Size-consistent wave functions for nondynamical correlation energy: The valence active space optimized orbital coupled-cluster doubles model

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The nondynamical correlation energy may be defined as the difference between full configuration interaction within the space of all valence orbitals and a single determinant of molecular orbitals (Hartree–Fock theory). In order to describe bond breaking, diradicals, and other electronic structure problems where Hartree–Fock theory fails, a reliable description of nondynamical correlation is essential as a starting point. Unfortunately, the exact calculation of nondynamical correlation energy, as defined above, involves computational complexity that grows exponentially with molecular size and is thus unfeasible beyond systems of just two or three heavy atoms. We introduce a new hierarchy of feasible approximations to the nondynamical correlation energy based on coupled-cluster theory with variationally optimized orbitals. The simplest member of this hierarchy involves connected double excitations within the variationally optimized valence active space and may be denoted as VOO-CCD, or VOD. VOO-CCD is size-consistent, has computational complexity proportional to the sixth power of molecule size, and is expected to accurately approximate the nondynamical correlation energy in such cases as single bond dissociation, diradicals, and anti-ferromagnetic coupling. We report details of our implementation of VOO-CCD and illustrate that it does indeed accurately recover the nondynamical correlation energy for challenging multireference problems such as the torsion of ethylene and chemical bond breaking. © *1998 American Institute of Physics.* [S0021-9606(98)30148-8]

I. INTRODUCTION

Recent advances in computer hardware and in *ab initio* methods have made it possible to achieve very high accuracy in electronic structure calculations.[1,2] However, it is still difficult to describe many chemically important situations such as bond breaking, transition states, and diradicals by using *ab initio* theory. The key methodological problem is the inherent multideterminantal nature of the wave function, often described as *nondynamical correlation*.[3–5]

As the simplest generic example of the bond breaking problem, consider the dissociation of the σ bond in H_2, shown schematically in Fig. 1. The simplest *ab initio* model, the Hartree–Fock (HF) approximation,[6,7] often called the self-consistent field (SCF) method, describes each electron in the molecule moving in the average field of the other electrons. The mean-field model describes chemical bonding by a *single* electronic configuration, with all electrons occupying variationally optimized orbitals. The resulting SCF wave function for H_2 is a doubly occupied σ orbital, which cannot properly describe the molecule at the dissociation limit because there are two electronic configurations, $(\sigma)^2$ and $(\sigma^*)^2$, that equally contribute to the wave function of two noninteracting H atoms. The interaction energy between these two configurations is the nondynamical correlation energy, which can be recovered by representing the wave function as a linear combination of two electronic configurations

$$\Psi = C_0 \Psi_0 + C_1 \Psi_1,$$
$$\Psi_0 = (\sigma)^2, \quad (1)$$
$$\Psi_1 = (\sigma^*)^2,$$

and optimizing both the coefficients C_i and the molecular orbitals at each nuclear geometry. Wave function (1), often referred as a two-configuration SCF (TCSCF) wave function, is the simplest example of a multiconfigurational SCF (MCSCF) wave function. In this example the orbitals σ and σ^* define the *active space*, which is the set of orbitals whose occupations vary among the different configurations included in an MCSCF wave function.

If a minimal basis set is used, then the σ and σ^* orbitals are determined by symmetry, and the two configurations $(\sigma)^2$ and $(\sigma^*)^2$ are the only ones allowed by symmetry for the ground state of H_2. Hence, for this particularly simple example, the TCSCF wave function (1) happens to be identical to a full configuration interaction (FCI) wave function in the active space of σ and σ^* orbitals. More generally, a FCI wave function defined in an active space of variationally optimized orbitals is called a complete-active-space SCF (CASSCF) wave function,[8] also known as full optimized reaction space (FORS).[9] For the H_2 molecule, when there are only two valence orbitals, wave function (1) recovers all nondynamical correlation.[5] For other molecules, however, the valence space contains more orbitals. Then, although two electronic configurations of the form $(\sigma)^2$ and $(\sigma^*)^2$ will dominate the dissociation of σ bonds, other electronic con-

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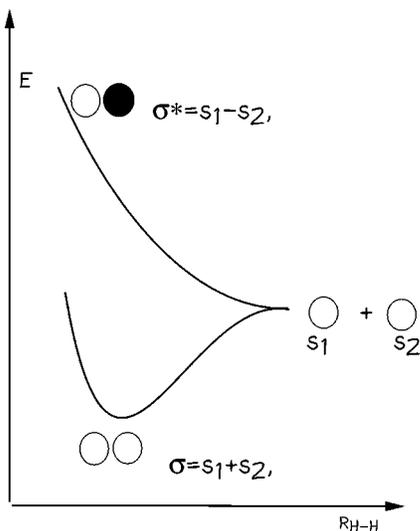
FIG. 1. Molecular orbital picture for H_2 dissociation. At equilibrium, the two hydrogen s orbitals form bonding σ and anti-bonding σ^* orbitals which are well separated in energy. The wave function describing chemical bond formation can be represented by doubly occupying the σ orbital. For a large nuclear separation, when σ and σ^* are degenerate, electrons are localized near individual H atoms and occupy orbitals s_1 and s_2.

figurations in the valence space can be important in the zero-order wave function. For instance, to describe the dissociation of each particular bond in a polyatomic molecule by a TCSCF wave function, different σ and σ^* orbitals should be included in the active space. However, describing the dissociation of two σ bonds at the same time (or one double bond) requires an MCSCF wave function including four electronic configurations. More generally, a zero-order wave function which includes all electronic configurations that can be formed by distributing the valence electrons among the valence orbitals (bonding, anti-bonding, and lone pair orbitals) is capable of describing the breaking of any type of chemical bond (double, triple, etc.) and, moreover, the simultaneous breaking of any number of bonds. In other words, *the non-dynamical correlation energy may be defined as the difference between full configuration interaction within the space of all valence orbitals, and a single determinant of molecular orbitals (Hartree–Fock theory).*[5] Hence, the CASSCF wave function incorporates all nondynamical correlation when the full valence active space is considered. Dynamical correlation energy, which is the difference between the FCI and CASSCF energies,[5] can be included later. Unfortunately, the exact calculation of nondynamical correlation energy, as defined above, involves computational complexity that grows exponentially with molecular size and is thus unfeasible beyond systems of just two or three heavy atoms.

