

# Symmetry breaking in a nutshell: The odyssey of a pseudo problem in molecular physics. The $\tilde{X}^2\Sigma_u^+$ BNB case revisited

Apostolos Kalamos<sup>a)</sup>

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 157 01, Greece

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The  $\tilde{X}^2\Sigma_u^+$  BNB state considered to be of symmetry broken (SB) character has been studied by high level multireference variational and full configuration interaction methods. We discuss in great detail the roots of the so-called SB problem and we offer an in depth analysis of the unsuspected reasons behind the double minimum topology found in practically all previous theoretical investigations. We argue that the true reason of failure to recover a  $D_{\infty h}$  equilibrium geometry lies in the lack of the correct permutational symmetry of the wavefunctions employed and is by no means a real effect.

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## I. INTRODUCTION

Symmetry<sup>1</sup> has played a decisive role in the development of classical mechanics since the early 17th century with the work of Kepler<sup>2</sup> and Galilei.<sup>3</sup> But it was only until 1918 that the complete set of continuous symmetries compatible with the structure of the Newtonian space-time were unified so gloriously in the celebrated Noether's theorem.<sup>4</sup>

In addition to the continuous symmetries associated to the Galilei group, transformations of discrete character are also applicable in quantum mechanics such as permutations of identical particles, inversion of space-spin coordinates, and time reversal. Permutations of indistinguishable particles (in the clamped nuclei approximation we are only concerned with electrons) are the most important ones among the discrete symmetries and their connection to the spin-statistics theorem places them at the very heart of physical sciences.

The molecular wavefunction  $\Psi$  may belong to any representation of the symmetric group, being degenerate or not. Coupled to the Pauli exclusion principle, we limit ourselves to states that are not degenerate under permutations and for a fermionic system belong to the antisymmetric irreducible representation of the associated symmetric group. Thus, any physically realizable state should satisfy two eigenvalue problems, the Schrödinger equation and a second one,  $P\Psi = (-1)^P\Psi$ ,  $P$  being any permutation of the symmetric group  $S_N$ . This second eigenvalue problem can be considered as a constraint<sup>5</sup> that every wavefunction must satisfy before being submitted to the Schrödinger equation. Long ago, it has been shown by Wigner<sup>6</sup> that the exact electronic wavefunction satisfying the Pauli principle and being simultaneously an eigenfunction of  $S^2$  and  $S_z$  should be written as (within the Coulombic approximation, the molecular Hamiltonian is spin free, thus,  $\langle S^2 \rangle$  is conserved for any

stationary state)

$$\begin{aligned}\Psi_{S,M}(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \\ = \left(\sqrt{f_N^S}\right)^{-1} \sum_{i=1}^{f_N^S} \Phi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Theta_i(\sigma_1, \sigma_2, \dots, \sigma_N), \\ \vec{x}_i = (\vec{r}_i, \sigma_i),\end{aligned}$$

where  $\Phi_i(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  are the exact solutions of the spinless Schrödinger equation,  $\Theta_i(\sigma_1, \sigma_2, \dots, \sigma_N)$  are spin eigenfunctions, while both sets  $\Phi_i$  and  $\Theta_i$  belong to dual representations of the symmetric group, and  $f_N^S$  is the number of all linearly independent spin eigenfunctions generated by  $N$  electrons with a total spin value  $S$ . It is clear that every trial function (within the Coulombic approximation) should be of the form given by Wigner.<sup>6</sup> By considering a Hartree product, being the simplest approximate spatial function, we find that the most elementary zeroth order wavefunction  $\Psi_{S,M}^0$  that should be considered in a variational procedure that also satisfies the Pauli principle should read  $\Psi_{S,M}^0 = \sum_{k=1}^{f_N^S} c_k^S \Psi_{S,M;k}^0$  with

$$\begin{aligned}\Psi_{S,M;k}^0 &= (N!)^{1/2} A(\Phi_0^N \Theta_{S,M;k}) \\ &= (N!)^{-1/2} \sum_P (-1)^P (P^r \Phi_0^N) (P^\sigma \Theta_{S,M;k}) \\ &= (N!)^{-1/2} \sum_P (-1)^P (P^r \Phi_0^N) \sum_{l=1}^{f_N^S} U_{lk}^S(P) \Theta_{S,M;l} \\ &= \left(\sqrt{f_N^S}\right)^{-1/2} \sum_{l=1}^{f_N^S} \Theta_{S,M;l} \left(\frac{f_N^S}{N!}\right)^{1/2} \\ &\quad \times \sum_P (-1)^P U_{lk}^S(P) P^r \Phi_0^N\end{aligned}$$

with  $A = (N!)^{-1} \sum_P (-1)^P P$ ,  $P = P^r P^\sigma$ , and  $U^S(P)$  being the antisymmetrizer and representation of the symmetric group generated by the spin functions  $\Theta_{S,M;k}$ ,

<sup>a)</sup>kalamos@chem.uoa.gr

$k = 1, 2, \dots, f_N^S$ , respectively. If the approximate wavefunction cannot be cast in the above form, the electrons will not be treated as indistinguishable particles. Since there are  $f_N^S$  spin functions to span the full space of the irreducible representations of the symmetric group that means we should consider them all. By considering them all, we are forced to consider  $f_N^S$  spatial functions that generate the dual representation of the symmetric group. Any failure to do that is effectively to fail considering indistinguishability properly, that is, to break the permutational symmetry.<sup>7</sup>

We will show in the present work that the symmetry breaking (SB)<sup>8</sup> problem is related to the lack of the “correct” permutational symmetry<sup>6</sup> of the wavefunctions adopted to attack the problem and is by no means a real effect.

## II. THE BNB SAGA

The  $\tilde{X}^2\Sigma_u^+$  BNB state seems to be the prototype system for the study of SB effects in molecular physics perhaps due to its rather small number of valence electrons (11e<sup>-</sup>). The very first paper on BNB is a 1989 Hartree-Fock (HF)/6-31 G\* study by Martin *et al.*,<sup>9</sup> while the latest one is a 2012 fixed-node Diffusion Monte Carlo (DMC) study by Al-Saidi.<sup>10</sup>

In a B<sub>3</sub>N<sub>2</sub>, B<sub>2</sub>N<sub>3</sub>, and BN<sub>4</sub> theoretical study, Martin *et al.*<sup>11</sup> examined the linear BNB radical by complete active space self-consistent field (CASSCF)/cc-pV(D,T)Z computational methods and found that it “exhibits definite symmetry breaking.” Since then, numerous theoretical investigations<sup>10–19</sup> have appeared that favor an asymmetric geometry with the exception of a 2004 study by Kalemos *et al.*<sup>14</sup>

Although it seems that an asymmetric ( $C_{\infty v}$ ) geometry is a rather comfortable situation since calculations tell us so, it is rather surprising that the double minimum nature of BNB is a recurring study case questioning in this way our confidence on the available computational methods. Such a persistence on something that seems logical to most of us is not compatible with a definitive explanation of such phenomena jeopardizing our general understanding of the subtle issues involved.

