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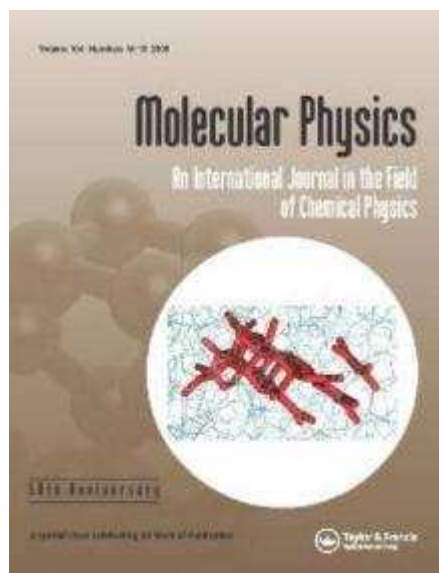
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Dissociating N₂: A multi-reference coupled cluster study on the potential energy surfaces of ground and excited states

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(Dated: December 2, 2008)

This article reports on the calculation of 12 low lying states of the nitrogen molecule along its dissociation using the multi-reference exponential wavefunction ansatz [J. Chem. Phys. **123** (2005) 84102], the single-reference formalism multi-reference coupled cluster [J. Chem. Phys. **94** (1991) 1229], and MRCI methods. Energies relative to full CI are given. The results show the multi-reference coupled cluster approaches generally applicable to very demanding problems at high accuracy. In comparison to MRCI both coupled cluster type approaches do not reproduce spatial symmetry exactly. Nevertheless, this error in the degeneracy is much less than the overall error of the MRCI calculations.

I. INTRODUCTION

The dissociation of N₂ along its potential energy surface (PES) is one of the most demanding problems in quantum chemistry since it requires a balanced treatment of dynamical and static correlation effects. All 3 *p*-electrons from each nitrogen are involved during the formation of its triple bond, giving rise to 6 active electrons in 2×3 *p* orbitals. Performing the calculations in the abelian subgroup D_{2h} of D_{∞h} the active space contains up to 56 determinants. While the X¹Σ_g⁺ ground state is essentially of single-reference character at the equilibrium geometry it becomes a linear combination of 44 determinants when assembling two atomic ⁴S states during dissociation. The excited states are most often of (modest) multi-determinantal structure already at equilibrium geometry and similarly to the ground state, they spread out into many determinants upon dissociation. Due to this difficulty the dissociation of N₂ has been used in the literature as a test system to benchmark multi-reference (MR) approaches.

Besides the numerical accuracy of the correlation energy with respect to full CI, N₂ offers several spatial and spin symmetry related properties that can be checked for. A good approximation method should, of course, conserve as many symmetry and other rigorous properties of the exact wavefunction as possible.

In the past the majority of calculations on N₂ were made with MRCI and CASPT2 methods [1–5]. However, N₂ should be a suitable test case for multi-reference coupled cluster (MRCC) methods. After the invention of the single-reference (SR) coupled cluster (CC) methods [6–9] there has been substantial research on the development of MRCC methods. Unfortunately, this task is by no means trivial and still unfinished. Up to now no MRCC approach having all the beautiful theoretical properties (e.g. size extensivity/connectivity) of the single-reference ansatz has been reported. Size extensivity of a method is

a necessary condition for an efficient calculation of the correlation energy of many-body systems.

In order to put some structure to the large number of MRCC type approaches they may be divided into several categories. The first category contains the so-called genuine multi-reference approaches which are the valence universal (Fock space, FSMRCC) [10–14] and state universal (Hilbert space, SUMRCC) [15–20] ansätze. Both approaches employ the Bloch equation and suffer (in their original formulation) from various limitations. The second category relies on further developments of the either the FSMRCC or SUMRCC approaches. Among the FSMRCC based approaches are the intermediate Hamiltonian IM-FSMRCC [21, 22] and the related EOM-CC [23–25] and ST-EOM-CC [26, 27] approaches. Among the SUMRCC based approaches there are general model space (GMS) SUMRCC approaches [28, 29], a state specific variant (MkMRCC) [30, 31] of the SUMRCC, Brillouin-Wigner based ansätze (BWMRCC) [32–35], and the multi-reference exponential (MR-expT) ansatz [36, 37]. Another category is not based on the SUMRCC or FSMRCC approaches but relies on extensions of the single-reference ansatz. Among these are the CC linear response approach [38, 39], the single-reference formalism based ansatz (SRMRCC) [40, 41], later variants [42–45] and related methods [46, 47]. Additionally, there are renormalized [48] and method of moment [49, 50] coupled cluster methods as well as dressed configuration interaction (CI) based ansätze [51–53], reduced MRCC [54, 55] and partially linearized reduced MRCC approaches [56, 57].

In the following we shall give a short (necessarily incomplete) history of quantum chemical calculations on N₂ with a focus on coupled cluster calculations. Among the first calculations on N₂ is the CISD calculation of Langhoff *et al.* [58] (1974) at the equilibrium distance. Later, there have been full CI calculations [59] and full CI and coupled cluster studies (FCI, CCS, CC2, CCSD, CC3, CCSDT) [60, 61]. More recently CCSDTQ5 results [62, 63], CCSDTQ6 results [64] and investigations of quadruple excitation approximations [65] have been published. Additionally, there are locally renormalized CCSD(T) [66], CI tailored CC [67] and method

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of moment CC calculations [68]. Recently Lyakh *et al.* [69] published CASCCSD calculations on the ground state PES of N₂. Several groups published FSMRCC [70, 70, 71], SUMRCC [72], GMS SUMRCC [73], and IM-FSMRCC [74] calculations. Based on the reduced MRCC approach [54] several calculations on N₂ [73, 75–77] were published. Very recently new results for the ground state potential surface were published [78].

However, to our best knowledge there has been no multi-reference coupled cluster study including the ground state and 11 low lying excited states along the PES simultaneously.

This study reports on correlation energy errors of spin-orbital based (i. e. not CSF based) multi-reference configuration interaction (SOMRCI), SRMRCC [40, 41], and MRexpT [36, 37] calculations for the N₂ PES including the ground state and a number of excited states. The paper is arranged into the following sections: In section II. we discuss the basic ideas of the SRMRCC and MRexpT multi-reference coupled cluster ansätze. Section III. describes the calculation parameters and procedures as well as the properties and difficulties arising in the course of the computation. Section IV. reports on the correlation energy errors and spatial degeneracy properties.

II. MREXP T AND SRMRCC ANSÄTZE

The single-reference based ansatz (SRMRCC) of Oliphant *et al.* [40] and Piecuch *et al.* [41] is given as

$$|\Psi_{\text{SRMRCC}}\rangle = e^{\hat{T}}|\mu_0\rangle \quad (1)$$

with $|\mu_0\rangle$ the Fermi vacuum and \hat{T} chosen to span the MRCI space according to

$$(1 + \hat{T})|\mu_0\rangle \sim |\Psi_{\text{MRCI}}\rangle \quad (2)$$

with “ \sim ” meaning spanning. Actually, SRMRCC is a kind of extended single reference ansatz as Eq. (1) and Eq. (2) correspond to a single-reference coupled cluster ansatz (e.g. CCSD) with additional specific higher excitations in \hat{T} . Alternatively one may view it as a single-reference CCSD... n with certain excitations missing and $n = m + m_{\text{act}}$ (for a complete active space) with m the base excitation level (for CCSD it is $m = 2$) and m_{act} the number of active electrons in the reference space. Obviously, ansatz Eq. (1) breaks the symmetry of the wave function as it makes one reference μ_0 (the Fermi vacuum) particular. The later variants of the SRMRCC ansatz [42–45] do not solve this fundamental problem of the SRMRCC approach. Although usually of reasonable accuracy in terms of the correlation energy when using the dominant determinant as Fermi vacuum, SRMRCC has been shown to have difficulties in case of avoided crossings [79, 80], potential surfaces, and low-spin/high-spin degeneracies [36, 79].

