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Revisiting the symmetry breaking in the $\tilde{X}^2\Sigma_u^+$ state of BNB

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In agreement with our previous work [A. Kalamos, J. Chem. Phys. **138**, 224302 (2013)], we established the centrosymmetric nature of the ground BNB state by means of the Restricted Coupled Cluster Singles and Doubles + Perturbative Triples (RCCSD(T)) computational method. We have also studied the symmetry adapted or broken behavior at the Configuration Interaction Singles and Doubles (CISD), CISD + Davidson Correction (CISD + Q), and RCCSD(T) computational levels based on various solutions of the Restricted Hartree-Fock (RHF) equations. Our theoretical conclusions are in agreement with the experimental results concerning the structure of the titled species. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4954061>]

I. INTRODUCTION

The Hartree-Fock (HF) orbital theory is the very first and simplest *ab initio* method employed for the study of the electronic structure of an n -electron system. It consists of finding the optimum single determinant wavefunction $\Phi_{\text{HF}} = \det(\chi_1\chi_2 \cdots \chi_n)$ by variation of its constituent one electron functions χ_k , known as spin-orbitals, that minimizes the energy functional $E[\Phi] = \langle \Phi | H | \Phi \rangle$. In case the spin-orbitals are allowed to exist in a superposition of spin-up and -down positions (the spin quantization axis can be freely rotated) and have complex spatial parts, the resulting Euler-Lagrange equations are known as the Generalized Hartree-Fock (GHF) equations. This method delivers spin and spatial symmetry broken (sb) solutions within the independent particle model, or in other words, the antisymmetrized product of the GHF spin-orbitals does not display the symmetries of the Hamiltonian used in the variational process and therefore it cannot be tagged by any good quantum number.

For reasons of both practical/computational convenience and aesthetics, several constraints are placed on the spin-orbitals that can only raise the energy in contrary to the spirit of the variational process. Under these circumstances, a stationary point in the constrained space may still be a local minimum or not, while the eventuality of bifurcations, *i.e.*, double wells in the vicinity of the constrained stationary solutions, may even arise. A stability analysis of these constrained HF solutions, or in other words the study of their second order variations pioneered by Thouless¹ and Adams,² is certainly in order. It is unambiguously clear though that within the premises of a single determinant wavefunction we cannot simultaneously insist on a true unconstrained variational minimum that also satisfies the exact symmetries. We are then faced with a symmetry dilemma first pointed out by Löwdin.³ It is legitimate though to ask for an obedience of the spatial and spin symmetries by our zeroth order wavefunction since

their restoration in a post HF treatment may be impossible. There are two ways to proceed.

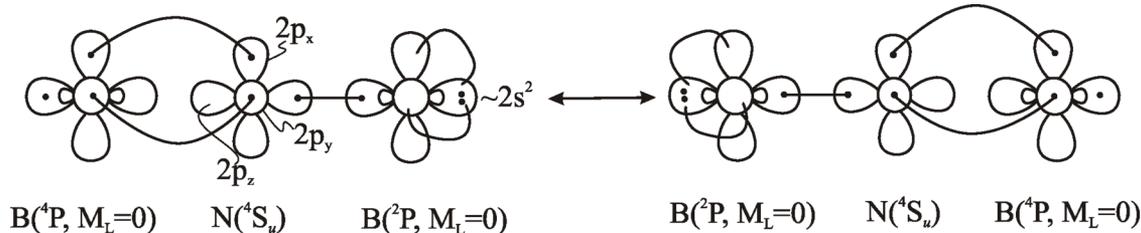
Within the single determinant approximation, this can only be achieved by placing constraints on the spin-orbitals conveying pathological characteristics improper to the HF model as a model of electronic structure theory. Generally speaking, the spin-orbitals are constrained to transform as the irreducible representations of the point group symmetry of the system (symmetry and equivalence restrictions) and/or the total wavefunction is supposed to be a spin eigenfunction and/or the spin-orbitals are eigenfunctions of s^2 and s_3 . In the case of absence of magnetic interactions or when there is no interest in spin dynamics, the spin and spatial degrees of freedom are rigorously separable and the spin-orbitals are eigenfunctions of s_3 . The spin symmetry constraint forces the doubly occupancy in closed shell cases (RHF) and doubly/singly occupancy in high spin open shell cases (ROHF). The doubly occupancy restricts the number of spin functions that can come into play and makes the operational character of the permutation operator ineffective.⁴ Relaxing this latter constraint (UHF) even in the simplest case of the ground He (1S) state shows that the RHF wavefunction possesses a saddle point character⁵ while the spatial orbitals acquire additional degrees of freedom and polarize; they are no longer eigenfunctions of l^2 . The use of two rather one radial orbitals gives much better results and the variational process sorts out orbitals differing considerably from each other.⁶ Although polarization/hybridization of atomic orbitals in a field free space sounds heretical, it is nevertheless theoretically sound due to the existence of an additional constant of motion known as the Laplace-Runge-Lenz vector.⁷ Similar results are obtained in the case of the isoelectronic H_2 system. Beyond the Coulson-Fischer point, the RHF wavefunction is unstable and the spatial orbitals tend to localize around their parental nuclear centers. Liberating the HF wavefunction from all spatial symmetry constraints with all their problematic effects, we obtain "sb" solutions and at the same time we are faced with the symmetry dilemma problem.