The pertaining literature up to 2003 is presented in Ref. 14 but for reasons of completeness we feel obliged to remind the most important points of both experimental and theoretical investigations.

The first experimental work is a matrix isolation ESR study by Knight *et al.*<sup>20</sup> Their results indicate a ground electronic state of  $\tilde{X}^2\Sigma_u^+$  symmetry with the spin density located on a boron  $sp_\sigma$  orbital. Geometry optimization (MP4/SDTQ/6-31G\*) conducted in association with hyperfine calculations predict a BN bond length of  $r_e = 1.338$  Å, while the insensitivity of the magnetic  $g$  and  $A$  parameters in three different rare-gas matrices revealed a strong internal bonding in BNB.

In a matrix infrared (IR) study, Andrews *et al.*<sup>21</sup> identified both a cyclic B<sub>2</sub>N ( $C_{2v}$ ) and a linear BNB ( $D_{\infty h}$ ) species and assigned the values of 882.3 and 1736.5 cm<sup>-1</sup> to the anti-symmetric stretching (as) fundamental of the cyclic and linear <sup>11</sup>B<sub>2</sub><sup>14</sup>N isotopologue, respectively.

Through CASSCF(7e<sup>-</sup>/8orb or 11e<sup>-</sup>/12orb)/cc-pV(D,T)Z calculations, Martin *et al.*<sup>11</sup> found a  $C_{\infty v}$

geometry arguing that the SB is physical and not an artifact of the calculations. In an anion photoelectron spectroscopy investigation of B<sub>2</sub>N<sup>-</sup>, Asmis *et al.*<sup>12</sup> assigned the value of 1143 ± 40 cm<sup>-1</sup> to the symmetric stretching (ss) mode of the  $\tilde{X}$  neutral B<sub>2</sub>N species while they observed a similar progression (855, 1197, and 1239 cm<sup>-1</sup>) to that found in the IR spectra of Andrews *et al.*<sup>21</sup> that was initially assigned to the <sup>2</sup>B<sub>2</sub> state of the cyclic B<sub>2</sub>N molecule. Based on the large variations of an asymmetry parameter  $\beta$  for some of the observed peaks and on the non-existence of a cyclic <sup>2</sup>B<sub>2</sub> state at the B3LYP and (coupled cluster + single + double + perturbative connected triples) CCSD(T)/aug-cc-pVTZ levels of theory, they revised the previous interpretation and assigned the above progression to the non-totally symmetric vibration of the linear BNB species. The appearance of odd quanta transitions for this vibrational mode was interpreted as a breakdown of the Franck–Condon approximation and that was explained on the basis of vibronic coupling between the  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$  states along the “as” coordinate. The linear BNB  $\tilde{X}$  state was found to be of  $D_{\infty h}$  symmetry with harmonic  $\omega(ss)$  frequencies of 1196 and 1143 cm<sup>-1</sup> at the B3LYP and CCSD(T) levels of theory, respectively, in excellent agreement with their experimental value of 1143 ± 40 cm<sup>-1</sup>. The B3LYP  $\omega(as)$  frequency of 1327 cm<sup>-1</sup> was not compatible though with the 855 cm<sup>-1</sup> value attributed to the fundamental frequency of that particular vibrational mode while problems were encountered during the CCSD(T) calculations due to the double minimum topology of the curve along the “as” coordinate. The vibrational levels of a Brueckner type orbital CCSD(T) “as” curve with either a single or double minima were both in very good agreement with the observed progression, so an asymmetry of the equilibrium geometry could not be inferred by such calculations. Based on a simple 2 × 2 linear vibronic coupling (LVC) model and making a number of approximations,<sup>22</sup> they have fitted the observed progression to the parameters of the LVC problem. A  $C_{\infty v}$  structure resulted for the  $\tilde{X}$  BNB state being lower than the  $D_{\infty h}$  one by only 18 cm<sup>-1</sup>. They finally concluded that the  $\tilde{X}$ BNB state is quasi-symmetric with respect to inversion based only on the LVC model but not on the CCSD(T) calculations.

In 2001, Gwaltney and Head-Gordon<sup>13</sup> concluded on the basis of Brueckner type orbital CC/DZP calculations that the linear ground BNB state undergoes a real second order Jahn-Teller (SOJT) distortion along the “as” coordinate with the  $C_{\infty v}$  structure ( $\Delta r = 0.09$  Å) lying 161 ± 20 cm<sup>-1</sup> lower than the  $D_{\infty h}$  one.

On the basis of state averaged SACASSCF + PT2 (and +1+2)/cc-pVQZ calculations, Kalemos *et al.*<sup>14</sup> found a  $D_{\infty h}$  equilibrium geometry and thoroughly discussed the SB problem in terms of valence-bond Lewis (vbL) structures. According to their study, one of the terminal B atoms is in an *in situ* <sup>4</sup>P state while the other is in its ground <sup>2</sup>P state. A Hartree-Fock or single state CASSCF wavefunctions cannot cope (generally speaking) with a  $glu$  combination of the two vbL structures that can be written (*vide infra*) and consequently any correlation treatment built on a SB reference fails.

A few months later, Russ *et al.*<sup>15</sup> studied the ability of HF, density functional theory (DFT), and CC methods to

describe the SOJT effect in both BNB and  $C_3^+$  linear species. Although their primary goal was not to provide a definitive answer on the ground state's geometry nor to simulate their spectra, they obtained wavefunctions that display a SB character at all CC variants and a stable  $D_{\infty h}$  structure at the DFT and  $MP_n$  ( $n = 2, 4$ ) levels of theory but with unphysical  $\omega$ (as) frequencies.

Two years later, Ding *et al.*<sup>23</sup> in a resonant two photon ionization spectroscopy (R2PI) experiment recorded vibronic bands in the range 470–510 nm. Analysis of the spectrum leads to a  $r_0(\tilde{X}^2\Sigma_u^+) = 1.312\,41(10)\,\text{\AA}$ <sup>24</sup> for the  $^{11}\text{B}^{14}\text{N}^{11}\text{B}$  isotopologue, while its spectrum displays a nuclear spin statistics pattern compatible with two equivalent  $^{11}\text{B}$  nuclei. They could not deduce on the perfect- or quasi-linearity or centrosymmetric nature of BNB but in case of a barrier to a  $D_{\infty h}$  structure, they asserted it would not be high.