SRMRCC inherits its size extensivity (connectivity) trivially from single-reference coupled cluster. In order to solve Eq. (1) for the amplitudes one inserts it into the Schrödinger equation, multiplies from the left by $e^{-\hat{T}}$, and projects onto $\langle\rho|$, with ρ element of the space spanned by $\hat{T}|\mu_0\rangle$ (e.g. a multi-reference singles doubles (MRSD) space *without* $|\mu_0\rangle$) yielding the residual equations

$$R_{\text{SRMRCC}}(\rho) = \langle\rho|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\mu_0\rangle. \quad (3)$$

Setting $R_{\text{SRMRCC}}(\rho) \stackrel{!}{=} 0$, $\forall\rho$ (with “ $\stackrel{!}{=}$ ” meaning the corresponding equality is imposed on the solution of the non-linear equation system) yields a non-linear equation system in t .

Recently Lyakh *et al.* [69] published CASCCSD calculations on the ground state PES of N₂. CASCCSD can be seen as a variant of the previously published SRMRCC approach [40]. Both rely on a single-reference Fermi vacuum and are not invariant to the choice of this vacuum. Most recently [81] the same authors tried to address the problem of symmetry breaking by a slight modification of CASCCSD they called XCASCCSD. By employing a symmetry adapted projection and symmetry adapting the t -amplitudes from their corresponding CI coefficients c they were able to improve the symmetry issues with CASCCSD. However, there are a few problems with this procedure. First of all using a truncated cluster operator (e.g. singles and doubles) it does not cure the symmetry breaking of the wavefunction as there is still one specific vacuum and the CI coefficient symmetrizing procedure has no effect on higher projection (product substitutions) levels. Another issue is the connectivity of the cluster amplitudes. Since SRMRCC and CASCCSD may be interpreted as special cases of the single-reference coupled cluster approach (SRCC) they inherit their connectivity from SRCC trivially. The proof of the cluster connectivity within SRCC relies on the projection of $e^{-\hat{T}}\hat{H}e^{\hat{T}}|\mu_0\rangle$ onto substituted determinants. Generating the cluster amplitudes by some other procedure (e.g. back-propagation from CI coefficients) will certainly not meet the connectivity property automatically and a special proof is to be given.

In contrast to SRMRCC [40, 41], MRexpT [36, 37], along with SUMRCC [15], MkmRCC [30, 31] and BWMRCC [33, 34], treats all references on the same footing. The wavefunction of MRexpT is given by

$$|\Psi\rangle = \sum_{\mu} e^{\hat{T}_{\mu}} c_{\mu} |\mu\rangle \quad (4)$$

with

$$\hat{T}_{\mu} = \phi(c_{\mu}) \sum_{\hat{\tau}_{\mu,i} \in \mathbb{T}_{\mu}} t_{\hat{\tau}_{\mu,i}|\mu} \hat{\tau}_{\mu,i} \quad (5)$$

with \mathbb{T}_{μ} the set of substitutions to be applied (e.g. singles and doubles) with respect to each reference $|\mu\rangle$ while excluding excitations from one reference to another. The

reference phase compensation factor $\phi(z)$ is given by $\phi(z) = e^{-i \arg z}$, $z \in \mathbb{C}$, and guarantees the potential completeness of the ansatz. It does not introduce a new variable. MRexpT is size consistent, core (i. e. inactive) connected, but not core-valence connected [82]. Therefore, MRexpT's accuracy may be expected to deteriorate in cases of large active spaces with many active electrons. From this perspective N_2 should be a very difficult test case for MRexpT.

Inserting Eq. (4) into the Schrödinger equation and projecting from the left onto $|\rho\rangle \in \bigcup_{\mu} \bigcup_{\hat{T}_{\mu,i} \in \mathbb{T}_{\mu}} \hat{T}_{\mu,i} |\mu\rangle \cup \bigcup_{\mu} |\mu\rangle$ (e.g. a multi-reference singles doubles (MRSD) space including the references $|\mu\rangle$) we get the residual equations

$$R_{\text{MRexpT}}(\rho) = \sum_{\mu} c_{\mu} \langle \rho | (\hat{H} - E) e^{\hat{T}_{\mu}} \mu \rangle \quad (6)$$

with $R_{\text{MRexpT}}(\rho) \stackrel{!}{=} 0$, \forall_{ρ} and $\sum_{\mu} |c_{\mu}|^2 = 1$ imposed yielding an equation system non-linear in t while linear in c .

The norm r_X , $X \in \{\text{SRMRCC}, \text{MRexpT}\}$ of the residuals Eq. (3) and Eq. (6) serves as a measure for convergence of the solution of the equation systems and is given as

$$r_X = \sqrt{\sum_{\rho} |R_X(\rho)|^2}. \quad (7)$$

If nothing else is stated all results are converged to a residual norm $r_X < 10^{-10}$.

III. CALCULATION DETAILS AND TECHNICALITIES

In the following we describe the main issues involved in the dissociation of N_2 and special characteristics of the calculation procedure employed in this article.

A. Basis set, orbital generation and reference space

In the calculations we used a 6-31G[83] [10s4p]/(3s2p) basis set. Since we wanted to employ the same orbitals for all states we decided to use $7\Sigma_u^+$ orbitals. Choosing the high spin component of the $7\Sigma_u^+$ state it is made up of a single determinant along the whole potential surface of N_2 . This allows for a more balanced treatment of the remaining states. Using MOLCAS [84] with an interface [85] we start from a 6-fold ionized N_2 cation allowing us to use a closed shell state while conserving the $D_{\infty h}$ symmetry among the orbitals. Those orbitals were fed into the RASSCF program of MOLCAS with the $1\sigma_g$, $2\sigma_g$ and $1\sigma_u$, $2\sigma_u$ inactive and 6 electrons in the $6(3\sigma_g, 1\pi_{ux}, 1\pi_{uy}, 3\sigma_u, 1\pi_{gx}, 1\pi_{gy})$ orbitals of the later SOMRCI and MRCC CAS space. Enforcing B_{1u} and septet state symmetry this actually corresponds to

R	N_2^{6+} SCF	$1^7\Sigma_u^+$ SCF	$X^1\Sigma_g^+$ FCI
1.5	-96.298 505	-106.245 291	-108.350 870
1.75	-97.545 227	-107.150 180	-108.849 522
2	-97.734 893	-107.639 325	-109.003 625
2.25	-98.376 313	-107.970 004	-109.013 599
2.5	-98.756 136	-108.226 199	-108.970 907
3	-99.284 824	-108.530 035	-108.870 370
3.5	-99.653 723	-108.665 398	-108.811 713
4	-99.935 011	-108.723 696	-108.791 925
4.5	-100.159 563	-108.747 964	-108.787 315
5	-100.343 670	-108.757 798	-108.786 287
7.5	-100.917 665	-108.764 118	-108.785 682
10	-101.213 222	-108.764 102	-108.785 588
20	-101.661 288	-108.764 102	-108.785 588
100	-102.021 159	-108.764 102	-108.785 588

TABLE I: Orbital generation: Ionized (symmetry conserving start guess) SCF, $1^7\Sigma_u^+$ SCF and $X^1\Sigma_g^+$ full CI energies in Hartree, [10s4p]/(3s2p) basis set, R in a. u.

