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Reply to the 'Comment on "Decoding real space bonding descriptors in valence bond language"' by S. Shaik, P. Hiberty and D. Danovich, *Phys. Chem. Chem. Phys.*, 2019, 21, DOI: 10.1039/C8CP07225F

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A recent Comment by Hiberty, Danovich and Shaik (Ref. 2) to our previous Communication on interpreting Valence Bond (VB) concepts in real space raises concerns about the map between Quantum Chemical Topology (QCT) concepts and those of other conceptual frameworks, such as VB theory. We clarify here why some of those discrepancies appear, particularly as resonance structures (RSs) are regarded. As originally shown in our communication, we do not redefine VB structures, but we compare them with their real space equivalent instead.

In our recent communication[1], the basic aim was was to show how and why QCT interpretations may (and sometimes do) differ from the standard non-orthogonal VB interpretation, and not to debunk or criticize the VB framework, which we think provides a very clear link between computational chemistry and chemical concepts in most cases.

This said, we fully agree with Shaik et al's final remark on Science being a democratic competition that tolerates simultaneously different points of view,[2] and we simply expect to contribute here to this healthy debate by pointing out where and why we cannot agree with many of the assertions made in the Comment. Before doing that, let us state clearly that QCT[3] is a means to analyze, not to compute, a given wavefunction in an orbital invariant way, through a given partition of space that may or may not coincide with the one provided by the quantum theory of atoms in molecules[4] (QTAIM) and with the only recourse to spatial density matrices. QCT thus provides a consistent set of results once a state vector $|\Psi\rangle$ is provided, without an specific knowledge of its previous genealogy, e.g. whether it was built through molecular orbital (MO) or VB recipes. Our purpose in Ref. 1 was to show that the *same* $|\Psi\rangle$ may be interpreted in different ways when it is the result of a VB calculation and the standard VB descriptors are used, or when it is analyzed through QCT arguments. Adopting one of these is, in a sense, a matter of taste, although reasons for and against each possibility may be obviously discussed and will, in the end, be Darwinistically selected by the community.

Another point which we tried to clarify in Ref. 1 is that a common problem chemical bonding theory is the relaxed use of basic chemical concepts like covalency, ionicity, etc. in different contexts *without a clear a priori statement of the particular definition the authors will be using*. In this sense, we were very careful in Ref. 1 in specifying that our use of *covalency*, for instance, refers to its real space instantiation, or that *population fluctuation* is used as a mathematically rigorous statistical variance or covariance of the number of electrons in a region, as specified in the theory of electron distribution functions.[5–8]

On mapping VB-RSs to QCT-RSs

Let us then write down the minimal set of premises underlying the *decoding* rules specified in Ref. 1 .

VB versus QCT resonance structures: In non-orthogonal VB theory,[9] the state vector is constructed as a linear combination of components, called resonance structures (VB-RSs, Eqs. 1 and 2 in Ref. 2, for instance): $|\Psi\rangle = \sum_i c_i |\Psi_i\rangle$. Each of the $|\Psi_i\rangle$ RSs is a single determinant, or a simple symmetry preserving combination of determinants, built from a set of non-orthogonal atom-centered atomic orbitals (AOs). The energy E obtained as $\langle\Psi|\hat{H}|\Psi\rangle$ obviously contains interference (i.e. *resonance*) terms coming from non-vanishing $\langle\Psi_i|\hat{H}|\Psi_j\rangle$ contributions. An example is the VB covalent-ionic resonance. Be that as it may, in a $|\Psi_i\rangle$ VB-RS one *assigns* a given number of electrons to each atom, just counting how many A-centered AOs are occupied in $|\Psi_i\rangle$. In dihydrogen, for instance, one electron comes from each atom in the covalent structure, while two electrons are associated to one of the hydrogens in each ionic structure.

