

A unitary multiconfigurational coupled-cluster method: Theory and applications

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(Received 21 July 1987; accepted 29 September 1987)

A unitary wave operator $\exp(G)$ is used to relate a multiconfigurational reference function Φ to the full, potentially exact, electronic eigenfunction $\Psi = \exp(G)\Phi$. If the reference function Φ is of a generalized complete-active-space (CAS) form, then the energy, computed as $\langle \Phi | \exp(-G) H \exp(G) | \Phi \rangle$ is size extensive; here H is the full N -electron Hamiltonian. The Hausdorff expansion of $\exp(-G) H \exp(G)$ is truncated at second order as part of our development. The parameters which appear in the cluster operator G are determined by making this second-order energy stationary. Applications to the widely studied H_2O (at the double zeta basis level) and lowest and first excited 1A_1 states of BeH_2 are performed in order to test this method on problems where "exact" results are known.

I. INTRODUCTION

The use of cluster expansions to describe electron correlation in molecules has become increasingly prevalent in the field of quantum chemistry and has been the subject of recent review articles.¹⁻³ In this paper, we propose a new variant of the coupled-cluster theory which admits multiconfigurational reference functions of the complete-active-space (CASSCF) variety, provides a compact size-extensive and approximately variational description of the electronic energy, and is capable of incorporating certain aspects of the so-called unitary group approach (UGA).⁴ Despite recent advances⁵⁻⁸ in the theory and application of coupled-cluster methods involving high excitations from a single determinant reference (e.g., CCSDT and CCSDT- n), progress in multideterminantal-based coupled-cluster theories has been notably slower. The need for a multideterminantal theory is manifest, especially for studies of potential energy hypersurfaces on which the configurations which provide the *essential* (or qualitative) description of the wave function change with nuclear coordinates.

Two general classes of solutions to the multideterminantal coupled-cluster problem exist. The earliest multideterminantal work by Mukherjee and co-workers,⁹ Coester,¹⁰ and Kümmel and co-workers¹¹ specify constraints above and beyond those used in single configuration coupled-cluster theories by considering the wave functions of related ionized species. As shown by Jeziorski and Monkhorst,¹² and by Bartlett and co-workers,¹³ the coupled-cluster wave function for a multideterminantal reference wave function can be determined by calculations similar to, but considerably larger than, those performed in a single-configuration-based CC treatment.

The alternative, application of a single coupled-cluster wave operator to the multiconfigurational reference wave function was pioneered by Lindgren,¹⁴ drawing on earlier work on multireference perturbation theory.¹⁵ Mention should also be made of the additional theoretical work in this area by Kvasnicka.¹⁶ The cluster operators used in our method are anti-Hermitian combinations of unitary group generators and products of such generators. Such generators and generator products were first considered in the context of

coupled-cluster by Banerjee and Simons.¹⁷ Baker and Robb¹⁸ extended these earlier works to consider anti-Hermitian combinations of *external* generator products. Here, we present a method whereby internal and semiinternal generator products are also considered as well as internal and external operators using the generators themselves.

The exact, correlated, electronic wave function Ψ within any finite-orbital basis can be related to a so-called reference wave function Φ by a unitary transformation U :

$$\Psi = U\Phi, \quad (1.1)$$

provided the overlap of Φ and Ψ is not zero and Φ is normalized to unity. An arbitrary unitary transformation may be written as the exponential of an anti-Hermitian operator G :

$$U = \exp(G) \quad (1.2a)$$

with

$$G = -G^\dagger. \quad (1.2b)$$

Using a unitary ansatz for the correlated wave function, the time-independent Schrödinger equation may be written as

$$e^{-G} H e^G \Phi = E\Phi. \quad (1.3)$$

An important yet straightforward consequence of using such an anti-Hermitian logarithmic wave operator is a variational principle for the resultant energy functional.¹⁹ As discussed in greater detail in Sec. II A, an anti-Hermitian total generator also facilitates a Lie algebraic formulation of the problem in which nonadditively separable contributions to the energy are eliminated.

The particular form of the theory developed here and the numerical examples given in this paper incorporate approximations beyond those absolutely necessary. The excitation space which results from generators and single generator products acting on our multiconfiguration reference function may be seen to be identical to that used in a multireference singles and doubles configuration interaction (MR-CISD) study and in Bartlett and co-workers' earlier MR-LCCM studies.¹³ The effective Hamiltonian $\exp(-G) H \exp(G)$ is truncated at second order in the Hausdorff expansion (cf. Sec. II C). The justification for this approximation lies in the assumption that the cluster

amplitudes will be small provided the reference wave function yields a qualitatively accurate representation of the total wave function.

In Sec. II of this paper, we develop our UCC theory and provide explicit formulas for the computational implementation of its second order approximation (in the energy functional). Then in Sec. III, we examine the results of two illustrative calculations. We report agreement with full CI results within ~ 1 kcal/mol for all geometries of H_2O investigated and essentially exact agreement for BeH_2 . In Sec. IV, we compare our UCC development with earlier related work. The ansatz of a nondegenerate MCSCF reference vs a quasidegenerate model space is discussed. Finally, Sec. V contains our conclusions.

II. THEORY

A. The unitary cluster ansatz

The use of unitary operators in a nonvariational method was pioneered by Primas^{20,21} in his studies of perturbation theory. Yaris²² elucidated the earlier work with emphasis on the general properties of the generator which maintain the size extensivity of the method. The present development is then related to earlier unitary perturbation work in much the same way as the usual coupled-cluster method, pioneered by Coester and Kümmel,²³ is related to conventional single determinant perturbation theories.² As Primas²¹ realized, reference functions Φ consisting of *arbitrary* (antisymmetrized products of) one-electron functions (e.g., MCSCF orbitals) do not give rise to unlinked clusters of Yaris's first kind²² in the energy expression which results from projecting Eq. (1.3) along $\langle\Phi|$. Yaris' analysis further demonstrated that the only *other* potential source of unlinked clusters lies exclusively in the functional form of G ; these unlinked clusters of the second kind are explicitly eliminated in an additively separable form of G . The absence of unlinked clusters is related to the size extensivity of the resulting energy expression.

The completeness of the set of all unitary transformations generated by an additively separable form was discussed by Yaris for the case of a multiplicatively separable reference function.²² Application of a later theorem by Dalggaard²⁴ ensures the completeness of the same set of unitary transformations for an essentially arbitrary reference function. Of course, we cannot, in practice, use the complete set of such generators, as this would be equivalent to performing a full configuration interaction (CI) calculation. Nevertheless, the completeness of the untruncated set of generators used in our work allows for systematic improvement in a series of calculations in which larger and larger approximations to the G operator are utilized.

