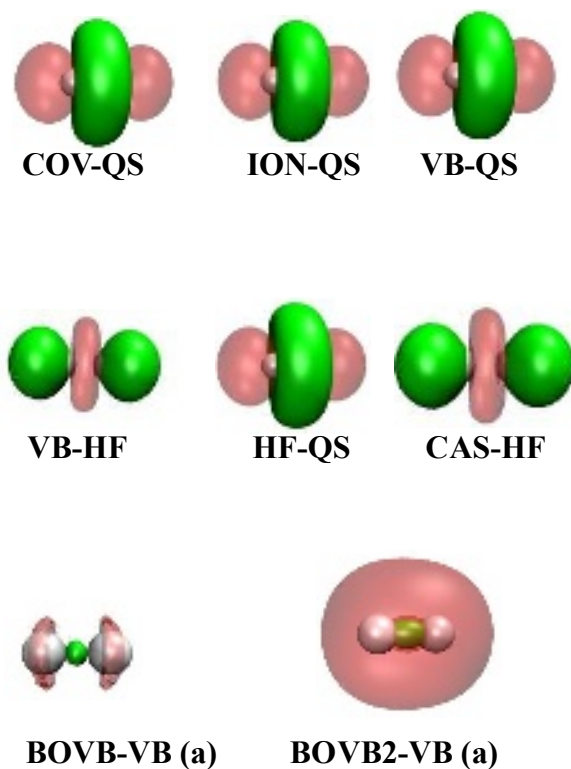


Figure 3: Isosurface of density differences in H_2 (isovalue ± 0.001 a.u. for all cases except (a) : ± 0.0001 a.u.) plain green is for positive values, translucent red for negative.

The F_2 case

The F_2 molecule is a specific case of bonding. As shown on the energetics (Table 1), the breathing orbital effect is much larger than in the H_2 case. Second difference with H_2 , the axial $2p_z$ orbitals allows new pattern in the charge density modification when the level of calculation is modified.

As shown earlier, covalent and ionic terms have the same electronic density, and, as it is built on these structures, the VB wave function looks then the same. The HF density apparently exhibits the same pattern as VB, but the VB-HF (or CAS-HF) density difference shows the depletion of the density in the center of the bond (See Figure 4). The same pattern was observed in H_2 . The breathing orbital effect in F_2 is large: $|\Delta E_{BOVB-VB}| > 85 \text{ kJ.mol}^{-1}$). Hence it is not surprising to see a large difference between the BOVB and the VB densities. In these pictures, the isovalue for the breathing orbital effect (BOVB-VB and BOVB2-VB) is ± 0.001 a.u., the same magnitude as the one obtained for VB-QS for instance. The pattern of the BOVB2-VB isosurface is close to that of the BOVB-VB, which is consistent with the small impact of the ionic splitting on the energies (Table 2, $|\Delta E_{BOVB2-BOVB}| < 2 \text{ kJ.mol}^{-1}$).

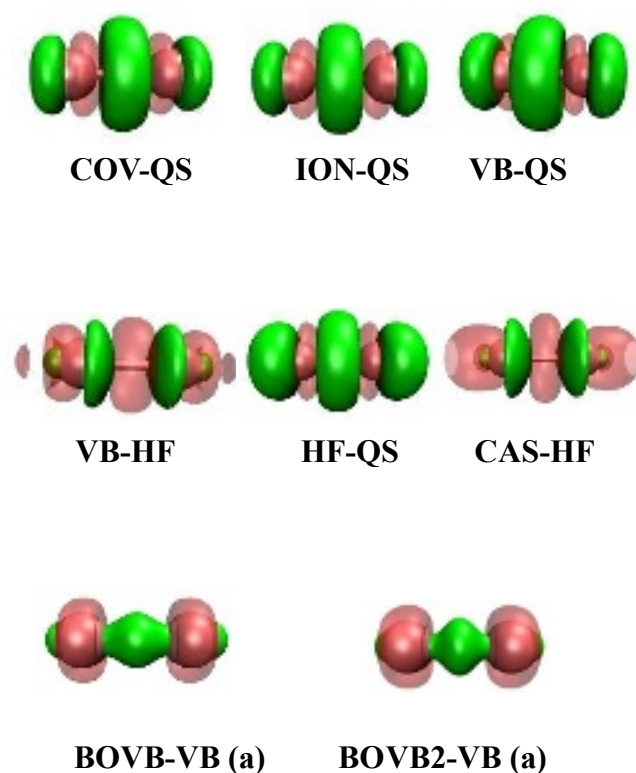


Figure 4: Isosurface of density differences in F_2 (isovalue ± 0.001 a.u. for all cases) Plain green corresponds to positive values, translucent red to negative ones.

The C_2H_4 case

The ethylene case is very similar to H_2 , but within the π system (that is in a lateral overlap). This is again a typical example of covalent bonding. The VB wave function and its covalent, and ionic components show the same density pattern. The VB (or CAS) vs HF density shows a density depletion very similar to that encountered in H_2 and F_2 . (See Figure 5). The breathing orbital effect is small (isovalues have been rescaled to ± 0.0001 a.u., otherwise no effect could be seen, as in H_2).