In a reduced multireference (RMR) CCSD(T) study, Li and Paldus<sup>16</sup> found a  $C_{\infty v}$  structure separated from the  $D_{\infty h}$  one by  $\sim 100\text{ cm}^{-1}$ , while a full configuration interaction FCI(11e<sup>−</sup>)/STO-3G calculation predicted a “real” SB effect with a barrier of  $2.45\text{ mE}_h$  ( $= 538\text{ cm}^{-1}$ ). Based also on a 2R(eference)-CCSD(T)/cc-pV(D,Q)/Z potential well along the “as” coordinate, they found the vibrational levels in close agreement with the ones found by Asmis *et al.*<sup>12</sup> Although all their calculations predict a double well curve, the barrier to the centrosymmetric structure is smaller than the zero point energy (ZPE) so no definitive conclusion could be drawn on the existence of such a barrier based on the existing experimental data. But at the level of theory used in their study the “symmetry breaking in BNB is real.”

In 2009, the Boggs group<sup>17</sup> investigated the SB problem by employing a series of multireference methods based on a SACASSCF reference wavefunction and concluded that the double well topology of the ground state's potential curve is real with a suggested barrier of  $20\text{ cm}^{-1}$ . They have fitted their *ab initio* results to a  $2 \times 2$  LVC model and extracted numerical values for the pseudo Jahn-Teller parameters employed that were subsequently used as an *a posteriori* physical explanation of the SB effect.<sup>25</sup>

In a 2010 CC study, a new parameter enters the rather obscure scene of the BNB problem. Stanton<sup>19</sup> published a paper entitled “An unusually large nonadiabatic error in the BNB molecule.” He constructed adiabatic “as” potentials for the  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$ <sup>26</sup> states by equation of motion coupled cluster EOMIP-CCSDT/[4s3p2d1f] calculations based on the HF orbitals of the anion  $\text{BNB}^-$  ( $\tilde{X}^1\Sigma_g^+$ ) system. The  $\tilde{X}$  curve displayed a double well topology as was also found in all previous CC studies but the purpose of his report was rather to assess the errors introduced by the adiabatic approximation than to enter in the seemingly endless quarrel of whether

BNB is SB or not. He fitted his *ab initio* curves on a three parameter  $2 \times 2$  LVC model used in a subsequent non-adiabatic calculation.<sup>27</sup> Although the experimental values<sup>12</sup> of the fundamental ( $855 \pm 40\text{ cm}^{-1}$ ) and first overtone ( $2052 \pm 40\text{ cm}^{-1}$ ) are in better agreement with his adiabatic ( $890.5$  and  $2061.7\text{ cm}^{-1}$ ) than with his nonadiabatic ( $812.5$  and  $1978.3\text{ cm}^{-1}$ ) results, he mysteriously claimed the greatest importance of nonadiabatic effects in the BNB case than “...to do better and better old-fashioned quantum chemistry” and that without even reporting the energies of the higher vibrational levels in both adiabatic and nonadiabatic regime that could be compared with the existing experimental data. He then concluded his report by suggesting that nonadiabaticity might be important even in cases where the energy separation ( $5638.6\text{ cm}^{-1}$  in the present case) between the pseudo JT couple of interacting curves is quite large and where there are no crossings or avoided crossings nearby.

The latest work on the BNB problem is a fixed node DMC study<sup>10</sup> where an asymmetric structure is found to lie lower than the symmetric one by only  $22(62)\text{ cm}^{-1}$  in agreement with the results of Ref. 17. The trial wavefunctions used in the fixed node DMC calculations were all subjected to the SB problem so it is not a surprise that a double minimum topology was found.

The above account on the ground state of the BNB radical reveals a thrilling story. Is it SB or not? Experimental data are not sufficient enough to conclude definitely while practically all theoretical calculations point to an asymmetric structure separated by the symmetric one by only a few wave numbers. Traditionally, this sort of problems were tackled either by non-orthogonal configuration interaction (CI) wavefunctions despite the extra labor or by carefully designed orthogonal CI wavefunctions that mimic the resonance of all SB structures entailed.<sup>28</sup> A common point of the above “solutions” in chemical terms is that they take into account the “resonance,” “charge separation,” and “orbital relaxation” energy through the “orbital doubling.” We will show in the present study that by enlarging the active space we restore the permutational symmetry<sup>6</sup> not present in the HF and insufficiently designed MCSCF wavefunctions. Respecting the fundamental symmetries of the problem at hand is the most secure way to deal with any molecular system for which a valence-bond reading may not be possible.

### III. RESULTS AND DISCUSSION

In 2004, Kalemos *et al.*<sup>14</sup> have shown that the  $\tilde{X}^2\Sigma_u^+$  BNB state can be written in chemical terms as the resonance of two vbL icons

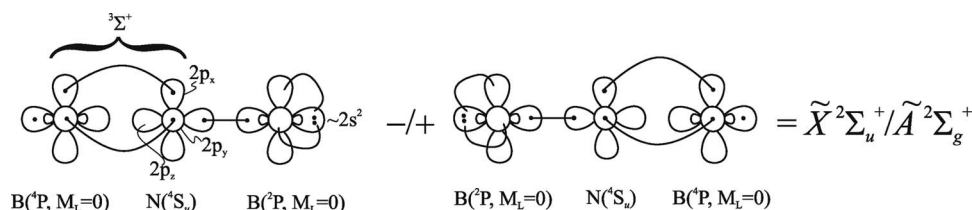


TABLE I. Energy ( $E_h$ ) and internuclear distances  $r_{B_1N}$ ,  $r_{B_2N}$  (Å) of the  $\tilde{X}^2\Sigma_u^+$  BNB state at the (SA)CASSCF, (SA)CASSCF+1+2(=MRCI), ACPF, and MRCI+Q/cc-pVTZ levels of theory.

| Method                                                                                | −E          | $r_{B_1N}$ | $r_{B_2N}$ |
|---------------------------------------------------------------------------------------|-------------|------------|------------|
| 9e <sup>−</sup> /11orb[ = (2s + 2p) <sub>B</sub> × 2 + (2p) <sub>N</sub> ]            |             |            |            |
| CASSCF                                                                                | 103.878 400 | 1.3854     | 1.2716     |
| SACASSCF <sup>a</sup>                                                                 | 103.866 236 | 1.3296     | 1.3296     |
| MRCI(9e <sup>−</sup> ) <sup>b</sup>                                                   | 104.009 545 | 1.3227     | 1.3227     |
| MRCI(9e <sup>−</sup> )+Q <sup>c</sup>                                                 | 104.018 967 | 1.3213     | 1.3213     |
| 11e <sup>−</sup> /12orb[ = (2s + 2p) <sub>B</sub> × 2 + (2s + 2p) <sub>N</sub> ]      |             |            |            |
| CASSCF                                                                                | 103.904 481 | 1.4030     | 1.2744     |
| MRCI(11e <sup>−</sup> )                                                               | 104.089 343 | 1.3861     | 1.2787     |
| MRCI(11e <sup>−</sup> )+Q                                                             | 104.101 130 | 1.3845     | 1.2815     |
| ACPF(11e <sup>−</sup> ) <sup>d</sup>                                                  | 104.099 702 | 1.3845     | 1.2814     |
| SACASSCF <sup>a</sup>                                                                 | 103.894 051 | 1.3739     | 1.3006     |
| 11e <sup>−</sup> /13orb[ = (2s + 2p) <sub>B</sub> × 2 + (2s + 2p + s') <sub>N</sub> ] |             |            |            |
| CASSCF                                                                                | 103.917 461 | 1.3976     | 1.2745     |
| SACASSCF <sup>a</sup>                                                                 | 103.908 589 | 1.3606     | 1.3057     |
| MRCI(11e <sup>−</sup> ) <sup>e</sup>                                                  | 104.091 809 | 1.3558     | 1.3023     |
| MRCI(11e <sup>−</sup> ) <sup>f</sup>                                                  | 104.073 225 | 1.3371     | 1.3371     |
| MRCI(11e <sup>−</sup> ) <sup>g</sup>                                                  | 104.087 950 | 1.3310     | 1.3310     |

