

Quadratic Coupled-Cluster Doubles: Implementation and Assessment of Perfect Pairing Optimized Geometries[†]

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We present orbital amplitude and orbital gradient equations for the quadratic coupled-cluster doubles (QCCD) theory. These expressions are size extensive and can be solved in $O(N^6)$ time with the use of $O(N^4)$ intermediates, which are efficiently defined. The optimized orbital formalism is naturally suited for excitations in only a valence space to describe nondynamical correlation. This also minimizes the additional cost relative to conventional CCD. The resulting valence QCCD is used to study the effects of correlation on equilibrium geometries of a range of small molecules in the perfect pairing active space. This enables comparison with generalized valence bond perfect pairing calculations on the same systems. Additionally, the use of valence QCCD as a supplement to complete active space (CAS) methods is illustrated with calculations of the transition structure for addition of hydrogen to *trans*-diazene (N_2H_2).

I. Introduction

Coupled-cluster theory (CC) has become the standard single reference wave function methodology in quantum chemistry because of its ability to achieve highly accurate predictions for equilibrium properties.^{1–3} The start of many applications is coupled-cluster with singles and doubles (CCSD),^{4–6} which performs well for predicting the properties of most molecules at or near equilibrium geometries. However, for more difficult problems, such as symmetry-broken molecules, CCSD suffers from underlying problems in the Hartree–Fock (HF) reference state. For symmetry-broken molecules like NO_3 ⁷ and O_4^+ ,⁸ the presence of orbital instabilities can be apparent in unexpectedly poor CCSD equilibrium properties, such as vibrational frequencies and infrared intensities. Even more extreme failures are seen for homolytic double or triple bond breaking, where CCSD energies with restricted orbitals yield pathological nonvariational failures at long bond lengths.⁹

Some of the symmetry-breaking problems can be alleviated by employing a different reference.¹⁰ The orbitals that minimize the coupled-cluster doubles (CCD) energy have proven to work well for symmetry-breaking molecules.^{11,12} We have used this method, which we call optimized doubles (OD), to study not only symmetry-breaking but also the breaking of molecular bonds.¹³ Both OD and the valence-only version (VOD), where the coupled-cluster equations are solved only in the space of optimized valence orbitals,¹³ work well for the breaking of single bonds but are incapable of breaking multiple bonds (unless the reference orbitals are permitted to break spin symmetry).

The inability of OD and VOD, which are based on the CCD energy functional, to properly dissociate multiple bonds is not so much a failure of the coupled-cluster wave function

where \hat{T}_2 is a double excitation operator and $|0\rangle$ is the reference state, as it is a result of the nonvariational nature of the CCD energy expression¹⁴

$$E_{\text{CCD}} = \langle 0 | (1 + \hat{S}_2^\dagger) (\hat{H} e^{\hat{T}_2})_c | 0 \rangle$$

$$= \langle 0 | (1 + \hat{S}_2^\dagger) (\hat{H} + \hat{H} \hat{T}_2 + \frac{1}{2} \hat{H} \hat{T}_2^2)_c | 0 \rangle \quad (2)$$

with \hat{S}_2^\dagger being a double de-excitation operator. We have previously determined¹⁴ that the coupled-cluster doubles wave function is qualitatively adequate to describe the stretching of multiple bonds, as long as one uses the Rayleigh–Ritz variational approach to minimize the expectation value of the coupled-cluster energy

$$E_{\text{VCCD}} = \frac{\langle \Psi_{\text{CCD}} | \hat{H} | \Psi_{\text{CCD}} \rangle}{\langle \Psi_{\text{CCD}} | \Psi_{\text{CCD}} \rangle} \quad (3)$$

instead of the standard projection scheme of eq 2. The variational CCD (VCCD) errors relative to the full configuration interaction (FCI) were on the order of 4 to 8 kcal/mol for the dissociation of double- and triple-bond systems in a minimal basis. This is in contrast to the conventional (nonvariational) CCD equations, which exhibited unphysical nonvariational collapse to energies well below FCI at long bond lengths. For variational CCD, larger errors were found in double- ζ basis sets, indicating that the simple CCD wave function could not simultaneously describe dynamical and nondynamical correlation as well as the latter alone. Of course the cost of variational CCD is factorial with molecular size (because it is a constrained FCI), which prohibits its use in anything other than model systems.

