Supporting Information

Na…B Bond in NaBH₃⁻: Solving the Conundrum

Slavko Radenković,*[a] Sason S. Shaik[b] and Benoît Braïda*[c]

1. The VB wave function and the BOVB method

The Valence Bond (VB) wave function is generally defined as the following. An active space of electrons is defined, which will occupy strictly local non-orthogonal orbitals, while the remaining (inactive) electrons occupy by pairs delocalized Molecular Orbitals. The VB wave function is then defined as an expansion onto a non-redundant set of classical valence bond structures, each structure being defined by a particular occupancy of the VB orbital set together with a specific spin coupling. A complete set of structures is then obtained by considering all possible (non-redundant) ways of distributing all active electrons into all active orbitals with a given spin-coupling, and the full VB wave function then expresses as:

$$\Psi_{VB} = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + \ldots c_N\Phi_N \tag{1}$$

where N is the total number of non-redundant structures.

Because the active VB orbitals are defined as atom or fragment centered, Classical VB wave functions thus achieve a quantum dressing of Lewis' model, each VB structure mapping a specific Lewis structure. This unique feature conveys to computed Classical VB wave functions direct interpretative capabilities, at the cost of dealing with non-orthogonal orbitals in order to ensure strict localization of the active VB orbitals. In this study, only the M–B bond pair is considered as active, so the problem is a simple two singlet-coupled electron in two strictly localized orbital problem. All B–H bonding electrons were treated as inactive, through doubly occupied delocalized Molecular Orbitals (MOs).

[a] Dr. Slavko Radenković, University of Kragujevac, Faculty of Science, 34000 Kragujevac, Serbia. E-mail: slavkoradenkovic@kg.ac.rs
[b] Prof. Dr. Sason Shaik, Institute of Chemistry, The Hebrew University of Jerusalem, 9190401 Jerusalem, Israel.
[c] Dr. Benoît Braïda, Sorbonne Université, Laboratoire de Chimie Théorique, 75005, Paris, France. E-mail: benoit.braida@sorbonne-universite.fr

In the BOVB method, the structure coefficients (c_N) and all the orbital coefficients onto the basis are simultaneously optimized to minimize the total energy following the variational principle. Besides, different sets of orbitals are used for different structures, which allows the orbitals to fluctuate in size and shape, so as to fit the instantaneous charges of the atoms on which these orbitals are located. This so-called "breathing orbital effect" brings into the VB wave function the necessary differential dynamical correlation to calculate accurate dissociation and resonance energies. The BOVB method has been extensively applied on many different systems over the time, and shown to provide consistently good observables for electronic ground states,[1,2] but also as shown more recently for excited states.[3] Different levels of the BOVB method exist. In this work, the U-D-BOVB level has been used, where "U" means "Unrestricted", and "D" that inactive orbitals are delocalized. Similarly to the standard D-BOVB method, different structures have different sets of orbitals, but in addition alpha and beta orbitals in each structure are also differentiated orbitals. By doing so, such a VB wave function no longer maps standard Lewis structures, but it rather maps Linnett structures,[4] which in particular in some radical molecules appears as a more adequate yet compact model to describe their electronic structure.[5] This U-D-BOVB method has previously shown to be particularly relevant in cases of two center three electron bonds,[6] which are of the same physical nature as two center one electron bonds that has been postulated as a component of the Na–B bond in $NaBH_3^-$. Going from standard ("restricted") VBSCF and BOVB levels to U-VBSCF and U-D-BOVB levels respectively has resulted in substantial improvements in BDE and RE_{CS} of $NaBH_3^-$. As such, the latter method has been selected and used throughout this study. More introductory details about BOVB and other "Classical" VB methods, together with an introduction to the XMVB program including commented input and outputs for several example cases and practical recommendations, can be found in a recent Valence Bond tutorial.[7]