<sup>a</sup>A two state SACASSCF wavefunction. The two states of  $^2A_1$  symmetry correlate to  $\tilde{X}^2\Sigma_u^+$  and  $\tilde{A}^2\Sigma_g^+$  at  $D_{\infty h}$  nuclear configurations.

<sup>b</sup>Nine out of the total number of 11 valence electrons are correlated. For the MRCI expansion, we used the natural orbitals of the SACASSCF wavefunction.

<sup>c</sup>+Q refers to the Davidson correction.

<sup>d</sup>Averaged coupled pair functional calculations based on CASSCF natural orbitals.

<sup>e</sup>The reference space consists of 246 972 configuration functions (CF), all single and double replacements generate 851 071 095 CFs internally contacted to 22 087 269 CFs.

<sup>f</sup>For the MRCI expansion, we used the natural orbitals of a SACASSCF wavefunction by state averaging  $^{12}A_1(2) + ^{12}B_1(4) + ^{12}B_2(4) + ^{12}A_2(5)$  states. Very tight convergence criteria were imposed during the geometry optimization; the optimized BN internuclear distances are identical at 7 decimal places. The MRCI energy rises by  $9.37 \times 10^{-5}$ ,  $3.59 \times 10^{-4}$ ,  $8.47 \times 10^{-4}$ , 0.002, 0.010, and 0.060  $E_h$  at  $\Delta r = 0.025, 0.05, 0.075, 0.10, 0.20$ , and 0.40 bohr.

<sup>g</sup>For the MRCI expansion, we used the natural orbitals of a SACASSCF wavefunction by state averaging  $^{12}A_1(2) + ^{21}A_1(2)$  states.

Each one of the building blocks is composed of an *in situ* B atom in its ground  $^2P$  state (the curved lines connecting the  $\sim 2s_B$  orbital with the empty  $2p_x$  and  $2p_y$  ones indicate the GVB type correlation of the  $\sim 2s_B^2$  electrons within the space provided) while the other terminal B atom is found in its excited  $^4P$  atomic state. The above vbL scheme is also consistent with the spin distribution revealed in the ESR investigation by Knight *et al.*<sup>20</sup> From a different but completely equivalent point of view, we can visualize the diabatic formation of the  $\tilde{X}^2\Sigma_u^+$  state as resulting from the linear approach of a B( $^2P$ ) atom to the BN( $^3\Sigma^+$ ) state;<sup>14</sup> the  $X^3\Pi$  BN state favors rather a  $C_{2v}$  B<sub>2</sub>N molecule than a linear BNB one, while the  $a^1\Sigma^+$  BN state, quasi-degenerate to the  $X$  one, is a “solid” closed shell molecule that does not offer a docking place to an incoming B atom.<sup>14</sup> In the vbL description, we can see 9 out of the 11 valence electrons, the rest being the  $\sim 2s_N^2$  not essential (pictorially) for the formation of the  $\sigma$  and  $\pi$  bonds between the N and the terminal B atoms.

In order to understand the physics of the so-called SB problem, we will analyze the results presented in Table I obtained with MOLPRO 2010.1<sup>29</sup> and by employing a Dunning cc-pVTZ basis set<sup>30</sup> on both B and N atoms.

When we optimize the geometry of one state of  $\tilde{X}^2\Sigma_u^+(^2A_1)$  symmetry (all calculations have been done under  $C_{2v}$  symmetry restrictions) with a CASSCF[9e<sup>−</sup>/11orb = (2s + 2p)<sub>B</sub> × 2 + (2p)<sub>N</sub>] wavefunction, we get a SB structure with  $r_{B_1N} = 1.3854$  Å and  $r_{B_2N} = 1.2716$  Å that corresponds to any one of the vbL resonance structures of the  $\tilde{X}^2\Sigma_u^+$  state (*vide supra*). The geometry optimization of the first root in a two state ( $\tilde{X}^2\Sigma_u^+ + \tilde{A}^2\Sigma_g^+$ ) SACASSCF wavefunction with the same specifications as above gives rise to the perfectly symmetric  $D_{\infty h}$  structure with  $r_{B_1N} = r_{B_2N} = 1.3296$  Å. The active space employed is good enough for the so-called “angular” correlation of the  $\sim 2s_B^2$  electron pairs (see the vbL diagram above), the true effect being the restoration of the permutational symmetry through the assignment of every electron of our 9e<sup>−</sup>/11orb problem to a different spatial function.<sup>6,31</sup> In the first case (CASSCF) not only the optimized geometry is of  $C_{\infty v}$  symmetry but the solution is of SB character since at a  $D_{\infty h}$  nuclear configuration the wavefunction is of  $C_{\infty v}$  nature (at  $\Delta r (= r_{B_1N} - r_{B_2N}) = 0.0$  bohr, the  $\langle\mu\rangle = 4.00$  D).

We subsequently performed a geometry optimization at the CASSCF [11e<sup>−</sup>/12orb = (2s + 2p)<sub>B</sub> × 2 + (2s + 2p)<sub>N</sub>, one state of  $^2\Sigma^+$  symmetry] and SACASSCF [11e<sup>−</sup>/12orb = (2s + 2p)<sub>B</sub> × 2 + (2s + 2p)<sub>N</sub>, two states of  $^2\Sigma^+$  symmetry] levels of theory. In both cases, a  $C_{\infty v}$  geometry was obtained with an asymmetry geometrical parameter  $\Delta r = 0.1286$  and 0.0733 Å, respectively; see Table I. It is interesting though to notice that although both wavefunctions predict a double minimum curve along the “as” coordinate, the SACASSCF wavefunction is not SB (at  $\Delta r = 0.0$  bohr the  $\langle\mu\rangle = 0.00$  D) while the CASSCF one is SB (at  $\Delta r = 0.0$  bohr the  $\langle\mu\rangle = 3.91$  D), thus any correlation treatment should be based only on a SACASSCF reference.<sup>14</sup>

The natural thing to ask is why a SACASSCF(9e<sup>−</sup>/11orb) calculation gives such a different result than the SACASSCF(11e<sup>−</sup>/12orb) one. The answer can be given after a careful inspection of the vbL description of the  $\tilde{X}^2\Sigma_u^+$  state. By distributing the  $\sim 2s_N^2$  electrons in the chosen active space (2s + 2p)<sub>N,B</sub>, we might have expected to “correlate” them in an angular way. Certainly, the B  $2p$  orbitals will not do the job since correlation (Coulomb law) is a local effect while the N  $2p$  related orbitals being singly occupied (N is in a  $^4S_u$  state) do not offer the necessary space for even a GVB type “correlation.” Single excitations of local type ( $2s^2 2p^3 \rightarrow 2s^1 2p^4$ ) would result in an *in situ* atom not in the  $^4S_u$  state and that will eventually break the total symmetry of the wavefunction.