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A second way to solve the above problem is through projection operators.⁸ The variational optimization of the spin projected UHF wavefunctions leads to the so called Generalized Valence Bond (GVB) or Spin Coupled (SC) equations. Practical evidence accumulated during the years shows that the obtained orbitals are of semilocalized nature in contrary to the incisively attractive conviction that the atomic or molecular orbitals should be symmetry orbitals and therefore delocalized.

The instabilities of restricted HF schemes are often associated with departures from a high symmetrical nuclear arrangement in polyatomic molecules but extreme care should be exercised in order to distinguish between a real and an artifactual symmetry breaking.⁹ We should not forget though that within the clamped nuclei approximation the internal nuclear coordinates are just parameters whose numerical value small (around the equilibrium configuration) or large (close to the dissociation limit), should be immaterial to the choice of the zeroth order wavefunction.¹⁰ In other words, we should not consider a wavefunction of limited flexibility just because it describes adequately well the equilibrium region. In this respect, an instability problem of any constrained HF scheme is a logical outcome of its restricted form and it should not be considered more seriously than that.

One of the most notorious problems in the “sb” literature is the $\tilde{X}^2\Sigma_u^+$ BNB state that is believed to exhibit a $C_{\infty v}$ equilibrium configuration as a result of a pseudo Jahn–Teller interaction with its first excited $\tilde{A}^2\Sigma_g^+$ state along the antisymmetric stretching (as) coordinate. A complete and critically presented account of the existing experimental and theoretical literature can be found in our earlier work.¹¹ The latest work on the “sb” problem in BNB following Ref. 11(b) is by Liu *et al.*¹² These authors established a small barrier to the centrosymmetric configuration of $\Delta E(D_{\infty h} \leftarrow C_{\infty v}) = 29 \text{ cm}^{-1}$ at the multireference configuration interaction + Davidson correction (MRCI + Q)/cc – pVTZ level of theory. By claiming the inappropriateness of the MRCI method, due to its lack of size extensivity, they relied upon an empirical correction such as



A carefully constructed CASSCF wavefunction resulting from the distribution of 9 e⁻ to 11 orbitals [= (2s + 2p)_B × 2 + (2p)_N] and state averaging the first two roots of $^2\Sigma_{(u/g)}^+$ symmetry results in a $D_{\infty h}$ minimum; this can be viewed as spatially projecting the two “sb” CASSCF wavefunctions (see Table I of Ref. 11(b)). We have presently tested the stability of the $D_{\infty h}$ minimum at the SACASSCF level by constructing part of the potential energy surface along the “as” × “s” coordinates (*i.e.*, computing the energy at $\Delta r = r(\text{BN}_1) - r(\text{BN}_2)$ for various values of $r(\text{BN}_1) = r(\text{BN}_2)$).

the +Q and the multireference analog of the averaged quadratic coupled cluster (AQCC) method to establish a disputed and a rather elusive barrier of such a small value.

We have recently detailed (see Ref. 11(b)) a solution to the “sb” problem following the projection operator route at the multireference correlation level. In that study, we have shown that the problem is caused by the distribution of the $N(\sim 2s^2)$ electrons in the usually chosen active space composed of the valence 2s and 2p B and N orbitals; see the first four entries of Table I in Ref. 11(b). By a carefully constructed active space, we have succeeded in both correlating the $N(\sim 2s^2)$ electrons and obtaining a “s” solution featuring a $D_{\infty h}$ minimum.