One strategy to approximate nondynamical correlation for larger systems is to perform CASSCF calculations in smaller active spaces. In that case, nondynamical correlation is no longer completely described in the zero-order wave function. Practically, this approximation introduces arbitrariness into theoretical descriptions because the active space is no longer uniquely defined and must be chosen based on physical considerations for each particular process. Often small active orbital spaces lead to significant errors, which

cannot be completely recovered by subsequent calculations of dynamical correlation. It has been shown by Davidson[10] that CASSCF calculations for the Cope rearrangement performed in a π-orbitals active space is qualitatively incorrect, and inclusion of σ-π correlation by subsequent second-order perturbation theory (CASMP2) calculations changes the energetics along the reaction coordinate significantly. Another case where a large active space is necessary is reported by Chaban *et al.*:[11] Their study of N_2O_2 isomers demonstrated that the CASSCF space should include not only four NO bonds and one NN bond, but also the oxygen lone pairs. The resulting CASSCF space—14 electrons distributed in 12 orbitals, denoted (14,12)—is very close to today's limit for the CASSCF method.

Another approach to the bond-breaking problem is to use the unrestricted Hartree–Fock (UHF) method, which allows the α and β orbitals to be different. The UHF solution can describe electron localization near individual H atoms for H_2 at the dissociation limit using a single Slater determinant constructed from different α and β orbitals

$$\Psi_{\text{UHF}} = |s_1(1)\alpha(1)s_2(2)\beta(2)\rangle. \qquad (2)$$

However, wave function (2) is only a *half* of the correct solution, and it no longer has the correct space or spin symmetry. At the dissociation limit the UHF-solution (2) is a mixture of triplet and singlet electronic configurations and is not an eigenstate of the $\hat{S}^2$ operator. To restore the correct symmetry we have to add $|s_1(1)\beta(1)s_2(2)\alpha(2)\rangle$ to Ψ_{UHF} [Eq. (2)]. As far as these two configurations are degenerate at the dissociation limit, the energy can be described reasonably well by the incomplete wave function (2), which results in a smooth, qualitatively correct potential energy curve. Quantitatively the shape of UHF curve is not very accurate, but can be corrected by post Hartree–Fock calculations using the UHF reference. For many chemical applications, however, the molecular wave function is also important, since observables other than the energy are often required. Spin-contaminated or symmetry-broken wave functions are inappropriate in such cases. Excited-state theories using UHF references yield wave functions which are even more spin contaminated than the ground state. The calculation of nonadiabatic or spin–orbital couplings using such wave functions is impossible (e.g., singlet and triplet electronic states become scrambled, making forbidden transitions allowed). The poor quality of the wave function restricts the use of the UHF model in chemical applications. For this reason, although in certain cases they can yield very accurate potential-energy surfaces, models using UHF references are not discussed in this paper. The MCSCF and CASSCF methods to which we compare our results also almost always employ restricted orbitals.

Single-reference configuration interaction (CI) and coupled-cluster (CC) methods approximate the total correlation energy and do not distinguish between nondynamical and dynamical contributions. Though these methods can be highly accurate when the electronic state is dominated by one configuration, they fail to describe multireference states even qualitatively correctly when truncated. Single-reference CI methods are not generally reliable for dissociation pro-

cesses, because a truncated CI wave function is not size-extensive: The product of the CI wave functions of two non-interacting fragments is not itself the same CI wave function. Size-extensive coupled-cluster methods[12,13] can describe molecules at their equilibrium geometries with state-of-the-art accuracy[14] but may fail for geometrically distorted molecules (such as transition states along a reaction coordinate). The reason for this is in the unbalanced description of the important configurations $[(\sigma)^2$ and $(\sigma^*)^2$ for $H_2]$: Excitations outside the valence space describe dynamical correlation for the reference $[(\sigma)^2]$ electronic configuration, whereas dynamical correlation for other important configurations $[(\sigma^*)^2]$ is neglected. Multireference configuration interaction[15] (MRCI) and multi-reference coupled-cluster[16–22] (MRCC) methods address these difficulties by explicitly modeling both dynamical and nondynamical correlation. Unfortunately, these methods are not suitable as ''model chemistries''[23] in the sense that there is some ambiguity in the choice of the active space and reference configurations.

Here we introduce a new hierarchy of computationally efficient approximations to the nondynamical correlation energy based on coupled-cluster theory. *We approximate the active-space full CI expansion in the CASSCF wave function by a coupled-cluster expansion.* We optimize the orbitals variationally to minimize the total energy, exactly as in CASSCF or any other MCSCF procedure. Since the coupled-cluster wave function[12,13] is size-extensive (i.e., containing only linked diagrams, making the total energy scale linearly with system size[24]), the resulting active-space coupled-cluster wave function will also be size extensive. Furthermore, the method will also be size consistent (implying qualitatively correct dissociation to products[25]) as long as the active space is chosen to be the full valence space and the maximum allowed excitation level is sufficient to describe the dissociation process. Always choosing the valence space as the active space makes the active space uniquely defined and enables us to describe any molecular process where non-dynamical correlation is important with uniform accuracy, without altering the active space and without selecting ''important'' electronic configurations. Models of increasing complexity are systematically defined by the maximum level of electronic excitations allowed in coupled-cluster wave function. This determines the type of chemical bonds which can be broken: The valence active space coupled-cluster doubles (CCD) model is capable of describing the dissociation of any single bond in the molecule (or any number of such bonds, if they are noninteracting), while the coupled-cluster doubles triples and quadruples (CCDTQ) model can describe any double bond dissociation, etc. *Our approach can be viewed as a systematic strategy of approximating the exponentially complex CASSCF wave function by polynomially complex CC models.* Our approach is similar in spirit to the restricted active space self-consistent-field (RASSCF) method,[26,27] which approximates CASSCF by limiting the maximum excitation level in the active space. However, by employing a coupled-cluster expansion instead of a configuration interaction expansion in the active space, we are able to treat the simultaneous breaking of any number of nonin-
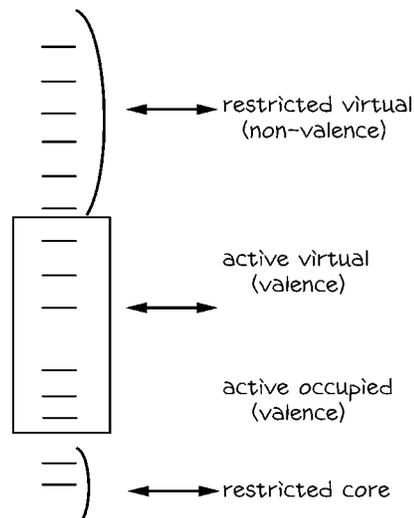

