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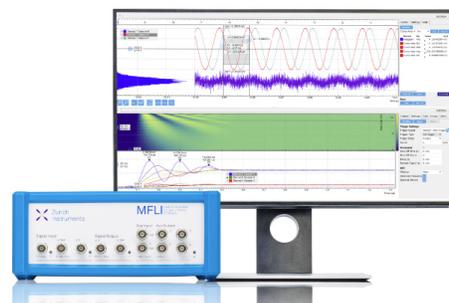
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Spin-restricted Brueckner orbitals for coupled-cluster wavefunctions

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The theory of spin-restricted Brueckner orbitals for high-spin open-shell coupled-cluster wavefunctions is presented. The orbitals are based on single-excitation amplitudes constructed using the symmetric spin-orbital basis coupled-cluster method of Jayatilaka and Lee. It is shown how this approach may be easily implemented within existing open-shell coupled-cluster programs. The method's performance is compared to conventional spin-unrestricted Brueckner orbitals for \tilde{C}^2A_2 NO₂ and $\tilde{X}^2A'_2$ NO₃, for which instabilities in the Hartree-Fock reference determinant cause serious difficulties for highly correlated wavefunctions. © 1997 American Institute of Physics. [S0021-9606(97)03747-1]

I. INTRODUCTION

Brueckner's theory for infinite nuclear matter¹ was first considered for the finite, non-uniform systems of atoms and molecules in 1958 by Nesbet.² By consideration of the problem of diagonalization of the electronic Hamiltonian within the basis of the reference and all singly and doubly excited determinants (i.e., the CISD approach), Nesbet explained that Brueckner theory provides a strict condition for the elimination of the singly excited determinants from the correlated wavefunction. That is, the theory provides for a set of orthonormal orbitals for which all single excitation coefficients are identically zero. Unfortunately, the construction of the set of orbitals which fulfill this "Brueckner condition," can only be determined *a posteriori*. As a result, the practical implementation of Brueckner-orbital-based methods has usually required the repeated construction of the correlated wavefunction (along with the associated integral transformation). Despite this drawback (which may perhaps be circumvented³), Brueckner orbitals have found new life within coupled-cluster (CC) theory^{4,5} in recent years.⁶⁻¹⁸

In 1981, Chiles and Dykstra⁶ introduced the first molecular application of the Brueckner coupled-cluster doubles (B-CCD) method, which they referred to as CCD ($\hat{T}_1 = 0$). Some years later, Handy and co-workers⁹⁻¹¹ also implemented B-CCD energies, along with a perturbational triple-excitation correction [known as B-CCD(T)] and analytic energy gradients. Following these important theoretical developments, numerous applications of the B-CCD and B-CCD(T) methods to "difficult" molecular systems have indicated the tremendous potential of these approaches for overcoming deficiencies in the Hartree-Fock reference wavefunction.^{12-14,16,17,19-22} This is particularly true in the case of symmetry-breaking instabilities,^{23,24} where it has recently been shown^{19,22,25} that even highly correlated methods

may fail dramatically in the prediction of non-symmetric harmonic vibrational frequencies when the Hartree-Fock reference determinant suffers from a singularity in its molecular orbital Hessian.

The application of the B-CCD method to open-shell systems (where symmetry-breaking instabilities are the most likely to occur) is straightforward when either a spin-unrestricted Hartree-Fock (UHF) or spin-restricted Hartree-Fock (ROHF) reference wavefunction is used as the initial guess for the Brueckner determinant. In the latter case, however, it is not possible to maintain spin restriction on the molecular orbitals because the single excitation amplitudes, which may be used as the rotation parameters for the iterative construction of the Brueckner orbitals, are not symmetric in the spin indices in the standard (α, β) spin basis. That is, $t_{I\alpha}^A \neq t_{I\beta}^A$, where I is a doubly occupied spatial orbital and A is an unoccupied spatial orbital. This asymmetry is a consequence of the uneven exchange contributions between the open- and closed-shell electrons. As a result, the repeated construction of the coupled-cluster wavefunction requires the transformation and storage of roughly three times the number of two electron integrals needed for the initial ROHF-CCSD (coupled-cluster singles and doubles) calculation.²⁶ This represents a significant obstacle for open-shell B-CCD implementations.

