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frequencies) and electrical (dipole moments, polarizabilities, and infrared intensities). The geometrical properties are well described at all levels except fixed DZ and DZ+. The improvements obtained by floating are small, particularly for bond distances. Floating DZ gives results slightly inferior to fixed DZP but is still an improvement on the fixed DZ results.

The situation is different for electrical properties, which are poorly described at the fixed-orbital level: the best agreement is obtained for the DZP basis dipole moment values, which differ from the Hartree-Fock limit values by some 7%. Floating produces drastic improvements in all cases. Indeed, for all the properties considered even the smallest floating basis set gives properties which are similar to or better than the best fixed basis set. Dipole moments at the fixed DZ level are in error by about 20%, compared to 3-4% when orbital floating is allowed. With addition of diffuse functions the computed values are somewhat larger than the Hartree-Fock limit, while the inclusion of both diffuse orbitals and polarization functions (floating DZP+) gives agreement with the Hartree-Fock limit to within 1%. Since experimental dipole moments are usually a few percent smaller than the Hartree-Fock limit, a floating DZ basis often gives dipole moments which are in fortuitously good agreement with experiment, as noted by Huber.²¹

The requirements for a fixed-orbital basis for calculating polarizabilities are quite demanding, and it is not surprising that even the largest fixed basis set (DZP+) produces polarizabilities which are 15% too low. When floating is allowed, the errors are 7% or smaller in all cases. In particular, when diffuse functions are added, the agreement with the Hartree-Fock limit is remarkably good.

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Perhaps the most difficult to calculate of these properties are infrared intensities, and fixed DZ and DZ+ calculations give intensities which are completely unreliable. Again, floating results in significant improvements, the best basis set giving errors about 3%.

It is clear that floating orbitals have a distinct advantage over fixed for the calculation of electrical properties. Even a modest basis set such as floating DZ+ gives errors less than 5% for electrical properties, while the floating DZP+ results are only 2% in error.

The optimization of floating orbitals is little more time-consuming than the optimization of geometries. With second-order techniques the number of iterations does not increase significantly, normally by only one or two iterations. The time spent in each iteration is also not significantly increased. The time-consuming step is the calculation of second-derivative integrals, and this takes the same time for floating and fixed orbitals. However, if the solution of the response equations is carried out in an iterative fashion, the number of iterations will necessarily increase with the increased number of perturbations. Nonetheless, with an appropriately adapted code the total time for calculation of wave functions and properties using floating orbitals should not exceed twice the time needed for the corresponding fixed basis (provided a geometry optimization is carried out). Given the dramatic improvements in calculated properties, floating orbitals appear more attractive than previously thought and considerably more attractive than extending fixed basis sets with the polarization functions that would otherwise be required.

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An Open-Shell Spin-Restricted Coupled Cluster Method: Application to Ionization Potentials in N₂

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In order to circumvent the problem of spin contamination in unrestricted Hartree-Fock based coupled cluster (CC) calculations, we present a new method of calculation for certain classes of open-shell systems. The approach ensures that the proper spin component of the resulting correlated wave function is projected out in the energy evaluation by the use of a reference function constructed from suitably chosen restricted open-shell Hartree-Fock or other orbitals. This single-reference open-shell spin-restricted CC method is applied to the calculation of ionization potentials in the N₂ molecule, and it is shown that highly accurate results can be obtained in a 5s4p1d basis. The mean error for all the principal ionization potentials of N₂ compared to experiment is 0.45%.

Introduction

In single-determinant reference coupled cluster (CC)¹⁻⁵ and many-body perturbation theory (MBPT) methods,^{4,6,7} the use of an unrestricted Hartree-Fock (UHF) wave function for open-shell systems is frequently employed.²⁻⁴ A UHF reference generally leads to a lowering of the total energy at the Hartree-Fock (HF) level since the α -spin electrons are chosen to occupy different spatial orbitals than the β -spin electrons. This procedure introduces important spin-polarization effects on the spin density, for example, while the corresponding open-shell RHF results would erroneously give zero.⁸ Also, UHF functions facilitate the correct separation of a single-determinant wave function in bond breaking.^{2,3} However, there are two prices paid for the additional

flexibility introduced by a UHF function. First, the wave function is not an eigenfunction of \hat{S}_z ,² and second, having to treat different

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orbitals for different spins (DODS) in the electron correlation calculation typically requires about 4 times as much computer time as in the RHF case.