FIG. 2. Schematic representation of active and restricted orbital spaces. Excitations are allowed within the window of active orbitals. Orbitals in each subspace are defined variationally, by minimizing total energy with respect to orbital rotations between occupied/virtual and restricted/active subspaces.

teracting (and, approximately, weakly interacting) single bonds at the CCD level. The corresponding RASSCF wave function, truncated at double excitations, could only describe one single bond dissociation: The simultaneous breaking of two single bonds, even if they are noninteracting, would require explicit quadruple excitations in the RASSCF.

The simplest member of this hierarchy involves connected double excitations within the variationally optimized valence active space and may be denoted as the valence optimized orbital coupled-cluster doubles model (VOO-CCD, or simply VOD). VOO-CCD is size-consistent for single-bond breaking, has a computational complexity proportional to the sixth power of the molecule size, and is expected to accurately approximate the nondynamical correlation energy in such cases as single bond dissociation, diradicals, and anti-ferromagnetic coupling.

The structure of the paper is as follows: Sec. II presents the theoretical model and introduces VOO-CCD. In Sec. III we illustrate that our method does indeed accurately recover the nondynamical correlation energy for challenging multi-reference problems such as dissociation and the torsion of ethylene. Comparison with other *ab initio* models demonstrates the importance of a balanced description of nondynamical correlation and supports our strategy for the accurate theoretical modeling of multireference electronic wave functions.

II. THE MODEL

We propose a systematic way to approximate the exponentially complex CASSCF wave function by polynomially complex coupled-cluster (CC) wave functions. The essence of the model is to define a CC wave function within a valence active space: Electronic excitations are allowed only within the small orbital active space shown in Fig. 2. Just as in any traditional MCSCF or CASSCF model,[8,9] the active

space is defined variationally, by minimizing the total energy with respect to orbital rotations between the four orbital subspaces (Fig. 2).

The choice of the active space is straightforward:[5,9] We select all valence orbitals, such as bonding, anti-bonding, and lone pairs, imitating the molecular orbital picture in a minimal basis set. The variational optimization of each orbital subspace makes the active space uniquely defined and optimal for each molecular geometry. As long as all valence orbitals are included in the active space, we can describe any reaction coordinate with uniform accuracy, without altering the active space and without selecting ''important'' electronic configurations. Increasingly accurate models are defined by the maximum level of electronic excitations allowed in the coupled-cluster wave function. Besides theoretical consistency and computational efficiency, this model enables us to interpret results of electronic structure calculations performed in large basis sets using a simple molecular orbital picture in a valence space of bonding and anti-bonding orbitals.

This work introduces the simplest model which includes connected double excitations. Recently, we have reported an optimized orbital coupled-cluster doubles (OO-CCD, or simply OD) electronic structure model in which the orbitals are obtained variationally by minimizing the energy with respect to orbital rotations between occupied and virtual subspaces,[28] and we have noted that the orbitals so obtained are approximate Brueckner orbitals. An algorithm for this method was introduced previously,[29] and it contrasts with the typical Brueckner CCD method,[30] which obtains orbitals by a projection equation involving singly substituted determinants. The method may be defined by the following set of coupled equations:[28]

$$\langle \Phi_0 | \hat{H} | (1 + \hat{T}_2) \Phi_0 \rangle = E, \tag{3}$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | (1 + \hat{T}_2 + \tfrac{1}{2} \hat{T}_2^2) \Phi_0 \rangle = E a_{ij}^{ab}, \tag{4}$$

$$\mathbf{C} = \mathbf{C}^o \mathbf{U}(\theta),$$

$$\frac{\partial E}{\partial \mathbf{U}(\theta)} \frac{\partial \mathbf{U}(\theta)}{\partial \theta} = 0, \tag{5}$$

where the operator $\hat{T}_2$ defines all double electronic excitations in an active orbital space, $\mathbf{C}$ is the molecular orbital matrix, $\mathbf{C}^o$ defines some set of guess orbitals, and $\mathbf{U}$ is the orbital transformation matrix defined by the set of orbital rotation angles θ. Equations (3) and (4) define the energy and $\hat{T}_2$ amplitudes in the CCD model, whereas Eq. (5) defines the variationally optimized orbitals. The final programmable equations for the energy, gradients with respect to orbital rotations and nuclear displacements, and an efficient new method for solving Eqs. (3)–(5) are given in Ref. 28, which focused on the model in which all orbitals are active. Here, we consider the case in which all nonvalence orbitals are made inactive, or restricted. The $\hat{T}_2$ excitation operator now works only in the active space of valence orbitals. We describe this as the valence optimized orbital coupled-cluster doubles model (VOO-CCD, or simply VOD). The presence of inactive orbitals requires us to generalize Eq. (5) to allow

additional orbital rotations: For OO-CCD only mixing between occupied and virtual orbital subspaces alters the total energy, whereas for VOO-CCD the total energy depends also on restricted–active orbital rotations. VOO-CCD is capable of describing diradical transition states and any number of noninteracting single bonds breaking simultaneously. Including triple and quadruple excitations (VOO-CCDTQ) will allow us to describe double bond breaking and tetraradicals.

