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UNVEILING THE BONDING IN NHBECO: A VALENCE BOND THEORY APPROACH

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ABSTRACT. In this study, the bonding and electronic structure of the HNBeCO molecule were investigated using high level classical Valence Bond (VB) theory. Starting from a full-structure calculation involving 175 VB structures, we identified and selected only seven dominant VB structures to describe the bonding between nitrogen and beryllium in HNBeCO. Our results showed that the employed set of VB structures accurately predicts the bond dissociation energy, closely matching the reference values obtained from CCSD(T) calculations. This study highlights the importance of both static and dynamic correlation in describing multiple bonding in beryllium-containing compounds. Notably, we confirmed that the N-Be bond in HNBeCO exhibits a triple bond character.

Keywords: valence bond theory, bonding, quantum chemistry.

INTRODUCTION

The year 2025 has been declared the International Year of Quantum Science and Technology. This year marks 100 anniversaries of Heisenberg's matrix mechanics, one of the foundational developments in quantum mechanics. Quantum mechanics has substantially influenced the development of theoretical chemistry throughout the 20th century, and it transformed chemistry from a phenomenological discipline into a fundamental science. The foundational work of Heisenberg and Schrödinger provided chemists with two theoretical frameworks for understanding chemical bonding: Valence Bond (VB) theory and Molecular Orbital (MO) theory (SHAIK and HIBERTY, 2008). Although both theories emerged around the same time, they soon became competing approaches. VB theory initially dominated the field of theoretical chemistry until the 1950s, after which MO theory gained prominence. Since the 1980s, however, VB theory has experienced a renaissance. While MO theory remains dominant today, VB theory offers the unique advantage of expressing the wavefunction as a linear combination of chemically intuitive Lewis structures. This contribution presents a case study that highlights the interpretative power of modern VB methods.

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Multiple bonding is a well-established phenomenon among *p*-, *d*-, and *f*-block elements, whereas its occurrence in *s*-block chemistry remains rare (CHIRIK, 2019). Within the *s*-block, beryllium is a notable exception, owing to its small atomic radius and high ionization energy, which favors the formation of covalent bonds (HAWTHORNE and HUMINICKI, 2002). Experimental and theoretical investigations have provided evidence for Be–Be multiple bonding in carbonyl complexes, as well as partial multiple bond character in heteronuclear Be–Fe species (WANG *et al.,* 2021; PURKAYASTHA *et al.*, 2024). In addition to metal–metal interactions, beryllium has demonstrated the ability to form multiple bonds with carbon and nitrogen (NIEMEYER and POWER, 1997). Several structurally characterized organoberyllium compounds exhibit significantly shortened Be–C and Be–N bond lengths, suggesting the presence of π-bonding contributions (ARROWSMITH *et al.*, 2016).

The recent paper reported the synthesis and characterization of a novel HNBeCO complex, formed by reacting beryllium with HNCO in a solid neon matrix (WANG *et al.*, 2022). Spectroscopic observations, complemented by computational analyses, reveal that the molecule adopts a linear geometry and exhibits an unusual Be–N triple bond (WANG *et al.*, 2022). It has been proposed that this bonding interaction consists of two strong π bonds and a weaker dative σ bond, representing a rare example of multiple bonding involving beryllium (WANG *et al.*, 2022). These findings provide new insights into the bonding capabilities of electron-deficient main group elements and highlight the potential of beryllium to engage in complex bonding scenarios previously considered exclusive to *p*- and *d*-block elements.

Motivated by these findings, we sought to examine the nature of bonding in the HNBeCO complex using VB theory (SHAIK and HIBERTY, 2008). While MO approaches have been widely applied to such systems, VB theory offers a complementary perspective, particularly well-suited for analyzing the resonance structures and the role of orbital hybridization in bond formation (HIBERTY and BRAÏDA, 2018; GALBRAITH *et al.*, 2021). Our aim was to gain a deeper understanding of the electronic structure of this unusual complex, with a focus on the bonding interactions between beryllium and neighboring atoms.

COMPUTATIONAL METHODS

The structure of HNBeCO was optimized at the B3LYP level of theory in combination with the 6-31G* basis set using the Gaussian 09 program (FRISCH *et al.*, 2009). The calculation of vibrational frequencies validated that this structure corresponds to a minimum on the potential energy surface.

Valence bond theory provides a localized and chemically intuitive description of molecular electronic structure, representing the wavefunction as a linear combination of spin-coupled electron-pairing structures (SHAIK and HIBERTY, 2008). The VBSCF method is the standard classical VB method that includes static electron correlation only. The breathing orbital valence bond (BOVB) method extends this framework by allowing each VB structure to employ its own optimized set of orbitals, thereby capturing dynamic correlation associated with orbital relaxation (SHAIK and HIBERTY, 2008).