2. The VB definition of covalent, ionic, and dative bonding
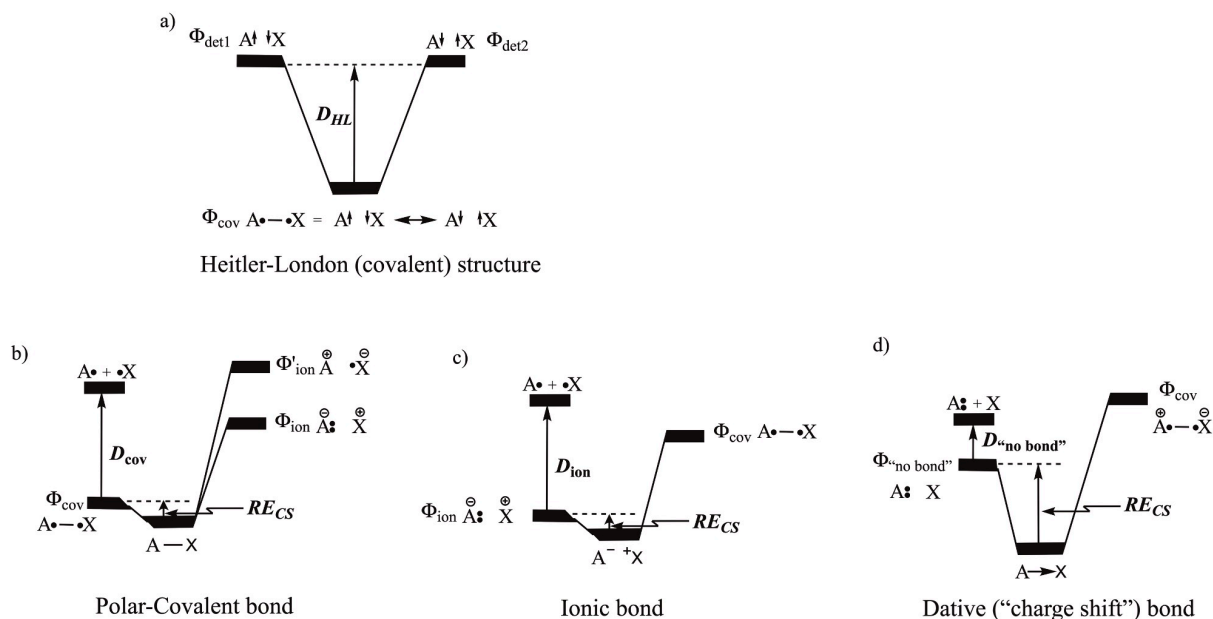
Scheme S1. VB interaction diagrams for: a) the Heitler-London function (also called covalent structure), b) a polar-covalent bond, c) a ionic bond, d) a Dative bond.

In Valence Bond theory, the 2 center – 2 electron (2c,2e) bonds are classified in three main families of bonding, the (polar-)covalent, ionic, and charge shift bonding (CSB) families.[8,9] In the case of a (polar-)covalent bond, the wave-function is dominated by the covalent VB structure, Scheme S1a. This structure, that is akin to the original Heitler-London function,[10] is a combination with equal coefficient of two alternating spin-determinant. The D_{HL} quantity in the diagram corresponds to the energy difference between the covalent structure and one of the two spin-determinants computed separately, but at the same equilibrium geometry. This quantity thus corresponds to the energy stabilization arising from the mixing of the two alternate spin-determinant, and could therefore be termed "spin-exchange stabilization energy". This effect is at the root of covalent bonding, and D_{HL} in a genuine (polar-)covalent bond is usually very large. This D_{HL} quantity is also called "in situ" covalent bonding energy, because it measures the bond strength energy right at the equilibrium geometry. The full VB interaction diagram for a (polar-)covalent case is displayed in Scheme S1b. The D_{cov} quantity here corresponds to the energy stabilization of the covalent structure by respect to the separate fragments in the homolytic dissociation limit. In neutral covalent bonded systems, D_{cov} is usually smaller than D_{HL}, because it is mitigated by the Pauli repulsion that build up between the interacting fragments from infinite separation to the equilibrium distance.