In the following, we introduce a CC spin-restricted method for open-shell systems described by a single reference determinant of pure spin at the Hartree–Fock level. Such a reference function can be either a single-determinant restricted open-shell Hartree–Fock (ROHF) solution or a more general determinant, constructed from non-Hartree–Fock orbitals. This latter reference function will here be designated quasi-RHF (QRHF) when it is obtained from orbitals optimized for a near-lying closed-shell state. Besides being eigenfunctions of S_z and S^2 , the use of such reference determinants permits CC calculations to be done in computer times closer to that for the closed-shell RHF case since most of the orbitals are doubly occupied. Unlike the open-shell RHF solution, the QRHF reference function is not optimum in energy. However, as we show elsewhere,⁹ CCSD theory introduces such relaxation effects through $\exp(T_1)$, so this is not usually a problem at the correlated level.

The QRHF reference function can be described as a Koopmans-like function. Such a function has previously been employed by Chong¹⁰ in perturbation studies of ionization potentials. Similarly constructed determinants have been proposed in MBPT¹¹ and used in CC¹² studies of excited states. Additional large classes of open-shell problems can be treated with such methods. For the more general open-shell cases, the use of a true open-shell RHF multideterminantal reference, which has been proposed as a reference for MBPT,¹³ introduces some of the difficulties associated with general multireference CC methods.¹⁴

Furthermore, multireference CC approaches, though suited to many of the same categories of open-shell problems,¹³ are more difficult formally and computationally. Consequently, the availability of a single-reference but spin-restricted CC approach for many types of applications is a highly desirable alternative.

The QRHF–CC and ROHF–CC methods will be illustrated with an application to the ionization potentials of N_2 .

Method

The CC formalism has been presented in detail elsewhere.^{1,6,15} Here, we will only give a short synopsis pertinent to the present discussion.

The exact solution of the many electron Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle \quad (1)$$

can be written

$$|\Psi_{\text{exact}}\rangle = |\Psi_{\text{CC}}\rangle = e^T|\Psi_0\rangle \quad (2)$$

where $|\Psi_0\rangle$ is a suitably chosen single reference determinant, frequently resulting from a Hartree–Fock calculation. The individual terms of the excitation operator

$$T = \sum_i T_i \quad (3)$$

can in the notation of second quantization be expressed as

$$T_i = \frac{1}{(i!)^2} \sum_{\substack{abc \\ ijk}} t_{ijk}^{abc} a^\dagger i b^\dagger j c^\dagger k \dots \quad (4)$$

The T amplitudes are obtained from solving the nonlinear equations

$$\langle \frac{abc\dots}{ijk\dots} | e^{-T} H e^T | \Psi_0 \rangle = \langle \frac{abc\dots}{ijk\dots} | (H e^T)_C | \Psi_0 \rangle = 0 \quad (5)$$

where C indicates the limitation to connected diagram components. The energy correction can be obtained by evaluating

$$E = \langle \Psi_0 | (H e^T)_C | \Psi_0 \rangle \quad (6)$$

with the converged T amplitudes.

For any open-shell case, even when Ψ_0 is a spin eigenfunction, $\exp(T)|\Psi_0\rangle$ introduces spin polarization unless T , and all products of T , are properly restricted to the appropriate spin case.¹⁷ To obtain a pure spin solution, we want to consider the spin projected (CC) function $\Psi_{\text{PCC}} = P \exp(T)|\Psi_0\rangle$. The spin-projection operator P ¹⁸ ensures that

$$S(S+1) = \langle \Psi_0 | \hat{S}^2 P \exp(T) | \Psi_0 \rangle / \langle \Psi_0 | P \exp(T) | \Psi_0 \rangle \quad (7)$$

and E_{PCC} is defined as

$$E_{\text{PCC}} = \langle \Psi_0 | H P \exp(T) | \Psi_0 \rangle / \langle \Psi_0 | P \exp(T) | \Psi_0 \rangle \quad (8)$$

There are two potential ways that such a projected CC method might be implemented. The first would be to actually project each of the components of $\exp(T)|\Psi_0\rangle$ before determining the equations for the amplitudes from eq 5. This would be analogous to the so-called projected Hartree–Fock (PHF)¹⁸ case, where you obtain the optimum coefficients after projection, and would be equivalent to a fully spin-adapted open-shell scheme. However, the implementation of such a method would require evaluating substantially different coupling coefficients for the amplitudes for each distinct case like doublets, triplets, etc.