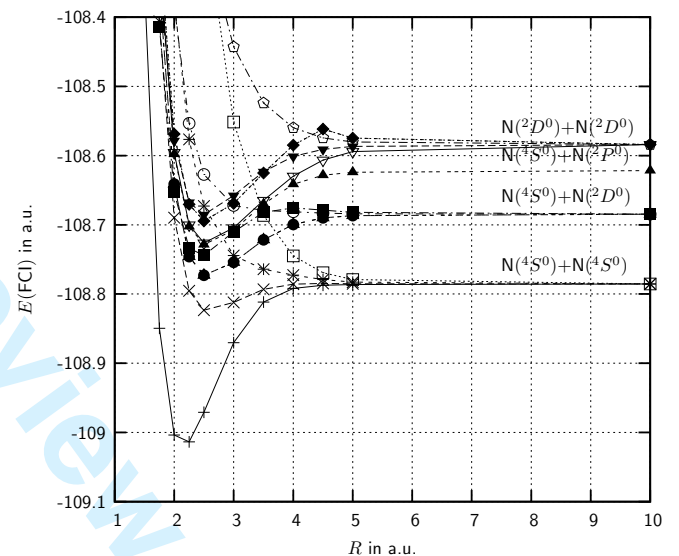


FIG. 1: N_2 : Potential energy surface calculated with Full CI, 6 electrons correlated using CAS($6e^-$, $3\sigma_g, 1\pi_{ux}, 1\pi_{uy}, 3\sigma_u, 1\pi_{gx}, 1\pi_{gy}$) and a [10s4p]/(3s2p) basis set.

a single determinant open shell SCF for the $7\Sigma_u^+$ state. After freezing the electrons in the $1\sigma_g$, $2\sigma_g$ and $1\sigma_u$, $2\sigma_u$ orbitals full CI calculations were carried out. The latter served as a reference for the succeeding MRCI and MRCC calculations. Table I shows the results of the ionized N_2^{6+} SCF, $1^7\Sigma_u^+$ SCF and $X^1\Sigma_g^+$ full CI calculations for reference.

$X^1\Sigma_g^+$ — —	$1^3\Delta_u(A_u)$ -- \triangle --
$1^3\Sigma_u^+$ -- \times --	$1^3\Sigma_u^-$ -- \blacktriangle --
$1^5\Sigma_g^+$ -- \ast --	$1^1\Sigma_u^-$ -- ∇ --
$1^7\Sigma_u^+$ -- \boxplus --	$1^1\Pi_g$ -- \blacktriangledown --
$1^3\Pi_g$ -- \blacksquare --	$1^1\Delta_u, 1^1\Gamma_u(B_{1u})$ -- \diamond --
$1^5\Pi_u$ -- \ominus --	$1^1\Delta_u, 1^1\Gamma_u(A_u)$ -- \blacklozenge --
$1^3\Delta_u(B_{1u})$ -- \bullet --	$2^1\Sigma_u^-$ -- \odot --

FIG. 2: N₂: Legend of state symbols.

B. Low lying states and potential energy surface of N₂

Figure 1 shows the full CI results for the states ($X^1\Sigma_g^+$, $1^3\Sigma_u^+$, $1^5\Sigma_g^+$, $1^7\Sigma_u^+$; $1^3\Pi_g$, $1^5\Pi_u$, $1^3\Delta_u$; $1^3\Sigma_u^-$; $1^1\Sigma_u^-$, $1^1\Pi_g$, $1^1\Gamma_u$, $2^1\Sigma_u^-$; $1^1\Delta_u$) and their corresponding atomic states for $R \rightarrow \infty$ ($N(^4S^0)+N(^4S^0)$; $N(^4S^0)+N(^2D^0)$; $N(^4S^0)+N(^2P^0)$; $N(^2D^0)+N(^2D^0)$) considered in this article. **Please note that the $1^1\Delta_u$ state dissociates to the $N(^2D^0)+N(^2P^0)$ channel which has not been considered explicitly in this work.** For clarity and efficiency we separated the state legend to figure 2. It holds for all plots (except the Δ , Γ -degeneracy plots).

At the correlated level all states in this study were calculated in their low-spin ($S_z = 0$) component leaving e.g. the $1^7\Sigma_u^+$ state with a single CSF made up from 20 determinants with 6 open shells. Table II shows the states, their mapping onto D_{2h} and the dominating determinants the states are made of. In particular the splitting of the Δ - and Γ -states onto the B_{1u} and A_u irrep of D_{2h} is given. There is a similar splitting of the $\Pi_{u/g}$ -states onto B_{2u} and B_{3u} as well as B_{2g} and B_{3g} .

In the last column of table II the dominating determinants for the considered states are given. In case of high degeneracy the latter choice may not be unique. In this case we started from the equilibrium and tried to stick to this determinant as long as possible. For the considered region of states for N₂ there is a crossing of the $1^1\Delta_u$ and $2^1\Sigma_u^-$ states at 4.3 Bohr. The $2^1\Sigma_u^-$ state changes its dominant determinant at about 3.5 Bohr. **Please note that for geometries $R \geq 4.5$ Bohr the $1^1\Delta_u$ state becomes a $1^1\Gamma_u$ state as shown in table II.** In order to analyze the spatial degeneracy in the $N(^2D^0)+N(^2D^0)$ dissociation channel, while leaving the number of states considered simultaneously limited, we switch to the $1^1\Gamma_u$ state and do not consider the $1^1\Delta_u$ state for $R \geq 4.5$. These state crossings have to be considered carefully while following the states.

C. Amplitude start guess generation

During early test calculations it turned out that targeting a certain state is a very delicate matter for the coupled cluster type methods and their large non-linear

State	D_{2h} irrep	Dominating determinant ^a
$X^1\Sigma_g^+$	A_g	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy}^2\rangle$
$1^3\Sigma_u^+$	B_{1u}	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gy}\rangle$
$1^5\Sigma_g^+$	A_g	$ \dots 3\sigma_g^2 \pi_{ux} \pi_{uy} \pi_{gx} \pi_{gy}\rangle$
$1^7\Sigma_u^+$	B_{1u}	$ \dots 3\sigma_g \pi_{ux} \pi_{uy} 3\sigma_u \pi_{gx} \pi_{gy}\rangle$
$1^3\Pi_g$	$B_{2g} (B_{3g})$	$ \dots 3\bar{\sigma}_g \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$
$1^5\Pi_u$	$B_{2u} (B_{3u})$	$ \dots 3\bar{\sigma}_g \pi_{ux}^2 \pi_{uy} \pi_{gx} \pi_{gy}\rangle$
$1^3\Delta_u$	B_{1u}	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gy}\rangle$
	A_u	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$
$1^3\Sigma_u^-$	A_u	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$
$1^1\Sigma_u^-$	A_u	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$
$1^1\Pi_g$	$B_{2g} (B_{3g})$	$ \dots 3\sigma_g \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$
$1^1\Gamma_u$ ^b	B_{1u}	$ \dots 3\sigma_g \pi_{ux} \pi_{uy} 3\sigma_u \bar{\pi}_{gx} \bar{\pi}_{gy}\rangle$
	A_u	$ \dots 3\sigma_g \pi_{ux}^2 3\sigma_u \bar{\pi}_{gx} \bar{\pi}_{gy}\rangle$
$2^1\Sigma_u^-$	A_u	$ \dots \pi_{ux} \pi_{uy} \pi_{gx} \pi_{gy}\rangle$ ^c
		$ \dots 3\sigma_g^2 \pi_{ux} \pi_{gx} \pi_{gy}\rangle$ ^d
$1^1\Delta_u$ ^e	B_{1u}	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gy}\rangle$
	A_u	$ \dots 3\sigma_g^2 \pi_{ux}^2 \pi_{uy} \pi_{gx}\rangle$

