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Spin Coupling and Resonance[†]

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The resonating block localize wave function (RBLW) method is introduced, a resonating modification of the block localized wave functions introduced by Mo et al. [Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687].This approach allows the evaluation of resonance energies following Pauling's recipe. The method is tested on two model molecules, hexagonal H_6 and benzene. Calculations have been done with (local) and without local restrictions (delocal). Resonance energies for both molecules have been obtained for each type of calculation, in agreement with Pauling's concept. From a comparison of the resonance energies obtained from RBLW and standard valence bond calculations, the resonating block localize wave functions prove to yield resonance energies close to standard valence bond delocal calculations.

1. Introduction

In the early years of quantum mechanics and its applications in chemistry, scientists concluded that the resonance between two Kekulé structures of benzene leads to it is hexagonal symmetry and great stability. This was deemed to be an indisputable fact. The past decades have shown however, that tremendous work has been done to undermine that belief. For example, in a series of a papers,[2−8] Shaik et al. stated, that the π system of benzene favors in fact a distorted geometry with localized bonds, with the σ system forcing the molecule to be symmetrical. Since the XIX-th century, when Kekulé derived his famous benzene structures[9] (Figure 1), until now, the resonance theory and the electronic delocalization of aromatic species has been a source of great confusion among chemists. Even after all these years, with basic concepts like delocalization and resonance energy (RE) deeply rooted in the minds of everyone, chemists still seek an improvement to the resonance picture.[10−15] In order to understand where this confusion might come from, we first have to understand the basic concept of Pauling's resonance energy (PRE) introduced in the 1930s of 20th century,[16] which was a basis for all future development in this area. In this memorable paper, Pauling sets up the benzene problem in essentially the same way as Hückel did in his approach.[17,18] With all of the assumptions and simplifications coming from the Hückel approach, he was able to treat the benzene molecule with the relatively simple Slater method[20] for formulating secular equation, combined with Rumer's diagrammatic method[21] and rules following from that[22] for finding the matrix elements. The fundamental historical interpretation of the resonance energy (PRE) was then defined by Pauling as the difference between the energy of the benzene molecule described with five, resonating Kekulé and Dewar structures and the energy of a single Kekulé structure (Figure 2)

$$E_{\mathrm{PRE}} = E_{5\mathrm{res.struc.}} - E_{1\mathrm{Kekule}} \tag{1}$$

Based on those calculations, he estimated the resonance energy and predicted quite accurately the contributions of the Kekulé and Dewar structures to the overall energy. Since no orbital optimization was performed, all energies were calculated with the same set of orbitals.

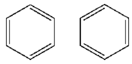

Figure 1. Two possible resonating structures of benzene proposed by Kekulé.

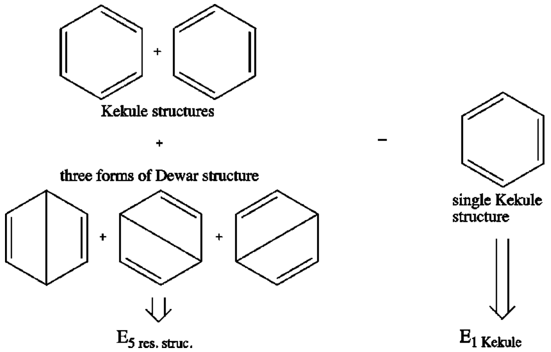

Figure 2. Pauling's resonance enegy definition showed on benzene example.