In this work, we describe an approach to spin-restricted open-shell B-CCD calculations, which we denote RB-CCD. The single excitation amplitudes are formulated within the symmetric spin-orbital basis of Jayatilaka and Lee,²⁷ which has been used recently as the foundation for the so-called Z-averaged perturbation theory (ZAPT),²⁸ a reformulation of the single-reference open-shell CCSD equations,²⁹ and a perturbational triple-excitation correction to the CCSD energy.³⁰ In Sec. II we describe the theoretical foundation of the spin-

restricted Brueckner theory, followed by a discussion of some of the practical aspects of the simple implementation of the method within existing ROHF-CCSD programs. Finally, in Sec. III, we test the performance of RB-CCD theory relative to the conventional, spin-unrestricted B-CCD approach for two systems for which instabilities in the Hartree–Fock reference determinant present a serious impediment to the coupled-cluster treatment of electron correlation effects.

II. THEORY

In order to force symmetric interactions between open and closed shells, Jayatilaka and Lee developed the symmetric spin orbital basis.²⁷ In their approach, new spin functions,

$$\sigma^+ = \frac{1}{\sqrt{2}}(\alpha + \beta), \quad \sigma^- = \frac{1}{\sqrt{2}}(\alpha - \beta),$$

are assigned to the open-shell electrons, with σ^+ assigned to the occupied half and σ^- assigned to the unoccupied half of each open shell orbital. The standard α and β functions are used for the doubly occupied and unoccupied orbital subspaces. In this new spin basis, the exchange interactions of α and β electrons in the same doubly occupied orbital with an electron in an open-shell orbital are equivalent. Jayatilaka and Lee have explored the consequences of this scheme in many-body perturbation theory²⁸ and coupled-cluster theory,²⁹ and have found that it is possible to take significant advantage of the resulting spin symmetry of the determinantal parameters in the correlated wavefunction.

For the perspective of a spin-restricted Brueckner theory, the most important result of the use of the symmetric spin orbital basis in open-shell coupled-cluster theory is the symmetry introduced in the \hat{T}_1 amplitudes. In particular, it may be shown that²⁹

$$\begin{aligned} t_{I\alpha}^{A\beta} &= t_{I\beta}^{A\alpha}, & t_{I\alpha}^{A\alpha} &= t_{I\beta}^{A\beta}, \\ t_{I\alpha}^{W\sigma^-} &= -t_{I\beta}^{W\sigma^-}, & t_{W\sigma^+}^{A\alpha} &= t_{W\sigma^+}^{A\beta}, \end{aligned}$$

where I , A , and W indicate doubly occupied, unoccupied, and singly occupied spatial orbitals, respectively. Since the α and β spin functions are not orthogonal to σ^+ and σ^- spin functions, the first class of \hat{T}_1 amplitudes, known as ‘‘spin-flip’’ \hat{T}_1 ’s, is generally non-zero in the symmetric spin orbital basis. However, as argued by Lee and Jayatilaka,²⁸ since the matrix element of the Hamiltonian operator between the reference determinant, $|\Phi\rangle$, and a singly excited determinant involving a spin-flip, $|I\alpha^{A\beta}\rangle$, contains no one-electron component, the spin-flip \hat{T}_1 ’s should be formally classified as double-excitation cluster operators. The remaining three classes of \hat{T}_1 amplitudes may be used to carry out a series of first-order rotations among the orbital subspaces, viz.³¹

$$\tilde{\phi}_I = \phi_I + t_{I\alpha}^{A\alpha} \phi_A + t_{I\alpha}^{W\sigma^-} \phi_W, \quad (1)$$

$$\tilde{\phi}_W = \phi_W + t_{W\sigma^+}^{A\alpha} \phi_A - t_{I\alpha}^{W\sigma^-} \phi_I. \quad (2)$$

At convergence the orbitals will obey the Brueckner conditions,

$$t_{I\alpha}^{A\alpha} = t_{W\sigma^+}^{A\alpha} = t_{I\alpha}^{W\sigma^-} = 0. \quad (3)$$