^acore orbitals $|1\sigma_g^2 2\sigma_g^2 1\sigma_u^2 2\sigma_u^2 \dots\rangle$

^b $R \geq 4.5$ bohr

^c $R < 3.5$ bohr

^d $R \geq 3.5$ bohr

^e $R < 4.5$ bohr

TABLE II: Dominant determinants of the individual states along potential surface aligned corresponding to the atomic dissociation channels

equation systems. Especially the solution of a non-linear equation system in the presence of degeneracy is rather difficult. Since we solve for a single state within one iteration cycle there is no simple way of selecting an "n-th" state. This is different for MRCI calculations. The latter usually employ some variant of the Davidson algorithm [86–90] which can handle several vectors simultaneously. The approximate eigenvectors within the Davidson algorithm are constructed as linear combinations from the projected (Krylov) space insuring the orthogonality of the vectors trivially. Additionally the calculation of the n-th eigenvector is a simple matter. Since there was no analogous tool at hand for simultaneously finding several solutions of a non-linear equation system (especially with degeneracy) we decided to **set up the following computational procedure**: 1. perform an MRCI calculation, 2. select the desired state and 3. propagate this MRCI state to the cluster amplitudes according to

$$\left. \begin{array}{l} \langle i | \Psi_{\text{MRexpT}} \rangle \\ \langle i | \Psi_{\text{SRMCC}} \rangle \end{array} \right\} \stackrel{!}{=} \langle i | \Psi_{\text{MRCI}} \rangle \quad (8)$$

with $\langle i |$ from the MRCI space. Solving Eq. (8) for SRM-RCC is rather straightforward according to $\hat{T}_1 = \hat{C}_1$, $\hat{T}_2 = \hat{C}_2 - \hat{T}_1^2$, and so on. For MRexpT, however, the solution of Eq. (8) becomes a non-linear equation system of its own. Consequently, before starting to solve the real coupled cluster equations a (simpler) non-linear equation system is solved in order to propagate the MRCI coefficients to coupled cluster amplitudes. This procedure usu-

ally proved to prepare starting amplitudes that allow the applied iteration scheme to securely lock onto a certain state. Although a simpler procedure is probably preferable for production type calculations this scheme served very well for the difficult N₂ calculations.

D. Initial reference space and removal of vanishing references

In order to get unbiased results all MRCI and MRCC calculations were carried out with the same CAS(6e⁻, 3σ_g 1π_{ux} 1π_{uy} 3σ_u 1π_{gx} 1π_{gy}) reference space for all states. For higher multiplicities determinants with too few open shells for the desired multiplicity were removed.

There is another reason for certain references to be removed. Considering Eq. (4) we see the exponentials of the cluster operators \hat{T}_μ to be weighted with the reference coefficient c_μ . This c_μ weighting originates from the wave operator formalism, that is $|\Psi\rangle = \hat{\Omega}|\Psi_0\rangle$ [15] with $|\Psi_0\rangle$ inherently carrying the reference weights. An analysis of the perturbative cluster amplitude expansion for MRexpT yields

$$t_{|\alpha\rangle} = \frac{A}{\sum_{\mu \in \mathbb{P}_\alpha} |c_\mu| (\epsilon_{|\mu\rangle} - \epsilon_{|\alpha\rangle})} \quad (9)$$

with \mathbb{P}_α containing those references from which a substituted determinant α may be generated, orbital energy differences $\epsilon_{|\mu\rangle} - \epsilon_{|\alpha\rangle}$, and some (for this discussion) irrelevant numerator A . Eq. (9) is explicitly derived and discussed elsewhere [82]. A similar expression to Eq. (9) holds for MkMRCC (cf. Eq. (27) of [31])

$$t_{|\alpha\rangle} = \frac{\dots + \sum_{\nu \neq \mu} \dots \cdot \frac{c_\nu}{c_\mu}}{E_0 - H_{\alpha\alpha}} \quad (10)$$

while SUMRCC and BWMRCC do not contain the c_μ weight in the denominator.

It may happen that a specific reference coefficient c_μ is nearly vanishing, causing amplitudes associated with any non vanishing determinant *solely* generated from this very reference to explode. This effect is quite different from the intruder state problem of the original SUMRCC since it is not related to a vanishing energy difference in the perturbative cluster amplitude expansion denominator but to a vanishing reference expansion coefficient. Therefore, it is less severe in the sense that it requires references to be removed which are (almost) useless anyway. "Almost" because their removal purges also all other determinants which were solely generated from this special reference. However, most of such determinants have a vanishing coefficient anyway and the effect on the energy is negligible.

In our implementation we remove references with coefficients below 10⁻¹² and substituted determinants if their summed reference weight $\sum_{\mu \in \mathbb{P}_\alpha} |c_\mu|$ is below 10⁻⁴ while their coefficient in the MRCI expansion is larger than 10⁻⁴. We monitor the effect of this truncation at MRCI

level. It turns out that the truncation error associated with the removal of vanishing references (and dependent substituted determinants) is usually a fraction of a μE_H with very few values of about $2\mu E_H$ for $R = 10$ Bohr. Slight variations of the truncation scheme show the MRexpT energies to vary at about the same size as the MRCI energies and we can rule out any effect of the truncation scheme to degeneracy properties.

Probably the issue with vanishing reference coefficients has been detected for the first time seriously with N₂ because of its high symmetry and large reference space. We would like to point out that we assume this kind of problem to appear also for the MkMRCC ansatz [30, 31]. Currently we are not aware of calculations in the literature regarding this method involving a reference space of comparable size and a symmetry of comparable degree simultaneously. However, in contrast to the intruder state problem of SUMRCC these problems can be removed easily in the above described manner without any substantial effect on the accuracy.

E. Reference CSF expansion for MRexpT

Approaching the dissociation limit ($R \rightarrow \infty$) we end up with two separated atomic systems carrying very many degeneracies. Actually, there are many more dissociation channels ending in atomic states than shown in figure 1. One source of degeneracy is the spin coupling. Consider for example the pair of ⁴S⁰ states of the nitrogen atom. Since the two atoms do not interact we may couple the total spin of the whole system to singlet, triplet, quintet and septet multiplicity without changing the total energy or the individual quartet multiplet (apart from S_z) on a single nitrogen atom. Due to this high degeneracy we were at first not able to converge these states to a residual norm of less than 10⁻¹⁰ for the MRexpT ansatz. An analysis of the iteration history in these cases shows the reference coefficients and amplitudes ("eigenvectors") to freely rotate between the degenerate states. After introducing a CSF based expansion of the reference determinants with respect to \hat{S}^2 these problems disappeared.