QCT starts by acknowleging that orbitals do not exist beyond

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one-electron systems. They are just fruitful important constructs. In its turn, the atomic concept which is needed for chemical interpretations is recovered in real space. An atom is a spatial region that defines an open quantum system, with a fluctuating number of electrons. Notice that this fluctuation is real, observable in principle, and not related to any particular way to partition the state vector. Through the use of electron distribution functions, one can determine the probability of finding a given number of electrons in each atomic region, *without recourse to artificial orbitals*. The *mapping* used and defined clearly in Ref. 1 is natural. A real space resonance structure (QCT-RS) is simply a distribution of the N electrons of the molecule in the set of regions in which the molecule has been divided. In the H_2 molecule, a QCT-RS refers to a distribution of the two electrons in A and B, the two spatial regions associated to H_A and H_B, respectively. In this way, three RSs appear $(n_A, n_B) = (2,0), (0,2)$, and $(1,1)$, where n_A and n_B refer to the number of electrons physically located in regions A and B, respectively. The *mapping* used and defined clearly in Ref. 1 between QCT-RSs and VB-RS is natural: a QCT-RS is mapped onto the VB-RS that possesses the same electron counting on each atom. In H_2, for instance, the $(1,1)$ RS is thus called the QCT *covalent* structure. Each QCT-RS is *observed* with a given probability, p_i, and has its own set of reduced density matrices.[6] A most important point is that the total energy E is a weighted sum of QCT-RS energies: $E = \sum_i p_i E_i$.[10] No interference terms appear, so when we talk of *resonance* between structures in QCT we refer simply to *coexistence* of RSs. The aim of Ref. 1 was to analyze the relation between VB- and QCT-RSs, e.g. how VB and QCT covalent structures relate to each other. We stress that no exclusivity for nomenclature exists in Science, so that the use of *covalent* and *ionic* labels for QCT-RSs is perfectly valid. Similarly evident to us is that the concept of RS is not exclusive of VB, although Shaik et al's clearly do not share this point of view.

Covalency and ionicity, covalent and ionic structures, electron population fluctuation: Covalency, as introduced by Lewis,[11] is one of the pillars of the theory of chemical bonding. Lacking an associated observable, it is a fuzzy construct, being related to *sharing* of electrons between *atoms*. Since atoms-in-molecules are also not observable, how electrons are thought to be shared between atoms must be defined in every theoretical framework, be that VB or QCT. Loosely speaking, covalency in VB is related to *covalent structures*, and in prototype covalent molecules like H_2, the covalent structure state function is able to describe binding rather accurately. In a similar way, ionicity, related to charge transfer between atoms is associated to the predominance of a VB ionic structure.

In QCT, the degree of sharing of electrons can be quantified. As pioneered by Bader and Stephens,[12] the number of shared pairs of electrons between two real space regions can be measured via the so-called delocalization index (DI): $\mathrm{DI}(A,B) = 2 \int_A \int_B d1\ d2\ \rho_{xc}(1,2)$, where the exchange-correlation density is integrated over the A and B atomic regions. Interestingly, if we understand the atomic electron population as a random variable the DI is related to the interbasin covariance of the electron population by: $\mathrm{DI}(A,B) = -2\mathrm{cov}(n_A, n_B)$. If electrons are shared between two spatial domains, their population *fluctuates*. Charge

transfer is similarly quantifiable.[13]

The aim of Ref. 1 was to show that QCT covalent structures alone, as well as any particular QCT-RS with fixed number of electrons in each atomic domain, lack covalency, and do not give rise to binding. The sharing of electrons in real space requires fluctuation of the atomic populations, thus the *coexistence* of several QCT-RSs. Why does a covalent VB-RS binds, i.e. why for instance the H_2 covalent VB-RS provides a reasonable potential energy curve? From the QCT point of view, because the AOs from which the VB covalent $|\Psi\rangle$ are constructed *overlap*. Thus they effectively include a combination of QCT-RSs. If the VB covalent RS is analyzed with QCT, the probability of finding the two electrons in each of the atoms is far from negligible. The VB covalent structure includes QCT ionic ones. This is recognized in Ref. 2.

The Shaik et al's critique

After these preliminary remarks, we now answer briefly to the main objections posed in Ref. 2. Some confusions are also pointed out.

1. What are the key conclusions in Ref. 1 ? Shaik et al's state that QCT-RSs mimic VB-RSs. However, QCT-RSs are general and perfectly well defined objects[5,14] which, as explained above, are *mapped* onto VB-RSs. No subordination exists whatsover between them. Similarly, covalency originates in QCT from the *coexistence* of RSs, which is not the VB covalent-ionic resonance.

2. Sources of confusion in the RS VB-ish approach. There is no artificial contradiction between the QCT-RS partition applied to CASSCF LiH and to VBSCF LiH. QCT reads any wavefunction, and the CAS LiH state vector was chosen as an academic well behaved model of the LiH molecule. Since, unfortunately, no QCT-RS is yet available for non-orthogonal VB functions, we cannot analyze a non-orthogonal VB description of LiH. Nonetheless, the QCT-RS results of any reasonable VB description of LiH would provide essentially the same results as for our CAS function: a very QCT-ionic molecule. In other words, the QCT-RS interpretation of VB LiH says it is QCT-ionic, the reading of its Chirgwin-Coulson weights that it is mainly VB-covalent. Although the comments in Ref. 2 regarding experimental facts are interesting, no coupling to experiments is needed here.