The difference between D_{cov} and D_{HL} provides a combined energetic measure of the electrostatic and Pauli repulsion interactions between the fragments. For a polar-(covalent) bond, secondary ionic structures also mix into the VB wave function, but this resonance mixing, RE_{CS} terms in Scheme S1, only lead to a secondary extra energy stabilization, the total Bond Dissociation Energy (BDE) being dominated by D_{cov} in this first family of (2c,2e) bonds. A similar situation occurs for an ionic bond (Scheme S1c), where this time one of the ionic structures dominates the wave function at equilibrium distance, and thus the BDE mainly arises from the electrostatic stabilization of the ion pair, RE_{CS} being here also a secondary component of the total BDE. The case of a "genuine" Dative bond, such as in the $H_3N{:}{\rightarrow}BH_3$ prototype, is last depicted in Scheme S1d. For Dative bonded systems a so-called "no bond" structure, corresponding to the heterolytic dissociation limit of the system ($H_3N{:} + BH_3$ in this example), is the major structure in the VB wave function from the dissociation limit up to equilibrium distance. However, quite in opposition to the case of a ionic bond, the stabilization of this major structure alone when the two fragments approach one another, i.e. the $D_{\text{"no bond"}}$ term in Scheme S1c, comes out to be only a *secondary* component of the total BDE, the latter being dominated by the resonance energy stabilization RE_{CS} between the major "no bond" and a minor "covalent" structure. As such, standard Dative bonds appear as a particular subclass of the "Charge Shift Bonding" family in the VB classification, which group all cases of two center bonds where the RE_{CS} is the major source of bonding.[9] Hence, the polar-covalent and Dative bonding mechanisms appear as very different in the VB classification, and could be unambiguously distinguished when working with classical VB wave functions.

3. Computational details

The high level *ab initio* BOVB method[1,11] has been used throughout this study, a method which incorporates both static and dynamical correlation at the orbital optimization step. BOVB single points calculations were carried out with the non-orthogonal Valence Bond XMVB 3.0 program,[12,13] using CCSD geometries optimized with the Gaussian 09 program.[14] The same def2-TZVP basis set has been used in all calculations. The dissociation energy curves of Figure 1 were obtained by rigid scan of the Na–B bond length from the equilibrium geometry. The U-VBSCF level was used for qualitative orbital

analysis, because it displays a unique set of active orbitals common to all structures. The obtained U-VBSCF orbitals (Figure 2) were plotted (isoval=0.05 a.u) using the GaussView software.[15] QTAIM analyses was carried out with the Multiwfn program,[16] using the CCSD and BOVB densities. In order to decompose the dipole moment into the local contributions coming from the Na and BH3 fragments, the dipole moment of the isolated fragments was calculated using the respective orbitals obtained for structure **1** in the BOVB ground state wave function of the $NaBH_3^-$ molecule.

Table S1. Bond dissociation energies (BDE), in kcal/mol, at the BOVB and CCSD(T) levels of theory in the same basis set (def2-TZVP). The CCSD/def2-TZVP geometries were employed in these calculations.

dissociation path	BDE	
	BOVB	CCSD(T)
$LiBH_3^- \rightarrow Li^- + BH_3$	20.37	20.25
$LiBH_3^- \rightarrow Li + BH_3^-$	35.80	37.09
$NaBH_3^- \rightarrow Na^- + BH_3$	16.83	15.72
$NaBH_3^- \rightarrow Na + BH_3^-$	36.39	34.66
$KBH_3^- \rightarrow K^- + BH_3$	10.20	13.83
$KBH_3^- \rightarrow K + BH_3^-$	30.21	29.92

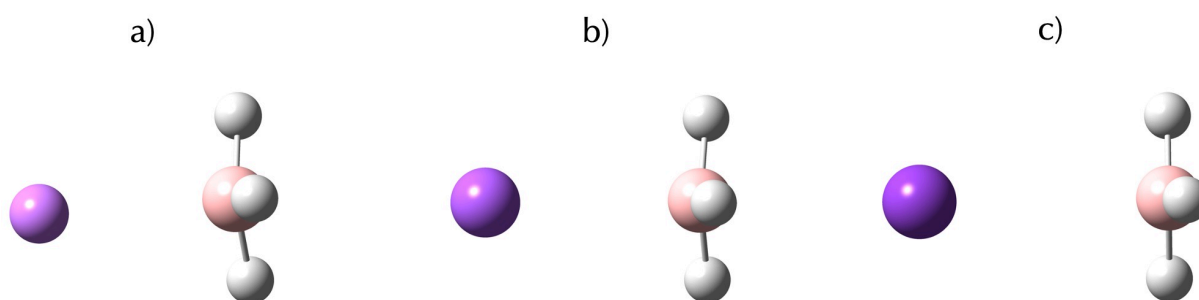a)   b)   c)