The introduction of the principal concept of resonance energy by Pauling was not the only important feature of that paper. By application of Rumer's diagrammatic method, the calculations became more feasible, to such an extent that they were not restricted anymore to just benzene and a few other simple aromatic compounds but could be easily applied to naphthalene and bigger conjugated aromatic systems. Moreover, the utilization of Rumer's method had very important impact on how a single bond has been described within valence bond theory. In the general case, a single bond in a molecule, is described by two orbitals, ϕ_1 of atom 1 and ϕ_2 of atom 2, coupled to a singlet, which can be written in the functional form:

$$\Psi_{12} = N(|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|) \tag{2}$$

where φ_i represents orbital ϕ_i multiplied by an α spin function and $\bar{\varphi}_j$ an orbital ϕ_j multiplied by a β spin function. Extending this idea to the description of a molecule with more than one bond, for example the π-bonds in a single benzene Kekulé

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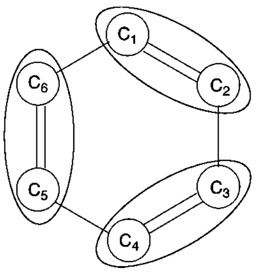

Figure 3. π-bond description with highlighted hybrid-like subgroups in the case of benzene Kekulé structure.

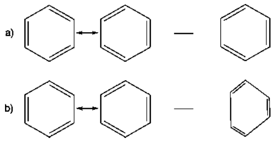

Figure 4. Vertical (a) and theoretical (b) resonance energy definitions in the case of benzene.

structure (Figure 3), we find that the resulting $\Psi_{12,34,56}$ function is simply a product of the three functions in (2):

$$\Psi_{12,34,56} = N(|\varphi_1\bar{\varphi}_2| - |\bar{\varphi}_1\varphi_2|)(|\varphi_3\bar{\varphi}_4| - |\bar{\varphi}_3\varphi_4|)(|\varphi_5\bar{\varphi}_6| - |\bar{\varphi}_5\varphi_6|) \quad (3)$$

The spin-coupling scheme arising from function (3) is of special importance in the valence bond (VB) method, since one can describe the whole molecule and its covalent bonds, by generating all possible functions of the form (3). Because we are interested only in an independent set of those functions, special noncrossing rules are available[21] that can ensure the selection of a proper subset of functions. In all VB methods, which have been developed over the years, like generalized valence bond (GVB),[23,24] valence bond self consistent field VBSCF),[25,26] spin-coupled valence bond (SCVB),[27] or complete active space valence bond (CASVB),[28−30] spin-coupling is a, sometimes implicit,[31,32] inseparable part.

1.1. Other Resonance Energy Definitions. Moving from the early Heitler-London approach,[33] in which the PRE was defined, to the modern VB approach, we are facing difficulties arising from orbital optimization.[41,53,54] Since orbital optimization is required to ensure a consistent answer which does not depend on the start, the original concept is no longer valid, because we would obtain different orbitals for resonating benzene and for one the Kekulé benzene structure. Many inconsistencies arose around this, which might be the cause of all of the confusion. Thus, many different resonance energy definitions were introduced over the years. In the modern VB approach, PRE can be defined as the difference between total energy and an energy of the most stable structure, from the same calculations. We emphasize here the concept "same calculations", which implies that both energies have to be obtained with the same set of orbitals, like in the original idea of Pauling. If one does allow the orbitals to adapt, one obtains the vertical resonance energy (VRE),[10,34] which is the energy difference between the molecule lacking resonance, i.e., one Kekulé benzene structure, and that same molecule described by resonating structures, i.e., resonating benzene (Figure 4a). The orbitals are optimized but the geometry is kept the same. Perhaps the limit of this approach is reached by employing "breathing orbitals".[13,14] Finally also the geometry may be adapted yielding the theoretical resonance energy (TRE)[11,40] Now the geometries of the molecule lacking resonance (1,3,5-cyclohexatriene) and of the molecule with resonance (resonating benzene) are optimized without any constrains, thus giving, for example, different bondlenghts for single and double bonds for the former[41] (Figure 4b)). In all of the models discussed so-far, the spincoupling defines the bond as in eq 2.