To avoid the intractable computational cost of variational CCD and yet improve the unsatisfactory results of standard CCD (or CCSD) for multiple bond-breaking, Van Voorhis et al. examined modifications to the conventional CCD equations in an attempt to make them more stable against nonvariational

$$|\Psi_{\text{CCD}}\rangle = e^{\hat{T}_2} |0\rangle \quad (1)$$

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collapse.¹⁵ Starting with the work of Arponen and co-workers,^{16,17}

$$E_{\text{ECCD}} = \langle 0 | e^{\hat{S}_2^\dagger} (\hat{H} e^{\hat{T}_2})_c | 0 \rangle$$

$$= \left\langle 0 \left| \left(1 + \hat{S}_2^\dagger + \frac{1}{2} \hat{S}_2^{\dagger 2} + \frac{1}{6} \hat{S}_2^{\dagger 3} \right) (\hat{H} e^{\hat{T}_2})_c \right| 0 \right\rangle \quad (4)$$

in which the \hat{S}_2^\dagger and \hat{T}_2 operators are treated on nearly equal footing rather than as in eq 2, we truncated the extended CCD (ECCD) equations to eliminate the $O(N^{10})$ scaling $\hat{S}_2^{\dagger 3} (\hat{H} e^{\hat{T}_2})_c$ term in eq 4 to end with the quadratic CCD (QCCD) equations,¹⁵

$$E_{\text{QCCD}} = \left\langle 0 \left| \left(1 + \hat{S}_2^\dagger + \frac{1}{2} \hat{S}_2^{\dagger 2} \right) (\hat{H} e^{\hat{T}_2})_c \right| 0 \right\rangle$$

$$= E_{\text{CCD}} + \left\langle 0 \left| \frac{1}{2} \hat{S}_2^{\dagger 2} \left(\frac{1}{2} \hat{H} \hat{T}_2^2 + \frac{1}{6} \hat{H} \hat{T}_2^3 \right) \right| 0 \right\rangle \quad (5)$$

QCCD can be seen as an extension of standard CCD (eq 2) through the inclusion of the $\hat{S}_2^\dagger (\hat{H} e^{\hat{T}_2})_c$ term. This term makes the coupled-cluster bivariational equations appear more variational. In other words, the left QCCD wave function $[\langle 0 | (1 + \hat{S}_2^\dagger + \frac{1}{2} \hat{S}_2^{\dagger 2}) e^{-\hat{T}_2}]$ is more similar to the right wave function $[e^{\hat{T}_2} | 0 \rangle]$ than is the corresponding left CCD wave function $[\langle 0 | (1 + \hat{S}_2^\dagger)]$. For double-bond dissociations, the QCCD energies are essentially the same as those of variational CCD. Even for a triple-bond dissociation, where QCCD yielded errors roughly three times larger than those of variational CCD, the structure of the QCCD dissociation curve remained qualitatively correct, especially when compared to the nonvariational collapse of conventional CCD.

Because the best performance for bond breaking was with a minimal basis, it would seem that QCCD should be used for this purpose with a valence active space (although equilibrium properties will usually be better with all orbitals active). This is a potentially significant extension of the work of Krylov et al.,¹³ which showed the effectiveness of VOD in describing the nondynamical correlation energy in a series of single-bond dissociations. Valence QCCD (VQCCD) will overcome the limitations of VOD for double-bond dissociations and is even reasonable for triple-bond dissociations. At the same time, its computational cost is such that active spaces on the order of 100 orbitals should be possible. This will permit the use of full valence active spaces on medium-sized molecules, which can serve as an important check on the validity of CASSCF calculations that are limited to only 13 or 14 active orbitals at present.

Here we describe a full implementation of the QCCD method and a series of additional test calculations that extend our initial report and pilot implementation.¹⁵ We present amplitude equations for the QCCD functional as well as the orbital gradient equations necessary to implement the optimized orbital version of QCCD. These equations are general for both valence active spaces and full correlation. They allow for arbitrary (e.g., nuclear as well as orbital) gradients and therefore allow geometry optimizations with analytical gradients.