Due to the symmetry breaking within SRMRCC the free rotation of the "eigenvectors" is impeded leaving SRMRCC less vulnerable to convergence problems in degenerate situations. In fact SRMRCC converged without imposing further restrictions on the wave function. Actually, there is no simple way to apply a reference CSF expansion to SRMRCC since the amplitudes spanning the reference space are 1. not unique for an individual reference and 2. reappear in product terms. It should be noted, that the very recently proposed scheme by Lyakh *et al.* [81] tries to address the symmetry adaption problem at CI level. It applies a symmetry adapted projection and requires an iterative procedure propagating the t amplitudes to c coefficients, symmetry adapting the latter, and back-propagation to t amplitudes. Nevertheless, the above mentioned issues regarding symmetry and connec-

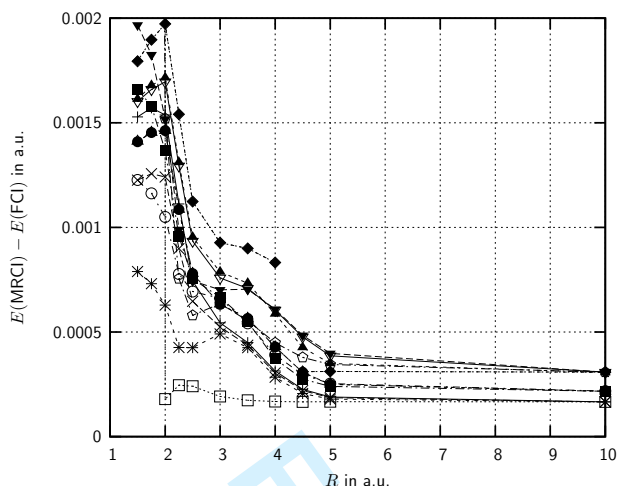


FIG. 3: Energy differences of MRCI with respect to FCI

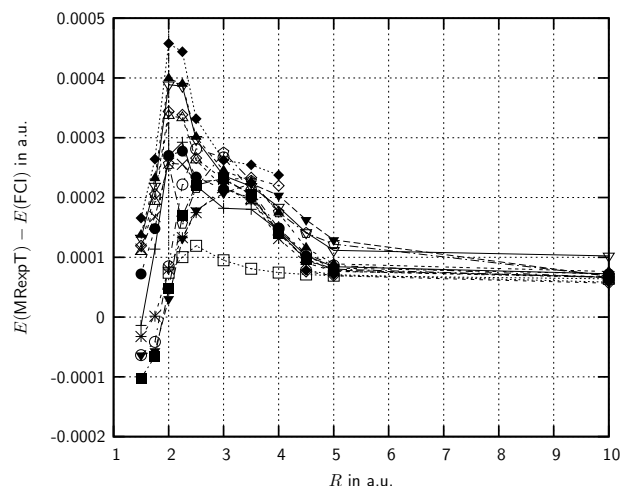


FIG. 4: Energy differences of MRexpT with respect to FCI

tivity remain.

Interestingly, the Fermi vacuum invariance of MRexpT treating all references on the same footing makes the approach more sensitive to "eigenvector" rotations in case of degeneracies. Actually, this is not an issue with MRexpT but with the solution of the non-linear equation system. Solving this problem in a general fashion requires the development of multi-root non-linear equation solvers similar to the multi-root Davidson procedure for MRCI [86–90]. This is however beyond the scope of this article and is to be addressed in the future.

We would like to emphasize that the reference space spin projection for MRexpT has been solely introduced because of convergence issues in case of spin degeneracy. It has *not* been applied to improve the spin projections of MRexpT. Actually, in case of no spin degeneracy it makes no difference if the reference space is expanded into determinants or CSFs.

IV. RESULTS AND DISCUSSION

Besides the usually probed correlation energy errors with respect to full CI N_2 offers a few rigorous properties related to its high symmetry that can be checked for. Of course the properties should be met exactly. However, it turns out that a few of them assemble a very challenging test for the considered multi-reference coupled cluster methods.

This section reports on the correlation energy errors of SOMRCI, MRexpT, and SRMRCC and spatial degeneracy errors.

A. Correlation energy errors with respect to Full CI

Tables III, IV, and V show the deviation from full CI at the various geometries and states for SOMRCI, MRexpT, and SRMRCC respectively while figures 3, 4, and 5 show the corresponding plots. All methods SOMRCI, MRexpT, and SRMRCC show the largest errors in vicinity of the equilibrium.

In table III and figure 3 SOMRCI shows errors ranging from 1973 to $165 \mu E_H$. All states converge smoothly and the non-parallelism error (NPE) ranges from 81 to $1665 \mu E_H$. The ${}^7\Sigma_u^+$ state shows the smallest errors for two reasons: 1. The orbitals have been made for this state and 2. for the septet state much of the correlation effect is covered by the Pauli correlation already. Since the reference space description of the ${}^7\Sigma_u^+$ and $2^1\Sigma_u^-$ states becomes very poor or the corresponding root very high at short distances we omitted them from the table.

In table IV and figure 4 MRexpT shows errors ranging from 457 to $-102 \mu E_H$ and the NPE varies between 56 and $399 \mu E_H$. The correlation energy errors are about a factor of 3 to 4 smaller with respect to SOMRCI. We note that it got very difficult to converge the MRexpT equations for cases with strong degeneracy. This happened at $R = 10$ Bohr for the states of the highly degenerate $N(2D^0)+N(2D^0)$ dissociation channel. From table II we see three singlet states ($1^1\Sigma_u^-$, $2^1\Sigma_u^-$, $1^1\Gamma_u$) to map onto A_u . In $D_{\infty h}$ only $1^1\Sigma_u^-$ and $2^1\Sigma_u^-$ are allowed to mix while all three of them may intermix in D_{2h} without application of a Λ_z projection. This happened for the $2^1\Sigma_u^-$ state at its crossing through the $1^1\Delta_u$ state (around $R = 4.5$ Bohr) and for the $2^1\Sigma_u^-$ and $1^1\Pi_g$ states at $R = 10.0$ Bohr. Without the employed spin related CSF expansion in the reference space there are more states which fail to converge to the desired residual norm of 10^{-10} . This is a strong indication that it becomes very difficult to converge the non-linear equations of MRexpT

R	$4S + 4S$				$4S + 2D$				$4S + 2P$	$2D + 2D$				
	$X^1\Sigma_g^+$	$3\Sigma_u^+$	$5\Sigma_g^+$	$7\Sigma_u^+$	$3\Pi_g$	$5\Pi_u$	$3\Delta_u$		$3\Sigma_u^-$	$1^1\Sigma_u^-$	$1\Pi_g$	$1\Delta_u, 1^1\Gamma_u$		$2^1\Sigma_u^-$
							B_{1u}	A_u				B_{1u}	A_u	
1.5	1527	1226	788	—	1660	1226	1409	1411	1613	1601	1967	1793	1795	—
1.75	1571	1256	730	—	1579	1162	1453	1453	1678	1659	1825	1896	1897	—
2	1537	1241	628	179	1367	1049	1462	1462	1715	1695	1518	1972	1973	1520
2.25	1112	898	425	246	957	777	1085	1085	1310	1294	989	1541	1541	754
2.5	743	646	424	240	753	693	778	779	953	934	744	1123	1124	579
3	544	524	490	192	666	661	632	632	787	758	701	926	926	635
3.5	449	436	425	173	548	541	564	564	733	708	704	899	899	553
4	313	304	284	167	371	390	428	428	586	604	608	831	831	448
4.5	226	220	205	166	274	296	307	307	426	477	483	310	310	379
5	189	186	179	166	239	253	250	250	349	385	397	311	311	344
10	165	165	165	165	216	217	216	216	306	308	308	308	308	308
NPE	1406	1091	623	81	1444	1009	1246	1246	1409	1387	1659	1664	1665	1212

TABLE III: Energy differences of SOMRCI with respect to FCI in micro Hartree, [10s4p]/(3s2p) basis set, R in a. u.