B. The specific choice of G

The form of the total generator that we choose to use is given as $G = \sum_{\alpha} t_{\alpha} e_{\alpha}$, where t_{α} is a so-called cluster amplitude (i.e., a scalar quantity whose value is determined numerically) and e_{α} is expressed in terms of generators e_{ij} of the unitary group $U(n)$ or single products of such generators (e.g., a two-body product has the form $e_{ijkl} \equiv e_{ij} e_{kl}$

$-\delta_{kj} e_{il}$).⁴ The generators $e_{ij} = \sum_{\sigma} a_{i\sigma}^{\dagger} a_{j\sigma}$ are given in terms of orbital excitations out of orthonormal molecular orbital ϕ_j into orbital ϕ_i . Thus the α index runs, in principle, through all nonredundant one-electron generators (e_{ij}) and two-electron generator products (e_{ijkl}), respectively. In practice, it is found that this operator list can be further truncated by a numerical screening procedure described in the Appendix without significant degradation of the wave function. We explicitly enforce anti-Hermiticity of G as follows: If e_{α} is included in the operator set, then its adjoint e_{α}^{\dagger} must also be included, and their amplitudes are restricted to obey $t_{\alpha}^{\dagger} = -t_{\alpha}$.

C. Second-order truncation of the Hausdorff expansion

Since the Hausdorff expansion of the effective Hamiltonian $e^{-G} H e^G$ appearing in Eq. (1.3) has an infinite number of terms, an exact solution to the resulting equations cannot practically be obtained. Observing that a Hausdorff expansion converges as an exponential, and assuming that Φ contains all of the *essential* (i.e., dominant) electronic configurations of Ψ , it is reasonable to *approximate* Eq. (1.3) through second order in the t_{α} amplitudes

$$\{H + [H, G] + 1/2[[H, G], G]\}|\Phi\rangle \cong E|\Phi\rangle. \quad (2.1)$$

This assumption that Φ contains the dominant configurations of Ψ is a crucial feature of our method. In practice, we satisfy this assumption by employing a multiconfiguration self-consistent field (MCSCF) wave function for Φ . Projecting Eq. (2.1) onto the reference (e.g., MCSCF) function Φ yields an expression for the total (electronic) energy as a function of the cluster amplitudes t_{α} . Requiring this energy to be stationary with respect to variations in the cluster amplitudes then yields an equation to be solved for the set of amplitudes. We note parenthetically that this procedure yields the variational energy for the approximate energy functional of Eq. (2.1) and *not* for the full untruncated energy functional of the Schrödinger equation given in Eq. (1.3). The difference in these two variational functionals will be small if the t_{α} amplitudes are small.

D. Evaluation of requisite matrix elements

The matrix elements of the single and double commutators appearing in Eq. (2.1) must be evaluated to implement our method. The earlier development of highly efficient algorithms⁴ for computing matrix elements of unitary group generators and single (but not double and higher!) generator products between spin-adapted configuration state functions (CSFs) suggests that a computationally attractive formulation for our equations might be obtained by the exclusive use of these matrix elements. In the case of the single commutator arising from projecting Eq. (2.1) onto the MCSCF reference state $\langle\Phi|$, we obtain

$$\langle\Phi|[H, G]|\Phi\rangle = 2 \sum_q \langle\Phi|H|\Phi_q\rangle \langle\Phi_q|G|\Phi\rangle. \quad (2.2)$$

The generalized Brillouin theorem within the configuration state space, which the MCSCF function obeys,²⁵ restricts the summation in Eq. (2.1) to CSFs *external* to the entire

MCSCF manifold. Moreover, the action of H on Φ can produce excited CSFs in which no more than two spin orbitals in the CAS MCSCF virtual orbital space are occupied and no more than two spin orbitals in the MCSCF core orbital space are unoccupied. Of course, if we choose to exclude some or all core or virtual excitations in G for chemical reasons, the

set of expansion CSFs is then further reduced.

A similar procedure involving the identification of those CSFs which yield nonzero matrix elements can also be applied to the double commutator term of the energy expression in Eq. (2.1). After rather tedious algebraic manipulations, we obtain

$$\begin{aligned} 1/2 \langle \Phi | [[H, G], G] | \Phi \rangle = & E_0 \sum_r \langle \Phi | G | \Phi_r \rangle \langle \Phi_r | G | \Phi \rangle + \sum'_{qq'} \langle \Phi | H | \Phi_q \rangle \langle \Phi | G | \Phi_{q'} \rangle \langle \Phi_{q'} | G | \Phi \rangle \\ & + \sum_{qr} \langle \Phi | H | \Phi_q \rangle \langle \Phi_q | G | \Phi_r \rangle \langle \Phi_r | G | \Phi \rangle - \sum_{rr'} \langle \Phi | G | \Phi_r \rangle \langle \Phi_r | H | \Phi_{r'} \rangle \langle \Phi_{r'} | G | \Phi \rangle \\ & - \sum_{qq'} \langle \Phi | G | \Phi_q \rangle \langle \Phi_q | H | \Phi_{q'} \rangle \langle \Phi_{q'} | G | \Phi \rangle - 2 \sum_{qr} \langle \Phi | G | \Phi_q \rangle \langle \Phi_q | H | \Phi_r \rangle \langle \Phi_r | G | \Phi \rangle. \end{aligned} \quad (2.3)$$

In Eq. (2.3) and throughout this work unless otherwise noted, E_0 denotes the MCSCF reference function's energy, q is an index labeling a CSF which has one or two virtual orbitals occupied (e.g., external or semiinternal excitations) or one or two core orbitals unoccupied (e.g., internal core-to-valence, external, or semiinternal excitations), r is an index labeling a CSF which is contained within the MCSCF reference function's expansion space (which therefore has no virtual orbitals occupied). A prime on the summation symbol denotes that the summation indices may not take the same value.

E. Simultaneous linear equations for t_α amplitudes

Differentiating the truncated Schrödinger equation [i.e., Eq. (2.1)], and requiring the energy to be stationary with respect to variations in the cluster amplitudes t_α yields a system of simultaneous *linear* equations of the form

$$\sum_\nu A_{\mu\nu} t_\nu = B_\mu, \quad (2.4)$$

where the dimension of the square A matrix and of the B vector in Eq. (2.4) is equal to the number of independent cluster amplitudes. Explicit forms for the A and B matrices are most easily obtained by direct differentiation of Eqs. (2.3) and (2.2), respectively. After some algebraic manipulation, we obtain

$$\begin{aligned} A_{\mu\nu} = & -2E_0 \sum_r S_{r\mu} S_{r\nu} + 2 \sum_r S_{r\mu} \sum_{r'} H_{rr'} S_{r'\nu} + \sum_{rq} \langle \Phi_q | e_\nu - e_\nu^+ | \Phi_r \rangle S_{r\mu} H_{q0} + 2 \sum_r S_{r\mu} \sum_q H_{qr} S_{q\nu} \\ & - 2E_0 \sum_q S_{q\mu} S_{q\nu} + 2 \sum_q S_{q\mu} \sum_{q'} H_{qq'} S_{q'\nu} + \sum_{qq'} \langle \Phi_{q'} | e_\nu - e_\nu^+ | \Phi_q \rangle S_{q\mu} H_{q'0} + 2 \sum_r S_{r\nu} \sum_q H_{qr} S_{q\mu} \\ & + \sum_{qr} \langle \Phi_q | e_\mu - e_\mu^+ | \Phi_r \rangle H_{q0} S_{r\nu} + \sum_{qq'} \langle \Phi_q | e_\mu - e_\mu^+ | \Phi_{q'} \rangle H_{q0} S_{q'\nu} \end{aligned} \quad (2.5a)$$

and

$$B_\mu = -2 \sum_q H_{q0} \langle \Phi_q | e_\mu - e_\mu^+ | \Phi \rangle. \quad (2.5b)$$