Figure S1. Optimized geometries obtained at the CCSD/def2-TZVP level of theory of: a) $[LiBH_3]^-$; b) $[NaBH_3]^-$ and c) $[KBH_3]^-$.

Table S2. Cartesian coordinates (in Å) of the studied systems obtained at the CCSD/def2-TZVP level of theory.

$[LiBH_3]^-$			
B	0.000000	0.000000	0.000000
H	1.035312	0.597687	-0.158210
H	-0.000000	-1.195446	-0.158210
H	-1.035263	0.597762	-0.158210
Li	0.000808	0.000500	2.485766
$[NaBH_3]^-$			
B	0.000000	0.000000	0.000000
H	1.037164	0.598776	-0.116449
H	-0.000000	-1.197595	-0.116449
H	-1.037132	0.598819	-0.116449
Na	0.000837	0.000480	2.771828
$[KBH_3]^-$			
B	0.000000	-0.000000	0.000000
H	1.038600	0.599644	-0.073942
H	0.000000	-1.199268	-0.073942
H	-1.038586	0.599653	-0.073942
K	0.001767	0.000945	3.211892

REFERENCES

[1]   P. C. Hiberty, S. Shaik, *Theor. Chem. Acc.* **2002**, *108*, 255–272.

[2]   W. Wu, P. Su, S. Shaik, P. C. Hiberty, *Chem. Rev.* **2011**, *111*, 7557–93.

[3]   B. Braïda, Z. Chen, W. Wu, P. C. Hiberty, *J. Chem. Theory Comput.* **2021**, DOI 10.1021/acs.jctc.0c00598.

[4]   J. W. Linnett, *J. Am. Chem. Soc.* **1961**, *83*, 2643–2653.

[5]   Y. Liu, T. J. Frankcombe, T. W. Schmidt, *Phys. Chem. Chem. Phys.* **2016**, *18*, 13385–13394.

[6]   B. Braida, T. Ribeyre, P. C. Hiberty, *Chem. – A Eur. J.* **2014**, *20*, 9643–9649.

[7]   A. Shurki, B. Braïda, W. Wu, in *Complementary Bonding Analysis* (Ed.: S. Grabowsky), De Gruyter STEM, Berlin, **2021**.

[8]   S. Shaik, D. Danovich, B. Braida, W. Wu, P. C. Hiberty, in *Chemical Bond II. Structure and Bonding* (Ed.: D.M.P. Mingos), Springer, Cham, **2015**, pp. 169–212.

[9]   S. Shaik, D. Danovich, J. M. Galbraith, B. Braïda, W. Wu, P. C. Hiberty, *Angew. Chem. Int. Ed.* **2020**, *59*, 984–1001.

[10] W. Heitler, F. London, *Zeits. für Physik* **1927**, *44*, 455–472.

[11] P. C. Hiberty, S. Humbel, C. P. Byrman, J. H. van Lenthe, *J. Chem. Phys.* **1994**, *101*, 5969–5976.

[12] L. Song, Y. Mo, Q. Zhang, W. Wu, *J. Comput. Chem.* **2005**, *26*, 514–521.

[13] Z. Chen, F. Ying, X. Chen, J. Song, P. Su, L. Song, Y. Mo, Q. Zhang, W. Wu, *Int. J. Quantum Chem.* **2015**, *115*, 731–737.

[14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, *Gaussian Inc., Wallingford CT* **2009**.

[15] R. Dennington, T. Keith, J. Millam, GaussView 5.0, Semichem Inc., Shawnee Mission, KS **2009**.

[16] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.