3. Traditional VB definitions differ from the VB-ish RS approach. We do not agree that QCT-RSs are not related to VB-RSs (see above). In Ref. 1 we try to *map* them easily, so that practitioners of one or the other frameworks may traverse their languages easily. Contrarily to what it is stated in Ref. 2, *there is a perfectly defined way to relate QCT-RSs and VB-RSs*. Take a VB structure and QCT-analyze it: this is a clean, mathematically rigorous, univocal procedure. If it is applied, for instance, to the VB-covalent structure of H_2, a mixture of QCT-covalent and QCT-ionic RSs will appear. It is the simultaneous *coexistence* of them which brings up population fluctuation, thus QCT-covalence. In other words, the VB-covalent RS is *covalent*, in the real space sharing electron sense, because it contains several coexisting QCT-RSs. Our statement "*no bonding without fluctuation*" is not presented as a new finding, but as an orbital invariant way to understand covalency. Shaik et al's write that our statement "*is nothing else than an alternative way of saying that in order for a covalent interaction*

to impart bonding, these two AOs must overlap; a principle that is known by all chemists for nearly 90 years.". This implies a computational method that uses orbitals. In the same vein, we think that the VB charge fluctuation leads to no confusion with our population fluctuations. The latter are statistically well-defined descriptors for which it is difficult to find another name. The QCT-RS description of charge-shift bonds (CSBs), a subject on its own, is completely uncoupled from all this. The fact that covalent bonding needs from population fluctuations in real space is unrelated, in principle, to CSBs. Unfortunately, there is no other way to refer to the *fluctuation of electron populations* than by using those four words.

4. Are there discrepancies between MO and VB descriptions? Shaik et al's state that MO and VB population analyses do match each other in their extense experience, in contrast with our statement about discrepancies between MO and VB interpretations. We stress that non-orthogonal VB and MO approaches converge when large expansions are used (be them orthogonal or not in the latter case [15,16]), and that non-orthogonal approaches lead to better overall quality for a given expansion size. This said, our point is that *interpreting* a VB wavefunction (which may be of high or low quality) using VB-RSs leads sometimes to results that do not match the interpretation of the *very same* function using invariant QCT techniques.

In Ref. 2, a comparison between Mulliken populations in the MO case with Chirgwin-Coulson weights in the VB one is offered to exemplify the compatibility of VB- or MO-interpretations. The LiH molecule is used as an example to show that the charge on Li, for instance, is about $0.30 - 0.40$ au in both cases. Although Shaik et al's explicitly recognize that Mulliken populations have been criticized, they claim that we single out VB from other methods by noticing the differences between the Chirgwin-Coulson weights and the QCT charges, a *scientifically untenable* position in their own words. We believe that these authors have misunderstood our position. Whatever method is used to obtain the LiH wavefunction (HF, DFT, CAS, CI, VB of any flavor, etc), the QCT analysis will lead to a charge on Li close to $+0.9$ au. It is not the method to obtain a state vector we are commenting on, but the procedure to interpret the state function. MO practitioners don't analyze their wavefunctions using Mulliken populations: they use the QTAIM, the NBO recipe, or any other modern method. However, VB practitioners tend to analyze their wavefunctions with Chirgwin-Coulson weights, which as recognized in Ref. 2 do not provide results far from the now forgotten Mulliken populations. It is here where the discrepancy is introduced. Reading the chemical *covalency* or *ionicity* from the VB weights produces results which may be very different from more modern approaches. In Ref. 1 we explain why. By the way, it is not only the QTAIM that provides a rather ionic picture of LiH. Iterative Hirshfeld populations, [17–19] for instance, do also reproduce these results.

5. Which VB sructure is the major one in LiH bonding - covalent or ionic? Disregarding the experimental side, since we are only interested on interpreting the electron distribution in a molecule, Shaik et al's turn to examine the VB picture of LiH to show that the covalent structure is the major contribution to the ground state, reproducing also the very large molecular dipole

moment. From this they conclude that "*The high dipole moment is an outcome od the mechanism of bonding in the covalent structures*". Any consistent framework like VB theory reproduces its results with its own chemical descriptors. Within non-orthogonal VB a highly hybridized 2s Li AO (Fig. 1 in in Ref. 2) is found in the covalent structure that justifies the large LiH dipole moment. However, as it is shown in the crystal clear pictures of the VB AOs of the Li and H atoms in Ref. 2, the bonding Li AO invades considerably the H atom. Actually, were it not constrained to be centered by construction on the Li nucleus, it is dubious that the "Li AO" would retain any major Li contribution. Be that as it may, a real space analysis of Fig. 1a in Ref. 2 shows that the LiH covalent structure is characterized by the overlap of one H AO residing mainly in the H region and one Li AO in which the probability of finding the electron close to the H is very large. In real space, the covalent VB-RS describes an electron distribution in which the two electrons have a large probability of being found close to the H atom. It contains a major QCT-RS ionic component.