The additional notation introduced in Eq. (2.5) is defined as follows:

$$H_{nn'} = \langle \Phi_n | H | \Phi_{n'} \rangle, \quad H_{n0} = \langle \Phi_n | H | \Phi \rangle,$$

and

$$S_{n\lambda} = \langle \Phi_n | e_\lambda - e_\lambda^+ | \Phi \rangle,$$

where, in all of these definitions, the indices n and n' can label either a *reference CSF* (i.e., r or r') or an *excited CSF* (i.e., q and q'). As mentioned earlier, the excited CSFs contain functions in which no more than two virtual orbitals are occupied and no more than two core orbitals are unoccupied. Nevertheless, this space contains functions which may be more highly excited than doubly with respect to several of the dominant CSFs in $|\Phi\rangle$.

F. Remarks on computational implementation

Even though we have not yet investigated the relative computational efficiencies of various formulations of our theory, a few remarks regarding our present form of its implementation are in order. Even the most elementary algorithm for solving the above simultaneous equations (i.e., an algorithm which forms A in blocks on peripheral storage from blocks of the H and S arrays also kept on peripheral storage, followed by the solution of the simultaneous equations by an elimination method capable of buffering from disk) yields a computationally viable formulation for small operator manifolds ($\sim 10^3$) and small MCSCF reference spaces. There are two factors which contribute to the success of such straightforward algorithms. First, the number of

generators $\{e_\alpha\}$ acting on Φ required to span the portion of Hilbert space necessary for a rather good description of the correlated wave function, may be much less than the number of CSFs necessary to span the same space (i.e., there may be redundancies or near redundancies in the $\{e_\alpha|\Phi\rangle\}$ space). Moreover, most of the numerical operations involved in solving Eq. (2.5) are matrix multiplications, and hence eminently computationally tractable. The vectorizability is, of course, obvious in as much as the constituent matrices are just modifications of the Hamiltonian used in more conventional configuration interaction (CI) treatments of electron correlation. Specific chemical examples using the algorithms mentioned above are presented in Sec. III of this paper.

The proposed theory as outlined above would indeed be seriously limited if it were not possible to circumvent the storage and solution by elimination methods of the full A matrix. Examination of Eq. (2.5) reveals that the most pernicious terms (i.e., terms involving $\langle\Phi_q|e_\mu - e_\mu^+|\Phi_i\rangle$) always appear in contractions between these terms and the vector H_{q0} . It is therefore clear that the step involved in forming $\Sigma_q H_{q0} \langle\Phi_q|e_\mu - e_\mu^+|\Phi_i\rangle$ is of the same computational difficulty as forming the so-called sigma vector in a direct CI procedure. More explicitly, the cluster amplitudes are analogous to the molecular integrals of the CI case, while the Hamiltonian projected on the reference is similar to the trial CI vector. We are not implying that such an implementation of our theory is straightforward; indeed the sequencing of matrix portions in the computer's core appears formidable. Nevertheless, we would like to emphasize that such a direct method is in principle as open ended here as it is in the CI case.

G. Energy expression

Advantage may be taken of the requirement that the correlated energy has been made *stationary* with respect to variations in the cluster amplitudes. Using the notation introduced in Eq. (2.5), the energy achieved as the projection of the truncated Schrödinger equation [i.e., Eq. (2.1)] on the reference function may be written as

$$E = E_0 + \sum_\mu t_\mu B_\mu + 1/2 \sum_{\mu\nu} t_\mu A_{\mu\nu} t_\nu,$$

which, after using Eq. (2.4), reduces to

$$E = E_0 - 1/2 \sum_\mu B_\mu t_\mu. \quad (2.6)$$

Of course, this result is not surprising; the same functional form results whenever a variational solution to a quadratic functional is obtained.

III. RESULTS

A *pilot* version of our unitary coupled-cluster method (UCC) has been implemented using the algorithm described in Sec. II F. We have chosen two well-studied molecules on which to test our theory. First, we examine the lowest two states of 1A_1 symmetry for the C_{2v} insertion of Be into H_2 , using a (10s3p/3s1p) Be basis and a (4s/2s) H basis. The contracted Gaussian atomic orbital basis and the particular nuclear geometries used in this study are exactly those

used previously by Bartlett and co-workers²⁶⁻²⁸, and by both of the authors in previous studies.^{17,29} As our second model problem, we chose to examine the H_2O molecule within a double zeta (DZ) basis at its equilibrium bond length R_e and with both bonds stretched to $1.5 R_e$ and $2.0 R_e$. Previous studies of DZ H_2O include the full CI results of Handy and co-workers,³⁰ the many body perturbation theory and earlier multireference coupled-cluster results of Bartlett and co-workers,^{13,31} and the multireference CI studies by Shavitt and co-workers³² and by Bartlett and co-workers.¹³ These model problems were chosen both because of the availability of comparative results and because a number of important aspects of the theory are tested between these two calculations.

In all applications of our theory, a converged MCSCF wave function of the *complete active space* (CAS) variety is first obtained.³³ The orbitals in each of the energy-invariant subspaces are then rotated to a so-called canonical form. The *core*- and *virtual*-space orbitals are each rotated among themselves to diagonalize the core Fock matrix^{34,35} defined as

$$\langle i|F^c|j\rangle = \langle i|h|j\rangle + 1/2 \sum_{kl}^{\text{occ}} \lambda_{kl} [2\langle ij|kl\rangle - \langle ik|jl\rangle], \quad (3.1)$$

where λ_{kl} is the MCSCF one-particle density matrix. The *valence* orbitals are rotated among themselves to diagonalize the Lagrangian matrix,^{35,36}

$$\epsilon_{ij} = \sum_k h_{ik} \lambda_{kj} + 2 \sum_{klm} \langle ik|lm\rangle \Gamma_{jklm} \quad (3.2)$$

which also involves the symmetrical two-particle density matrix Γ_{jklm} . The configuration amplitudes for configurations in which these canonical orbitals appear are then recalculated (by performing one final CI calculation) and the resulting MCSCF wave function is used as the reference for our unitary coupled-cluster theory.