Presently we adhere to the same computational strategy but at the single reference zeroth order level. We have managed to obtain a “s” solution of the RHF equations not by imposing symmetry constraints but by mimicking the state average procedure previously employed^{11(b)} (*vide infra*). Single and double excitations out of the RHF(s) wavefunction resulted in symmetric solutions with a $D_{\infty h}$ minimum, see also Ref. 33 in Ref. 11(b). In both single- and multi-reference levels, we have successfully simulated the nonorthogonal post HF computational schemes used in similar cases and with much less computational effort.¹³

II. RESULTS AND DISCUSSION

For both atoms, the Dunning¹⁴ correlation consistent polarized valence of quadruple and quintuple cardinality (cc-pV(Q or 5)Z) has been employed in conjunction with the HF, CASSCF, CISD, CISD + Q, and RCCSD(T) methods as implemented in the MOLPRO 2012.1 suite of programs.¹⁵ All calculations have been done under C_1 symmetry.

In our previous work,^{11(b)} we analyzed in great detail the source of the “sb” problem at the multireference level and proposed a step by step approach to its solution. The $\tilde{X}^2\Sigma_u^+$ BNB state can be pictorially (vbL scheme) viewed as the combination of two symmetry broken HF solutions, *i.e.*,

There is no sign of bifurcation in the vicinity of the $D_{\infty h}$ minimum. The “sb” problem at the CASSCF level appears when the $\sim(2s^2)_N$ electron pair enters in the above active space which is ill defined for its GVB type (local type) correlation; see Ref. 11(b) for details.

A RHF wavefunction can converge to either a “sb” solution (RHF(sb)), that is exhibiting a $C_{\infty v}$ character at a $D_{\infty h}$ nuclear arrangement, pictorially represented by one of the two resonating vbL structures, or to a “s” solution (RHF(s)) that exhibits a $D_{\infty h}$ character at a $D_{\infty h}$ nuclear

structure, pictorially represented by the resonance of both vBL schemes. If we consider the HF solution of one or the other “sb” structures, then all doubly occupied orbitals are slightly asymmetric while the singly occupied orbital is highly localized to one or the other end. Let us call these HF solutions $\Phi_L(\text{sb})$ (the singly occupied electron is localized on the left B atom) and $\Phi_R(\text{sb})$ (the singly occupied electron is localized on the right B atom). Then the linear combination of these two “sb” HF wavefunctions will give rise to the HF description of the ${}^2\Sigma_u^+/{}^2\Sigma_g^+$ states. The converged “s” HF wavefunction is composed of SCF optimized orbitals that can be viewed as the average of the “sb” orbitals; see Figure 1. This HF solution should be considered *per se* and in any post HF treatment since it respects the point group symmetry at any nuclear configuration without imposing any symmetry constraints or by performing block diagonalization.

We have optimized the geometry at the CISD, CISD + Q, and RCCSD(T) computational levels based on both the RHF(sb) and RHF(s) solutions; see Table I and Figure 2. All curves tagged “sb” in Figure 2 are based on the “sb” RHF wavefunction and these offer a graphical representation of Löwdin’s symmetry dilemma problem. The slope of all these curves is not zero at $\Delta r = 0.0$ bohr attesting to the noncentrosymmetric character, or in other words the solutions are symmetry broken. Also, their potential minima are of $C_{\infty v}$ character; see also Table I. On the contrary, a post RHF(s) correlation scheme generates not only symmetric solutions at the centrosymmetric structures but also leads to