1.2. Block Localize Wave Function Approach. Resonance energy is in general an energy difference between the real system described by all possible resonating structures and its most stable structure. One would thus expect problems defining this concept within the molecular orbital (MO) framework, since usually in MO calculations all molecular orbitals are delocalized over the whole system. The first who tried to overcome this problem were Mulliken and Parr.[34] They evaluated the energy of a single Kekulé benzene structure, simply by replacing the three delocalized π MOs in benzene with three nonresonating ethylene-like π MOs. Later a similar approach has been used by Daudey et al.[35] and Kollmar,[36] who also considered the electronic relaxation of the σ frame, and by Glendening et al.[37] The delocalized nature of MO's still made those developments impractical, even though the post-SCF analyses such as the natural bond order (NBO)[38,39] method by Weinhold et al. was able to estimate the delocalization energy. Trying to combine the best of both VB and MO worlds, Mo et al.[1] introduced the block localized wave function method (BLW).[1,42] The BLW approach divides all basis functions into subgroups. All MOs then are expanded in terms of the basis functions in only one of the subgroups. Full orthogonality of orbitals within given subgroup is imposed, while those belonging to different subgroups are obviously nonorthogonal to each other. The implication of such an approach is that each bond is described now by one, doubly occupied orbital, and the whole molecular wave function is only one, close shell determinant. This leads to the situation where no explicit spin-coupling between singly occupied orbitals is in use anymore. Considering now the single Kekulé benzene structure from Figure 3 and its π bonds only, each ellipse around the π bond represents a given subgroup, a doubly occupied hybrid-like orbital. From the standard hybrid definition[43] we know, that a hybrid is an orbital, localized on one atom, and defined as a linear combination of atomic orbitals belonging to that atom. Now in the case of the BLW approach, each π bond from the considered example in Figure 3 is a doubly occupied orbital or, in fact, a doubly occupied hybrid, but localized over two atomic centers, so it is a linear combination of atomic orbitals belonging to both atoms. Now, assuming that Θ_{ij} represents a hybrid localized over carbon atom i and j, the whole π system from Figure 3 can be described as

$$\Psi = |\Theta_{12}\bar{\Theta}_{12}\Theta_{34}\bar{\Theta}_{34}\Theta_{56}\bar{\Theta}_{56}| \quad (4)$$

where Θ_{ij} is a linear combination of atomic orbitals, φ_i belonging to atom i and φ_j belonging to atom j

$$\Theta_{ij} = b_1\varphi_i + b_2\varphi_j \quad (5)$$

and $\bar{\Theta}_{ij}$ represents the same hybrid with opposite spin.

Mo et al. have defined the resonance energy within BLW approach as a difference between the total Hartree−Fock energy of a given molecule and an energy of molecule described within the block localized wave function approach (Figure 5a)

$$E_{\text{res-blw}} = E_{\text{HF}} - E_{\text{BLW}} \quad (6)$$

Apart from the mentioned resonance energy definitions, which are the most important, and widely used, ones, there are many

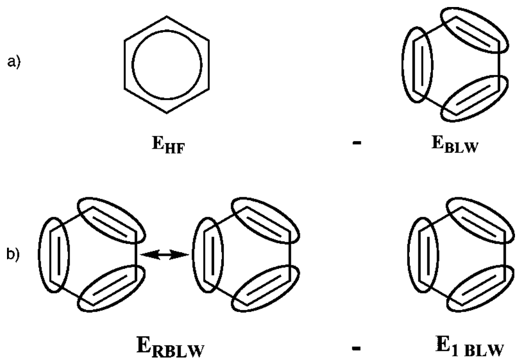

Figure 5. Resonance energy definitions within block localize wave function (a) and resonating BLW approach (b).