As an initial application of this new implementation, we use the geometry optimization capability to study the performance of the VQCCD method (with the 1:1 or perfect pairing (PP) active space where each valence occupied orbital has a correlating orbital in the active space) for equilibrium geometries of small closed-shell molecules. This is a prerequisite to applying the method later in studies of more reactive systems, including transition structures. Furthermore, there is a recent comprehen-

TABLE 1: CCD Energy Functional^a

$$E_{\text{CCD}} = E_0 + t_{ij}^{ab} \langle ij || ab \rangle + s_{ab}^{ij} [\langle ij || ab \rangle + 2 \bar{H}_{ij}^{ba} t_{ij}^{ae} - 2 \bar{H}_j^{ma} t_{im}^{ab}]$$

$$+ \frac{1}{2} \langle ef || ab \rangle t_{ij}^{ef} + \frac{1}{2} \bar{H}_{ij}^{mn} t_{mn}^{ab} - 4 \bar{H}_{ie}^{ma} t_{mj}^{eb}]$$

$$\bar{H}_b^a \equiv f_b^a - \frac{1}{2} \langle mn || eb \rangle t_{mn}^{ea} \quad \bar{H}_j^i \equiv f_j^i + \frac{1}{2} \langle mi || ef \rangle t_{mj}^{ef}$$

$$\bar{H}_{kl}^{ij} \equiv \langle ij || kl \rangle + \frac{1}{2} \langle ij || ef \rangle t_{kl}^{ef} \quad \bar{H}_{bi}^{ja} \equiv \langle ib || ja \rangle - \frac{1}{2} \langle jm || be \rangle t_{im}^{ae}$$

^aAll repeated indices are summed over.

sive study¹⁸ of the performance of the generalized valence bond perfect pairing (GVB-PP) method along these lines against which we can compare.

Finally, having established the baseline performance of the VQCCD method in the PP space, we apply this model to the problem of the transition structure for the addition of hydrogen to *trans*-diazene. This has been previously studied using the complete active space SCF (CASSCF) method with active spaces up to full valence in size^{19,20} as well as by single reference methods.²¹ We can compare against those results, using exactly the same active spaces and basis set employed for CASSCF, to test the fidelity of VQCCD as an approximation to CASSCF, as a function of active space size. This is a model problem for one possible area in the future application of VQCCD: testing the effect of small active spaces against full valence or PP active spaces, which are not feasible for most polyatomic molecules using CASSCF.

II. Theory

We begin with the conventional formulation of the CCD wave function (eq 1) with the standard second quantization definition of the CCD excitation operator

$$\hat{T}_2 = \frac{1}{4} \sum_{ab} t_{ij}^{ab} a^\dagger b^\dagger j i \quad (6)$$

and the double de-excitation operator

$$\hat{S}_2^\dagger = \frac{1}{4} \sum_{ab} s_{ab}^{ij} i^\dagger j^\dagger b a \quad (7)$$

where i, j, k, \dots (a, b, c, \dots) denote active orbitals that are occupied (unoccupied) in the reference determinant $|0\rangle$ and t_{ij}^{ab} and s_{ab}^{ij} are the amplitudes. We will use i', j', k', \dots (a', b', c', \dots) to denote inactive occupied (unoccupied) orbitals from/to which excitations are not allowed.

A. CCD Energy and Amplitude Equations. The standard CCD energy (eq 2) may be expressed in terms of amplitudes and dressed Hamiltonian elements as in Table 1. To determine the amplitude equations for this energy, we wish to find the stationary points as functions of \hat{S}_2^\dagger and \hat{T}_2 . Symbolically, we want to enforce

$$\frac{\partial E_{\text{CCD}}}{\partial \hat{S}_2^\dagger} = 0 \quad \frac{\partial E_{\text{CCD}}}{\partial \hat{T}_2} = 0 \quad (8)$$

Because E_{CCD} is linear in \hat{S}_2^\dagger (eq 2), $\partial E_{\text{CCD}} / \partial \hat{S}_2^\dagger$ is independent of \hat{S}_2^\dagger ; therefore, the two amplitude equations (eq 8) are uncoupled. This greatly simplifies the evaluation of the CCD

energy because one never needs to compute \hat{S}_2^\dagger (only \hat{T}_2) to obtain the energy. However, for the computation of CCD energy derivatives, the $\partial E_{\text{CCD}}/\partial \hat{T}_2$ stationary equation is required. We shall also see later that both stationary conditions must be satisfied to evaluate the QCCD energy.