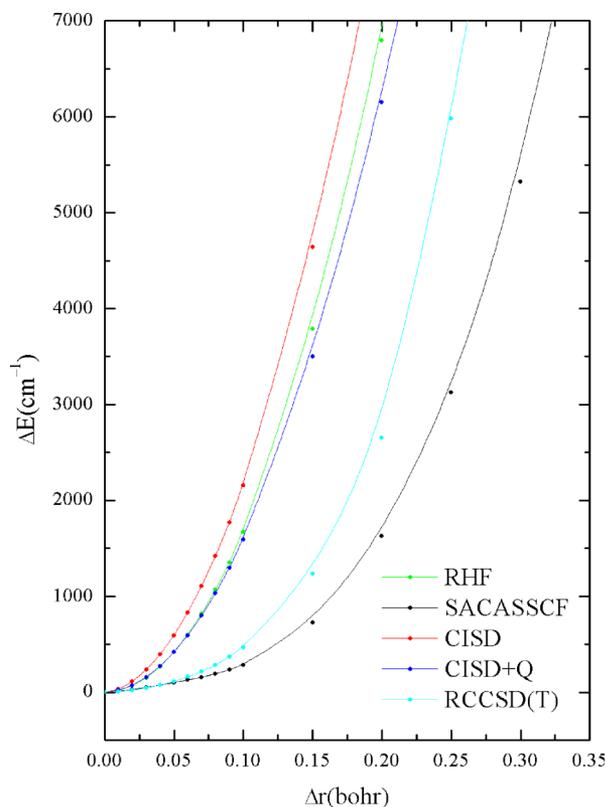


FIG. 1. Potential energy curves along the asymmetric coordinate $\Delta r (=r_1 - r_2)$ at the RHF(s), SACASSCF, CISD(s), CISD+Q(s), and RCCSD(T)(s) computational levels (cc-pVQZ). The zero of energy corresponds to the equilibrium $D_{\infty h}$ geometry at each computational level.

TABLE I. Energy (E_h) and internuclear equilibrium distances $r_{e1}(\text{NB}_1)$ and $r_{e2}(\text{NB}_2)$ (Å) of the $\tilde{X}^2\Sigma_u^+$ BNB state at the RHF (“sb” and “s”), CISD (“sb” and “s”), CISD+Q (“sb” and “s”), and RCCSD(T) (“sb” and “s”)/cc-pVQZ levels of theory.

Method	-E	$r_{e1}(\text{NB}_1)$	$r_{e2}(\text{NB}_2)$
RHF(sb)	103.749 199	1.245 0	1.364 2
CISD(sb) ^a	104.072 873	1.255 1	1.373 3
CISD+Q(sb) ^a	104.111 402	1.262 8	1.381 7
RCCSD(T)(sb) ^a	104.126 326	1.273 6	1.379 6
RCCSD(T)(sb) ^{a,b}	104.134 056	1.272 8	1.378 7
RHF(s)	103.711 655	1.298 9	1.298 9
CISD(s) ^c	104.059 338	1.308 1	1.308 1
CISD+Q(s) ^c	104.107 468	1.316 5	1.316 5
RCCSD(T)(s) ^c	104.127 112	1.322 6	1.322 6
RCCSD(T)(s) ^{c,b}	104.134 844	1.321 8	1.321 8
Expt. ^d		1.31241(10)	1.31241(10)

^aCorrelation treatment based on the RHF(sb) wavefunction.

^bResults obtained with the cc-pV5Z basis set.

^cCorrelation treatment based on the RHF(s) wavefunction.

^dReference 16, the reported value refers to r_0 .

$D_{\infty h}$ equilibrium geometries; see Table I and Figure 2. As can be seen in Table I, the global minimum at both the RCCSD(T)/cc-pV(Q and 5)Z levels is of centrosymmetric nature and lies lower than the $C_{\infty v}$ one by 173 cm^{-1} while the geometrical characteristics are in agreement with the experimental results.¹⁶ We have also tested the stability of