Alternatively, we can project *after* determining the coefficients. In the Hartree–Fock case this is known as PUHF,¹⁸ and, of course, the coefficients are not as optimum but much easier to obtain. The second viewpoint is that taken here. After obtaining $\exp(T)|\Psi_0\rangle$, by treating the open-shell system with a single-determinant ROHF or QRHF reference, and using our standard DODS CC methods,^{2,16} we would then project. This exploits the fact that at convergence the CC solution is independent of any iterative starting point. Of course, even though eq 7 is satisfied, $\langle \Psi_{\text{CC}} | \hat{S}^2 | \Psi_{\text{CC}} \rangle_C \neq S(S+1)$. However, the evaluation of S in the projected form is consistent with energy evaluation from eq 6.

In addition, since $[\hat{S}^2, P] = [H, P] = 0$, we are free to commute P to obtain $\langle P \Psi_0 |$ in the bra of the numerator and denominator of eq 7 and 8. If we now simply require Ψ_0 to be an eigenfunction of S^2 , we can absorb the projector into Ψ_0 , i.e., $P\Psi_0 = \Psi_0$, and no actual projection need ever be performed. We simply employ the DODS form of the CC programs while choosing our reference as an ROHF or QRHF function, and since they are spin eigenfunctions, we have an open-shell spin-restricted CC method.

Furthermore, since all of P is used, the current procedure does not correspond to just annihilating one contaminating spin component, like some MBPT methods.¹⁹ In fact, in the proceedings of this meeting Schlegel shows that coupled cluster singles and doubles (CCSD) excitation model,¹⁶ based upon UHF, will naturally benefit from annihilating the *first spin contaminant* without any projection. This fact has also been observed numerically.²⁰ In our new scheme, by use of an ROHF or QRHF reference, all spin contaminants are removed. Finally, the unity of the method is appealing, since for all single-configuration spin eigenfunction possibilities, the approach and code are the same regardless of the multiplicity. The deficiency would be that

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TABLE I: Vertical Ionization Potential of N₂ (in eV) Using a 5s4p1d Basis^a

leading config	RHF-UHF				RHF-QRHF				RHF-ROHF				expt ^b	GF ^c
	SCF	CCD	CCSD	CCSDT-1	<i>d</i>	CCD	CCSD	CCSDT-1	SCF	CCD	CCSD	CCSDT-1		
3σ _g ⁻¹	15.69	15.54	15.44	15.29	17.27	17.08	15.39	15.36	15.96		15.46	15.29	15.5	15.70
1π _u ⁻¹	15.34	16.72	16.72	16.85	16.78	18.24	16.69	16.87	15.42		16.72	16.85	16.8	16.85
2σ _u ⁻¹	19.95	18.88	18.78	18.50	21.12	20.24	18.71	18.57	20.15		18.80	18.50	18.6	18.96
1σ _g ⁻¹	419.46		411.43	410.93	426.80		411.07	411.29					409.9	

^a RHF-UHF refers to a calculation where the ground-state calculation is based on an RHF reference and the ionic-state calculations on a UHF reference. RHF-QRHF indicates that the ionic calculations are based on a QRHF reference, and RHF-ROHF that they are based on an open-shell RHF reference function. See text for further discussion. ^b ESCA experimental results of Siegbahn et al.²⁰ ^c Green's function results of von Niessen et al.¹⁸ ^d Equivalent to the result obtained by using Koopmans' theorem.

regardless of what is put on the right side of eq 7 and 8; we retain only the proper spin components. Consequently, $\exp(T)\Psi_0$ should not be too far from the true spin-adapted CC result.

The relationship of this method to certain spin-projected UHF-based MBPT methods should be mentioned. In Schlegel's scheme,¹⁹ a single annihilator is used and no projection of the correlated wave function is made, but instead a recipe to eliminate overcounting is employed. Another UHF-MBPT method presented here by Knowles and Handy²¹ projects the correlated wave function and uses more than a single annihilator. Neither of these methods uses ROHF or other open-shell spin eigenfunctions as a reference as we do.

What makes using ROHF or QRHF references conveniently possible in CCSD theory is that, unlike perturbation theory, the actual form of H_0 (which can be complicated for ROHF) is not relevant, since infinite-order (CC) methods are independent of H_0 . Also, as long as the diagrams containing off-diagonal Fock operators which are nonvanishing for arbitrary molecular orbital basis sets are included, CC theory permits the use of any set of orbitals. Our codes have this flexibility.¹⁶

For eq 2 to be exact T should include all T operators. However, very accurate results can be obtained by truncating T to include only a few terms. The level of truncation defines different CC models. The restriction $T = T_2$ is referred to as the coupled cluster doubles (CCD) model.^{1,2,5} The addition of the single excitation operator, i.e., $T = T_1 + T_2$, defines the CCSD model.^{16,20} Below we will also present results using the CCSDT-1¹⁵ model which includes the "connected" triplet excitations in a linear fashion. If a system is well-described by a single HF determinant, the CCD model is generally able to recover about 90–95% of the correlation energy,⁶ while CCSD improves upon that. The CCSDT-1 results are usually extremely close to the full CI limit.^{20a}

The first choice for a single-determinant open-shell spin eigenfunction reference is ROHF. Such a function is optimum for each state subject to maximum double occupancy with the electrons occupying the open-shell orbitals, all having parallel spin. The orbitals for one open-shell state like N₂⁺(²Σ_g) are not the same as for N₂⁺(²Π_u), however. Different orbitals for different states can complicate evaluating transition probabilities among different possible states because of the orbital nonorthogonality.