The Chirgwin–Coulson weights of seven VB structures were computed at four different theoretical levels: VBSCF, BOVB, S-BOVB, and SD-BOVB. These weights reflect the importance of each structure in the total VB wavefunction and provide insight into the electronic structure and resonance character of HNBeCO.

The split-BOVB (S-BOVB) method further improves the flexibility of the VB wavefunction by allowing active two-electron bonding orbitals to be split into separately optimized orbitals, each single occupied (SHAIK and HIBERTY, 2008). Hence, at this “S” level, all active electron pairs are described as two-electron singlet coupled into a pair of orbitals. Splitting the electron pairs basically includes radial dynamical correlation into the active space. The highest level of BOVB variants, known as the SD-BOVB level, combines the S-BOVB approach with delocalization of the inactive orbitals across multiple centers (Shaik and Hiberty, 2008). Thus, the SD-BOVB basically reduces the Pauli repulsion between inactive pairs in comparison to the S-BOVB level. Together, BOVB, S-BOVB, and SD-BOVB provide a progressively refined hierarchy of valence bond methods suitable for multi-reference systems with both localized and delocalized bonding features. In this study all VB calculations were performed using the XMVB 3.0 program (Song *et al.*, 2005; Chen *et al.*, 2015).

RESULTS AND DISCUSSION

The optimized structure of HNBeCO investigated in this study was obtained using a significantly smaller basis set compared to that used by Wang and coauthors (Wang *et al.*, 2022). However, the chosen level of theory was found to be capable of accurately reproducing subtle geometric features such as critical bond length alternation (Fig. 1), consistent with the findings reported in the previous paper (Wang *et al.*, 2022).

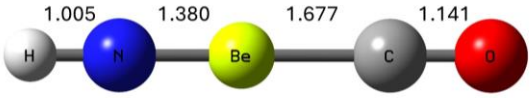
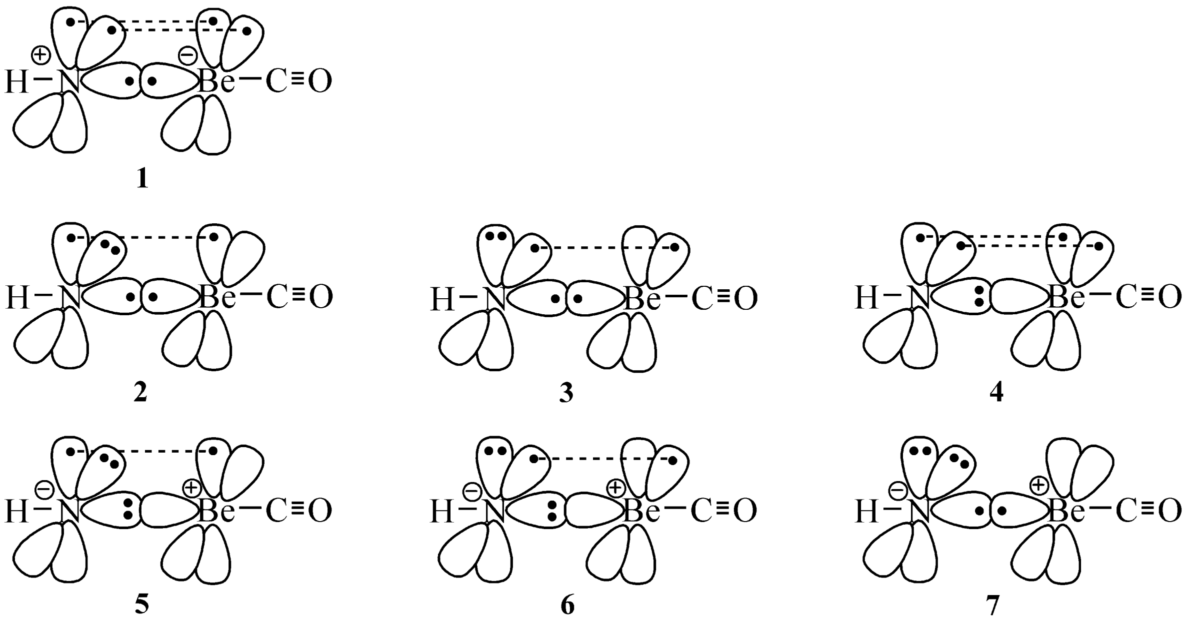


Figure 1. Optimized structure of HNBeCO with bond distances (in Å).