A. BeH₂

The perpendicular C_{2v} insertion of Be into H_2 (cf. Fig. 1) samples a number of chemical environments, including: the atom-diatomic environment at which the $1a_1^2 2a_1^2 3a_1^2$ configuration (i.e., $1s_{\text{Be}}^2 1\sigma_g^2 2s_{\text{Be}}^2$) dominates, the quasidegenerate "transition state" geometry at which the $1a_1^2 2a_1^2 1b_2^2$ configuration also contributes in an essential manner and the linear HBeH geometry at which $1a_1^2 2a_1^2 1b_2^2$ dominates. The atom-diatomic and linear triatomic limits are of interest since we use abelian point group molecular orbitals in our program. Hence, potential instabilities due to the existence of higher symmetries, local in the case of the separated atom-diatomic and global for the linear triatomic, are investigated at the end points of this model problem. It is well known that quasidegeneracy is a serious problem in single-reference-configuration perturbation theory and in overly truncated single-reference coupled-cluster expansions. The region near the transition state tests the ability of our theory to handle the quasidegeneracy within the MCSCF reference function. We also examine the lowest excited 1A_1 state for this perpendicular insertion of Be into H_2 to investi-

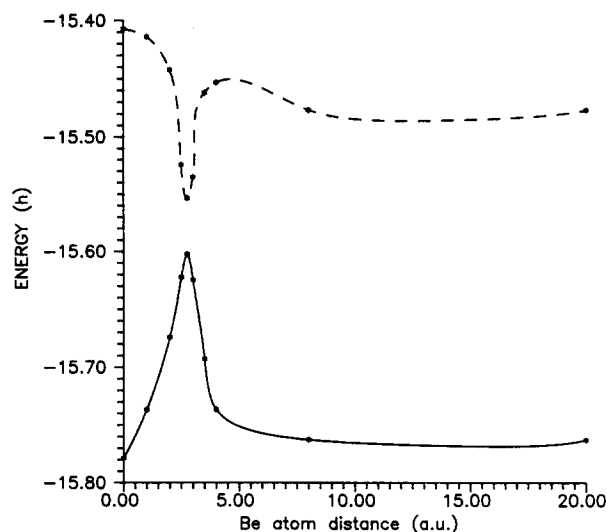


FIG. 1. Comparison of UCC with FCI energies for the lowest and first excited 1A_1 states of BeH_2 at various geometries (see the text). The * denote our UCC results, the solid and dashed lines are cubic spline fits to the FCI results.

gate the accuracy of our unitary coupled-cluster method in describing excited states and also to check the *relative* accuracy of our ground and excited states (cf. Fig. 2). This second concern definitely deserves attention in any method such as ours where the operator manifold $\{e_a\}$ varies between the two states in question because of the use of a screening procedure (see the Appendix) to eliminate unnecessary operators.

The MCSCF calculation on the reference function may be described in terms of the orbital occupancy $1a_1^2(2a_13a_14a_11b_11b_22b_2)^4$; this procedure yields 37 CSFs. We should note that a separate MCSCF calculation is performed for the ground and the excited 1A_1 states (i.e., the excited state is *not* taken to be the second root of the ground-

state variational problem with optimal ground-state orbitals). For comparison, valence space full-CI (FCI) calculations were performed in which the four valence electrons were distributed over all nine valence and excited orbitals leaving the $1a_1$ orbital doubly occupied (i.e., frozen core); this procedure yields 197 CSFs. It should be noted that the MCSCF energy itself accounts for a substantial ($\approx 90\%$) portion of the correlation energy ($E_{\text{MC}} - E_{\text{SCF}}/E_{\text{FCI}} - E_{\text{SCF}}$) in this model problem; nonetheless, the question of the utility of our unitary coupled-cluster work in describing the remaining correlation energy is important to consider. The second model problem which we examined (DZ H_2O) represents an example in which the MCSCF reference function's energy recovers a considerably smaller portion of the electron correlation energy.

At the linear geometry, the 1A_1 ground state of BeH_2 is dominated by the single configuration $2a_1^21b_2^2$ (i.e., $2\sigma_g^21\sigma_u^2$) ($C_1 = 0.986$); the first excited state of 1A_1 symmetry is also dominated by a single configuration $2a_1^13a_1^11b_2^2$ (i.e., $2\sigma_g^11\pi_u^11\sigma_u^2$) (with $C_1 = 0.975$) and corresponds to a singlet $\sigma \rightarrow \pi$ state. Use of a complete valence space reference function (in which both components of the Be π orbital are included and treated equally) ensures that the total electronic wave function transforms as an irreducible representative of $D_{\infty h}$. Though this guarantee does *not* extend to a coupled-cluster wave function using an incomplete operator manifold formed from this CAS reference; examination of the dominant cluster amplitudes indicates no propensity to break symmetry in this model problem. For the ground state, 46 cluster operators based on the one dominant configuration were chosen in our screening procedure. For the excited state, there were two configurations with amplitudes larger than 0.1 and the set of cluster operators derived from consideration of these two CSFs numbered 89. In both cases, a total of 173 CSFs would be required to span the image of the entire MCSCF reference function under the action of all of the chosen cluster operators. The dominant cluster amplitudes for all three nuclear geometries discussed in detail are presented in Table I.

The error (compared to the FCI value) in the ground-to-excited 1A_1 state energy gap for the MCSCF reference wave function is 1.1 kcal/mol; application of our unitary coupled-cluster method reduces this to 0.1 kcal/mol (see Fig. 1).

At the bent geometry $\text{Be}(0.0, 0.0, 0.0)$, $\text{H}(0.0, \pm 1.62, 2.0 \text{ a.u.})$, a second CSF ($2a_1^13a_1^1$), $1b_2^12b_2^1$ has an amplitude greater than 0.1 in the ground-state MCSCF reference wave function. (The subscripted t is used to indicate triplet coupling.⁴) The number of cluster operators chosen via our screening process at this geometry then becomes 66. At this bent geometry, the excited state becomes decidedly multi-configurational; there are 8 CSFs with amplitudes larger than 0.1; those with amplitudes larger than 0.2 include $2a_1^23a_1^2$ (0.647), $2a_1^13a_1^11b_2^2$ (-0.534), $3a_1^11b_2^2$ (-0.260), $2a_1^11b_2^2$ (0.254), and $2a_1^21b_2^1$ (-0.227). The large number of *essential* configurations thereby increases the number of cluster operators chosen through our screening process to 100. The error in the ground-to-excited state energy gap at the MCSCF level at this geometry is 1.6 kcal/