R	$4S + 4S$				$4S + 2D$				$4S + 2P$	$2D + 2D$				
	$X^1\Sigma_g^+$	$3\Sigma_u^+$	$5\Sigma_g^+$	$7\Sigma_u^+$	$3\Pi_g$	$5\Pi_u$	$3\Delta_u$		$3\Sigma_u^-$	$1^1\Sigma_u^-$	$1\Pi_g$	$1\Delta_u, 1^1\Gamma_u$		$2^1\Sigma_u^-$
							B_{1u}	A_u				B_{1u}	A_u	
1.5	-14	113	-32	—	-102	-63	72	109	137	132	-63	119	165	—
1.75	113	168	1	—	-66	-41	147	192	232	219	-56	205	264	—
2	269	257	80	74	46	85	270	337	399	388	30	343	457	255
2.25	292	255	132	100	169	221	277	333	389	386	131	338	443	155
2.5	219	225	174	119	220	281	234	262	301	297	178	265	331	216
3	182	230	217	94	232	267	213	216	244	236	207	229	262	275
3.5	180	205	196	80	204	211	199	194	226	218	223	233	254	227
4	144	142	131	74	139	147	148	142	174	184	203	219	237	175
4.5	102	96	90	71	96	106	102	96	115	141	162	76	78	140
5	84	78	76	69	80	86	82	76	88	111	129	69	70	121
10	72	66	67	63	66	66	72	66	76	102	68 ^a	56	58	68 ^a
NPE	306	191	249	56	334	344	205	271	324	308	286	287	399	180

^anot converged to residual norm of 10^{-10} due to degeneracyTABLE IV: Energy differences of MRexpT with respect to FCI in micro Hartree, [10s4p]/(3s2p) basis set, R in a. u.

at the presence of high degeneracy. However, it suggests that this problem can be fixed by the use of CSFs not only with respect to the total spin operator \hat{S}^2 but also with respect to the angular momentum operator $\hat{\Lambda}_z$. Since the latter operator was not implemented in the calculation procedure, the convergence problems caused by the Λ_z degeneracy did not get resolved.

In table V and figure 5 SRMRCC shows errors ranging from 576 to $-282 \mu E_H$ and the NPE varies between 63 and $621 \mu E_H$ taking only the calculations based on the dominating determinants into account. Likewise the plots in figure 5 show results from calculations with dominating determinants taken as Fermi vacuum. Both ranges are slightly poorer than those for MRexpT but with respect to SOMRCI they are still about a factor of 3 smaller. There are no convergence issues with SRMRCC but the $2^1\Sigma_u^-$ state requires a change of the Fermi vacuum at $R = 3.5$ Bohr. Refusing to change the vacuum along the potential surfaces results either in poorer

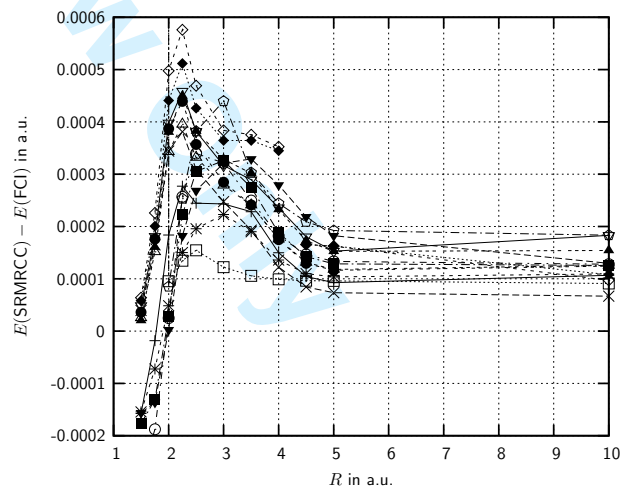


FIG. 5: Energy differences of SRMRCC with respect to FCI

R	$4S + 4S$				$4S + 2D$				$4S + 2P$	$2D + 2D$				
	$X^1\Sigma_g^+$	$3\Sigma_u^+$	$5\Sigma_g^+$	$7\Sigma_u^+$	$3\Pi_g$	$5\Pi_u$	$3\Delta_u$		$3\Sigma_u^-$	$1^1\Sigma_u^-$	$1\Pi_g$	$1\Delta_u, 1\Gamma_u$		$2^1\Sigma_u^-^a$
							B_{1u}	A_u				B_{1u}	A_u	
1.5	-157	39	-154	—	-176	-282	36	25	20	48	-156	63	58	—/—
1.75	-18	164	-72	—	-131	-187	176	151	160	181	-136	225	200	—/—
2	183	344	48	95	27	24	387	342	380	397	2	497	440	85 ^b /232
2.25	277	380	150	134	222	256	439	395	449	458	182	576	511	253 ^b /234
2.5	244	309	195	154	305	339	356	331	382	381	268	469	426	382 ^b /332
3	243	247	223	122	326	321	284	278	328	316	321	383	364	439 ^b /369
3.5	228	192	190	105	274	249	241	240	301	289	329	375	364	371/302 ^b
4	149	122	135	99	187	181	174	175	232	235	279	352	344	292/244 ^b
4.5	104	84	109	96	142	146	129	131	172	180	218	165	165	240/208 ^b
5	92	73	103	96	128	133	116	118	152	152	182	162	162	214/192 ^b
10	106	66	109	91	125	127	124	125	154	183	129	96	107	— ^c /183 ^b
NPE	434	341	377	63	502	621	403	370	429	410	485	513	453	359 ^d

^aFermi vacuum: $|\dots\pi_{ux}^2\bar{\pi}_{uy}\pi_{gx}\pi_{gy}^2\rangle / |\dots3\sigma_g^2\bar{\pi}_{ux}\pi_{gx}\pi_{gy}\rangle$

^bDominant determinant

^cNo convergence

^dNPE based on dominant determinant

TABLE V: Energy differences of SRMRCC with respect to FCI in micro Hartree, [10s4p]/(3s2p) basis set, R in a. u.

performance or lack of convergence.

Switching from one vacuum to another for $2^1\Sigma_u^-$ state leaves a significant gap between the two calculations. At certain geometries this gap may become of the same size as the overall error in the correlation energy. As we usually do not have full CI values at hand there is no way to select the "optimal" switching point.

