

Lewis-Based Valence Bond Scheme: Application to the Allyl Cation

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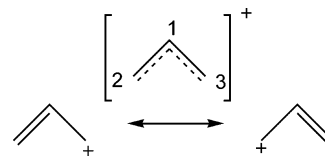
A method for expressing the wave function in terms of Lewis structures is proposed and tested on the allyl cation. This computational scheme is called valence bond BOND (VBB). The compact VBB wave function gives consistent results with the breathing orbital valence bond method (BOVB) for the resonance energy of the allyl cation (54 and 55 kcal/mol for VBB and BOVB, respectively). The optimization of the σ orbitals, in such a way they adapt to each resonance structure, makes use of the breathing orbital effect. It is shown that this "breathing" of the σ frame is more efficient in the resonant hybrid than in the localized state, so that a resonance energy of 63 kcal/mol is obtained at this level of computation.

Introduction

Although there have been these past years a wide spread of computational concepts and tools to the chemists, one shall recognize that the usual wave function's concept is sometimes very broad from the usual chemist's way of thinking, that is, Lewis structures,¹ mesomery, and resonance.² The molecular orbital (MO) and density functional theory (DFT) theory of course give an accurate view of the electronic structure and contribute significantly to major advances in understanding chemical reactivity and structural properties. Yet, the orbital delocalization across the whole molecule in these methods does not provide a directly readable wave function in terms of Lewis structures. Significant advances have been made in using fragments' densities (or orbitals) to further analyze how fragments interact.³ Several other methods are also available to re-express the wave function in terms of usual Lewis bonding schemes such as lone pairs and bonds between two atoms.^{4–6} Those proceed *a posteriori*, on a wave function that has been optimized in the MO (or DFT) fully delocalized scheme.

One of the key chemical concepts in relation with the language of Lewis structures is resonance. This concept shows up when several Lewis pictures (resonance forms) have to be invoked to reach a correct physical description of a molecule.⁷ However, the computation of the resonance energy between contributing structures is always a challenge. One of the simplest examples is the allyl cation that can be written as the resonance between two contributing structures (Scheme 1). Its resonance energy has been the subject of numerous contributions and controversies.^{8,9} The most recent of them, from Mo¹⁰ and from Barbour et al.,¹¹ gave quite different values for the resonance energies. While Mo suggested for the cation a resonance of about 45 kcal/mol, Barbour et al. found a value about 2 times smaller, around 21 kcal/mol. One reason for such discrepancies is related to the geometric relaxation of resonance contributors. In the dehydrogenation strategy used by Barbour et al. (eq 1),

SCHEME 1



such a relaxation is included in the resonance evaluation. We can thus attribute a part of the discrepancy to the resonance definition. Using a relaxed geometry for the resonant contributors, Mo proposed to use the adiabatic resonance energy (ARE) instead of the vertical resonance energy (VRE). Because the geometrical relaxation lowers the energy of the resonant contributor by a little less than 10 kcal/mol, the ARE is found to be about 38 kcal/mol, in slightly better agreement with the Barbour result.



Such a definition facilitates the comparison with the dehydrogenation reactions such as the one described in eq 1. However, if we restrict ourselves to the resonance energy as defined by Pauling and Wheland,² then VRE is the valid definition. This is the difference between the energy of the resonant state and that of the lowest localized contributor taken at the geometry of the resonant state. Because the Lewis structures are somehow localized, the valence bond (VB) theory appears as a most valuable tool to gain knowledge about resonance. Each bond can indeed be individually described through its covalent and ionic structures.

VB theory suffered from a lack of accuracy in the past time,¹² for dynamic correlation was not included and orbitals were not optimized. Bond dissociation energies were thus poorly reproduced. However, it has been shown that a crucial part of the dynamic correlation can be brought into the compact VB wave function through what has been called the breathing orbital effect (BOE).¹³ The BOE is included in the VB wave function using *different orbitals for different resonating structures*. Each set of individual orbitals can adapt in size and shape to best

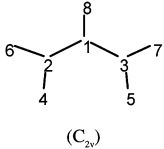
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TABLE 1: Geometrical Parameters (Å and deg) for the Allyl Cation (MP2/cc-pvdz)