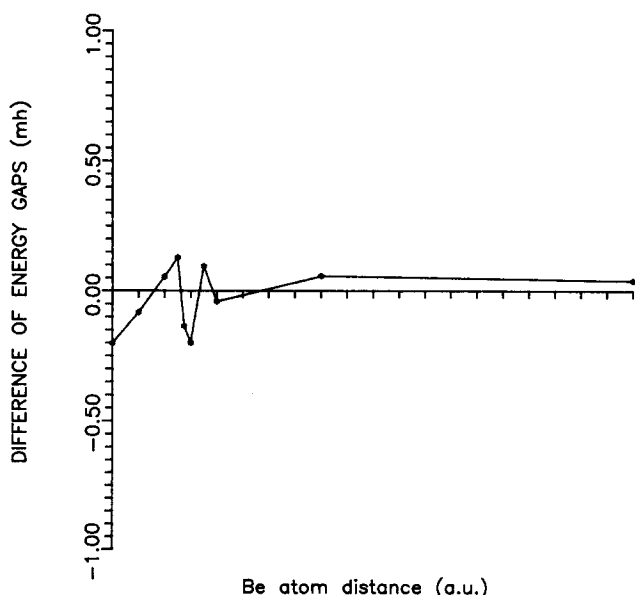


FIG. 2. Comparison of UCC and FCI energy gaps between the lowest and first excited 1A_1 states of BeH_2 at various geometries. The * denote our UCC results, the FCI results define the x axis.

TABLE I. Amplitudes of dominant cluster operators^a at various geometries of BeH₂.

	(0.0, ± 2.54, 0.0) ^b	(0.0, ± 1.62, 2.0)	(0.0, ± 0.70, 20.0)
	1 ¹ A ₁		
1b ₂ ² → 3b ₂ ²	0.0246
3a ₁ 1b ₂ → 5a ₁ 3b ₂	...	0.106	...
3a ₁ 1b ₂ → 6a ₁ 3b ₂	...	-0.0958	...
2a ₁ 2b ₂ → 3b ₂ 5a ₁	...	-0.0946	...
1σ _g ² → 2σ _g ²	0.0483
2s ² → 3s ²	0.0433
	2 ¹ A ₁		
1b ₂ ² → 3b ₂ ²	0.0259
4a ₁ → 5a ₁	0.0582
4a ₁ → 6a ₁	0.0355
2a ₁ 4a ₁ → 5a ₁ ²	...	0.485	...
1b ₂ ² → 5a ₁ ²	...	0.220	...
2a ₁ 4a ₁ → 3b ₂ ²	...	0.212	...
1σ _g ² → 2σ _g ²	0.0483

^aThe symbol $ik \rightarrow jl$ is used to denote the unitary excitation operator $e_{ijkl} - e_{jikl}$.

^bCoordinates refer to positions of hydrogen in a.u., Be is taken to be at the origin.

mol; the UCC calculation reduces this error to less than 0.1 kcal/mol. In the excited-state calculation three external excitations dominated, but it is interesting to note that two *internal* excitations had cluster amplitudes greater than 0.1:

$$4a_1^2 \rightarrow 1b_1^2 (-0.152) \quad \text{and} \quad 2a_1^1 4a_1^1 \rightarrow 2b_2^2 (-0.158).$$

At the nuclear geometry closest to the transition state, H (0.0, ± 1.275, 2.75 a.u.), we find that the wave functions of the ground and excited states are dominated by the configurations $2a_1^1 3a_1^1$ and $2a_1^1 1b_2^1$; for the ground state the amplitudes are -0.600 and 0.722, while for the excited states the relative magnitudes and signs are reversed, 0.714 and 0.564. Thus, at this geometry, the lowest excited ¹A₁ state is "doubly excited" relative to the ground state. As was pointed out earlier by one of the authors,¹⁷ a number of additional configurations are needed in the *qualitative* description of the wave function at this geometry. Both of the configurations $2a_1^1 1b_2^1$ and $2a_1^1 1b_2^1 2b_2^1$ are important in both the ground state (amplitudes 0.108 and 0.161, respectively) and the excited state (amplitudes -0.195 and 0.195, respectively). Three additional CSFs have substantial contributions to the ground state: $(2a_1^1 3a_1^1), 1b_2^1 2b_2^1$ (-0.154), $2a_1^1 3a_1^1 1b_2^1$ (0.147), and $(2a_1^1 3a_1^1), 1b_2^1 2b_2^1$ (0.110); while two additional CSFs have amplitudes greater than 0.1 in the excited state: $3a_1^1 1b_2^1$ (-0.186) and $2a_1^1 2b_2^1$ (-0.144). Cluster operator screening based on the preceding enumerated configurations yields 82 and 87 operators for the ground and excited states, respectively. As for the previously examined nuclear geometries, application of the unitary coupled-cluster method substantially reduces the error in the ground-to-excited-state energy gap from 2.8 kcal/mol at the MCSCF level to less than 0.1 kcal/mol.

Examination of the cluster amplitudes for both the ground and excited states reveals that many of the largest amplitudes correspond to internal and semiinternal excitations. In particular, of the ten largest cluster amplitudes in

the ground-state calculation, four correspond to semiinternal excitations and one to an internal excitation. Of the ten largest cluster amplitudes for the excited state, again four are semiinternal excitations and now two are internal excitations. This result surprised us since it might be argued that the use of a rather high quality MCSCF reference function would preclude the need for further correlation among the valence orbitals. Apparently, optimal correlation between valence and virtual orbitals requires significant redistribution of electron density in the valence region beyond that contained in the MCSCF reference.

The last nuclear geometry we examine in detail is the separated-atom-diatomic molecule limit [i.e., H(0.0, ± 0.70, 20.0 a.u.)]. The ground state is described by three essential configurations, $1\sigma_g^2 2s^2$ (0.954), $1\sigma_g^2 2p^2$ (-0.160), and $2s^2 1\sigma_u^2$ (-0.107). In *C*_{2v} symmetry, three distinct configurations corresponding to $1\sigma_g^2 2p^2$ (with $2p_x$, $2p_y$, and $2p_z$ included) were observed; these symmetry equivalent configurations were indeed found to have coefficients within 1×10^{-6} of one another. The lowest singlet excited state (¹Σ_g⁺ H₂ + ¹P_{Be}) is described by two essential configurations, $1\sigma_g^2 2s^1 2p^1$ (0.994) and $2s^1 2p^1 1\sigma_u^2$ (-0.111). The error in the energy gap between the ground and lowest excited ¹A₁ states calculated at the MCSCF level is 0.9 kcal/mol, and our unitary coupled-cluster method reduces this to (substantially) less than 0.1 kcal/mol. The number of cluster operators used to describe the ground-state wave function was 88 and for the lowest excited state the number was 87. A difficulty in our automatic operator selection procedure is highlighted by the excited-state calculation. The largest resulting *t*_α amplitudes (± 0.742) corresponded to a pair of excitations which break the degenerate point group: $2s^1 2p^1 \rightarrow 3s^1 1\sigma_g^1$ and $2s^1 2p^1 \rightarrow 1\sigma_g^1 3s^1$. We hasten to point out that this pair cancel each other to 1×10^{-11} and no breaking of the overall symmetry was observed. Nonetheless, this illustrates two points: First, our theory is robust enough to handle hidden additional symmetry; and second, a screening procedure with knowledge of higher symmetry would complement the straightforward screening procedure which we presently have in place. Ignoring the above spurious operator pair, only one cluster operator had a relatively large amplitude (0.0483) and corresponded to the excitation $1\sigma_g^2 \rightarrow 2\sigma_g^2$.