In the iterative scheme, the new orbitals $\tilde{\phi}_I$, $\tilde{\phi}_W$ must be orthonormalized, and virtual orbitals $\tilde{\phi}_A$ are then obtained by orthonormalization to these. This presents no significant difficulties. The orbitals may then be used in a ‘‘macroiteration’’ algorithm in which in each step the two-electron integrals are transformed to the new basis and a new coupled-cluster wavefunction is computed. Such an approach would benefit considerably from convergence acceleration procedures, such as those based on the ‘‘direct inversion in the iterative subspace’’ (DIIS) method.^{4,32,33} One such DIIS implementation was described for the closed-shell B-CCD method by Hampel, Peterson, and Werner,³ and was found to dramatically improve the convergence of the B-CCD iterative procedure by simultaneously optimizing the cluster amplitudes and the orbital rotation matrix.

Similar to the ROHF wavefunction, the spin-restricted Brueckner determinant is an eigenfunction of the \hat{S}^2 operator. As a result, the RB-CCD energy is completely spin-projected, though the CC wavefunction itself still contains contaminants from higher-order spin states.^{26,34,35} This may be considered a theoretical advantage of the RB-CCD method over the conventional spin-unrestricted B-CCD approach, where the Brueckner determinant is not in general an \hat{S}^2 eigenfunction and therefore does not necessarily produce a spin-pure energy. However, it is not certain whether such a difference between the RB-CCD and B-CCD methods is of any practical importance, since both schemes may generally be expected to produce coupled-cluster wavefunctions with only a small amount of spin contamination.^{13,35} In addition, while it is clear that at convergence of the RB-CCD equations there will be fewer terms which contribute to spin contamination of the wavefunction relative to ROHF-CCSD,²⁹ the magnitude of these terms is unknown, and it is therefore not possible to make quantitative comparisons of spin impurity in the wavefunctions produced in the RB-CCD and ROHF-CCSD methods.

While the discussion presented so far has focused on the single-excitation amplitudes constructed within the symmetric spin-orbital basis, it should be noted that it is not necessary to implement the open-shell coupled-cluster equations within this same basis in order to take advantage of the RB-CCD method. In either the standard (α, β) or symmetric spin-orbital basis, the CCSD equations give the same answer at convergence, as pointed out by Jayatilaka and Lee.²⁷ Therefore, once the \hat{T}_1 amplitudes have been computed using a standard (α, β) ROHF-CCSD program, they may be trivially transformed to the symmetric spin orbital basis using the following equations:

$$t_{I\alpha}^{A\alpha} = \frac{1}{2}(t_{I\alpha}^{A\alpha} + t_{I\beta}^{A\beta}), \quad (4)$$

$$t_{I\alpha}^{A\beta} = \frac{1}{2}(t_{I\alpha}^{A\alpha} - t_{I\beta}^{A\beta}), \quad (5)$$

$$t_{I\alpha}^{W\sigma^-} = \frac{1}{\sqrt{2}} \tilde{t}_{I\beta}^{W\beta}, \quad (6)$$

and

$$t_{W\sigma^+}^{A\alpha} = \frac{1}{\sqrt{2}} \tilde{t}_{W\alpha}^{A\alpha}, \quad (7)$$

where \tilde{t}_i^a indicates a single-excitation amplitude in the (α, β) basis.

Another perspective on the RB-CC method is based on the requirement that the Brueckner reference determinant Φ should have maximal overlap with the exact, correlated wavefunction Ψ ,

$$\frac{\partial}{\partial \phi} [\langle \Phi | \Psi \rangle] = 0, \quad (8)$$

where $\partial\phi$ indicates a variation in the component molecular orbitals. It may be shown that this condition is equivalent to the requirement that the overlap between all singly excited determinants and the exact wavefunction is zero.^{7,36,37} In the RB-CC theory, we impose the additional constraint that the rotations needed to achieve this maximum-overlap condition must not break the spin restriction on the orbitals. The Brueckner conditions may therefore be obtained by writing down the conditions that $\langle \Phi | \Psi \rangle$ is stationary when orbital changes $\phi_I \rightarrow \phi_I + \epsilon_1 \phi_A$; $\phi_W \rightarrow \phi_W + \epsilon_2 \phi_A$; $\phi_I \rightarrow \phi_I + \epsilon_3 \phi_W$; $\phi_W \rightarrow \phi_W - \epsilon_3 \phi_I$. This leads to the conditions