Parameter	Value
C ₁ -C ₂	1.392
C ₂ -H ₄	1.098
C ₂ -H ₆	1.097
C ₁ -H ₈	1.094
C ₂ C ₁ C ₃	117.4
H ₄ C ₂ C ₁	120.6
H ₆ C ₂ C ₁	121.7
H ₈ C ₁ C ₂	121.3



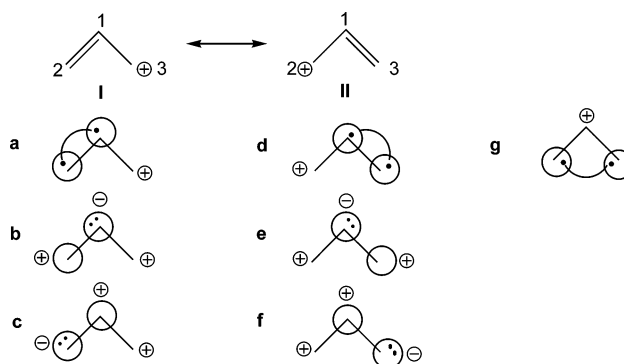
describe its valence bond structures, while being fully optimized to minimize the energy of the total wave function and remaining strictly local (i.e., each orbital is defined on only one atom). The corresponding method, the breathing orbital valence bond (BOVB), has been tested on correlation demanding systems and provides valuable information and concepts.¹⁴ It has been shown to accurately reproduce the bond dissociation energies given by experiments or most accurate MO schemes such as coupled cluster methods. Yet, the BOVB wave function dissociates to the Hartree–Fock fragments, that is, the zero correlation reference. The BOE is thus to be attributed to the *differential* dynamic correlation that is involved during bond breaking processes.¹⁵

Despite its accuracy, the Pauling valence bond (VB) scheme, where each bond is described by one covalent and two ionic structures, is not always much more readable than is the delocalized MO wave function. With each bond being expanded in its three components, the number of VB structures tends to increase rapidly with the size of the system considered. Such a wave function is the most localized one can think about and is still far from the usual Lewis structure because it is too much localized.

In the present contribution, we wish to propose a Lewis-based valence bond wave function that exactly mimics the chemists' way of writing. Our scheme resembles in its principle to previous valence-bond-like studies of the resonance in π systems such as the R-GVB method from Goddard¹⁶ or the bond distorted orbitals approach proposed by Mo for the description of 1,3-butadiene.¹⁷ However, while the previous methodologies concentrated on the π system and neglected to pay attention to the σ frame, in our approach, we will make full use of the breathing orbital concept for the σ orbitals (*different sets of orbitals for different Lewis structures*). As we will see, this extra ingredient can improve significantly the predictions and in particular the resonance energy. Similarly to the bond distorted orbital approach, the π bonds are explicitly considered in their natural meaning with a delocalization between only two atoms. Because of both the BOE on the σ frame and the natural π delocalization, we called the present scheme valence bond BOND (breathing orbitals naturally delocalized). It is abbreviated as VBB in the following. We first investigate the allyl cation resonance energies using the BOVB framework. We then detail the VBB scheme and apply it to the allyl cation. Comparisons are made between the VBB and BOVB results as for the resonance energy, and between the VBB wave functions and the weights we obtain from an NBO–NRT analysis.^{6,18}

Computational Details

Our study used MP2/cc-pvdz¹⁹ geometry (Table 1) as optimized with the Gaussian package.²⁰ The VB calculations

SCHEME 2

were held with the same basis set. For these calculations, we used the XMVB program from Wu and co-workers.²¹ The XMVB program is a modern and efficient spin-free valence bond code. It allows a full flexibility for the definition of the valence bond wave function, including VBSCF, BOVB,^{12,13} or VBCI methods.^{21c} Additional computations with the natural resonance theory (NRT) were held using the NRT code embedded in the NBO 5.0 program.²²

Results and Discussion

Valence Bond Description of the Allyl Cation. The wave function is composed of a set of VB structures that forms a complete and minimal set (also called Rumer basis) for the description of a given electronic state. Among the electrons and orbitals, one distinguishes an active space and active electrons, which will be described at the VB level. Here, the carbon atoms' p orbitals orthogonal to the molecular plane form the active orbitals, while the two π electrons are the active electrons. All the σ orbitals are held "inactive", that is, they will be described by delocalized MO. The Rumer basis of VB structures describing the π system of allyl cation is made of all of the possible arrangements of two electrons into the three active orbitals that can form a singlet state. To find the VB structures of the allyl cation, it is more convenient to start from the traditional Lewis description for this molecule (structures **I** and **II**) and expand them into their covalent and ionic contributions (Scheme 2). Doing so for structures **I** and **II**, six VB structures are obtained (**a–f**). Because structures **b** and **e** are identical, one can remove either **b** or **e** from the total wave function. To reach a complete description, we also considered the additional structure **g**. This structure has no charge separation and has some relevance in the wave function, as pointed out earlier.²³ The set of VB structures **a**, **b**, **c**, **d**, **f**, and **g** then forms a Rumer basis.