Summarizing this discussion of our BeH₂ data, it appears that the unitary coupled-cluster method is capable of yielding energy results uniformly accurate to within 0.1 kcal/mol, when the MCSCF reference is itself reasonably accurate (~1 kcal/mol).

B. H₂O

The simultaneous symmetric breaking of the two OH bonds in water has been the subject of several previous studies.^{13,30,31} We chose to study this model problem for two primary reasons: First, an MCSCF description of the wave function accounts for a modest and variable (with nuclear geometry) portion of the correlation energy, 35.8% at 1.0 *R*_e, 57.2% at 1.5 *R*_e, and 74.8% at 2.0 *R*_e. Second, the core (i.e., O_{1s}) orbital was included in the full CI study of this problem,³⁰ as a result of which the number of electrons to

correlate (10) is considerably larger than the number in the BeH₂ study (4).

The orbital and configuration spaces used in our MCSCF calculation are identical to those used earlier by Laidig and Bartlett.¹³ The energetically lowest two orbitals of a_1 symmetry were kept doubly occupied in all reference MCSCF configurations as was the lone pair orbital ($1b_1$), although excitations are permitted out of these orbitals by the coupled-cluster operators e_α . The remaining 4 electrons were distributed in all possible ways consistent with spin- and space-symmetry restrictions among 2 a_1 orbitals and 2 b_2 orbitals to yield a 12 configuration MCSCF reference function.

Configurations with amplitudes greater than 0.1 (0.06 for the equilibrium bond length) are displayed in Table II. Consideration of the configurations with amplitudes greater than 0.06 in the 1.0 R_e H₂O, rather than the 0.1 employed at other geometries, reduces the error in the absolute energy of the 1A_1 ground state (compared to the full CI energy) from 1.3 to 1.0 kcal/mol. It is evident that an operator screening procedure based on the amplitude of a CSF in the reference function is susceptible to the omission of many small contributions. The importance of such numerous additive contributions was emphasized, for the case of CI calculations, by Harrison and Handy.³⁰ Possible remedies for this difficulty include an operator set defined as the union of operator sets at individual geometries³⁷ or a perturbation-theory-based operator screening criterion.³⁸ We wish to emphasize two points here: First, the agreement of our results with the full-CI result is quite good, even when we use the coarser 0.1 amplitude operator screening criterion; second, the remaining difficulty is not an inherent limitation of the unitary coupled-cluster method, but rather one related to our ancillary screening procedure which can, and probably should, be improved.

The energies of our unitary coupled cluster calculation on DZ H₂O are plotted in Fig. 3. For comparison, we also include the (multireference) coupled-cluster results of Laidig and Bartlett,¹³ as well as multireference CISD,¹³ and single reference CISDTQ results of Handy and co-workers.³⁰ Casual inspection of Fig. 3 shows that all of these methods

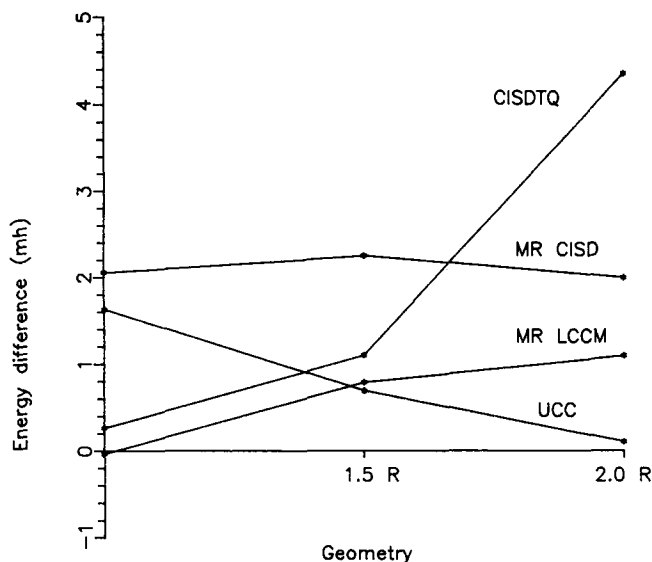


FIG. 3. Comparison of UCC, MR LCCM (Ref. 13), MR CISD (Ref. 13), and CISDTQ (Ref. 24) with FCI (Ref. 24) electronic energies for DZ H₂O at various nuclear geometries.

describe the electron correlation at a level of "chemical accuracy" (≤ 1 kcal/mol) at all nuclear geometries, except for the CISDTQ method at geometries with stretched bonds where its single configuration reference is inaccurate. The MR CISD energy is notably flat, indicating that a *uniform* error is present; both Bartlett and Laidig's earlier MR LCCM and our present UCC have variable accuracies at different bond lengths, although both yield quite accurate energies.

To achieve an accurate comparison of our results with those of other workers, we report here further details of our calculation. Using 612 cluster operators chosen using the reference function CSFs with amplitudes greater than 0.06, a correlated energy of $-76.156\,234$ hartree was obtained at the equilibrium geometry. At the 1.5 R_e geometry, 612 cluster operators are chosen using our screening process for a MCSCF amplitude criterion of 0.1. The resulting UCC correlated energy is $-76.013\,827$ hartree. At 2.0 R_e , a UCC correlated energy of $-75.905\,141$ was calculated using 576 cluster operators with a cutoff criterion of 0.1. At all three geometries, the dimension of the image of the full MCSCF reference function under the e_α operator manifold (including the identity) was 2867, while the dimension of the associated second-order CI (SOC) space was 4141. The largest-amplitude cluster operators at various bond lengths are given in Table III.

Summarizing the discussion of our H₂O data, it appears that the absolute accuracy of our UCC method can be quite good. The relative accuracy (compared to the FCI energy) varies as a function of geometry more than the relative accuracy of the MRCISD method but we feel this is probably due to variations introduced by our operator screening process. This point of view is supported by the fact that we achieve a 20.5% reduction in energy error when we expand our operator manifold further at R_e by lowering our CSF amplitude cutoff from 0.1 to 0.06.

TABLE II. Amplitudes of dominant configurations at various geometries of H₂O.