III. RESULTS AND DISCUSSION

In this section we consider two examples of chemically important situations when the accurate description of nondynamical correlation is essential. We discuss chemical bond dissociation in diatomic and polyatomic molecules and consider diradical transition states, and we compare the VOO-CCD model against the CASSCF method, to which VOO-CCD can be considered an approximation. The CASSCF and VOO-CCD calculations reported here are always performed in a full valence active space, with core orbitals restricted (except for BH results when core orbitals were included into the active space). We also show examples of single-reference calculations: Restricted Hartree–Fock self-consistent-field (SCF); configuration interaction singles and doubles (CISD); second-order Møller–Plesset perturbation theory (MP2); coupled-cluster singles and doubles (CCSD);[31] coupled-cluster singles, doubles, and full triples (CCSDT);[32] and CCSD with triple excitations treated perturbatively [CCSD(T)].[33] For all calculations we used a restricted Hartree–Fock reference. Some comparisons with full CI (FCI) are also reported.

The present study employs a double-ζ plus polarization (DZP) basis set of contracted Gaussian functions, comprised of the standard Huzinaga–Dunning[34,35] double-ζ basis augmented by six d-type polarization functions for first-row atoms [$\alpha_d(\text{B}) = 0.5$, $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{N}) = 0.8$, $\alpha_d(\text{O}) = 0.85$] and three p-type polarization functions [$\alpha_p(\text{H}) = 0.75$] for hydrogen. For BH, we used the p exponent for hydrogen [$\alpha_p(\text{H}) = 1.0$] employed by Harrison and Handy.[36] The contraction scheme for the DZP basis is $(9s5p1d/4s2p1d)$ for first-row atoms and $(4s1p/2s1p)$ for hydrogen. To elucidate the theoretical difficulties encountered for triple-bond breaking in N_2, some additional results were obtained with the minimal STO-3G basis.[37]

Calculations were performed using two *ab initio* packages: Q-CHEM[38] and PSI.[39] Our program for VOO-CCD calculations is linked to both platforms. Full CI results were obtained using the determinant-based CI program DETCI,[2,40] and most CASSCF calculations were performed using a new program written by C.D.S., which has been interfaced to DETCI. Additional CASSCF results were obtained using the GAMESS[41] electronic structure program.

A. BH molecule

The failure of single-reference methods when applied to dissociation problem, an inherently multiconfigurational situation, is well known.[1,14,42] However, *quantitative* demonstrations of this failure are relatively rare, due to the lack of benchmark full CI surfaces. In Fig. 3, we compare potential-energy curves calculated by the SCF, CISD, MP2, CCSD,
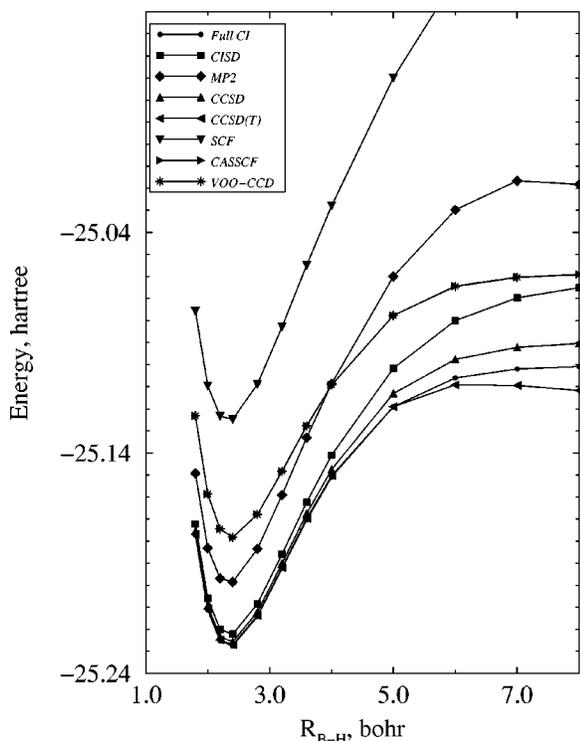
FIG. 3. Potential-energy curves for the BH molecule using a DZP basis set.

FIG. 4. Relative error against FCI calculation for BH molecule, DZP basis set.

CCSD(T), CASSCF(6,6), and VOO-CCD methods for BH to the full CI curve. Note that for chemical applications the absolute error in the energy is not important; we are interested only in the relative error along the potential-energy curve. Figure 3 demonstrates that although the potential-energy curves close to the equilibrium geometry are reproduced reasonably well by the uncorrelated Hartree–Fock method and much better by the CISD and MP2 methods, the errors in the dissociation energy are enormous. This behavior is completely expected and is due to the inherent multireference character of the dissociated molecule, which is not included in the SCF zero-order description since the single Slater determinant places both electrons in the same molecular orbital. Hence, the SCF approximation results in a too ionic wave function at the dissociation limit—both electrons can be localized near one of the atoms. MP2 theory, which treats the second electronic configuration as a perturbation to the Hartree–Fock wave function, obviously should not be applied at the dissociation limit, where both configurations are of the same importance. The CISD method fails to describe the dissociated molecule because it is not size-consistent: The product of the two fragment CISD wave functions is not itself a CISD wave function (it contains triple and quadruple excitations). The error for the CCSD method is much smaller, because coupled-cluster wave functions are size-extensive and include important higher excitations through nonlinear terms. However, the description of the two important configurations is not balanced: Excitations outside the valence space describe dynamical correlation for the reference $[(\sigma)^2]$ electronic configuration, whereas dynamical correlation for the second configuration $[(\sigma^*)^2]$ is incompletely described. Figure 3 shows also results for the
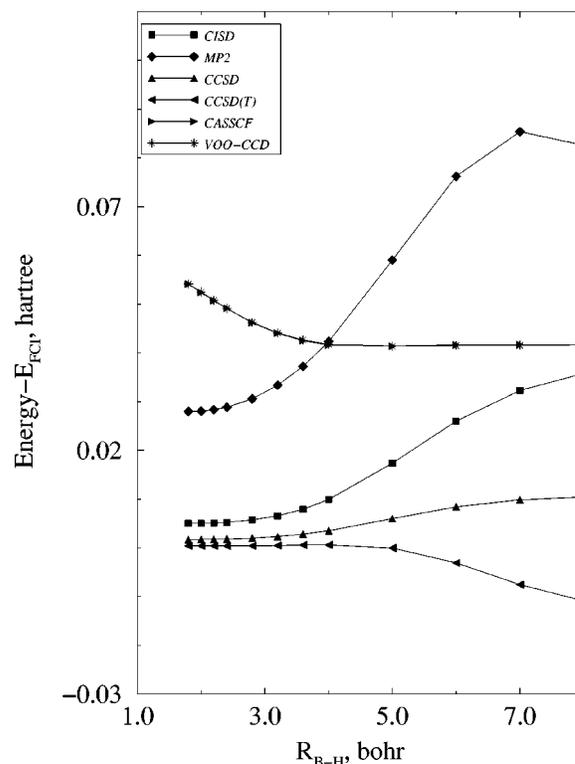
CCSD(T) model. At small nuclear separations, when the reference configuration is dominant, the CCSD(T) curve almost coincides with the FCI one. However, the perturbative treatment of triple excitations by the CCSD(T) model fails at dissociation: The near-degeneracies of orbitals in the course of nuclear separation make the perturbative approach invalid. VOO-CCD and CASSCF(6,6) curves are indistinguishable, with the maximum relative error of VOO-CCD against CASSCF(6,6) is about 0.0001 hartree (0.06 kcal mol^{-1}).