We prefer to be verbose here. Real space-minded researchers see no orbitals, just spatial distributions of electrons. For them, if an electron is close to a nucleus it should be associated to it. From their point of view, the VB-covalent wavefunction in LiH is a mixture of a minor QCT-covalent and a major QCT-ionic component. On average, the two binding electrons will be found much more likely close to the H than to the Li atom. Asserting that when two electrons are in the neighborhood of the hydrogen atom one of the electrons *belongs* to the lithium is a difficult to assume concept for real space-minded researchers, although a perfectly valid one for orbital-minded ones. In this way, the same wavefunction can be interpreted in two very different manners. Chemical concepts obtained from Chirgwin-Coulson weights (much as those obtained from Mulliken populations) can be at odds with those coming from other methods.

6. Conclusion. Shaik et al's conclude their comment by noticing that the QCT *fluctuation* has its equivalent in AO overlap. We agree, although what it is stated in Ref. 1 is that *without orbitals* we can still use fluctuations, i.e. that the fluctuation point of view is more general, than, although obviously compatible with, the atomic overlap argument. Moreover, it is perfectly legitimate to use "*fluctuation*" in the QCT context, since this is the term by which the statistical measures to which we refer are universally known. The fact that charge-shift bonding parlance uses also *fluctuation* should pose no problem, as in many other cases where the same wording is used in different contexts (simply think of the several uses of "*charge transfer*" in NBO and perturbation theory which coexist without problem). Finally, it is clear that MO and VB (and any other methodology) will converge if correlation is correctly taken into account. What it does not converge is the analysis of the same and the very same wavefunction with different interpretational tools. QCT-RS interpretations are more general than VB-RS ones. The former can be applied to *all* kinds of wavefunctions, the latter to those obtained through the VB recipes.

Final remarks

QCT-RSs for the VB-covalent RS in H_2. As stated, at the time be-

ing QCT-RS calculations from non-orthogonal VB wavefunctions are still to be implemented in VB computational packages. However, an approximate analysis for the simple Heitler-London function in dihydrogen (H_A-H_B) can be performed easily. Let us write

$$\Psi_{VB}^{cov} = N[a(1)b(2) + b(1)a(2)]\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \quad (1)$$

where $a \equiv 1s_A$, $b \equiv 1s_B$, $N = [2 + 2S^2]^{-\frac{1}{2}}$, and $S = \langle a|b \rangle$. If the assumption is made that the overlap integral between the $g \equiv 1\sigma_g$ and $u \equiv 1\sigma_u$ orbitals built from the a and b AOs restricted to the A domain, $\langle g|u \rangle_A$, is equal to $1/2$ (we have found it to evolve from 0.44 at $R = 0.5$ au to 0.50 at $R = 5$ au), then it is easy to show that

$$p^{cov}(2,0) \approx \frac{1}{4}\left[1 - \frac{1-S^2}{1+S^2}\right]. \quad (2)$$

Using a typical value for $S \approx= 0.7$ at equilibrium, the previous expression leads to $p^{cov}(2,0) \approx 0.16$. The full configuration interaction result is close to 0.21. Thus the simple H_2 VB-covalent RS is about 70% QCT-covalent and $2 \times 16 \approx 30\%$ QCT-ionic. The pure covalent VB-RS is a mixture of covalent and ionic QCT-RSs.

The unbound character of the covalent QCT-RS in H_2. A back of the envelope argument proves that a covalent QCT-RS is unbound in a two-electron system like H_2. To that end, we force one electron to lie in each of the two symmetric spatial regions between two protons, at any internuclear distance. An interacting quantum atoms (IQA) perspective is useful.[20,21] The binding energy of the system is written as $E_b = 2E_{def}^H + E_{clas} + E_{xc}$. We have already shown[20] that the deformation energy of an atom, E_{def} in a homodiatomic is necessarily positive definite, as it is its classical interaction energy, E_{clas}. The only stabilizing energy component must come from the exchange-correlation energy. However, if each of the electrons is localized in its atomic domain, the pair density is purely Coulombic, $\rho^2(1,2) = \rho(1)\rho(2)$, and the exchange-correlation density vanishes. This implies that $E_{xc} = 0$, and that $E_b > 0$. In the case of many electron homodiatomics a similar proof is also easy. The absence of fluctuation of the electron populations forbids electron sharing and thus real space covalency.

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