	1.0 R_e	1.5 R_e	2.0 R_e
$3a_1^2 1b_2^2$	0.986	0.921	0.716
$(3a_1^4 4a_1^1), 1b_2^1 2b_2^1$	0.0798	0.133	...
$3a_1^2 2b_2^2$	-0.0797	-0.155	-0.247
$4a_1^2 1b_2^2$	-0.0762	-0.180	-0.296
$(3a_1^4 4a_1^1), 1b_2^1 2b_2^1$	-0.0604	-0.192	0.380
$3a_1^4 4a_1^1 1b_2^1$...	-0.116	0.265
$3a_1^2 1b_2^1 2b_2^1$	0.199
$4a_1^2 2b_2^2$	0.191
$3a_1^4 4a_1^1 2b_2^1$	-0.129
$4a_1^2 1b_2^1 2b_2^1$	-0.110

TABLE III. Amplitudes of dominant cluster operators^a at various geometries of H₂O.

	1.0 R_e	1.5 R_e	2.0 R_e
$1b_1^2 \rightarrow 2b_1^2$	0.0583	0.0566	0.0569
$1b_1 1b_2 \rightarrow 2b_1 2b_2$	-0.0381	-0.0415	...
$1b_1 3a_1 \rightarrow 2b_1 4a_1$	0.0376	0.0398	...
$3a_1 2b_2 \rightarrow 4a_1 3b_2$...	0.0374	...
$4a_1 1b_2 \rightarrow 5a_1 2b_2$...	0.0366	...
$2a_1 2b_2 \rightarrow 3b_2 4a_1$	-0.0462
$2a_1 3a_1 \rightarrow 3b_2 1b_2$	-0.0455
$2a_1 1b_2 \rightarrow 3b_2 3a_1$	-0.0419
$2a_1 4a_1 \rightarrow 3b_2 2b_2$	-0.0410

^aSee footnote a of Table I.

IV. DISCUSSION

A. Multideterminantal coupled-cluster method

In the preceding sections, we developed the theory of our unitary coupled-cluster method and presented two illustrative examples. We now compare the formal structure of our work with that of earlier workers. One criterion by which multideterminantal coupled-cluster theories can be categorized involves whether the reference function is treated as nondegenerate or quasidegenerate. Earlier works, notably those of Lindgren,¹⁴ Monkhorst,¹² and Bartlett,¹³ assume that reference functions are made up of combinations of configurations which lie "close" in energy (i.e., are quasidegenerate).³⁹ This ansatz is indeed the only reasonable one for atomic calculations, which provided the initial focus of these theories. The notion of a quasidegenerate valence space also has great utility for diatomic and pi-electron system polyatomic species. However, the character of "quasidegeneracy" is sorely strained when one considers a more typical polyatomic molecule in which valence orbital interactions cause *large* splittings of the resulting molecular orbitals.²⁹ Nonetheless, a formalism based on a quasidegenerate ansatz might still work. The alternative ansatz, that of a nondegenerate yet multiconfigurational reference, becomes increasingly valid as one considers molecules in which the valence orbitals span large energy ranges. Works by one of the authors¹⁷ and by Baker and Robb¹⁸ have demonstrated the chemical utility of a nondegenerate multiconfiguration reference, and have even included works on species where a quasidegenerate model space might be more appropriate (e.g., N₂).

Previous nondegenerate (but multideterminantal) coupled-cluster methods have been subject to criticism aimed at their neglect of internal and semiinternal excitations. With the present work, we are able to include all classes of excitation operators, including the internal and semiinternal excitations. Based on the experience gained in our work and reported herein, the earlier criticisms are found to have merit; many of the largest-amplitude excitations in our numerical studies were indeed found to belong to the class of semiinternal excitations.

A legitimate concern about the use of a nondegenerate reference is the utility of the method for a physically quasidegenerate situation (e.g., near an avoided crossing). As discussed in greater detail in the previous section, the BeH₂

model problem was partially chosen to address such concerns. The results of that study support the adequacy of the initial assumption and the robustness of our method.

Since our unitary coupled-cluster method is nondegenerate, it does not describe (to any useful approximation) correlation of the orthogonal-complement MCSCF states beyond that achieved within the MCSCF process itself. As a result, the number of cluster operators required to achieve a satisfactory description of the beyond-MCSCF correlation effects for the one state under investigation is relatively small. In our study of DZ H₂O (cf. Sec. III B), the number of CSFs in the full CI calculation was 256 473; in the CISDTQ calculation there were 17 678 CSFs and in the MR CISD calculation there were 3277 CSFs. Although the exact number of cluster amplitudes used by Laidig and Bartlett¹³ in their MR LCCM treatment was not given, consideration of their algorithm suggests that a number similar to the number of CSFs in the MR CISD study was used. As detailed in the preceding section, we attain results similar in quality to the above methods using approximately 600 cluster amplitudes. Because the time needed to solve the linear equations [Eq. (2.4)] varies as the square of the number of cluster operators, such savings are significant. Since our implementation of the UCC method is presently at a pilot or rudimentary level, we defer detailed discussion of its computational efficiency to future publications. Nonetheless, it may be appreciated that a compact description of the correlated wave function ought to lead to an efficacious description of electron correlation.

In earlier work, one of the authors¹⁷ has shown the utility of a coupled-cluster energy functional truncated at second order acting on an MCSCF reference. In that work, the cluster operators were expressed as undetermined amplitudes multiplying a generator or generator product of the unitary group. The resulting $\exp(G)$ was not of a unitary type. Specification of the spin and space symmetry of the correlated wave function is straightforward in a theory using generators of the unitary group. Later work by Baker and Robb¹⁸ drawing on this earlier study replaced the cluster operators by closely related anti-Hermitian operators. This enabled a stationary condition to be used to determine the cluster amplitudes, thereby reducing the requisite equations from quadratic to linear.

We drew upon these earlier works for the functional form and the definition of the $\exp(G)$ operator, but we increased the operator set to admit entire classes not previously included and we circumvented the computational difficulties of higher order density matrices. As a result, the rate determining step of our theory is computationally similar to the rate determining step of a multireference-CI calculation, namely construction of $H\phi$, where ϕ is a trial vector of the dimension of the CSF space and H is the CSF-space representative of the Hamiltonian \hat{H} . We, therefore, expect our theory to be computationally applicable to whatever systems are accessible to the MR-CISD method.