Figure 4 shows the errors against FCI. The CASSCF and VOO-CCD potential-energy curves are almost parallel to the FCI curve *at the dissociation limit*, while they introduce a relative error of around 0.01 hartree for small internuclear separations (the error decreases monotonically with increasing internuclear distance). By contrast, CC methods yield a small error near equilibrium which monotonically increases with atomic separation. This is because the nature of the error is different for the CC and CASSCF models: CASSCF recovers all nondynamical correlation but completely lacks dynamical correlation. Dynamical correlation is local, and, therefore, is more important for small internuclear distances. The locality of dynamical correlations results in a systematic overestimation of bond lengths by MCSCF models. Such behavior of the error is rather encouraging and suggests that when a description of dynamical correlation is added to the CASSCF or VOO-CCD wave functions (e.g., by perturbation theory), the resulting potential-energy curve should be nearly parallel to the FCI one. Indeed, the success of the CASPT2[43,44] model when the CASSCF is performed in a full valence space supports our expectations. For reference,

TABLE I. Total energies (hartree) for BH dissociation using the VOO-CCD, CASSCF(6,6), and full CI methods with a DZP basis set.[a]

R_{BH} (bohr)	VOO-CCD	CASSCF	FCI
1.8	−25.123 112	−25.123 143	−25.177 247
2.0	−25.158 668	−25.158 696	−25.211 118
2.2	−25.174 435	−25.174 471	−25.225 193
2.4	−25.178 286	−25.178 335	−25.227 417
2.8	−25.167 874	−25.167 956	−25.214 156
3.2	−25.148 281	−25.148 394	−25.192 401
3.6	−25.127 643	−25.127 772	−25.170 278
4.0	−25.109 155	−25.109 273	−25.150 922
5.0	−25.077 674	−25.077 645	−25.119 025
6.0	−25.064 497	−25.064 366	−25.105 991
7.0	−25.060 360	−25.060 250	−25.101 928
8.0	−25.059 160	−25.059 088	−25.100 770

[a]The SCF energy at 2.4 bohr is −25.124 742 hartree. Core electrons were correlated.

Table I contains VOO-CCD, CASSCF(6,6), and FCI total energies for several points shown in Figs. 3 and 4.

B. CH₃OH

VOO-CCD and CASSCF(14,12) potential-energy curves for C–O bond dissociation in methanol are compared in Fig. 5. Excellent agreement between the CASSCF and VOO-CCD results demonstrates that VOO-CCD approximates the CASSCF energy successfully for the dissociation of a single bond between two heavy atoms. The maximum relative error along the dissociation curve is about 0.0015 hartree
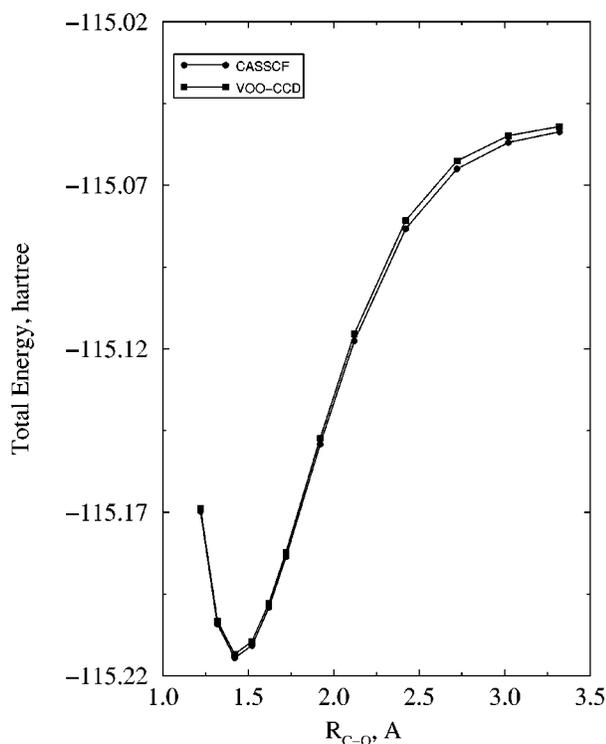
TABLE II. Total energies (hartree) for C–O bond breaking in CH₃OH using the VOO-CCD and CASSCF (14,12) methods with a DZP basis set.[a]

R_{CO} (Å)	VOO-CCD	CASSCF
1.321	−115.203 242	−115.204 206
1.421	−115.213 390	−115.214 466
1.621	−115.197 829	−115.199 165
2.421	−115.080 734	−115.083 278
3.321	−115.052 036	−115.053 618

[a]Other coordinates fixed at $R_{CH}=1.094$ *A*, $R_{OH}=0.963$ Å, $\theta_{HOC}=108.0°$. The SCF energy at $R_{CO}=1.421$ Å was −115.072 788 hartree.