In these calculations (Table 2), we used fixed σ orbitals that were taken from an Hartree–Fock calculation on the allyl cation (restricted Hartree–Fock (RHF) orbitals). So, at this level of description, all σ orbitals are common in the different structures composing the BOVB wave function. The RHF energy is indicated here as a convenient, well-defined, reference energy for the tables. Following the BOVB framework, the VB orbitals were held strictly localized, mono-occupied, and are free to optimize in each VB structure. Because they bear no charge separation, the structures **a**, **d**, and **g** are the lowest in energy, followed by **b** and **e** where the charge separation is alternated (+/–/+). The energy of the nonalternating structures (–/+ /+) **c** and **f** is as high as 294 kcal/mol over the Hartree–Fock reference (Table 2).

The Lewis structure **I** corresponds to a mixture of VB structures **a**, **b**, and **c**. The energy of **abc** can be used as the

TABLE 2: BOVB Results on the Allyl Cation with the cc-pvdz Basis Set (RHF σ orbitals)

	E (hartree)	$\Delta E/\text{HF}$ (kcal/mol)	$\Delta E/\text{abc}$ (kcal/mol)
RHF	-116.20131	0.0	
a (or d)	-116.09792	64.9	
b (= e)	-116.00582	122.7	
c (or f)	-115.73292	293.9	
g	-116.01160	119.0	
abc or def	-116.14411	35.9	0.0
ad	-116.17456	16.8	-19.1
adg	-116.20970	-5.3	-41.2
abcdf	-116.20339	-1.3	-37.2
abcdfg	-116.22985	-17.9	-53.8
CAS(2,3)	-116.21478	-8.5	
I (σ RHF)	-116.14190	37.3	0.0 ^a
I–II–III (σ RHF)	-116.22934	-17.6	-54.9 ^a
I–II–g (σ RHF)	-116.22930	-17.6	-54.9 ^a

^a Relative to structure **I** computed within the Lewis-based VBB approach with common RHF σ orbitals. See text.

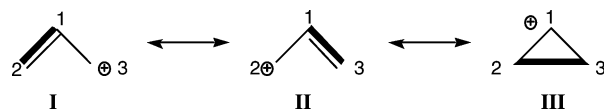
zero energy to evaluate the resonance energy in the allyl cation. By comparing the energy of **abc** to that of the full BOVB wave function (**abcdfg**), we found that the resonance energy is as large as 53.8 kcal/mol, a value that is to be compared to the most recent vertical resonance energy published by Mo (~ 45 kcal/mol).¹⁰ The resonance energy obtained by the BOVB scheme is thus larger than Mo's results by about 10 kcal/mol. This is partly because, in the localized state (**I**), we are using frozen RHF orbitals as the σ orbitals of the wave function, while these orbitals are relaxed in the block-localized wave function (BLW) used by Mo. By lowering this localized state's energy, Mo's BLW method might tend to underestimate the resonance energy. As a matter of fact, other computations by the same group with Hartree–Fock frozen σ orbitals gave a resonance energy much closer to the BOVB results, 55.7 kcal/mol.²³ The role of structure **g** is evaluated by taking the energy difference between the **abcdf** and **abcdfg** BOVB wave functions. We find that its contribution to the resonance energy amounts to 16.6 kcal/mol, that is to say, as much as a third of the total resonance energy.

It is to be noted that the absolute energy obtained with the complete BOVB wave function **abcdfg** is about 10 kcal/mol lower than the energy of the complete active space wave function involving the two π electrons in the three valence π orbitals: CAS(2,3). This difference indicates which amount of dynamic correlation is included in the BOVB wave function (~ 10 kcal/mol).