At this point, we should comment on the FCI results by Li and Paldus.<sup>16,18</sup> In Ref. 16, they employed a STO-3G minimal basis set and correlated all 11 valence electrons. They found a barrier of 2.45  $mE_h$  ( $= 538$  cm<sup>−1</sup>) between the  $C_{\infty v}$  and  $D_{\infty h}$  structures. In Ref. 18, they employed a cc-pVDZ basis set yielding 45 molecular orbitals (MO). They used “truncated” spaces for the FCI expansion and correlated 3 (in 38/45 MOs), 5 (in 39/45 MOs), and 7 (in 33/45 MOs) electrons out of the total number of 11. They found a double minimum curve with barriers of 2040, 1603, and 542 cm<sup>−1</sup>, respectively.

We have performed a geometry optimization of the first root of  $^2\Sigma^+$  symmetry at the SACASSCF(9e<sup>−</sup>/11orb, two

states of  $^2\Sigma^+$  symmetry) level of theory in a series of basis sets whose quality ranges from STO-3G to cc-pVnZ ( $n = 2-6$ ). At the SACASSCF( $9e^-$ )/STO-3G level of theory (equivalent to a FCI( $9e^-$ /STO-3G)), we obtained a  $C_{\infty v}$  structure with geometrical parameters  $r_{B_1N} = 1.4065$  Å,  $r_{B_2N} = 1.2860$  Å, and  $E = -102.462\,180$   $E_h$ . When using the cc-pVnZ,  $n = 2-6$ , basis sets, we obtained a perfect centrosymmetric molecule with internuclear distances  $r_{B_1N} = r_{B_2N} = 1.3374, 1.3296, 1.3268, 1.3265$ , and  $1.3264$  Å, respectively, while the harmonic frequencies with the largest cc-pV6Z basis set are  $\omega(ss)/\omega(as)/\omega(b) = 1182/1568/68$   $\text{cm}^{-1}$ . The complete disagreement between the STO-3G and any of the cc-pVnZ ( $n = 2-6$ ) SACASSCF( $9e^-$ /11orb) calculations is as expected. The “elementary” STO-3G([ $2s1p$ ]) basis set cannot describe simultaneously both  $^2P(2s^22p^1)$  and  $^4P(2s^12p^2)$  B states that are necessary for the formation of the  $\tilde{X}^2\Sigma_u^+$  BNB state (*vide supra*). The smallest basis set that should be used is a [ $3s1p$ ] (the  $s$  and  $p$  functions are taken from the cc-pVDZ basis set). At the SACASSCF( $9e^-$ /11orb)/[ $3s1p$ ] level of theory, we obtained a  $D_{\infty h}$  geometry with  $r_{B_1N} = r_{B_2N} = 1.4165$  Å and  $E = -103.744\,224$   $E_h$ . Qualitatively, the same result was obtained when we considered a [ $3s2p$ ] basis set ( $r_{B_1N} = r_{B_2N} = 1.3498$  Å and  $E = -103.813\,299$   $E_h$ ) while the smallest basis set that could “correlate” the  $\sim 2s_N^2$  electrons is a [ $3s2p_N\,3s1p_B$ ]. Based on the above analysis, the FCI( $11e^-$ /STO-3G) results of Ref. 16 is hardly a surprise (at the SACASSCF( $11e^-$ )/STO-3G level of theory, equivalent to FCI( $11e^-$ /STO-3G), we obtained  $r_{B_1N} = 1.4237$  Å,  $r_{B_2N} = 1.2810$  Å, and  $E = -102.488\,179$   $E_h$ ). In Ref. 18, the choice of the cc-pVDZ basis set was correct but the choice of the electrons to be correlated was rather unfortunate. From the vbL description of the  $\tilde{X}^2\Sigma_u^+$  state (*vide supra*), we see that at least  $9e^-$  play a fundamental role in the formation of the  $\sigma$  and  $\pi$  bonds in both resonant structures. By considering less electrons (3, 5, or 7) than this “absolutely” necessary number, we deliberately discriminate and break the symmetry of the problem from the very beginning (this is also evident from the trend of the barrier height  $\Delta E(D_{\infty h} \leftarrow C_{\infty v})$  when they correlated 3(2040  $\text{cm}^{-1}$ ), 5(1603  $\text{cm}^{-1}$ ), and 7(542  $\text{cm}^{-1}$ ) electrons; see Ref. 18). Also the elimination of some of the highest lying MOs can break the cylindrical symmetry if unwisely chosen. We have performed FCI( $9e^-$ )/[ $3s1p$ ] and FCI( $9e^-$ )/[ $3s2p$ ] calculations based on the natural orbitals of a two state SACASSCF( $9e^-$ /11orb) wavefunction. The minimum of the “ss” curve is located at  $r_{B_1N} = r_{B_2N} = 1.4136$  and  $1.3504$  Å, respectively, with  $E_{FCI}([3s1p]) = -103.756\,981$   $E_h$  and  $E_{FCI}([3s2p]) = -103.858\,007$   $E_h$ . By asymmetrically stretching the linear molecule by  $\Delta r = 0.01, 0.02, 0.03, 0.05$ , and  $0.1$  bohr, the FCI/[ $3s1p$ ]/[ $3s2p$ ] energy rises by  $1.57 \times 10^{-5}$  ( $2.04 \times 10^{-5}$ ),  $6.09 \times 10^{-5}$  ( $7.87 \times 10^{-5}$ ),  $1.29 \times 10^{-4}$  ( $1.67 \times 10^{-4}$ ),  $3.08 \times 10^{-4}$  ( $4.01 \times 10^{-4}$ ), and  $9.0 \times 10^{-4}$  ( $0.001$ )  $E_h$ , respectively. So, there is no trace of SB in our FCI( $9e^-$ ) calculations. We believe that the SB FCI results in Refs. 16 and 18 are an artifact due to the combination of small basis sets and the number of correlated electrons and not a real effect.