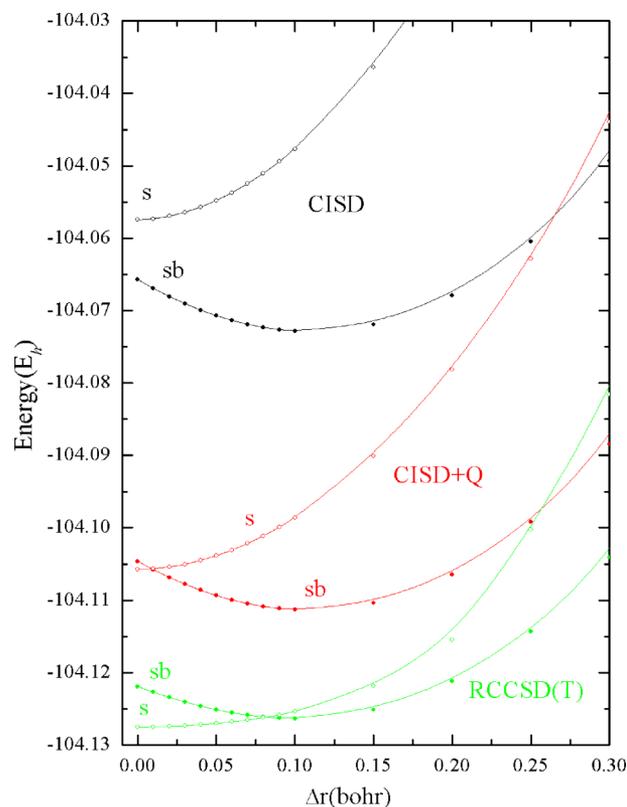


FIG. 2. Potential energy curves along the asymmetric coordinate $\Delta r (=r_1 - r_2)$ at the CISD(s and sb), CISD+Q(s and sb), and RCCSD(T)(s and sb) computational levels (cc-pVQZ). Each curve contains the lowest energy point either of “s” or “sb” character.

the centrosymmetric minimum by computing the RCCSD(T) (based on the RHF(s) orbitals) potential energy surface along the “as” \times “s” coordinates and found no evidence of bifurcations in the vicinity of the minimum.

The essential difference between the current and our previous study lies on the point we decide to differentiate the spatial part of the $N(\sim 2s^2)$ electrons. In Ref. 11(b), we accomplished that at the zeroth order CASSCF level while in the present case at the post HF correlated level. In either case, delicate care should be exercised for the correct description of all valence electrons and in particular for the $N(\sim 2s^2)$ ones.

At this point, we should compare our results to the reduced multireference (RMR) CC results by Li and Paldus.¹⁷ In Table I of their study, they show CCSD(T), 2R-, and 4R-RMR-CCSD(T) data based on different choices of RHF orbitals obtained with a STO-3G basis set. In our previous work,^{11(b)} we have extensively discussed the pitfalls of the STO-3G basis set, it is largely deficient for the description of both the ground (2P) and first excited (4P) B states necessary for the formation of the ground BNB state. They then employed the 2R-RMR-CCSD(T) method based on the RHF orbitals of the closed shell cationic species BNB^+ that change smoothly from symmetric to asymmetric geometries. Their decision was based on the better agreement between the 2R-RMR-CCSD(T)/STO-3G and FCI/STO-3G results. Although the cationic system (BNB^+) is perfectly symmetric and insensitive to the “sb” problem, it is a two configuration problem (with coefficients of ~ 0.73 and ~ -0.58) and at some regions of the “as” coordinate even more configurations are needed. This means that there is not a single configuration that describes it adequately well.¹⁸ It is interesting to mention though that the CCSD(T) results based on the ROHF(s)/STO-3G orbitals show the smallest barrier between the $C_{\infty v}$ and $D_{\infty h}$ structures; just $0.71 mE_h$ in contrast to $1.85 mE_h$ at the 2R-RMR-CCSD(T)/QRHF(BNB^+) level. Had they used a more flexible basis set this barrier would be nonexistent and their results would be similar to ours. As presently shown, just a single reference CCSD(T) wavefunction is enough to capture correctly the physics of the BNB problem if based on RHF(s) orbitals.¹⁹

In Ref. 12, the authors obtained a very small barrier of 6.93 (1R-MRCI+Q), 12.78 (2R-MRAQCC), and 29.19 (2R-MRCI+Q) cm^{-1} . Claiming the size nonextensivity of the MRCI they employed the empirical Davidson correction and the multireference modification of the AQCC method instead of relying on the most robust CCSD(T) method for such a tiny quantity. Additionally the CC method obtains a barrier of at least three times bigger ($\sim 100 \text{ cm}^{-1}$,¹⁷ $\sim 140 \text{ cm}^{-1}$,²⁰ and 161 cm^{-1} ²¹) and this is rather incompatible with their results ($\sim 29 \text{ cm}^{-1}$) and the nature of their motivation to obtain a size extensive result.

III. CONCLUSIONS

In a symmetry breaking problem, we have to include all necessary structures in order to restore the symmetry of either spatial and/or spin nature and this is usually accomplished

when we go beyond the single determinant approximation. At the multireference level, extreme caution is needed with regard to the choice of the active space after a careful inspection of the physics entailed in the particular problem. Depending on the nature of the species, it may arise that the problem can even be solved at the single reference level through a computational strategy that should closely follow the essence of nonorthogonal post HF schemes.