The derivative with respect to \hat{S}_2^\dagger is trivial because the energy is linear in \hat{S}_2^\dagger . After referring to the CCD energy in Table 1, we find that

$$\frac{\partial E_{\text{CCD}}}{\partial s_{ab}^{ij}} = P(i/j)(a/b) \left[\langle ij||ab \rangle + 2\bar{H}_{ij}^{bae} - 2\bar{H}_{ij}^{maab} + \frac{1}{2} \langle ef||ab \rangle t_{ij}^{ef} + \frac{1}{2} \bar{H}_{ij}^{mnab} - 4\bar{H}_{ei}^{maeb} \right] \quad (9)$$

The derivative with respect to \hat{T}_2 , however, is *not* trivial because we have not only the explicit derivatives of \hat{T}_2 , including the \hat{T}_2^2 term, but also the implicit derivatives of \bar{H} to consider. To maintain the $O(N^6)$ scaling, and to aid in subsequent definition of the QCCD amplitude equations, we first define a set of intermediaries that are contractions of \hat{S}_2^\dagger with \hat{T}_2 :

$$\begin{aligned} u_a^b &= s_{ea}^{mn} t_{mn}^{eb} & u_i^j &= s_{ef}^{mj} t_{mi}^{ef} \\ u_{ij}^{kl} &= s_{ef}^{kl} t_{ij}^{ef} & u_{aj}^{ib} &= s_{ae}^{im} t_{mj}^{eb} & u_{ab}^{cd} &= s_{ab}^{mn} t_{mn}^{cd} \end{aligned} \quad (10)$$

With the use of these intermediaries, along with the definitions of the dressed Hamiltonian elements in Table 1, we can now state the derivative of the CCD energy with respect to \hat{T}_2 to be

$$\begin{aligned} \frac{\partial E_{\text{CCD}}}{\partial t_{ij}^{ab}} &= P(i/j)(a/b) \left[\langle ij||ab \rangle + 2\bar{H}_{ij}^{bae} - 2\bar{H}_{ij}^{maab} + \frac{1}{2} \langle ab||ef \rangle s_{ef}^{ij} + \frac{1}{2} \bar{H}_{mn}^{ij} s_{ab}^{mn} - 4\bar{H}_{am}^{ie} s_{mj}^{eb} - u_a^e \langle ij||eb \rangle - \right. \\ &\quad \left. u_i^m \langle mj||ab \rangle + \frac{1}{4} u_{mn}^{ij} \langle mn||ab \rangle + 2u_{am}^{ie} \langle ej||bm \rangle \right] \end{aligned} \quad (11)$$

With the definition of an additional Hamiltonian term

$$\bar{H}_{bi}^{ja} \equiv \langle ib||ja \rangle - \langle jm||be \rangle t_{im}^{ae} \quad (12)$$

we can rearrange the stationary equation to

$$\begin{aligned} \frac{\partial E_{\text{CCD}}}{\partial t_{ij}^{ab}} &= P(i/j)(a/b) \left[\langle ij||ab \rangle + 2\bar{H}_{ij}^{bae} - 2\bar{H}_{ij}^{maab} + \frac{1}{2} \bar{H}_{ab}^{ef} s_{ef}^{ij} + \frac{1}{2} \bar{H}_{mn}^{ij} s_{ab}^{mn} - 4\bar{H}_{am}^{ie} s_{mj}^{eb} - u_a^e \langle ij||eb \rangle - u_i^m \langle mj||ab \rangle \right] \end{aligned} \quad (13)$$

to give an efficient final form.