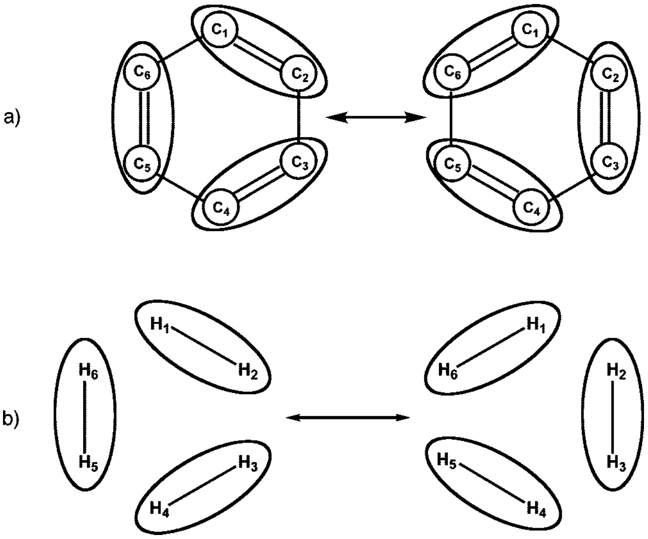

Figure 6. Resonating block localize wave functions in the case of benzene (a) and hexagonal H_6 (b).

TABLE 1: Geometries of Considered Molecules (Legths in Å)

molecule	CC1	CC2	HC	molecule	HH1	HH2
benzene	1.397	1.397	1.087	H_6 cycled	0.740	0.740

TABLE 2: Hexagonal H_6 Total Energies (au)

basis set	method	E_{HF}	E_{RBLW}	E_{RBLW} struc	E_{VB}	E_{VB} struc
6-31G	local	−3.068967	−2.956032	−2.764622	−2.906863	−2.774565
6-31G	delocal	−3.068967	−3.071512	−3.025661	−3.106965	−3.052446
tzvp	local	−3.097497	−2.986240	−2.812897	−2.977412	−2.865810
tzvp	delocal	−3.097497	−3.099904[a]	−3.054957[a]	−3.133662	−3.081974

[a] Generalized Brillouin theorem converged at 10^{-4}.

others, which we have not mentioned because this publication is not meant to be an exhaustive literature overview on resonance energy definitions.

2. Method

Looking at valence bond theory, one can conclude that, from its very beginning, VB is based on two major aspects: nonorthogonality and spin-coupling. Since removing the nonorthogonality of orbitals would cause a lack of interaction between the atoms, and removing spin-coupling of the singly occupied orbitals, as another crucial ingredient in valence bond calculations, is readily possible, we felt inclined to expand the BLW idea even further.

TABLE 3: Hexagonal H_6 Resonance Energies (kcal/mol)

basis set	method	$E_{RBLW\ res}$	$E_{VB\ res}$
6-31G	local	120.11	83.02
6-31G	delocal	28.77	34.21
tzvp	local	108.78	70.03
tzvp	delocal	28.21[a]	32.44

[a] Generalized Brillouin theorem converged at 10^{-4}.

We believe that Mo's definition of resonance energy, based on block localized wave functions, is heavily basis set dependent,[44] vide infra, and no explicit resonance is actually present in the wave functions considered. Since the omission of spin-coupling of the singly occupied orbitals in VB calculations seems interesting, we decided to expand the BLW idea into the resonating block localize wave function approach (RBLW), where we're letting two, or possibly more, block localized wave functions resonate with each other, just like different structures in standard valence bond calculations resonate. By considering two resonating block localize wave functions, we can define the resonance energy in agreement with Pauling's concept, just like we define it in standard valence bond with spin-coupling. The resonance energy definition, in the case of benzene, in the RBLW approach is defined then as the energy difference between benzene described with both resonating Kekulé-like block localized wave functions E_{RBLW} and one, most stable block localized wave function E_{1BLW}, where both energies come from the same calculations with the same orbitals (Figure 5b)

$$E_{res-rblw} = E_{RBLW} - E_{1BLW} \tag{7}$$

A consequence of this is that our standard VB approach is affected. As previously mentioned, a bond in BLW approach is described by one, doubly occupied orbital which, in fact, is a doubly occupied hybrid-like block, localized over two atomic centers. Each hybrid-like block is expanded as a linear combination of atomic orbitals belonging to atoms over which given block is localized. By allowing two Kekulé-like block localized wave functions from Figure 6a to resonate, a situation is created where two hybrids of the two block localized wave functions share the same atomic orbitals, a situation not intended in an original hybrid definition. This means that the system is severely overdetermined, and new orbital schemes had be devised.