$$c_{I\alpha}^{A\alpha} + c_{I\beta}^{A\beta} = c_{W\alpha}^{A\alpha} = c_{I\beta}^{W\beta} = 0, \quad (9)$$

which is equivalent to Eq. (4) when truncated-CC amplitudes are used to replace the general correlated wavefunction coefficients above. As a result, the *average* of the α and β components rather than the individual single-excitation amplitudes in the CC wavefunction will approach zero at convergence in the RB-CC method. When considered in the symmetric spin-orbital basis, however, this condition may be viewed as requiring that *all* single-excitation amplitudes approach zero, and that no approximations are made.

III. APPLICATIONS

We have implemented the RB-CCD method within the PSI³⁸ program package. In order to evaluate the performance of this approach, we have carried out a series of calculations on the \tilde{C}^2A_2 state of NO₂ and the ground $^2A'_2$ state of NO₃. Both of these systems have presented serious difficulties for a variety of theoretical methods due in part to instabilities in the Hartree-Fock reference wavefunction.

A double-zeta basis, including polarization functions (DZP) was used for both systems. This basis consisted of the standard Huzinaga-Dunning^{39,40} set of contracted Gaussian functions with one additional set of higher-angular-momentum polarization functions⁴¹ on each atom. The contraction scheme for this basis is $(9s5p1d/4s2p1d)$. Pure angular momentum functions were used for all *d*-type orbitals. All spin-unrestricted B-CCD calculations were carried out using the ACESII program package.⁴²

All optimized geometries and harmonic vibrational frequencies were determined using finite-differences of energy points. However, due to the occasional existence of nearby symmetry-broken solutions of the Hartree-Fock equations, the determination of non-symmetric harmonic vibrational frequencies was complicated due to variational collapse if the ROHF reference determinant was used as the initial guess for the Brueckner iterative procedure. This problem was circumvented, however, by the use of a so-called quasi-restricted Hartree-Fock (QRHF) reference wavefunction^{13,26} as the initial guess. The QRHF determinant is composed of orbitals which are optimized for a nearby closed-shell state; in both systems studied here, the closed-shell anion was chosen. Stanton and Bartlett have advocated the use of the QRHF reference wavefunction in coupled-cluster calculations (QRHF-CC) as an alternative to B-CCD for avoiding instabilities in the ROHF or UHF reference wavefunctions.¹³ Their calculations suggest that QRHF-CC may be a powerful and efficient method for such purposes, in spite of the fact that the reference molecular orbitals are not optimum for the electronic state of interest. In the present work, it was found that the QRHF reference wavefunction provided an adequate initial guess for the convergence of the RB-CCD conditions at every relevant geometry.

A. \tilde{C}^2A_2 NO₂

The \tilde{C} state of NO₂ has been under scrutiny in recent years due to unexpected discrepancies between the theoretical^{22,43} and experimental^{44,45} predictions of the equilibrium *N-O* bond distance. High-level coupled-cluster studies have provided strong evidence that this excited state exhibits a pseudo-Jahn-Teller distortion along the asymmetric stretching coordinate, and, as a result, the true symmetry of the molecule may in fact be C_s , rather than C_{2v} as has previously been assumed. CCSD(T) computations based on UHF, QRHF, and spin-unrestricted Brueckner determinants all concur in their prediction of a symmetry-broken equilibrium structure. CCSD(T) computations based on a ROHF reference determinant, on the other hand, fail to predict the correct shape of the asymmetric stretching potential curve due to a nearby instability in the ROHF wavefunction at the CCSD(T) optimized geometry.