B. QCCD Energy and Amplitude Equations. With the standard CCD amplitude equations defined above in eqs 9 and 13, we wish to consider the gradient of the additional energy term introduced by QCCD (eq 5). The inclusion of higher orders of \hat{S}_2^\dagger not only makes the coupled-cluster equations appear more variational but also *couples* the amplitude equations. This not only complicates the evaluation of the energy expression, because now both \hat{T}_2 and \hat{S}_2^\dagger are required for the energy, but also complicates the evaluation of the derivative with respect to \hat{S}_2^\dagger because the equations are no longer linear in \hat{S}_2^\dagger . Although the QCCD equations introduce higher-order interactions (quadruples and hexuples), through a prudent choice of $O(N^4)$ intermediaries, one can still calculate the energy in $O(N^6)$

TABLE 2: QCCD Energy Functional^a

$$\begin{aligned} E_{\text{QCCD}} &= E_{\text{CCD}} + [u_e^b u_f^d - u_{ef}^{ba} u_a^d - u_{ef}^{ad} u_{ae}^{cb} - 4u_{ej}^{kb} u_{jk}^{id} + 2x_{jk}^{bd} s_{ef}^{jk}] \times \bar{H}_{bd}^{ef}/8 \\ &\quad + [4x_{il}^{bc} s_{ce}^{im} - 4u_{ei}^{jc} u_{cj}^{mb} + 2u_{ij}^{mb} - 2u_{ei}^{kb} u_{mi}^{kl}] \\ &\quad + 2u_{d}^{bm} u_{el}^{md} - 2u_{ed}^{ab} u_{al}^{md} - y_{kl}^{ab} s_{ae}^{kn} - u_e^b u_l^m] \times \bar{H}_{bm}^{le}/4 \\ &\quad + [u_j^m u_l^n - u_{ji}^{mn} u_l^i - u_{il}^{kn} u_{kj}^{im} - 4u_{cj}^{mb} u_{bl}^{nc} + 2x_{jl}^{bc} s_{bc}^{mn}] \times \bar{H}_{mn}^{il}/8 \\ x_{ij}^{ab} &= t_{ik}^{ac} u_{cj}^{kb} & y_{ij}^{ab} &= u_{ij}^{kl} t_{kl}^{ab} \\ \bar{H}_{kl}^{ij} &\equiv \langle ij||kl \rangle + \frac{1}{2} \langle ij||ef \rangle t_{kl}^{ef} & \bar{H}_{ab}^{cd} &\equiv \langle ab||cd \rangle + \frac{1}{2} \langle mn||ab \rangle s_{mn}^{cd} \\ \bar{H}_{bi}^{ja} &\equiv \langle ib||ja \rangle - \langle jm||be \rangle t_{im}^{ae} \end{aligned}$$

^a All repeated indices are summed over.

time. Table 2 presents the QCCD energy using the intermediaries defined in eq 10.¹⁵

To determine the QCCD stationary conditions of eq 5, we begin by defining three additional intermediaries

$$\xi_{ab}^{ij} = \bar{H}_{ab}^{ef} s_{ef}^{ij} \quad \eta_{ab}^{ij} = s_{ae}^{im} \bar{H}_{bm}^{je} \quad \xi_{ab}^{ij} = s_{ab}^{mn} \bar{H}_{mn}^{ij} \quad (14)$$

that will be used along with the x_{ij}^{ab} and y_{ij}^{ab} intermediaries from Table 2. With these intermediaries, we can state the derivative of the QCCD energy with respect to \hat{S}_2^\dagger as

$$\begin{aligned} \frac{\partial E_{\text{QCCD}}}{\partial s_{ab}^{ij}} &= \frac{\partial E_{\text{CCD}}}{\partial s_{ab}^{ij}} + P(i/j)(a/b) [t_{ij}^{cd} \chi_{cd}^{ab} + t_{ik}^{ac} \chi_{cj}^{kb} + \chi_{ij}^{kl} t_{kl}^{ab} + \\ &\quad \chi_{i}^{k} t_{kj}^{ab} + t_{ij}^{ac} \chi_{c}^{b} + x_{ij}^{cd} \bar{H}_{cd}^{ab} + (4x_{ik}^{ca} + y_{ik}^{ca}) \bar{H}_{cj}^{kb} + \bar{H}_{ij}^{kl} \chi_{kl}^{ab}] \end{aligned} \quad (15)$$

where most of the complexity has been wrapped up in a set of χ intermediates,

$$\chi_{ab}^{cd} = -\frac{1}{2} u_a^e \bar{H}_{eb}^{cd} - u_{ae}^{cf} \bar{H}_{fb}^{ed} + 2u_{am}^{nc} \bar{H}_{bn}^{md} - \eta_{ab}^{mn} t_{mn}^{cd} \quad (16)$$