Thus, the root of the problem lies in the inadequate reference wavefunction due to the lack of permutational invariance.<sup>6</sup> In order to solve the problem, we need to en-

large our active space by at least one orbital that should be of the appropriate “shape” for a GVB like “correlation” of the  $\sim 2s_N^2$  electron pair. For reasons of computational convenience, we have chosen to add only one orbital of  $\sigma$  symmetry giving rise to a reference SACASSCF[ $11e^-$ /13orb = ( $2s + 2p$ )<sub>B</sub>  $\times$  2 + ( $2s + 2p + s'$ )<sub>N</sub>] wavefunction. In order to enforce the GVB shape of that additional orbital, a number of  $^{12}\Lambda$  states<sup>32</sup> was included in the SACASSCF optimization. Based on such orbitals, a geometry optimization at the multireference configuration interaction (MRCI) level resulted in a perfect  $D_{\infty h}$  geometry,  $r_{B_1N} = r_{B_2N} = 1.3310$  Å, with  $E = -104.087\,950$   $E_h$ ; see Table I. The MRCI energy rises by  $3.08 \times 10^{-6}$ ,  $1.35 \times 10^{-5}$ ,  $7.29 \times 10^{-5}$ ,  $2.29 \times 10^{-4}$ , and  $0.001$   $E_h$  at  $\Delta r = 0.01, 0.02, 0.04, 0.06$ , and  $0.10$  bohr, respectively.

A last comment on the geometrical parameters found is in order. The optimized internuclear distance  $r_{B_1N} = r_{B_2N} = 1.331$  Å is found in much better agreement with the value  $r_e = 1.338$  Å reported by Knight *et al.*<sup>20</sup> than with the R2PI value of  $r_0(\tilde{X}^2\Sigma_u^+) = 1.312\,41(10)$  Å by Ding *et al.*<sup>23,24</sup> It is interesting though to notice that the optimized geometry at the RHF + 1 + 2/cc-pVTZ<sup>33</sup> level of theory,  $r_{B_1N} = r_{B_2N} = 1.3130$  Å ( $E = -104.035\,978$   $E_h$  and  $\omega(ss)/\omega(as)/\omega(b) = 1222/2176/58$   $\text{cm}^{-1}$ ) is in perfect agreement with the R2PI value.

## IV. CONCLUSIONS

The  $\tilde{X}^2\Sigma_u^+$  BNB state has been studied by MRCI( $11e^-$ )/cc-pVTZ and FCI( $9e^-$ )/[ $3s2p$ ] methods. We have analyzed its bonding characteristics in terms of vbL structures and by respecting the electronic permutational symmetry we have carefully constructed a reference wavefunction upon which true dynamical correlation has been extracted. We have checked our MRCI results by FCI( $9e^-$ )/[ $3s2p$ ] calculations and we found no trace of symmetry breaking in qualitative disagreement with practically all previous theoretical investigations that predicted a barrier to a centrosymmetric structure either of 20  $\text{cm}^{-1}$  (based on MRCI methods)<sup>17,34</sup> or 100–160  $\text{cm}^{-1}$  (based on CC methods).<sup>13,16,19,35</sup> We have also shown that it is indeed possible to solve such SB problems with “conventional” electronic structure packages but a deep understanding of the subtleties entailed is necessary at least for the time being, perhaps such peculiarities will not be a problem in the future when “intelligent” programs do the thinking for us.<sup>36</sup>

The computational strategy that should be adopted in related SB problems can be synopsized as follows. By considering that molecular orbitals do not have to sort out as symmetry orbitals in a completely unconstrained optimization process,<sup>37</sup> we should average all symmetry related SB structures in a SACASSCF step that is equivalent to a spatially projected wavefunction. That was done in our SACASSCF( $9e^-$ /11orb) wavefunction. When valence electrons not directly used in bond formation (the  $\sim 2s_N^2$  in our case) are distributed in the active space, then the active space should be such that the additional electrons should be singly occupied or can be “correlated,” so that the correct permutational symmetry is

respected.<sup>6</sup> That was done in our SACASSCF(11e<sup>-</sup>/13orb) wavefunction.

In summary, we have explicitly shown in this study where the SB problem is hidden and offered the most general way to circumvent this sort of peculiarities and this is perhaps the most important feature of this work. We simply cannot expect something to be symmetrical when the fundamental symmetries are not respected from the very beginning. Although existing experimental data are in line with an equal bond length BNB structure, we strongly believe that additional experimental work is in order to unambiguously clarify the nature of its equilibrium geometry.

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<sup>1</sup>The proper translation of the Greek word *symmetria* (from the prefix *syn* [together] and the noun *metro* [measure]) is commensurability or in proportion with. During the classical era, the Greeks interpreted this word as the harmony of the different parts of an object, the good proportions between its constituent's parts. In some way, symmetry was always related to beauty, truth, and good. In a generalized and contemporary meaning, one can speak about symmetry of an "object" if under any kind of transformation at least one property of the "object" is left invariant.

<sup>2</sup>The germ of the idea of symmetry in natural philosophy appeared in *Astronomia Nova*, Kepler's 1609 book in which his first two laws of planetary motion are described. In 1619, he published *Harmonices Mundi* where he attempted to explain the geometrical forms and physical phenomena in terms of harmony and congruence.

<sup>3</sup>In a celebrated passage of his *Dialogo*, Galilei enunciated what is now called the Galilean relativity principle that forms the foundation of Newtonian mechanics.

<sup>4</sup>E. Noether, Nachr. D. König. Gessesch. D. Wiss. Zu Göttingen, math-phys. Klasse, 235 (1918) [*Transp. Theory Stat. Phys.* **1**, 186 (1971)]. The curious reader should consult the marvelous book *Les Théorèmes de Noether: Invariance et lois de Conservation au XXe Siècle* by Y. Kosmann-Schwarzbach and L. Meersseman, Éditions de l'École Polytechnique, 2006, for its authoritative historical and scientific commentary on both of Noether's theorems.

<sup>5</sup>In most of the cases, additional constraints are imposed on approximate wavefunctions due to their incomplete form. These constraints are often related to the point group of the associated geometry. It should be mentioned though that an exact solution will have the correct symmetry of the problem, e.g., in the Kepler problem all points ( $\vec{r}(t)$ ,  $\vec{p}(t)$ ) of the phase space will be such that both the angular momentum and the so-called Laplace-Runge-Lenz vectors will be conserved without imposing them from the outset. In the atomic case, the Hartree-Fock orbitals are restricted to be eigenfunctions of  $L^2$ ,  $L_z$ ,  $s^2$ ,  $s_z$  while orbitals with the same value of  $L^2$  are constrained to have the same radial part.

<sup>6</sup>E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press, New York, 1959), p. 259, formula 22.20b and the paragraph that follows it. The German edition of the book appeared in 1931.