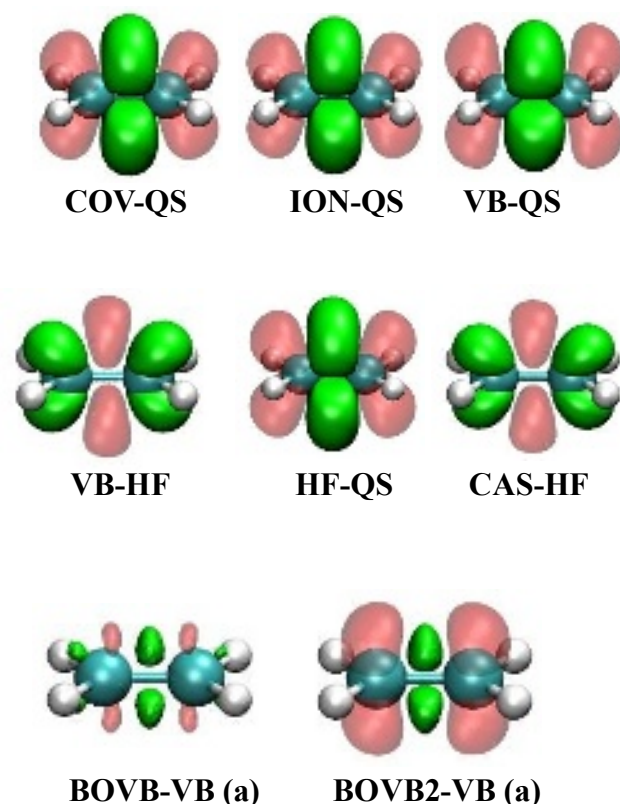


Figure 5: Isosurface of density differences in C_2H_4 (isovalue ± 0.001 a.u. for all cases except (a) : ± 0.0001 a.u.) Plain green corresponds to positive values, translucent red to negative ones.

Discussion

At a first glance, when the same orbitals are used, the covalent and the ionic terms have the same expression for the density. Moreover, the density difference obtained for the Valence Bond wave function looks the same. Both “facts” might give the impression that the addition of the ionic terms to the VB wave function does not bring anything for the bonding. However, the coupling terms between ionic and covalent determinants in the wave function bring some modifications on the density, as shown below in (3) and (4). This explains why there are density differences between the VB wave function and the covalent (or ionic) part, while the densities of each of its components are equal. The density difference between the VB wave function and the covalent is plotted in Figure 6 in the case of H_2 .

$$\langle |a\bar{b}| + |b\bar{a}| | \hat{\rho}(r) | | a\bar{a} | \rangle = 2 \times \mathcal{N}^2 \{ a(r)^2 S_{ab} + a(r)b(r) \} \quad (3)$$

$$\langle |a\bar{b}| + |b\bar{a}| | \hat{\rho}(r) | | b\bar{b} | \rangle = 2 \times \mathcal{N}^2 \{ b(r)^2 S_{ab} + a(r)b(r) \} \quad (4)$$

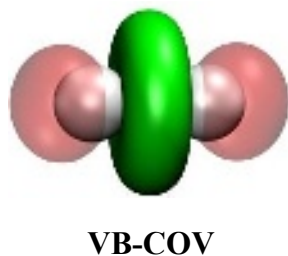


Figure 6: Density difference in H₂, electronic density difference between the VB wave function and its covalent contributor; isovalue ± 0.001 a.u., plain green corresponds to positive values, translucent red to negative ones.

Conclusion

We showed density patterns of HF, CAS and BOVB wave functions by isovalue plots of their differences with respect to the quasi-classic state. This was done for a few emblematic bonds. Covalent and ionic contributors display the same density pattern, but the coupling leads to an adapted electronic density. These modifications can be seen with the density difference. In the F₂ case the Breathing Orbital Effect is large and the density difference with the quasi-classical term can be drawn, even for rather large isovalues (0.001 a.u.). The density difference isosurfaces with the quasi-classical state clearly show how bonding occurs in between the nuclei, as Klaus Ruedenberg significantly contributed to describe.