The reference bond dissociation energy (BDE) was obtained at the CCSD(T)/6-31G* level of theory. Generally, the CCSD(T) is widely accepted as the gold-standard in quantum chemistry. To describe the N-Be bonding within the VB framework, we selected an active space of 6 hybrid orbitals (sp_z, p_x and p_y on both N and Be atoms) populated by a total of 6 electrons. From a full structure VBSCF calculation, which involving 175 possible VB structures, only 7 structures with Chirgwin–Coulson weights larger than 4.5% were selected. These VB structures are shown in Figure 2.



1

2 3 4

5 6 7

Figure 2. Set of 7 VB structures.

The selected 7 VB structures yield a BDE approximately 11 kcal/mol lower than that obtained with all 175 VB structures (Table 1). When including the breathing orbital effect at the BOVB level, this reduced set of 7 VB structures provides very similar results to the full-structure VBSCF calculation. In the next step, at the S-BOVB level, all active orbitals occupied with 2 electrons were split in all selected VB structures. Including radial dynamical correlation at the S-BOVB level improved the BDE by ~ 6 kcal/mol relative to the BOVB result. At the SD-BOVB level, the BDE is further improved, and the obtained value is about 9 kcal/mol less than the reference CCSDT energy. Considering that the VB description relies on a relatively small subset of VB structures, this discrepancy is acceptable. Based on these results, the SD-BOVB wavefunction can be confidently used for further bonding analysis in the molecule.

Table 1. Calculated BDE energies

	BDE [kcal/mol]
CCSD(T)	165.53
VBSCF (175 structures)	147.23
VBSCF (7 structures)	136.53
BOVB	146.88
S-BOVB	152.87
SD-BOVB	156.19

Previous discussion reveals that seven VB structures are relevant to describe the bonding in HN–BeCO. Structures **2** and **3** represent the dominant neutral covalent forms, featuring σ-bonding between N–Be, and contribute the most across all computational levels. Structure **1** is an ionic form (N^+–Be^-), while structure **4** involves partial π-donation from nitrogen to beryllium. Structures **5**, **6** and **7** are ionic forms with varying charge distributions (e.g., N^-–Be^+). All these VB structures confirmed previous results that the N-Be bond in HNBeCO exhibits a triple bond character.

The most significant contributions across all levels arise from structures **2** and **3**, with each maintaining a weight close to or slightly above 25% (Table 2). This consistency across all computational levels suggests that these two structures dominate the resonance hybrid. In contrast, structure **1**, which carries a relatively minor weight at the VBSCF level (2.48%), gains substantial importance at the BOVB level (11.02%) and retains a higher weight in subsequent models. This increase is a clear manifestation of the importance of orbital relaxation: BOVB allows for separate orbital optimization for each VB structure. Structures **4**–**7** exhibit intermediate weights, and their contributions slightly vary with the inclusion of dynamic correlation. Notably, the weight of structure **4** decreases when going from VBSCF (21.49%) to BOVB (15.57%), likely due to competition with more stabilized structures upon orbital relaxation. However, its contribution increases slightly in SD-BOVB (16.31%), indicating that dynamic correlation partially recovers its energetic significance. Within the VB framework, the "Charge Shift resonance energy" (RE_{CS}), is defined as the difference between the energies of the full-VB-structure wavefunction and the wavefunction consisting of the most stable VB structure. In our case, the most stable structure is **2**, which is isoenergetic with structure **3**. At the SD-BOVB level, we found that RE_{CS} equals 66.25 kcal/mol. This reveals that nearly one third of the BDE originates from charge shift resonance stabilization.

Table 2. Chirgwin-Coulson weights of structures at different levels.

	VBSCF	**BOVB**	**S-BOVB**	**SD-BOVB**
1	2.48	11.02	10.17	8.84
2	25.34	24.84	25.11	25.72
3	25.34	24.76	24.73	25.10
4	21.49	15.57	15.31	16.31
5	8.68	7.18	6.79	6.43
6	8.68	7.27	7.29	7.04
7	8.00	9.36	10.60	10.56

CONCLUSIONS

In this study,Valence Bond (VB) theory was employed to investigate the bonding and electronic structure of HNBeCO. The bonding between nitrogen and beryllium in HNBeCO can be described as a resonance among seven dominant VB structures, all displaying multiple bonding interactions between N and Be. Two neutral covalent structures play a dominant role, collectively contributing nearly 50% of the total wavefunction. These structures highlight a dative σ-bond alongside two π bonds between N–Be atoms. Overall, the bonding in HNBeCO cannot be captured by a single classical structure, but rather emerges from a delicate balance of covalent, ionic, and delocalized interactions. Furthermore, our study revealed that the charge shift resonance stabilization significantly influences the bonding between N and Be atoms.

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