<sup>7</sup>As an example, consider the Li atom, its RHF representation is  $\sim |1s(1)a(1)1s(2)\beta(2)2s(3)a(3)|$ , the assumed spatial function  $1s(1)1s(2)2s(3)$  can be coupled only to the spin eigenfunction  $\Theta_{1/2,1/2,1} = 1/\sqrt{2}[a(1)\beta(2) - \beta(1)a(2)]a(3)$  and not to the second one  $\Theta_{1/2,1/2,2} = 1/\sqrt{6}[2a(1)a(2)\beta(3) - a(1)\beta(2)a(3) - \beta(1)a(2)a(3)]$ , so RHF does not conform to the Wigner's way of writing down a properly antisymmetric wavefunction being simultaneously a spin eigenfunction. The spatial part of its UHF representation can be in general coupled to both spin eigenfunctions. By applying a spin projection operator to UHF, we finally get the wavefunction written the Wigner's way.

<sup>8</sup>A wavefunction which is not invariant under all symmetry operations of the point group is said to be symmetry broken (SB). In classical mechanics, SB occurs when a stable minimum undergoes bifurcation and splits into two stable minima. Although the above cases are distinct, we will use the term in both of its meanings.

<sup>9</sup>J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **90**, 6469 (1989).

<sup>10</sup>W. A. Al-Saidi, *Chem. Phys. Lett.* **543**, 41 (2012).

<sup>11</sup>J. M. L. Martin, J. El-Yazal, J. P. François, and R. Gijbels, *Mol. Phys.* **85**, 527 (1995).

<sup>12</sup>K. R. Asmis, T. R. Taylor, and D. M. Neumark, *J. Chem. Phys.* **111**, 8838 (1999). It is a combined experimental and theoretical study of BNB.

<sup>13</sup>S. R. Gwaltney and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **3**, 4495 (2001).

<sup>14</sup>A. Kalemos, T. H. Dunning, Jr., and A. Mavridis, *J. Chem. Phys.* **120**, 1813 (2004).

<sup>15</sup>N. J. Russ, T. Daniel Crawford, and G. S. Tschumper, *J. Chem. Phys.* **120**, 7298 (2004).

<sup>16</sup>X. Li and J. Paldus, *J. Chem. Phys.* **126**, 224304 (2007).

<sup>17</sup>Y. Liu, W. Zou, I. B. Bersuker, and J. E. Boggs, *J. Chem. Phys.* **130**, 184305 (2009).

<sup>18</sup>X. Li and J. Paldus, *J. Chem. Phys.* **130**, 164116 (2009).

<sup>19</sup>J. F. Stanton, *J. Chem. Phys.* **133**, 174309 (2010).

<sup>20</sup>L. B. Knight, Jr., D. W. Hill, T. J. Kirk, and C. A. Arrington, *J. Phys. Chem.* **96**, 555 (1992).

<sup>21</sup>L. Andrews, P. Hassanzadeh, T. R. Burkholder, and J. M. L. Martin, *J. Chem. Phys.* **98**, 922 (1993).

<sup>22</sup>Both the  $\tilde{X}$  and  $\tilde{A}$  diabatic states of the LVC model were assumed to have the same harmonic frequency while the separation constant  $\Delta$  was evaluated by considering the experimental energy gap  $T_0 = 0.785$  eV and the calculated zero point energies of both adiabatic states for a given value of the interaction parameter  $\lambda$ . But most importantly they fitted experimental data on a completely decoupled (1D instead of 3D) model that is parametrized by a three parameter  $2 \times 2$  matrix. Taking into account the assumptions and oversimplifications made the barrier  $\Delta E(D_{\infty h} \leftarrow C_{\infty v})$  of  $18 \text{ cm}^{-1}$  should be viewed with extreme caution.

<sup>23</sup>H. Ding, M. D. Morse, C. Apetrei, L. Chacaga, and J. P. Maier, *J. Chem. Phys.* **125**, 194315 (2006).

<sup>24</sup>The bond length was obtained by measuring the rotational constant of the ground vibrational state, converting this to a moment of inertia, then assuming a rigid symmetric linear structure, and solving for the bond length. However, even in its ground vibrational level there is a ZPE motion, and for this molecule the bending motion will have fairly large amplitude motion because of its small bending frequency. This means that in the (0, 0, 0) vibrational level, the two B atoms spend a significant amount of time with a shorter distance between them than they do when they are in the linear configuration. This decreases the vibrationally averaged moment of inertia, which makes the bond length computed from the measured rotational constant shorter than what is found at the equilibrium position. Private communication with Professor M. D. Morse; see Ref. 23.

<sup>25</sup>In Ref. 17, we read "The physical reason of this instability in terms of bonding is that the two electronic states, which are orthogonal in the high-symmetry configuration, become mixed under the odd nuclear displacements thus producing additional (covalent) energy gain that offsets the losses by distortion." We believe that the argumentation presented in Sec. III C of Ref. 17 is of tautological nature. Both electronic states at all points of the configurational space are orthogonal and not only in the high symmetry nuclear configuration. Their highly correlated methods give rise to a double well curve, using this fact as a starting point in the  $2 \times 2$  problem they gain nothing new. They get as an output what they entered as an

input. The fundamental question is whether the double minimum well is correct or not and not to rename the configuration interaction as a pseudo Jahn–Teller effect.

<sup>26</sup>It was mistakenly reported as  $^2\Sigma_g^-$ .

<sup>27</sup>As was also done in Ref. 12, the model employed decouples all modes of vibration and uses a three parameter  $2 \times 2$  matrix for the description of the  $\tilde{X}-\tilde{A}$  system.

<sup>28</sup>S. L. Guberman and W. A. Goddard III, *Chem. Phys. Lett.* **14**, 460 (1972), discussions on a spatially projected wavefunction are older and given by several authors; C. F. Jackels and E. R. Davidson, *J. Chem. Phys.* **64**, 2908 (1976); L. Engelbrecht and B. Liu, *ibid.* **78**, 3097 (1983); A. D. McLean, B. H. Lengsfeld III, J. Pacansky, and Y. Ellinger, *ibid.* **83**, 3567 (1985); W. D. Allen, D. A. Horner, R. L. Dekock, R. B. Remington, and H. F. Schaefer III, *Chem. Phys.* **133**, 11 (1989); E. Hollauer and M. A. C. Nascimento, *Chem. Phys. Lett.* **184**, 470 (1991); P. C. Hiberty, S. Humbel, and P. Archirel, *J. Phys. Chem.* **98**, 11697 (1994); A. Ricca, J. Weber, M. Hanus, and Y. Ellinger, *J. Chem. Phys.* **103**, 274 (1995); F. Mota and J. J. Nova, *ibid.* **105**, 8777 (1996); P. Y. Ayala and H. Bernhard Schlegel, *ibid.* **108**, 7560 (1998).