Consider a standard valence bond calculation including spin-coupling and an arbitrary wave function $\Psi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3|$. Then, in the orbital optimization, orbital ϕ_1 can be changed by adding infinitesimal small (δ_{14}) part of orbital ϕ_4

$$\phi_1 \rightarrow \phi_1 + \delta_{14}\phi_4$$

Such an orbital change has an impact on Ψ_0

$$\Psi_0 = |(\phi_1 + \delta_{14}\phi_4)\overline{(\phi_1 + \delta_{14}\phi_4)}\bar{\phi}_2\bar{\phi}_2\phi_3|$$

which after simple mathematical operations leads to

$$\Psi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3| + \delta_{14}C_{1\rightarrow4}|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3|$$

Operator $C_{1\rightarrow4}$ is the unnormalized excitation operator which, in this case, replaces orbital ϕ_1 with orbital ϕ_4, once for α spin and once for β spin per Slater determinant. In general, each $C_{i\rightarrow j}$ operator generates a singly excited Brillouin state Ψ_{ij}, and each of those Brillouin states corresponds to an orbital change. When all possible singly excited Brillouin states Ψ_{ij} are generated, a Super CI wave function can be created:

$$\Psi_{\mathrm{SuperCI}} = b_0\Psi_0 + \sum_{i}^{n}\sum_{j}^{m} b_{ij}\Psi_{ij} \qquad (8)$$

where i runs over n occupied orbitals and j runs over m virtual orbitals. If hybrid restrictions are imposed on orbitals, only excitations within given local subgroups are treated, and all other are being discarded. The variational coefficients b_{ij} from eq 8 are being obtained by solving the secular equation

$$(\mathbf{H} - E\mathbf{S})\mathbf{b} = 0 \qquad (9)$$

and are subsequently used to make improved orbitals. In (9), **H** and **S** are the Hamiltonian and metric matrices in the basis of singly excited states, E is the lowest eigenvalue and **b** is the corresponding eigenvector. Upon successful convergence, when the orbitals are optimal, and Ψ_0 coincides with $\Psi_{\mathrm{Super\ CI}}$, the coefficients b_{ij} are equal to zero and the generalized Brillouin theorem is satisfied

$$\langle \Psi_0 | \hat{H} - E_0 | \Psi_{ij} \rangle = 0. \qquad (10)$$

In practice, molecular orbitals are being mixed with virtual orbitals. The latter are generated from the doubly occupied orbitals, as an orthogonal complement to them

$$1 - \mathbf{c}\cdot\mathbf{c}^{\dagger}$$

where **c** is a matrix containing vectors of occupied orbitals, and $\mathbf{c}\cdot\mathbf{c}^{\dagger}$ is a projection operator. In this set the (partial) singly occupied are included. For standard valence bond calculations we're generating one set of virtual orbitals, common for all structures. But now, since different hybrids in the two different block localized wave functions share part of their basis functions, we had to generate separate virtuals for each hybrid-like block, and perform excitations only within the blocks.[46] Of course, in the cases considered, the occupied orbitals are completely equivalent. However due to the overlap of the orbitals and the extreme linear dependency in the optimization process, even a slight numerical discrepancy can result in the loss of this equivalence. Thus we applied equivalence restrictions[45] to ensure that the orbitals stay equivalent. Setting up those conditions means, in fact, adding all equivalent Brillouin states Ψ_{ij}, and using the resulting mixing coefficient b_{ij} from (8) for all the excitations concerned.

An interesting feature of the general hybrid definition, we introduced, is that there are no restrictions on the number of atomic centers over which a given hybrid-like block can be localized. This can be used to aid convergence. In the calculations without local restrictions for hexagonal H_6 and benzene molecules, multicenter hybrid-like blocks, localized over the whole molecule were used to ensure the equivalence of the orbitals.