We would like to point out that larger particle numbers are expected to show the coupled cluster methods much more superior to MRCI. Anyway, the small test system N_2 with 6 electrons correlated puts the considered coupled cluster approaches to a strong test as MRCI is already quite accurate.

B. Spatial symmetry properties

An interesting point of the N_2 potential energy surface is the analysis of the validity of spatial degeneracies. Symmetry issues for MRCC type calculation have been considered previously by Piecuch and Paldus [91, 92] and Berkovic and Kaldor [72]. There are two different types of spatial degeneracies within N_2 that may be tested for:

- (i) Degeneracies originating from the two dimensional irreducible representations of $D_{\infty h}$ appearing for angular momentum projections in z -direction larger than 0 (e. g. $\Lambda_z = \{\pm 1, \pm 2, \dots\}$ according to Π , Δ , etc. states).
- (ii) Degeneracies at $R \rightarrow \infty$ originating from
 - (a) the full rotation group for the individual atoms (e. g. 3-fold P , 5-fold D , etc. degeneracies)

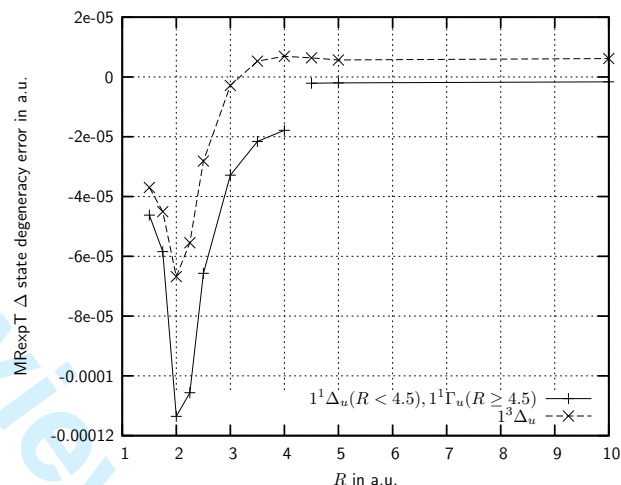


FIG. 6: $1\Delta_u$, $1\Gamma_u$, and $3\Delta_u$ degeneracy error for MRexpT

- (b) different couplings of the total spin located at the individual atoms to the resulting molecular total spin (e.g. $(X^1\Sigma_g^+, 1^3\Sigma_u^+, 1^5\Sigma_g^+, 1^7\Sigma_u^+) \rightarrow (4S + 4S)$).

In the following we analyze the Δ - and Γ -state degeneracy and the $R \rightarrow \infty$ degeneracy separately.

1. Δ and Γ state degeneracy

A linear molecule like N_2 should show perfect degeneracy between the two components of the Π -, Δ -, and Γ states. While the Π -state degeneracy is reproduced smoothly the symmetry conservation of the Δ -states

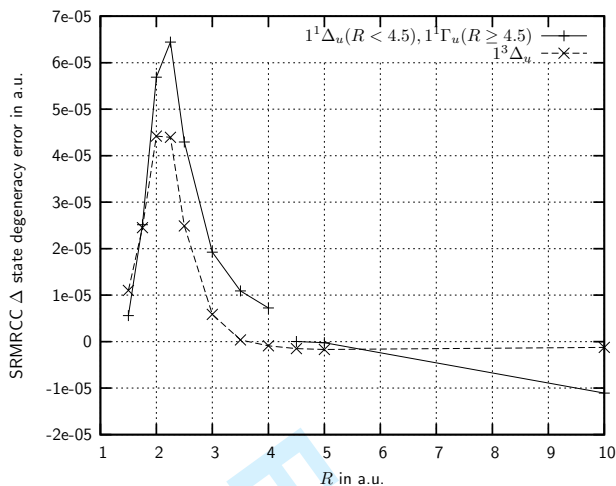


FIG. 7: ${}^1\Delta_u$, ${}^1\Gamma_u$, and ${}^3\Delta_u$ degeneracy error for SRMRCC

turns out to be very difficult for the coupled cluster approaches. This has been reported before by Berkovic *et al.* [72] who performed SUMRCC calculations on N_2 and found degeneracy errors of about 0.3 eV (11 mE_h).

As can be seen from figures 6 and 7 both MRexpT and SRMRCC show very significant errors in the Δ -state degeneracy. The errors are largest (114 μE_H and 65 μE_H for MRexpT and SRMRCC respectively) at the vicinity of the equilibrium distance and fall off for $R \rightarrow \infty$. Although the reason for this behavior is not yet entirely clear to us we will try to give some explanation.

An analysis of the subduction of $\Pi_{u/g}$ states of $D_{\infty h}$ shows them to appear at the B_{3u}/B_{2u} and B_{3g}/B_{2g} irreducible representations (irreps) of D_{2h} for the ungerade and gerade symmetry respectively. Since these two pairs of irreps are populated with (x, y) -degenerate states (e.g. $\Phi_{u/g}$ and higher Λ_z) only, the irreps of each pair B_{3u}/B_{2u} and B_{3g}/B_{2g} are completely equivalent. Consequently a calculation in D_{2h} reproduces this degeneracy trivially and in the previous section we reported a single component only.

In contrast to this the subduction of $\Delta_{u/g}$ and $\Gamma_{u/g}$ states of $D_{\infty h}$ shows them to appear at the B_{1u}/A_u and A_g/B_{1g} irreducible representations of D_{2h} for the ungerade and gerade symmetry respectively. However, the A_g , B_{1g} , B_{1u} , A_u irreps are also populated with Σ_g^+ , Σ_g^- , Σ_u^+ , Σ_u^- states respectively with the latter all having possibly different energies. In D_{2h} a symmetry broken wavefunction could couple to those Σ states removing the degeneracy. Unfortunately, we could not calculate the Λ_z projection with the current implementation to check for this directly. Therefore, we calculated all $\langle {}^M\Delta | {}^M\Sigma \rangle$ overlaps of same multiplicity M close to the equilibrium geometry (that are: $\langle {}^3\Delta_u | {}^3\Sigma_u^+ \rangle$, $\langle {}^1\Delta_u | {}^1\Sigma_u^- \rangle$, $\langle {}^2^1\Sigma_u^- | {}^1\Delta_u \rangle$, and $\langle {}^1^3\Sigma_u^- | {}^3\Delta_u \rangle$). All of them show an overlap of the order 10^{-16} which corresponds to a calculated zero. This does of course not rule out a coupling to any other (higher) Σ -state but it seems to be very unlikely that