$$\begin{aligned} \chi_{aj}^{ib} &= (\xi_{ac}^{ik} + 4\eta_{ca}^{ik} + \xi_{ac}^{ik}) t_{kj}^{cb} + 2u_a^c \bar{H}_{cj}^{ib} + 2u_i^k \bar{H}_{aj}^{kb} - 4u_{aj}^{kc} \bar{H}_{ck}^{ib} - \\ &\quad 4\bar{H}_{aj}^{kc} u_{ck}^{ib} + 4u_{al}^{kb} \bar{H}_{jk}^{li} - 2u_{jk}^{li} \bar{H}_{al}^{kb} + 4u_{cj}^{id} \bar{H}_{da}^{bc} - 2u_{da}^{bc} \bar{H}_{cj}^{id} \end{aligned} \quad (17)$$

$$\chi_{ij}^{kl} = -\frac{1}{2} \bar{H}_{ij}^{km} u_m^l - u_{in}^{km} \bar{H}_{mj}^{nl} + 2u_{fi}^{ke} \bar{H}_{ej}^{lf} \quad (18)$$

$$\chi_a^b = \bar{H}_{ae}^{bf} u_f^e - u_n^m \bar{H}_{am}^{nb} - \frac{1}{2} \xi_{ae}^{mn} t_{mn}^{be} + 2\eta_{ae}^{mn} t_{mn}^{be} \quad (19)$$

$$\chi_i^j = \bar{H}_{im}^{jn} u_n^m - \bar{H}_{ei}^{jf} u_f^e - \frac{1}{2} t_{ik}^{ef} \xi_{ef}^{jk} + 2t_{kl}^{ef} \eta_{ef}^{kj} \quad (20)$$

Through the use of the χ intermediates, we have reduced the $O(N^{12})$ computational cost to a series of $O(N^6)$ steps with $O(N^4)$ storage. For the CCD $\partial E_{\text{CCD}}/\partial \hat{S}_2^\dagger$ equation (eq 9), the most expensive step is the $O(O^2 V^4)$ step, whereas the most expensive term in the corresponding QCCD equation is the $O(V^6)$ piece in the χ_{ab}^{cd} intermediate.

For the derivative of the QCCD energy with respect to \hat{T}_2 , we use two different sets of intermediaries (κ and $\bar{\Gamma}$) to define the terms needed in addition to those in eq 13. For the derivative

of the QCCD energy with respect to \hat{T}_2 , we have

$$\frac{\partial E_{\text{QCCD}}}{\partial t_{ab}^{ij}} = \frac{\partial E_{\text{CCD}}}{\partial t_{ab}^{ij}} + P(i/j)(a/b) \left[\kappa_{ab}^{cd} s_{cd}^{ij} + \kappa_{ak}^{ic} s_{cb}^{kj} + s_{ab}^{kl} \kappa_{kl}^{ij} + \kappa_{cb}^c s_{cb}^{ij} + s_{ab}^{ik} \kappa_k^j - \frac{1}{2} u_a^c s_{cb}^{ij} - \frac{1}{2} s_{ab}^{ik} u_k^j + 2u_b^c \eta_{ac}^{ij} + 2\eta_{ab}^{ik} u_k^j + u_{ak}^{ic} (2s_{cb}^{kj} + 2s_{cb}^{kj} + 4\eta_{cb}^{ik} + 4\eta_{bc}^{kj}) - u_{ab}^{cd} \eta_{cd}^{ij} - \eta_{ab}^{kl} u_{kl}^{ij} + \tilde{\Gamma}_{ab}^{cd} \langle cd || ij \rangle + \tilde{\Gamma}_{ak}^{ic} \langle cb || kj \rangle + \langle ab || kl \rangle \tilde{\Gamma}_{kl}^{ij} \right] \quad (21)$$

with the set of κ intermediates

$$\kappa_{ab}^{cd} = -u_{ae}^{cf} \tilde{H}_{fb}^{ed} + 2u_{am}^{nc} \tilde{H}_{bn}^{md} \quad (22)$$