3. Calculations

All VB calculations were performed using the ab-initio program TURTLE,[46] which has been integrated into the GAMESS-UK[47] package. Geometries of the model molecules considered in this paper were optimized in GAMESS-UK using density functional theory[48] with the B3LYP[49] functional in a 6-31G**[50] basis set and are presented in Table 1. All VB and RBLW calculations were performed with 6-31G[51] and TZVP(Ahlrichs),[52] basis sets. Throughout all calculations, only Kekulé-like structures were included in the description of hexagonal H_6 and benzene, since the three Dewar structures contribute only about 6−7%[53,54] each in the case of benzene and they would obscure the view of the resonance of the former structures. For the benzene calculations, the σ orbitals were included in optimization and the 1s orbitals of the carbons were kept as frozen core.

3.1. Results and Discussion. ***3.1.1. Hexagonal H_6.*** In the case of H_6, a hexagonal arrangement with a fixed H−H bond length of 0.74 Å has been used. The total energies from the resonating block localized wave function (E_{RBLW}), standard valence bond (E_{VB}) calculations, and the energies of the most stable structures from RBLW ($E_{\mathrm{RBLW\ struc}}$), VB ($E_{\mathrm{VB\ struc}}$) calculations and Hartree−Fock energies (E_{HF}) for 6-31G[51] and tzvp[52]basis sets are presented in Table 2. Both types of VB calculation have been done with (local) and without any local restrictions on the orbitals (delocal). We have to emphasize here that local restrictions differ when considering RBLW or VB calculations. In the case of the RBLW method with local restrictions, we're dealing with hybrid-like blocks, localized over two atomic centers. In case of the standard VB calculations, the well-known hybrid definition is used, where each hybrid is localized only on one atom.[43] In the delocal calculations, we start from the end-result of the local calculations and no restrictions are used. The orbitals are free to delocalize over the whole molecule. In the case of the RBLW calculations, special care was taken to ensure the equivalence of the orbitals.

Resonance energies according to Pauling from RBLW ($E_{\mathrm{RBLW\ res}}$) and VB ($E_{\mathrm{VB\ res}}$) calculations are presented in Table 3. As expected, both Kekulé-like structures (Figure 6b), have the same weight, after convergence. Considering the total energies from Hartree−Fock, RBLW and standard VB calculations in the 6-31G[51] basis set with local restrictions (cf. Table 3), we can conclude that all "VB" energies are higher than Hartee-Fock energy. The delocalization of the orbitals in the MO calculation provides a better description, due to the complete delocalization, whereas the local restrictions imposed on orbitals in both types of VB calculations, stop them from tailing onto neighboring atoms. We can observe the same effect when moving to bigger basis sets. The total energies obtained from local RBLW calculations are always lower than total energies obtained from local VB calculations, which is due to hybrid-like blocks being localized over two atomic centers in the case of RBLW method as opposed to one atomic center hybrids in the local VB approach.

Considering now proper RBLW and VB calculations, without any local restrictions (delocal), and comparing their total energies with the Hartree−Fock energy, in the 6-31G[51] basis set (cf. Table 2), we see that both VB calculations give lower energies than the Hartree−Fock calculations. The RBLW calculations were checked that the generalized Brillouin theorem was satisfied without any restrictions after convergence to ensure

TABLE 4: Benzene Total Energies (au)

basis set	method	E_{HF}	E_{RBLW}	$E_{\mathrm{RBLW\ struc}}$	E_{VB}	$E_{\mathrm{VB\ struc}}$
6-31G	local	−230.623206	−230.564082	−230.486581	−230.542991	−230.499684
6-31G	delocal	−230.623206	−230.626666	−230.597931	−230.692657	−230.660998
tzvp	local	−230.769906	−230.696877	−230.620422	−230.672199	−230. 627816
tzvp	delocal	−230.769906			−230.834378	−230.803434