In order to assess the utility of the RB-CCD method, we have determined the C_{2v} -constrained optimized geometry and harmonic vibrational frequencies at that level of theory. These results are presented in Table I, along with the ROHF-CCSD and unrestricted B-CCD predictions taken from Ref. 22. The orbital rotations included in the RB-CCD method are clearly sufficient to overcome the instability in the ROHF reference determinant, without the need of the additional relaxations which break orbital spin restriction. The RB-CCD method predicts a somewhat sharper negative curvature ($861i \text{ cm}^{-1}$) of the asymmetric stretching coordinate relative to the conventional B-CCD approach ($689i \text{ cm}^{-1}$). However, it is uncertain which value is to be preferred. In any case, the correct, qualitative prediction for the asymmetric

TABLE I. Absolute energies (E_h), geometrical parameters (Å and degrees), and harmonic vibrational frequencies (cm^{-1}) for the \tilde{C}^2A_2 state of NO_2 using a DZP basis. ROHF-CCSD and B-CCD results are taken from Ref. 22. RB-CCD denotes the spin-restricted Brueckner method described in the text.

	ROHF-CCSD	B-CCD	RB-CCD
Energy	-204.569 662	-204.569 979	-204.568 454
r_e (N–O)	1.281	1.281	1.279
θ_e (O–N–O)	109.6	109.6	109.6
$\omega_1(a_1)$	1362	1356	1368
$\omega_2(a_1)$	778	778	781
$\omega_3(b_2)$	549	689i	861i

stretching frequency given by the RB-CCD method is encouraging.

B. $\tilde{X}^2A'_2 \text{NO}_3$

The geometrical symmetry of the ground state of the nitrate radical presents an intriguing theoretical problem. Three structures have been found to be energetically most favorable: (1) A high-symmetry D_{3h} structure, (2) a C_{2v} structure with one long and two short N–O bonds (1L2S), and (3) a C_{2v} structure with one short and two long N–O bonds (1S2L). In spite of intense theoretical and experimental analysis,^{13,46–49} it is not definitively known which of these three corresponds to the equilibrium configuration, or if the dynamic structure observed experimentally results from a pseudorotational average of all three. The theoretical analysis has been complicated by the existence of instabilities in Hartree–Fock reference wavefunctions.

Table II presents relative energies and optimized geometries for the D_{3h} and 1L2S C_{2v} configurations of NO_3 . Conventional B-CCD theory predicts that the C_{2v} structure is the lowest-energy configuration, lying 2.7 kcal/mol below the D_{3h} structure. The RB-CCD method agrees completely with these predictions, giving nearly identical optimized geometries and a relative energy which differs by only 0.22 kcal/mol from that of the B-CCD method. However, the basis set used here (DZP) is not large enough to make any direct comparisons to experimental data. In addition, it is known that high-level correlation effects are very important for the nitrate radical. Stanton, Gauss, and Bartlett¹³ showed that inclusion of limited triple excitations [via the B-CCD(T) approach] instead favored the high-symmetry structure, though the potential energy surface remained very flat. It is expected

TABLE II. Relative energies (kcal/mol) and geometrical parameters (Å and degrees) for the D_{3h} and C_{2v} isomers of the $\tilde{X}^2A'_2$ state of NO_3 using a DZP basis.

	B-CCD		RB-CCD	
	D_{3h}	C_{2v}	D_{3h}	C_{2v}
Relative energy	0.00	-2.77	0.00	-2.99
r_e (N–O _A)	1.234	1.344	1.234	1.346
r_e (N–O _B)	1.234	1.206	1.234	1.206
θ_e (O _A –N–O _B)	120.0	114.3	120.0	114.2

that the addition of a perturbational triple-excitation correction³⁰ would give predictions in quantitative agreement with those of the B-CCD(T) method, though at significantly reduced computational cost.

IV. CONCLUSIONS

We have developed a spin-restricted Brueckner theory for coupled-cluster wavefunctions (RB-CCD) as an alternative to the conventional, spin-unrestricted B-CCD method. The RB-CCD approach is shown to be more efficient than B-CCD, as it requires transformation and storage of only one-third the number of two-electron integrals needed by the latter. We have described RB-CCD in terms of the symmetric spin orbital basis,²⁷ within which its derivation is straightforward. Furthermore, this approach may be easily implemented within existing ROHF-CCSD programs. Through test applications to the \tilde{C} state of NO_2 and the ground state of NO_3 , we have demonstrated that RB-CCD appears to provide predictions of molecular properties in quantitative agreement to those of B-CCD, and should therefore be very useful in the avoidance of problems due to instabilities in the Hartree–Fock reference determinant. Further developments are currently in progress, including large-basis-set applications and the extension of the method to analytic gradient techniques.

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