One way to avoid this problem is to pick *one* set of orbitals for *all* possible open-shell and closed-shell states, sacrificing some of the optimum property. The QRHF reference does this. Since QRHF orbitals are non-Hartree-Fock for the specific open shell, we now have to require that the CC iterations recover not only the energy correction (now defined relative to the QRHF) but also the orbital relaxation energy. As we will find in the numerical example below, the T_2 operator will still be primarily responsible for the "correlation" energy in a QRHF calculation whereas in order to permit "orbital relaxation" we further have to include T_1 . The operator $\exp(T_1)$, in effect, works as an orbital transformation operator allowing the system to relax in the presence of the open-shell electron(s), which is related to Thouless' theorem.²² See ref 9 for a more detailed discussion of the CC theory for orbital relaxation. Thus, the QRHF approach requires that

the CC calculation be performed, at least, at the CCSD level. This is true for ROHF as well.

A further consideration is the specific choice of the QRHF orbitals. The regular HF based scheme provides a well-defined recipe for determining orbitals for a correlated calculation. This property is lost when using the present method since we are now left free to choose from different sets of orbitals. In order for the CC iterations to have reasonable convergence properties, however, the orbitals should be chosen "sufficiently close" to the optimum orbitals for the open-shell state in question.

Usually there exists a natural choice of orbitals. In the case of a singly excited or singly ionized state of a closed-shell molecule, for example, one would first optimize the ground state at the RHF level. These orbitals would then subsequently be used in correlated calculations of the ground state as well as the excited/ionized state. Such a choice of reference could be called the Koopmans' choice of reference⁹ since it is in the spirit of Koopmans' theorem at the HF level. The Koopmans' choice is particularly useful since we use the same set of orthonormal orbitals for both the ground state and all the excited/ionized states which considerably simplifies the evaluation of transition matrix elements among the states.

In other more general cases such as a ground state with one open shell, we are presented with two natural choices of reference orbitals: one obtained from an RHF calculation of the closed shell resulting from ionizations from the open shell and one from a calculation on some closed-shell negative ion, or, perhaps, even some average of the two.²³ A third choice of orbitals that might be used would be to use UHF orbitals, but just from the α -spin block, for example. To make the present approach useful, the difference in the results from the different orbital choices should be relatively small. We will return to this question in a subsequent paper.

Calculations and Discussion

The method presented above has been applied to the calculation of the principal ionization potentials in the N₂ molecule using QRHF as well as ROHF reference determinants. In terms of the closed-shell RHF reference function $|\Psi_0\rangle$, the QRHF wave function for the ionic state can be expressed as

$$|\Psi_{\text{ion,CC}}\rangle = \exp(T)|\Psi_0\rangle$$

where i is the relevant spin-orbit annihilation operator for the ionization process and T will be determined for the open-shell state.

In the present calculations we employ one of the basis sets defined by Salez and Veillard.²⁴ From this work we selected contraction no. 14 for the s-functions and no. 8 for the p-functions. We further add one Cartesian d-function with exponent $\alpha_d = 0.75$. The basis set can be described as a (11s7p1d)/[5s4p1d] set which gives it the character of an extended basis for this system. The same extended basis set has previously been used in the Green's function calculations of von Niessen et al.²⁵ The experimental equilibrium geometry $R = 2.0693$ au is used; i.e., we obtain "vertical" ionization potentials. No orbitals are frozen in any of the correlated calculations.