¹D. J. Thouless, *Nucl. Phys.* **21**, 225 (1960).

²W. H. Adams, *Phys. Rev.* **127**, 1650 (1962).

³P.-O. Löwdin, *Rev. Mod. Phys.* **35**, 496 (1963).

⁴Let us consider, for example, the Li atom in its ground 2S state. For a three electron system, there are two linearly independent spin functions $\Theta_1 = 1/\sqrt{2}[a(1)\beta(2) - \beta(1)a(2)]a(3)$ and $\Theta_2 = 1/\sqrt{6}[2a(1)a(2)\beta(3) - a(1)\beta(2)a(3) - \beta(1)a(2)a(3)]$. It is obvious that only Θ_1 can be coupled to the spatial part $1s1s2s$. Although the antisymmetrizer generates all spin functions, the operational character of the permutation operator is lost since permuting two identical particles placed in the same spatial orbital has no physical meaning. Moreover, the spin eigenfunctions Θ_1 and Θ_2 have nonvariational coefficients in the RHF wavefunction but those dictated by the symmetric group.

⁵C. A. Coulson, *Quantum Theory of Atoms, Molecules and the Solid State* (Academic Press, NY, 1966).

⁶W. Heisenberg, *Z. Phys.* **38**, 411 (1926); E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929); C. Eckart, *Phys. Rev.* **36**, 878 (1930).

⁷E. Schrödinger, *Ann. Phys.* **80**, 437 (1926).

⁸P.-O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).

⁹E. R. Davidson and W. T. Borden, *J. Phys. Chem.* **87**, 4783 (1983).

¹⁰The simplest example is the H_2 problem. At infinity the σ_g^2 and σ_u^2 electronic configurations are degenerate so according to perturbation theory both should be considered which leads us to the Coulson-Fischer wavefunction. Once the second configuration is needed (σ_u^2) it should be present at all nuclear configurations. This small (2×2) MCSCF wavefunction is a variationally optimized spin projected UHF. What it actually does is to place the two electrons in different spatial orbitals so that their permutation operator becomes effectively operational. See also, A. C. Hurley, J. Lennard-Jones, and J. A. Pople, *Proc. R. Soc. London, Ser. A* **220**, 446 (1953) for a MCSCF transcription of a GVB wavefunction.

¹¹(a) A. Kalemos, T. H. Dunning, Jr., and A. Mavridis, *J. Chem. Phys.* **120**, 1813 (2004); (b) A. Kalemos, *ibid.* **138**, 224302 (2013).

¹²Y. Liu, W. Zou, and I. B. Bersuker, *Chem. Phys. Lett.* **603**, 18 (2014).

¹³P. Y. Ayala and H. B. Schlegel, *J. Chem. Phys.* **108**, 7560 (1998).

¹⁴T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).

¹⁵H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györfy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O'Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and M. Wang, *MOLPRO 2012.1*, a package of *ab initio* programs, 2012, see <http://www.molpro.net>.

¹⁶H. Ding, M. D. Morse, C. Apetrei, L. Chacaga, and J. P. Maier, *J. Chem. Phys.* **125**, 194315 (2006).

¹⁷X. Li and J. Paldus, *J. Chem. Phys.* **126**, 224304 (2007).

¹⁸In Ref. 17, we read “The energy differences in Table I indicate that the (2R) RMR CCSD(T) method employing QRHF(+) MOs gives the closest result to FCI, even though it slightly underestimates the SB effects. The reason for a better performance of the QRHF(+) MOs relative to the QRHF(-) ones is the weaker MR character in the former case. We will thus employ the QRHF(+) MOs in our subsequent calculations.”

¹⁹The adopted computational strategy is reminiscent of the resonating coupled cluster CI method, see e.g., S. Yamanaka, S. Nishihara, K. Nakata, Y. Yanezawa, M. Okumura, T. Takada, H. Nakamura, and K. Yamaguchi, *Int. J. Quantum Chem.* **109**, 3811 (2009).

²⁰J. F. Stanton, *J. Chem. Phys.* **133**, 174309 (2010).

²¹S. R. Gwaltney and M. Head-Gordon, *Phys. Chem. Chem. Phys.* **3**, 4495 (2001).