(0.9 kcal mol^{-1}). Table II contains VOO-CCD and CASSCF(14,12) total energies for several points shown in Fig. 5.

C. Multiple bond dissociation

Since VOO-CCD includes only double excitations, it is only capable of describing the dissociation of a single bond (or an arbitrary number of noninteracting single bonds). The following example demonstrates the limitations of the VOO-CCD model. To describe the dissociation of the triple bond in the N₂ molecule, the wave function should contain quadruple and, in principle, sextuple excitations. Figure 6 compares the potential-energy curves for the N₂ molecule calculated by the CASSCF(10,8) and VOO-CCD methods using a DZP basis. At small internuclear distances, up to ≈$1.75r_e$, the agreement between VOO-CCD and CASSCF models is surprisingly good. Nevertheless, the VOO-CCD model fails at larger internuclear separations. The reason for this failure
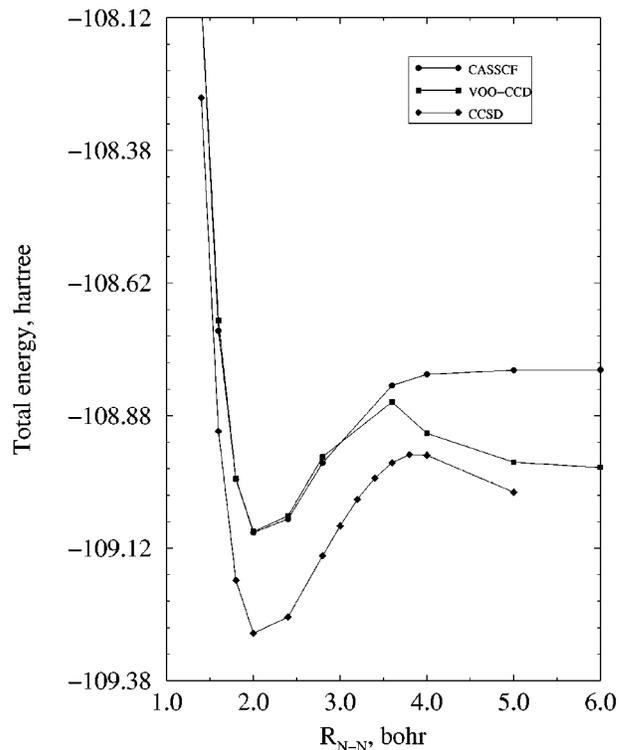

FIG. 5. C–O bond breaking in CH₃OH using the VOO-CCD and CASSCF(14,12) methods with a DZP basis set.

FIG. 6. Potential-energy curve for N₂ using a DZP basis set. Total VOO-CCD energy at the experimental equilibrium geometry ($r_e=1.0977$ Å) is −109.103 639 hartree.
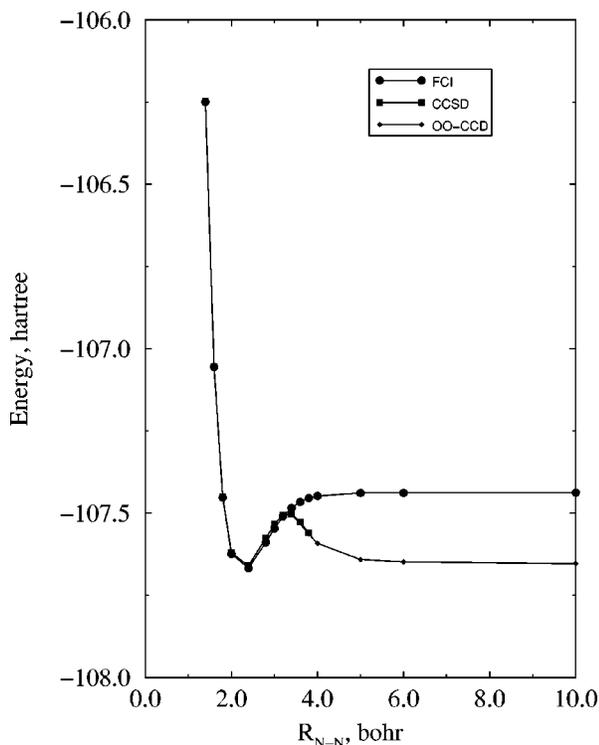
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FIG. 7. Potential-energy curve for N_2 using a minimal STO-3G basis set.

is an absence of quadruple and sextuple excitations essential for the correct breaking of a triple bond. Since the CCD model does not include these excitations, the amplitudes of double electronic excitations can be overestimated by the truncated nonlinear Eq. (4), when the weight of higher excitations in the FCI wave function is large. This results in an overestimation of the correlation energy defined by Eq. (3). Such behavior of the nonvariational CCD energy is similar to that of the MP2 model, and we note that the CCSD method (all orbitals active) behaves the same way as VOO-CCD at large internuclear distances. To strengthen this comparison, additional calculations were performed for CCSD and VOO-CCD using a minimal basis set (STO-3G), for which VOO-CCD and CCSD become more similar. The results are compared to FCI in Fig. 7: Again, VOO-CCD (which here is the same as OO-CCD if the core orbital is made active) greatly overestimates the correlation energy at the dissociation limit and yields a curve nearly identical to that of CCSD.