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The $X^1\Sigma_g^+$ HF ground state of N_2 can be written $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4$. We consider four main ionization potentials from this state: three resulting from ionization of valence shells and one from a vacancy in an inner shell. Comparing the results presented in Table I, we note that at both the CCSD and the CCSDT-1 levels the QRHF, ROHF, and the UHF based calculations differ by at most 0.09 eV for the valence ionizations. The coincidence of the results at the CCSD level attests to the effectiveness of $\exp(T_1)$ in introducing the requisite orbital relaxation. The example for which orbital relaxation is most important is for the inner-shell case, when the absolute difference is a considerably larger ~ 7 eV. However, the difference between the relaxed UHF-CCSDT-1 and QRHF-CCSDT-1 results is a miniscule $< 0.1\%$. The coincidence of QRHF-CCSD and UHF-CCSD is primarily a measure of orbital relaxation introduced by $\exp(T_1)$, but barring difficult multireference character, the CCSDT-1 model has been shown to essentially give the full CI result.^{20a} Since the full CI is invariant to the choice of MO basis set, we would expect nearly identical results at the CCSDT-1 level for a variety of choices of MO's. We further note that the UHF results and the ROHF results are identical at the CCSDT-1 level, showing that at this level the spin contamination of the UHF based scheme is negligible. For the sake of comparison we also include the Green's function results of von Niessen et al.²⁵ and the experimental results of Siegbahn et al.²⁶ The method of von Niessen et al. employs an expansion of the self-energy, Σ , which is complete to third order. This method is unable to adequately introduce the relaxation effect in the inner shell unlike the present methods, which is why the $1\sigma_g$ ionization is not included. For other electron propagator results obtained by using a basis set of comparable size, see ref 27.

From Table I, at the Hartree-Fock level we note the incorrect ordering of the IP's for the $3\sigma_g^{-1}$ and $1\pi_u^{-1}$ states. We further note the Koopmans' value for the $1\pi_u^{-1}$ and the UHF value for the $3\sigma_g^{-1}$ IP's show accidentally good agreement with the correlated results. At the CCD level all the UHF results show good agreement with the higher level CCSD and CCSDT-1 correlated results, which attests to CCD alone accounting for the essentials of electron correlation. However, the QRHF-CCD values, which neglect $\exp(T_1)$, are too high. The erroneous ordering of IP's mentioned above is however rectified even for the QRHF reference which confirms that this problem is purely caused by the lack of correlation at the HF level. As the single excitations are introduced into the correlation operator at the CCSD level, the UHF and QRHF results agree very well, showing that $\exp(T_1)$ on top of CCD introduces the orbital relaxation contained in the UHF-CCD results.

The final inclusion of linear triples only modifies the results slightly, showing that "connected" triples, T_3 , as opposed to

"disconnected" triples like T_1T_2 and $T_1^3/3!$, are not important correlation effects for this ionization process.

The agreement with experiment is excellent with the errors for the four ionization potentials (valence to core) being 0.9%, 0.4%, 0.2%, and 0.3%, respectively. Of course, the agreement is about equally good for the CCSDT-1 and CCSD results and with either a UHF, ROHF, or QRHF reference. For N_2^+ the QRHF scheme works very well, since the orbitals are a reasonable choice and additional relaxation is easily introduced by $\exp(T_1)$. However, there are obvious limits to the suitability of the QRHF-CC method. For example, an attempt to obtain the 3P state of Be by using a QRHF starting point built upon RHF orbitals for the B state of Be is subject to failure. The reason is simple; since the 3P state requires occupying a p-orbital that lies in the continuum of Be, the CC theory is not likely to converge for the 3P state. However, once orbitals for the 3P state are obtained, moving the p-orbital below the Fermi level, convergence is found to be quite good.

In conclusion, we present a method for calculating accurate ionization energies for classes of open-shell systems using a single-reference spin-restricted coupled cluster method. This method avoids most of the problem of spin contamination and effectively introduces orbital relaxation. The approach requires using at least the CCSD model and the inclusion of non-Hartree-Fock terms in the CC equations. Appropriate iterations of the CCSD or CCSDT-1 equations could provide non-Hartree-Fock MBPT results,^{10,28} except that one would have to define a suitable H_0 for the ROHF cases.¹³ The orbital relaxation terms arising from T_1 and part of its coupling with T_2 give rise to the so-called coupled-perturbed Hartree-Fock (CPHF) diagrams.^{10,29} Their evaluation alone could be used to introduce orbital relaxation for any level of correlation, such as MBPT(4). In fact, such a hybrid model may be used to sum the CPHF terms to infinite order while "correlation" is only evaluated to some lower order.³⁰ Then, MBPT based upon a QRHF or ROHF reference, would be as accurate as the corresponding UHF-MBPT while avoiding both spin contamination and the fourfold increase in computer time due to DODS. The proposed single-reference open-shell spin-restricted CC method, unlike MBPT, is independent of any choice for H_0 and properly introduces off-diagonal Fock matrix elements, which is why it offers such a convenient computational formalism for open-shell states starting from an ROHF single-determinant reference.

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Registry No. N_2 , 7727-37-9.

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