Lewis-Based Valence Bond Description of the Allyl Cation. The previous section considered the traditional VB picture for the allyl cation system. It has its advantages and its limitations. Among the limitations is the fact that the weights of the Lewis structures cannot be obtained directly. Another limitation concerns the computational price one would have to pay for taking into account the breathing of the σ frame (vide infra). Doing so in each of the six VB structures would require a total of six different sets of all the σ orbitals. Evident computational requirements would render such an approach expensive.

To better fit to the usual Lewis-based description, we propose using the VBB scheme, that is, a partially delocalized wave function. Such a wave function is composed of different terms, each corresponding exactly to one of the Lewis structures involved in the chemical description of the molecule considered. To best describe the allyl cation, we use a three-structure wave function (**I**, **II**, **III**). The additional Lewis structure **III** allows

us to include the VB structure **g** in our description and will be discussed later. We thus define here a wave function that sticks strictly to Lewis language and is, in addition, significantly more compact than the six-structure VB picture.

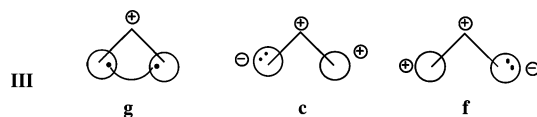


$$\Psi_{\text{VBB}-\sigma(\text{HF})} = c_{\text{I}} \times |\sigma_{\text{HF}}(\pi_{12}\bar{\pi}'_{12})| + c_{\text{II}} \times |\sigma_{\text{HF}}(\pi_{23}\bar{\pi}'_{23})| + c_{\text{III}} \times |\sigma_{\text{HF}}(\pi_{13}\bar{\pi}'_{13})| \quad (2)$$

In the VBB scheme, the π orbitals are all considered as pure GVB (Coulson–Fisher) pairs: they are singly occupied and delocalized between only two atoms (eq 2).²⁴ The delocalization of the pair orbitals allows the indirect inclusion of ionic terms for each two-electron π bond. Thus, for each pair bond, the valence bond covalent–ionic description is built in the Coulson–Fischer pair. For the third structure (**III**), for instance, the GVB pair naturally includes the structures **g**, **c**, and **f**. With this approach, one can either fix or optimize the σ orbitals. When they are held fixed to their RHF values (noted σ -RHF), the VBB scheme is equivalent to the aforementioned BDO approach.¹⁷ The σ frame can also be optimized, either as a set of orbitals that is common for all the structures or with specific sets for each resonating structure. When each Lewis structure possesses its own set of σ orbitals, the BOE is taken into account in the σ frame.

The orbitals (σ and π) can be variationally optimized during the calculation of the total wave function of either the resonant hybrid **I–II–III** or a specific isolated Lewis structure such as **I** or **III**. This allows the variational adjustment of the optimal covalent–ionic mixing, through π orbital optimization. In other terms, our description includes the nondynamic (left–right) correlation for each bond. In any case, the different sets of orbitals in the multireference VBB wave function and the weights of its components are optimized simultaneously.

The computation at the VBB level normally includes the σ BOE. However, to compare to the BOVB results, we first present the scheme with σ orbitals held fixed to their RHF values (that is, without the BOE for the σ frame).



The energy of structure **I**, with the RHF σ orbitals held fixed, is 37.3 kcal/mol over the Hartree–Fock reference energy (Table 2). This value is slightly higher than that of the BOVB computed Lewis structure **abc**. This is because the VBB wave function with only structure **I** does not include any dynamic correlation, while the “**abc**” description does, thanks to the breathing orbital effect. The resonance energy, as computed directly from the energy difference between **I** and **I–II–III**, is similar to that obtained with the BOVB method (54.9 vs 53.8 kcal/mol).

The flexibility of the XMVB code allows us to replace Lewis structure **III** with VB structure **g**, by simply restricting the optimization of the GVB orbitals to their corresponding atomic Gaussian functions. This calculation has been carried out to ensure that **c** and **f**, which are already included in the Lewis structures **I** and **II**, do not muddle the VBB wave function. The last entry in Table 2, **I–II–g**, has the same energy as **I–II–**

TABLE 3: Valence Bond BOND Results on the Allyl Cation with the cc-pvdz Basis Set (with the σ frame optimized in each structure; see eq 3)

	E (hartree)	$\Delta E/\text{HF}$ (kcal/mol)	$\Delta E/I$ (σ opt) (kcal/mol)	weights (%)
HF	-116.20131	0.0		
I (σ opt) or II (σ opt)	-116.15817	27.1	0.0	
III (σ opt)	-116.06978	82.5	55.4	
I–II–III (σ opt)	-116.25833	-35.8	-62.9	37/37/26
I–II–g (σ opt)	-116.25771	-35.4	-62.4	38/38/24
I–II (σ opt)	-116.22278	-13.5	-40.5	50/50/–

III. Because both calculations give identical results, we conclude that Lewis structure **III** only brings the contribution from VB structure **g**.