<sup>29</sup>H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see <http://www.molpro.net>.

<sup>30</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).

<sup>31</sup>It is interesting to consider the following results on the  $N(^4S_u)$  atomic state based on different CASSCF/cc-pVQZ calculations. The RHF energy is  $E_{RHF} = -54.400\,176\,E_h$ . When an orbital of  $s$  type is added into the active space, the CASSCF energy obtained is  $E_{(2s+2p+s)} = -54.407\,805\,E_h$ . The same energy is obtained by a spin coupled wavefunction. The  $\sim 7\,mE_h$  energy lowering is traditionally attributed to the radial correlation of the  $\sim 2s_N^2$  electron pair. The true origin though is the restoration of the permutational symmetry (A. G. H. Barbosa and M. A. C. Nascimento, *Int. J. Quantum Chem.* **99**, 317 (2004)). The coefficients of the four linearly independent spin functions associated to a  $5e^-/2S + 1 = 4$  problem are  $c_1 = 0.9740$  (the HF spin function),  $c_2 = 0.1688$ ,  $c_3 = 0.1194$ , and  $c_4 = 0.0924$ . Although the  $c_2$ – $c_4$  coefficients are extremely small their presence is vital for the permutational invariance of the total wavefunction; see Ref. 6. When orbitals of  $p$  symmetry are included in the active space, then the GVB-like optimized wavefunction has an energy  $E_{(2s+2p+s+p)} = -54.409\,152\,E_h$ , while the inclusion of  $d$  type orbitals has a dramatic effect in the energy stabilization,  $E_{(2s+2p+s+p+d)} = -54.433\,463\,E_h$ . In all these wavefunctions, the additional three  $p$  and five  $d$  orbitals were used as the GVB complement of the  $\sim 2s_N$  one and not in a CASSCF way. For a “traditional” approach to the subject, see J. W. Hollett and P. M. W. Gill, *J. Chem. Phys.* **134**, 114111 (2011); C. A. Nicolaides, *Int. J. Quantum Chem.* **111**, 3347 (2011); A. D. Becke, *J. Chem. Phys.* **138**, 074109 (2013).

<sup>32</sup>The geometry optimization of the first root of  $^2\Sigma^+$  symmetry of a two state SACASSCF([11e<sup>-</sup>/13orb =  $(2s + 2p)_B \times 2 + (2s + 2p + s')_N$ ] wavefunction gives rise to a SB structure with  $r_{B_1N} = 1.3606\,\text{\AA}$ ,  $r_{B_2N} = 1.3057\,\text{\AA}$ , and  $E = -103.908\,589\,E_h$ . Since it is hard to optimize the GVB companion

of the  $\sim 2s_N$  orbital in the  $a_1$  symmetry block, we “forced” the additional orbital to be of the “correct shape” by including two states of  $^{12}A_1$  symmetry in the optimization procedure. This way it is certain that the  $\sim 2s_N^2$  electrons will be in different orbitals along the  $\sigma$  frame of the molecule. We tested the energy loss due to the above followed SACASSCF procedure by calculating the CASSCF ( $5e^-/5orb$ ) + 1 + 2 (+Q)/cc-pVQZ ( $C_1$  symmetry) energy of the  $N(^4S_u)$  atomic state based on orbitals optimized for a  $^4A$  reference [ $E = -54.521\,480\,(-54.525\,51)\,E_h$ ] and on orbitals optimized for a  $^6A$  reference [ $E = -54.519\,195\,(-54.528\,06)\,E_h$ ]. In the molecular BNB case, the energy loss is  $\sim 4\,mE_h$ .

<sup>33</sup>It is well known that the HF equations being nonlinear admit many solutions for the same nuclear configuration. It is indeed possible to find a symmetry adapted (SA) solution for the  $\tilde{X}^2\Sigma_u^+$  BNB state at the RHF level of theory;  $E_{RHF}^{(SA)} = -103.704\,892\,E_h$  with  $r_{B_1N} = r_{B_2N} = 1.3013\,\text{\AA}$  and positive harmonic frequencies  $\omega(ss)/\omega(as)/\omega(b) = 1270/2178/9\,\text{cm}^{-1}$ , while for the symmetry broken (SB)  $\tilde{X}^2\Sigma^+$  structure  $E_{RHF}^{(SB)} = -103.742\,274\,E_h$  with  $r_{B_1N} = 1.2470\,\text{\AA}$ ,  $r_{B_2N} = 1.3669\,\text{\AA}$  and positive harmonic frequencies  $\omega(ss)/\omega(as)/\omega(b) = 1190/2060/178\,\text{cm}^{-1}$ . A geometry optimization at the CISD, CISD + Q, ACPF, and RCCSD(T) levels of theory based on either the SA or SB RHF solutions give a  $D_{\infty h}$  or a  $C_{\infty v}$  structure, respectively. A one state CASSCF wavefunction is practically always localized on a SB structure while a two state SACASSCF averages the two mirror related SB structures and sorts out solutions of  $u/g$  symmetry. The different results ( $D_{\infty h}$  or  $C_{\infty v}$ ) obtained above by the same computational methods are mainly due to the initial asymmetrical geometry considered for the geometry optimization. When  $\Delta r = 0.1$  bohr, the final optimized geometry was of  $D_{\infty h}$  character while when  $\Delta r = 0.3$  bohr, the solution obtained was of  $C_{\infty v}$  nature. That explains the disagreement between the MRCI results in Refs. 14 and 17.

<sup>34</sup>It is interesting to notice that in Ref. 17 the barrier  $\Delta E(D_{\infty h} \leftarrow C_{\infty v})$  diminishes when the level of the correlation treatment increases. By extrapolating their results, they may even obtain a zero barrier, i.e., no SB. By ameliorating the quality of the wavefunction, they partly restore the permutational symmetry.

<sup>35</sup>A resonating CC wavefunction would eliminate the spurious double minimum, see, e.g., S. Yamanaka, S. Nishihara, K. Nakata, Y. Yonezawa, M. Okumura, T. Takada, H. Nakamura, and K. Yamaguchi, *Int. J. Quantum Chem.* **109**, 3811 (2009).

<sup>36</sup>Towards that direction is the interesting work described in G. E. Scuseria, C. A. Jiménez-Hoyos, T. M. Henderson, K. Samanta, and J. K. Ellis, *J. Chem. Phys.* **135**, 124108 (2011), where they deliberately break any kind of symmetry and then by applying all suitable projection operators they restore it piece by piece.

<sup>37</sup>A mathematically sound proof is given in E. H. Lieb and B. Simon, *J. Chem. Phys.* **61**, 735 (1974). To the best of our knowledge, the imposition of symmetry and equivalence restrictions to the HF orbitals is described for the first time in R. K. Nesbet, *Proc. R. Soc. London, Ser. A* **230**, 312 (1955); see also *Rev. Mod. Phys.* **33**, 28 (1961).

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