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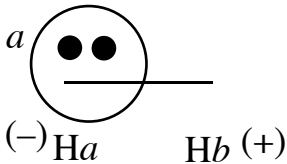
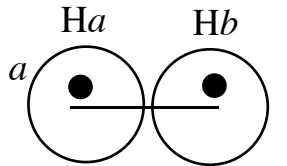
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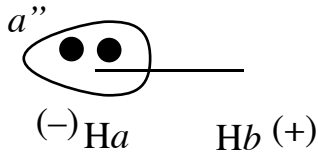
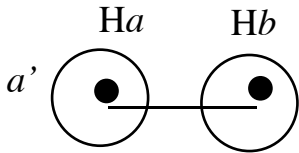
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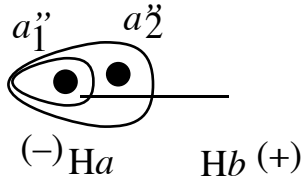
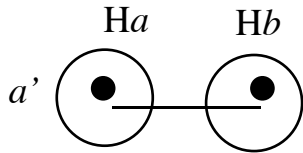
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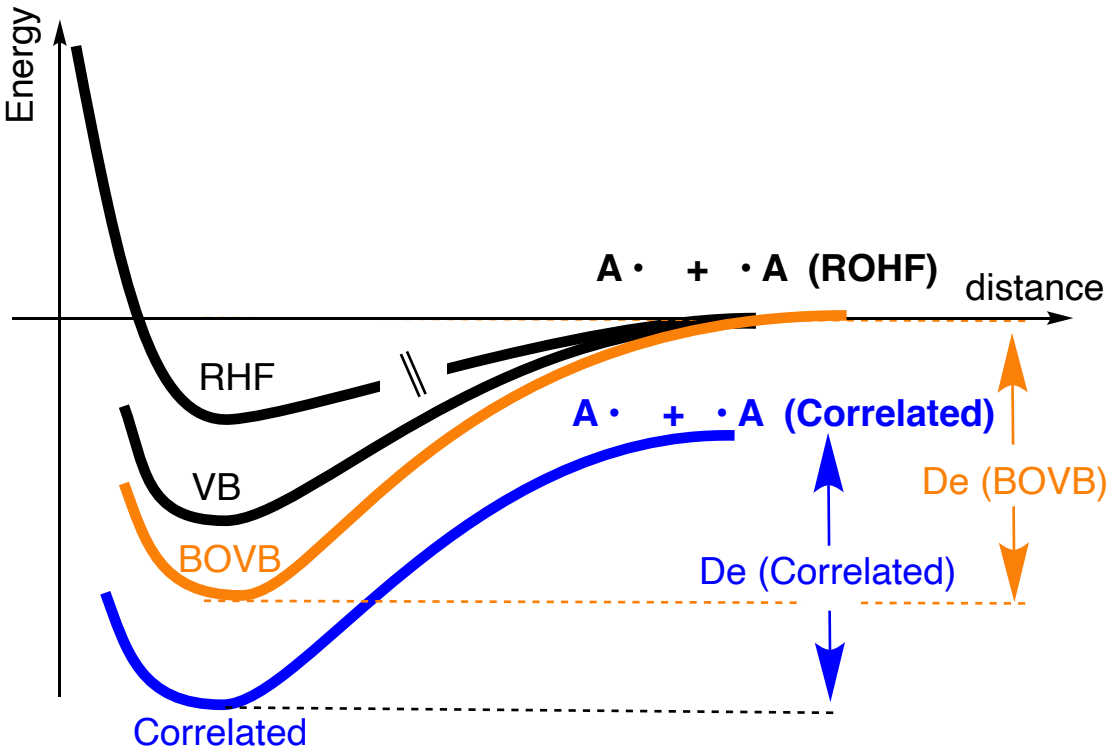
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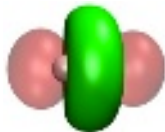


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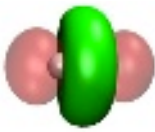


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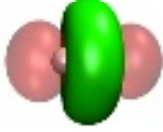




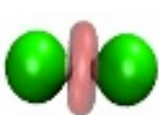
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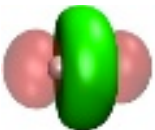
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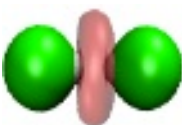
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VB-HF



HF-QS



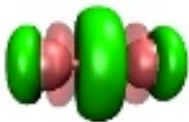
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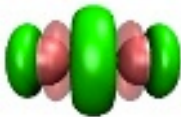
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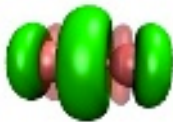
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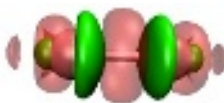
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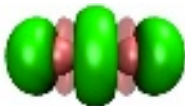
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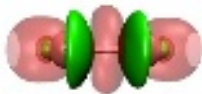
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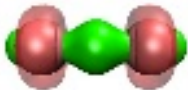
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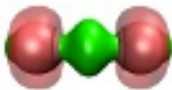
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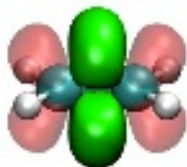
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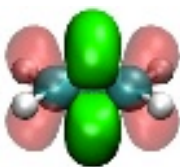
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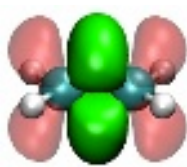
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COV-QS



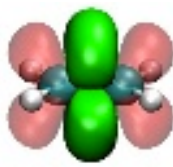
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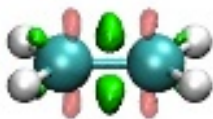
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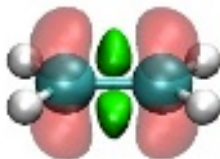
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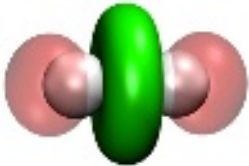
CAS-HF



BOVB-VB (a)



BOVB2-VB (a)



VB-COV