TABLE 5: Benzene resonance energies (kcal/mol).

basis set	method	$E_{\mathrm{RBLW\ res}}$	$E_{\mathrm{VB\ res}}$
6-31G	local	48.63	27.18
6-31G	delocal	18.03	19.87
tzvp	local	47.98	27.85
tzvp	delocal		19.42

that the equivalence restrictions did not actually constrain our calculations. The RBLW delocal calculations result in higher energies than standard delocal VB calculations, due to the fact that the BLW functions are Hartree−Fock like, whereas the VB includes electron correlation. Unfortunately, for the RBLW delocal calculations in the tzvp[52] basis set, the generalize Brillouin theorem has converged only to 10^{-4}.

Comparing resonance energies obtained from delocal calculations with the RBLW method (28.77 kcal/mol) and the standard VB method (34.21 kcal/mol) in the 6-31G[51] basis set, and in a bigger basis set, 28.21 and 32.44 kcal/mol for RBLW and VB, respectively, we notice that the resonance energies from both calculations behave and are quite similar and rather basis set independent. In contrast to this, the behavior of resonance energies from calculations with local restrictions suggest a heavy basis set dependency.[41]

From the definition of hybrids in RBLW method, where two neighboring hybrid-like blocks (each coming from two separate block localize wave functions) overlap, we can expect much bigger overlaps than between two hybrids in standard valence bond calculations. That is indeed the case, as the overlap between the RBLW orbitals H1H2 and H6H1 (Figure 6b) is approximately 0.84, compared to 0.59 between the orbitals on H1 and H2, both in delocal calculations.

3.1.2. Benzene. We can follow the same reasoning when considering the benzene molecule. From the calculations we obtained the same weights for both Kekulé-like block localize wave functions (Figure 6a), as expected. Comparing the total energies of Hartree−Fock, RBLW and VB delocal calculations in the 6-31G[51] basis set (cf. Table 4), again shows that delocal calculations of both VB types give lower total energies than Hartree−Fock calculations. Unfortunately the total energy for RBLW delocal calculations in the tzvp[52] basis set is not available yet, due to program restrictions. Looking at the total energies from RBLW and VB local calculations in the 6-31G[51] basis set and comparing them to the Hartree−Fock energy (cf. Table 4) also confirms that local calculations of both VB types give higher total energies than Hartree−Fock calculations. The resonance energies obtained within RBLW (18.03 kcal/mol) and VB (19.87 kcal/mol) (delocal,6-31G)[51] are almost equal, as was also observed in the case of hexagonal H_6. As RBLW calculations utilize separate sets of orbitals for hybrid-like blocks per resonating block localize wave function, we might expect resonance energy obtained from RBLW delocal calculations to be close to the one obtained from breathing orbital valence bond (BOVB) method (−44.13 kcal/mol[41]). However, resonance energies from RBLW delocal calculations are close to those of delocal VB, which might be due to fact that the “breathing” effect in RBLW is compensated for by the extra correlation in normal VB. Resonance energies obtained for RBLW (48.63 kcal/mol) and VB (27.18 kcal/mol) local calculations in the 6-31G[51] basis set, again show big differences between those two types of calculations. Performing these calculations in a tzvp[52] basis set confirms the results from H_6, that the resonance energy obtained from both types of VB calculations with local restrictions, is rather basis set dependent.

The overlap of the RBLW orbitals C1C2 (cf. Figure 6a) is 0.68, substantially bigger than that of the VB orbitals C1 and C2 at 0.53, suggesting that the RBLW orbitals do resemble breathing orbitals.[41]

4. Conclusions

Our calculations for the resonating block localize wave function method show, that removing spin-coupling between singly occupied orbitals, as one of the two crucial ingredients for valence bond calculations, is possible and yields perfectly consistent results. Resonance energies obtained from RBLW delocal calculations converge to values obtained by standard VB. Thus by removing spin-coupling and having only resonating closed shell determinants, normal resonance is obtained.

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