B. Formal structure

In recent years several authors^{3,40-42} have compared the formal structure of single reference nonvariational methods

with each other and with the configuration interaction method. Though our UCC method is inherently a multideterminant-reference theory, certain aspects of the theory may be directly compared with the other methods. Examination of Eqs. (2.2) and (2.3) or, perhaps, more clearly the precursor of these equations,

$$0 = \frac{\partial}{\partial t_\alpha} \left\{ 2 \sum_q \langle \Phi | H | \Phi_q \rangle \langle \Phi_q | T | \Phi \rangle + E_0 \sum_n \langle \Phi | T | \Phi_n \rangle \langle \Phi_n | T | \Phi \rangle + \sum_{qn} \langle \Phi | H | \Phi_q \rangle \langle \Phi_q | T | \Phi_n \rangle \langle \Phi_n | T | \Phi \rangle - \sum_{nn'} \langle \Phi | T | \Phi_n \rangle \langle \Phi_n | H | \Phi_{n'} \rangle \langle \Phi_{n'} | T | \Phi \rangle \right\} \quad (4.1)$$

shows that the terms of a CEPA(0) (or L-CPMET) theory⁴⁰ are present (i.e., the first, second, and fourth terms) together with an additional term. In Eq. (4.1), we maintain our convention of using the index q for elements of the *external* state space (cf. Sec. II D), and the indices n and n' for unrestricted configuration state functions (or linear combinations thereof) orthogonal to the MCSCF reference function. A more detailed discussion of the relation of our UCC theory to an approximate (CEPA-type) theory related to it is the subject of a forthcoming publication.⁴³

As was shown by Paldus and co-workers,⁴⁰ the information content which enters in to a CISD calculation and a L-CPMET calculation is identical (i.e., the Hamiltonian in the basis of single and double excitations). Examination of Eq. (4.1) shows that our UCC theory also uses the Hamiltonian in the "singles and doubles" basis. The third term of Eq. (4.1), which is not present in the L-CPMET theory, allows the clusters to couple directly (i.e., not across the Hamiltonian but through $\langle \Phi_q | T | \Phi_n \rangle$); this direct coupling is not usually found in theories which are described as "linear." Furthermore, using a multideterminant-reference function enables the aforementioned term to include contributions from what may be described as triple and quadruple excitations *relative to the dominant CSFs* in the MCSCF reference. As was indicated in Sec. II D, the most accurate description of the level of excitation is a second-order CI space, which our UCC method fully exploits the information content thereof.

The *primary* difference between our present UCC theory and Bartlett and co-workers' MR-LCCM theory¹³ was discussed in the preceding subsection in the context of a quasidegenerate vs nondegenerate reference function. In their initial reported implementation, Laidig and Bartlett chose to neglect the cluster operator coupling the external space (i.e., T_{0Q} in their notation) because of its anticipated unimportance. Our present theory and implementation includes this term [in the second line of Eq. (4.1)], which had been neglected in earlier formulations.⁴⁴

V. CONCLUSIONS

We described the theory of a new multideterminantal coupled-cluster procedure and demonstrated its effective-

ness with two illustrative calculations on species which have been studied by many earlier workers. Our method uses a single multiconfigurational-reference wave function and appears capable of achieving "chemical accuracy" (\lesssim few kcal/mol) not only at stationary points on a Born-Oppenheimer hypersurface but also at distorted geometries.

Correlated energies calculated using our theory are additively separable (i.e., the method is size extensive), provided the energy of the reference function is also additively separable. In our opinion, the unitary coupled-cluster method described in this work is a promising procedure for high accuracy chemical studies, especially for systems with qualitatively different electronic structures in different regions of interest on the potential energy hypersurface.

Future directions of this work include analyzing algorithms for more effective implementation (especially on vector processors) and the analytical calculation of molecular responses to perturbations, including atomic displacements.

ACKNOWLEDGMENTS

The authors wish to acknowledge the financial support of the U.S. Army Research Office (Grant No. DAAG-2984K0086), the National Science Foundation (Grant No. 8206845), and the donors of the Petroleum Research Fund, administered by the American Chemical Society (PRF 14446AC6).

APPENDIX: OPERATOR MANIFOLD SCREENING PROCESS

The selection of an operator manifold to use in our UCC method within the list of all single and double excitations is important for the stability of the simultaneous equations [Eq. (2.4)] as well as for the overall efficiency of the method. Heuristically, linear combinations of excited configurations which are coupled in a manner "similar" to the MCSCF reference function interact stronger than an arbitrary linear combination of the same CSFs. This observation has been made for the coupled electron pair approximation (CEPA) in the form of the self-consistent electron pairs (SCEP) variant.^{45,46} Inclusion of excitations from the MCSCF reference to the aforementioned arbitrary linear combinations may have little effect on the energy, yet doing so is computationally costly. Concomitantly, the simultaneous linear equations which must be solved are of larger dimension and are more ill behaved.

We now describe a screening procedure in detail which is designed to circumvent the difficulty. Let $|I\rangle$ denote an, in principle, arbitrary CSF in the MCSCF reference space, and suppose we have already included some excitations $\{e_\alpha\}$ in the operator manifold M . In practice, the set of reference CSFs $\{|I\rangle\}$ is determined by a numerical dominance criterion (typically, an MCSCF coefficient greater than 0.1). The screening procedure described here is then applied sequentially to the predetermined set in order of dominance. The reference $|I\rangle$ together with the extant operator manifold M defines a set of configurations—those formed by members of M acting on $|I\rangle$. Let us assume that we have selected a subset C of the full set of configurations generated by M acting on $|I\rangle$ such that there is a one-to-one mapping from M

to C . When screening a "new" operator e_α for potential inclusion in our operator set M , we will include this operator e_α in M if $\langle K | e_\alpha | I \rangle \neq 0$ for some $|K\rangle$ not already included in C . Implementation of this algorithm is relatively straightforward, since the operator manifold M (and the set $\{|I\rangle\}$) are used to determine C , the set of excited configurations, and not vice versa. In practice, one pass through a so-called formula tape is required for screening each reference CSF.

The propriety of using a single CSF from an MCSCF function in the screening has been proven by Dalgaard. Nonetheless, we cannot apply Dalgaard's Theorem 1 from Ref. 24 without some modification, as we only have available generators e_{ij} and single products e_{ijkl} of these unitary group generators. However, it can be seen that the application of generators and generator products subsequently to other CSFs within the MCSCF configuration space (i.e., using the above process for a sequence of $|I\rangle$ s) has much the same effect as application of higher than single generator products to any one CSF. We have not rigorously studied the completeness of this particular set of operators; indeed the point is somewhat peripheral to our purpose since we desire a truncated set which embodies the essential chemistry.

Our screening procedure can be seen to select excitation operators which preferentially correlate the dominant CSFs in the MCSCF reference space. The set of operators so chosen then constitutes our $\{e_\alpha\}$ manifold. We must emphasize that these excitation operators *do* act on the entire MCSCF reference function $|\Phi_{MC}\rangle$, even though they were selected by considering their effect on individual dominant CSFs $|I\rangle$ in $|\Phi_{MC}\rangle$. The selection procedure outlined above is capable of giving rise to external and semiinternal as well as internal excitations. We have not encountered particular difficulties from any class of operators chosen by this screening process (cf. Sec. III).

The screening procedure discussed in this Appendix may be seen to be a viable, but certainly not unique, prescription for choosing a chemically reasonable truncated set of excitation operators for use in our UCC method.

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