D. Ethylene torsional barrier

Next, we consider the torsional barrier in the ethylene molecule. This example, though simple, represents a wide class of chemically important problems such as transition states and diradicals.[45,46] The molecular orbital picture of ethylene at the equilibrium geometry and along the twisting coordinate is sketched in Fig. 8. At the equilibrium geometry, the two carbon p orbitals perpendicular to the molecular plane form bonding π and anti-bonding π^* orbitals. The ground state (labeled the N state) doubly occupies the π-orbital. A $\pi \to \pi^*$ excitation results in the V state. Doubly occupying the π^* orbital results in the Z state. As we twist ethylene around the C–C bond, the overlap between the two
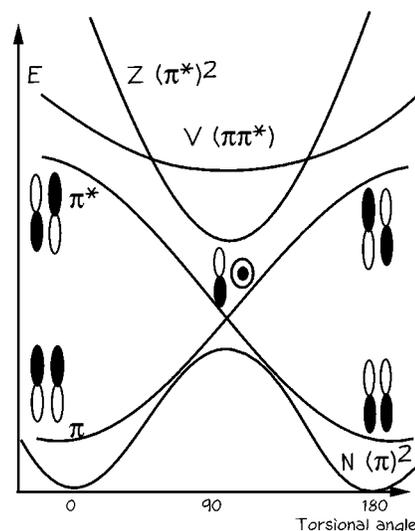

FIG. 8. Schematic molecular orbital picture of ground and excited states of ethylene along the torsional coordinate. Twisted ethylene at 90° can be considered as a simple diradical transition state.

p orbitals decreases and becomes zero at 90°. Therefore, at 90° the π and π^* orbitals become degenerate and the π bond is broken. In order to describe twisted ethylene at 90°, we have to introduce the two configurations $(\pi)^2$ and $(\pi^*)^2$ consistently into our zero-order description.

Figure 9 shows potential-energy curves along the ethylene torsional coordinate, with all other degrees of freedom frozen at the experimental equilibrium values[47] (see Table III). The restricted Hartree–Fock potential-energy curve has
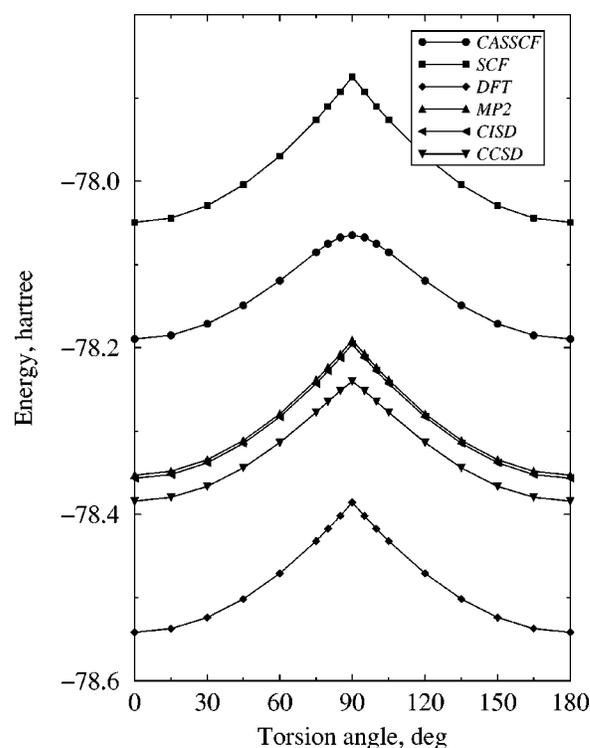

FIG. 9. Ethylene torsional barrier using a DZP basis set. The RHF SCF energy at for the planar structure is $-78.049\ 241$ hartree.

TABLE III. Total energies and geometries for planar ethylene (D_{2h}).

Method	Energy (hartree)	R_{CC} (Å)	R_{CH} (Å)	θ_{HCH}
VOO-CCD/DZP[a]	−78.192 135	1.358	1.102	116.84
MRDCl (Ref. 49)	−78.3452	1.328	1.10	117.
Exp. (Ref. 47)	n/a	1.334	1.081	117.36

[a]Core electrons correlated.

a pronounced cusp at 90° because it completely lacks the second important configuration. Restricted density functional theory (DFT) with the B3LYP[48] hybrid exchange-correlation functional also yields a sharp cusp. Neither MP2 or CISD can eliminate the cusp due to the inconsistent treatment of double excitations. The CCSD curve exhibits a cusp at 90° because the configuration $(\pi^*)^2$ is undercorrelated with respect to the reference $(\pi)^2$, whereas both configurations are of the same importance at the barrier. Perturbative treatment of higher excitations in the coupled-cluster wave function does not eliminate the cusp: We have found that CCSD(T) also has a small cusp. CASSCF, however, results in a smooth curve.

Figure 10 compares two different approximations of the CASSCF(12,12) wave function in the full valence active space: VOO-CCD and TCSCF. TCSCF is a CASSCF(2,2) calculation which describes only the two most important electronic configurations for this process: $(\pi)^2$ and $(\pi^*)^2$. The TCSCF curve is shifted down by 0.113 hartree to show all curves on the same scale. All three curves are smooth and almost coincide at small torsional angles. The maximum er-

FIG. 11. C–H bond dissociation in ethylene using CASSCF(12,12) and VOO-CCD with a DZP basis set.
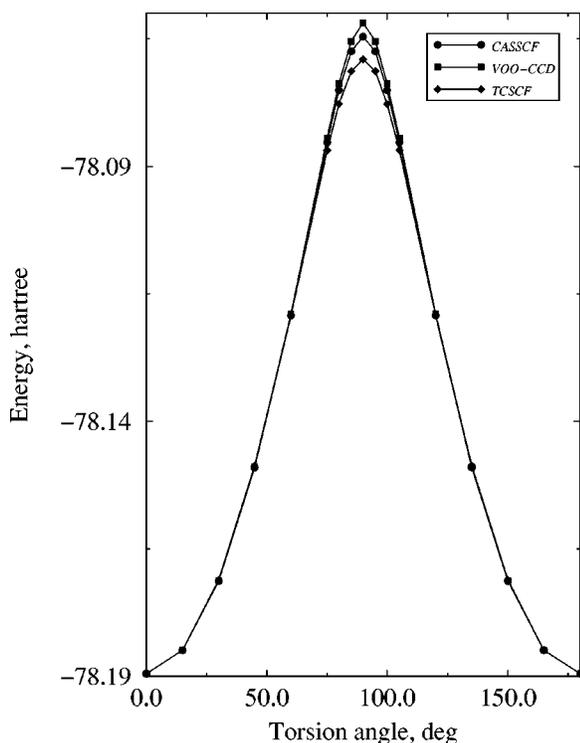