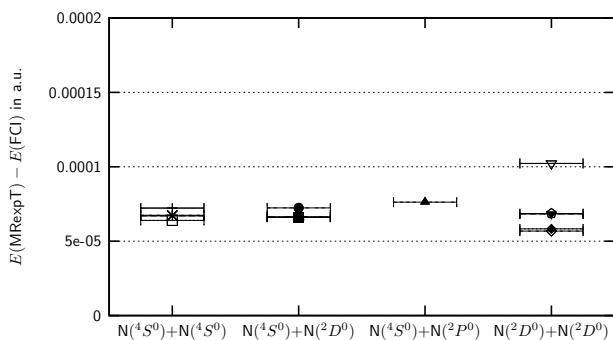
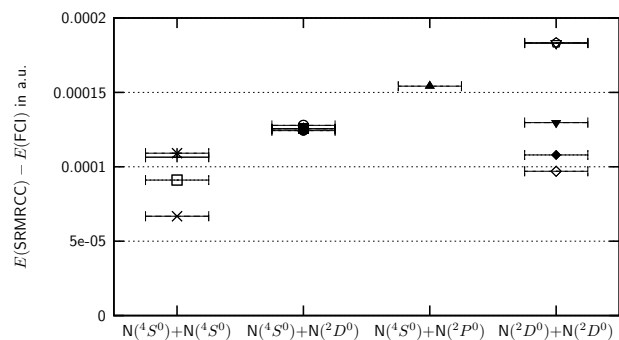
No. of open shells	No. of ref. conf.			
	${}^3\Delta_u$		${}^1\Delta_u$	
	B_{1u}	A_u	B_{1u}	A_u
0	0	0	0	0
2	18	12	18	12
4	0	4	0	4
6	1	0	1	0
dets.	56	48	56	48
CSFs	26	24	23	20

TABLE VI: Number of reference configurations having a certain number of open shells as well as number of determinants and CSFs for the ${}^3\Delta_u$ and the ${}^1\Delta_u$ states close to the equilibrium geometry

the considered Δ -states show an overlap with higher Σ -states while they do not with the lowest ones. Therefore, practically we can rule out Δ/Σ mixing to cause the lack of degeneracy. Additionally, after careful inspection we can rule out the truncation procedure due to vanishing reference coefficients to be the origin of the symmetry breaking.

There is some evidence that there is another reason for the poor Δ -degeneracy. Table VI shows the open shell structure of the two calculated Δ states for their two D_{2h} components. Table VI is to be read as follows: For the B_{1u} component of the ${}^3\Delta_u$ state (second column) there are 18 configurations having 2 open shells while there is only one configuration having six open shells. The reference space consists of 56 determinants corresponding to 26 CSFs (the numbers of CSFs in the last line differs for the triplet and singlet state due to the different spin eigenfunction degeneracy at a given multiplicity). We note that the B_{1u} and A_u components of both Δ -states show a significant difference in their open shell structure. Similarly, the corresponding exponential (the real coupled cluster) wavefunctions show a very different open shell structure for the two components. Using a linear wavefunction CSF based ansatz the open shell structure does not matter and both states are reproduced degenerately, of course. However, a wavefunction ansatz containing product terms of substitution operators contains determinants which do not carry their own coefficient but are made from disconnected clusters. Now, for an increasing number of open shells the spin degeneracy is growing accordingly and in order to span the spin space we needed a larger number of freely optimized coefficients. However, this cannot be achieved with the product type wavefunction. In other words: The fundamental problem is that the spin degeneracy may increase during the substitution process but the product excitations do not allow for a proportionally growing number of free parameters. Therefore, we get a wavefunction which differs in its level of correlation for the two Δ -state components destroying the exact symmetry.

In order to get a deeper understanding we simplified the system to a single nitrogen atom. Due to the full

FIG. 8: $R = 10$ degeneracy errors for MRexpTFIG. 9: $R = 10$ degeneracy errors for SRMRCC

rotation group symmetry we expect e.g. the 2D state to be five-fold degenerate (for a fixed S_z). The five components of 2D state map onto the B_{3u} , B_{2u} , B_{1u} and two times A_u irreps of D_{2h} . What we find is a perfect degeneracy within the three B-type irreps and slightly different energy for the two states in A_u . The reference spaces of the B-type irreps consist of two determinants with one closed and one open shell while the two A_u components consist of three determinants with three open shells. Due to the tiny number of references we could carry out an explicit wavefunction analysis supporting our suggestion. However, a final answer to this issue can be only given using a spin averaged based implementation of MRCC approaches. It remains puzzling why MRexpT shows slightly larger Δ -state degeneracy errors than SRMRCC.

Finally we would like to mention that already at linear level (SOMRCI) there is an issue related to the Δ state degeneracy. At very close inspection of table III we also find a small ($1 \mu E_H$) degeneracy error for the Δ -states (e.g. the ${}^3\Delta_u$ state at $R = 2.25$ Bohr) due to the lack of completeness of the singles doubles substitution space within a spin orbital picture.

2. $R \rightarrow \infty$ degeneracy

An analysis of the full CI calculations shows the the atomic channels $N(4S^0)+N(4S^0)$, $N(4S^0)+N(2D^0)$, $N(4S^0)+N(2P^0)$, $N(2D^0)+N(2D^0)$ to be degenerate up to at least six digits for $R \geq 10$. However, from tables III, IV, and V we see only MRCI to reproduce these degeneracies. For convenience figures 8 and 9 assemble the errors for MRexpT and SRMRCC with respect to full CI at $R = 10$ Bohr grouped by the corresponding dissociation channel respectively in a single plot with the spread showing the degeneracy errors. Although certainly not being exact MRexpT shows a moderate degeneracy error. On exclusion of the $1^1\Sigma_u^-$ state the degeneracies of MRexpT are below about $12 \mu E_H$ (max-min) with the $1^1\Sigma_u^-$ being off about $46 \mu E_H$. Due to its symmetry broken reference SRMRCC shows larger errors of about $87 \mu E_H$ (max-min). There is some evidence that these $R \rightarrow \infty$ degeneracy errors have a similar origin as the Δ

degeneracy errors before. Further investigations are to be made.

Previous studies on the $R \rightarrow \infty$ degeneracy using EOMCCSDt have been carried out by Kowalski *et al.* [93] for the CH^+ molecule. In this case the $2^1\Sigma^+$ and $1^1\Delta$ states should become degenerate for $R \rightarrow \infty$. However, the reported degeneracy error at $R = 5$ a.u. was $10 mE_h$ which is about two orders of magnitude larger than the errors found in this work. Although the two studies did not consider the same molecule the number of correlated electrons was exactly the same. We therefore expect the two orders of magnitude between the errors of the previous [93] and this study to be significant.

V. CONCLUSION

To our best knowledge we presented the first full potential surface (including dissociation) calculations of 12 low lying states of N_2 with multi-reference coupled cluster approaches so far. Although we used a small basis and correlated only 6 electrons the calculations contain the whole complexity of the dissociation of the N_2 molecule at ground and excited state level. We reported energy differences with respect to full CI and analyzed spatial degeneracy errors.

Besides the poor degeneracy of the Δ -states the results for MRexpT are very satisfactory. SRMRCC shows slightly larger correlation energy errors with respect to full CI and suffers from its lack of Fermi vacuum invariance. SRMRCC shows a poorer degeneracy for the atomic fragments when approaching $R \rightarrow \infty$ while it performs slightly better for the $1^1\Delta_u$ state than MRexpT.

Nevertheless, in view of the complexity of the N_2 system with all its difficulties and traps this study can be regarded as a successful application of multi-reference coupled cluster methods to problems which were accessible mainly with MRCI and CASPT2 based methods so far. We also point out that the reported degeneracy errors of order $0.1 mE_H$ are much smaller than the typical errors in the MRCI correlation energy with respect to full CI. Additionally, by correlating a larger number of electrons this relation will improve substantially in favor of the

coupled cluster type methods.

Further investigations of the origin of the degeneracy errors are to be made. As we expect many of the observed issues with MRexpT and SRMRCC to appear with other MRCC approaches as well an analogous investigation of N₂, e.g. for MkMRCC and BWMRCC, would be very interesting.

Acknowledgments

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