The compactness of the VBB description allows the relaxation of the σ orbitals independently for each structure in the multireference VBB wave function (eq 3). In the new wave function, the coefficients c'_i as well as the σ and π orbitals are reoptimized to minimize the energy of the total wave function. Similarly to the breathing orbital effect of the BOVB method, the optimization of *different σ orbitals for different Lewis structures* brings a part of the dynamic correlation into the VBB wave function (eq 3), that is, the instantaneous adaptation of σ orbitals to the charge fluctuation. As the different sets of orbital are optimized in the presence of each other, the resulting Lewis structures are a compromise between an optimal individual description and an optimal resonance between each other.

Such a σ orbital optimization lowers the energy of **I** by some 10 kcal/mol and that of the resonant hybrid (**I–II–III**) by almost 20 kcal/mol (Table 3 compared to Table 2). The resonance energy in the allyl cation is thus increased up to 62.9 kcal/mol when we allow different σ orbitals for different Lewis structures. Although the “Lewis” structure **III** is about 55 kcal/mol higher than the traditional bonding pattern (**I** or **II**), its weight in the wave function is as large as 26%. This value is consistent with the coefficients reported earlier by Mo with a fixed σ frame.²³

$$\Psi_{\text{VBB}-\sigma(\text{opt})} = c'_1 \times |\sigma_1(\pi'_{12}\bar{\pi}''_{12})| + c'_{\text{II}} \times |\sigma_{\text{II}}(\pi'_{13}\bar{\pi}''_{13})| + c'_{\text{III}} \times |\sigma_{\text{III}}(\pi'_{23}\bar{\pi}''_{23})| \quad (3)$$

The NRT theory can be applied to this system. This method allows an interpretation of any wave function (Hartree–Fock, post-Hartree–Fock, DFT, etc.) in terms of Lewis structures. It only requires the density matrix to be computed. In this study, we have carried out the NRT analysis of a B3LYP/cc-pVDZ wave function. Through its automatic procedure, the program only managed to find a description in terms of structures **I** and **II**. Their weights are of approximately 49% for each, with additional structures that weigh less than 0.3%. These additional structures are scattered in numerous structures with C–C or C–H bonds broken into C \cdots C⁺ or C \cdots H⁺ and C \equiv C triple bonds. However, the NRT implementation in the NBO 5.0 code permits us to indicate other specific bonding schemes, and the through space bond in **III** can be explicitly requested. When explicitly requested for a description in terms of structures **I**, **II**, and **III**, the NRT program finds the weights 39/39/22, respectively. This result is in good agreement with the VBB results (Table 3).

The last entry in Table 3 reports the energy of the two-structure VBB wave function **I–II**. It corresponds the usual description of the allyl cation, as given in Scheme 1. The resonance energy of this wave function represents only two-thirds of the total resonance energy (40.5 vs \sim 63 kcal/mol).

The VBB method appears here as a valuable tool to assess for the validity of a Lewis representation. It can be used to show if an additional structure is significant by either its weight or its effect on the total energy.

Conclusion

The valence bond BOND (VBB) scheme, presented here on the case of the allyl cation, allows a direct correspondence between each component of the multideterminant VBB wave function and a specific Lewis structure. The method gives results that are consistent with the BOVB calculations for the energy and with the NRT analysis for the weights of the Lewis structures. Thanks to the compactness of the description, σ orbitals can be optimized within the “breathing orbital” frame, that is, using different σ orbitals for the different Lewis structures composing the VBB wave function. The resonance energy is found about 10 kcal/mol larger when this adaptation to the instantaneous charge fluctuation is allowed.

The VBB scheme appears as a valuable tool to compute all the resonance parameters, such as the resonant contributor’s energy, resonant hybrid’s energy, overlap between structures, and so forth. As for the weights of the different Lewis structures, it converges here to the same results as an NBO–NRT analysis on a MO-based wave function, which is a good sign for both methods.

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