FIG. 10. The torsional barrier for ethylene as computed by CASSCF(12,12), TCSCF [CASSCF(2,2)] and VOO-CCD using a DZP basis set. An absolute error of 0.113 hartree is subtracted from the TCSCF energy in order to compare all three curves on the same scale. The VOO-CCD total energy is −78.188 456 at equilibrium and −78.061 061 at the barrier.
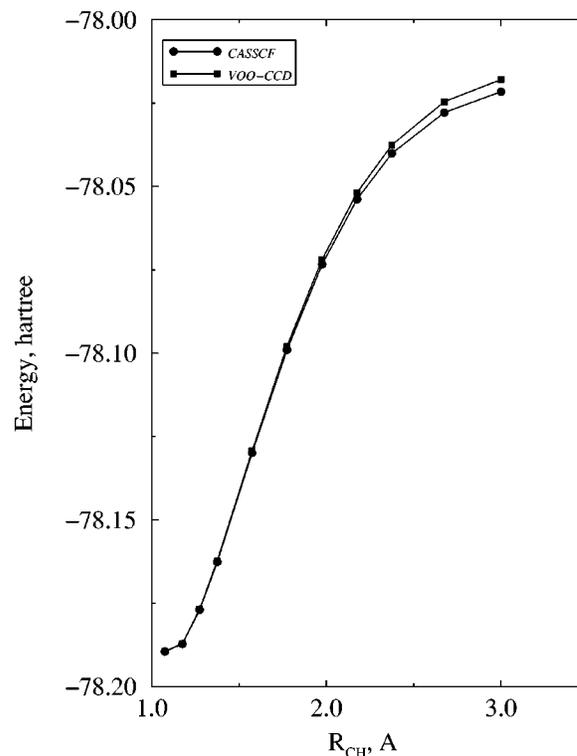
ror against CASSCF(12,12) occurs at the barrier and is small for both methods. The maximum error for VOO-CCD is 0.0025 hartree (1.6 kcal mol^{-1}), while the error for TCSCF is twice as large, −0.005 hartree (3.1 kcal mol^{-1}). The excellent agreement between VOO-CCD and CASSCF(12,12) shows that our approach indeed approximates nondynamical correlation very accurately. The larger error for the TCSCF calculations shows that our strategy for approximating nondynamical correlation gives better results than the traditional one, when CASSCF calculations are performed in smaller active spaces. For this particular case, when only two electronic configurations $[(\pi)^2$ and $(\pi^*)^2]$ are of the major importance, the effect on the energy is rather small; however, other properties can be affected much more dramatically. It has been reported[10] that σ-π correlation, which is omitted in the TCSCF wave function, is indeed very important and is difficult to recover when it is not present in the zero-order wave function. Our model is free from this type of difficulty, since we always choose the full valence space as our active space. The drastically reduced computational expense of CCD compared to full CI allows us to treat much larger molecules using the full valence space than is possible for CASSCF.

Another important advantage of our strategy is that we can describe with the same accuracy *any* single bond-breaking in ethylene without altering the active space. By contrast, for small active space CASSCF calculations, the active space must be carefully chosen for each particular reaction coordinate. This advantage is of tremendous importance where chemistry in polyatomic molecules is concerned: Very often several reaction channels can be open for

TABLE IV. Total energies, geometries, and barrier heights for twisted ethylene (D_{2d}).

Method	Energy (hartree)	R_{CC} (Å)	R_{CH} (Å)	θ_{HCH}	Barrier (eV)
VOO-CCD/DZP[a]	−78.084 796	1.494	1.105	116.88	2.92
MRDCl (Ref. 49)	−78.2451	1.484	1.104	117	2.72
Exp. (Refs. 50–54)	n/a	n/a	n/a	n/a	2.8,2.59

[a]Core electrons correlated.

the same molecule, and it is impossible to calculate reliable relevant energetics for them when the active space is different for each channel. Figure 11 compares the potential-energy curve along the CH bond dissociation coordinate for ethylene as calculated by the VOO-CCD and CASSCF(12,12) methods. The maximum difference of 0.0035 hartree (2.2 kcal mol^{-1}) between the two curves occurs at the dissociation limit. The error is of the same order of magnitude as for the torsion of ethylene.

We have also performed geometry optimizations for ethylene at equilibrium and at the barrier. Geometry optimization was performed with core orbitals included into the active space. The results are summarized in Tables III and IV. Bond lengths are overestimated by the VOO-CCD model, since dynamical correlation is not included. We would expect bond lengths to decrease for larger basis sets. The torsional barrier in ethylene is still a subject of controversy which we consider too intricate to discuss here in any further detail. However, we hope to examine this issue more closely in a future study.

IV. CONCLUSIONS

We have introduced a new approach for the size-extensive treatment of nondynamical correlation based on coupled-cluster theory and the concept of a variationally defined valence active space. We have presented the simplest member of this hierarchy, the valence optimized orbital coupled-cluster doubles (VOO-CCD) model, which approximates the CASSCF wave function using the CCD model. VOO-CCD is size-consistent and has a computational complexity proportional to the sixth power of the molecule size in contrast to exponential scaling of CASSCF model (hence, it can be applied to moderate size polyatomic molecules). We have demonstrated by numerical examples that VOO-CCD accurately approximates nondynamical correlation energy for single chemical bond dissociation and diradical transition states.

The variationally optimized full valence active space is uniquely defined and enables us to describe any type of molecular process with uniform accuracy, without altering the active space, or selecting important electronic configurations. We consider this to be a tremendous advantage versus traditional models of nondynamical correlation. The VOO-CCD model enables us to study multichannel reactions in polyatomic molecules, diradicals, and anti-ferromagnetic coupling. It is possible to define a related theory for electronically excited states, and to augment VOO-CCD model by dynamical correlation corrections; such work is currently in progress.

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