$$\kappa_{aj}^{ib} = -4u_{aj}^{kc} \tilde{H}_{ck}^{ib} - 4\tilde{H}_{aj}^{kc} u_{ck}^{ib} + 4u_{al}^{kb} \tilde{H}_{jl}^{li} - 2u_{jk}^{li} \tilde{H}_{al}^{kb} + 4u_{cj}^{id} \tilde{H}_{da}^{bc} - 2u_{da}^{bc} \tilde{H}_{cj}^{id} \quad (23)$$

$$\kappa_{ij}^{kl} = -u_{in}^{km} \tilde{H}_{mj}^{nl} + 2u_{fi}^{ke} \tilde{H}_{ej}^{lf} \quad (24)$$

$$\kappa_a^b = \tilde{H}_{ae}^{bf} u_{ef}^e - u_n^m \tilde{H}_{am}^{nb} - \frac{1}{2} s_{ae}^{mn} t_{mn}^{be} + 2\eta_{ae}^{mn} t_{mn}^{be} \quad (25)$$

$$\kappa_i^j = \tilde{H}_{im}^{jn} u_n^m - \tilde{H}_{ei}^{jf} u_f^e - \frac{1}{2} t_{ik}^{ef} s_{ef}^{jk} + 2t_{ki}^{ef} \eta_{ef}^{kj} \quad (26)$$

and the QCCD two-particle density matrices ($\tilde{\Gamma}$) intermediates

$$\tilde{\Gamma}_{ab}^{cd} = \frac{1}{4} u_a^c u_b^d - \frac{1}{4} u_{ab}^{ce} u_e^d - \frac{1}{4} u_{ae}^{cf} u_{fb}^{ed} - u_{ak}^{lc} u_{bl}^{kd} + \frac{1}{2} s_{ab}^{kl} s_{kl}^{cd} \quad (27)$$

$$\tilde{\Gamma}_{aj}^{ib} = u_j^i u_a^b - 2u_{aj}^{ic} u_c^b - 2u_j^k u_{ak}^{ib} + 4u_{aj}^{kc} u_{ck}^{ib} + 2u_{ai}^{kb} u_{jk}^{li} - 2u_{cj}^{id} u_{da}^{cb} + s_{ac}^{ki} (4x_{jk}^{cb} + y_{jk}^{cb}) \quad (28)$$

$$\tilde{\Gamma}_{kl}^{ij} = \frac{1}{4} u_k^i u_l^j - \frac{1}{4} u_k^m u_{ml}^{ij} - \frac{1}{4} u_{km}^{in} u_{nl}^{mj} - u_{dk}^{ic} u_{cl}^{jd} + \frac{1}{2} s_{kl}^{ab} s_{ab}^{ij} \quad (29)$$

Note that all the terms in the κ intermediates were computed in the χ intermediates used in the derivative of the energy with respect to \hat{T}_2 to the extent that the χ_a^b and χ_i^j terms are identical to their respective κ intermediates. In coding the amplitude equations, the individual κ expressions were constructed and then used in the formation of the new s_{ab}^{ij} term. Then the additional terms required to form the χ intermediates were computed and used for the new t_{ij}^{ab} term.

Although the second step in the evaluation of the new \hat{S}_2^{\dagger} term, the contraction of the QCCD two-particle density matrices with the two-electron integrals, is simple, the work involved in obtaining the $\tilde{\Gamma}$'s (eqs 27–29) contributes to the limiting step in a QCCD calculation. The computation of the $\tilde{\Gamma}_{ab}^{cd}$ term requires $O(V^6)$ work and $O(V^4)$ storage, similar to the four virtual index κ and χ intermediates.

Upon closer inspection of the QCCD energy in Table 2 and the $\tilde{\Gamma}$'s in eqs 27–29, one observes the QCCD energy terms that are contracted with the dressed Hamiltonian elements, and the QCCD two-particle density matrices are exactly the same. Therefore, a natural consequence of obtaining the QCCD two-particle density matrices in the course of calculating the derivative with respect to \hat{T}_2 is that one can define the QCCD energy as contractions of the full one- and two-particle density matrices with Fock elements and two-electron integrals. This makes the most of the $O(V^6)$ work done to determine the updated \hat{S}_2^{\dagger} . One can obtain the QCCD $\tilde{\Gamma}_{ij}^{ab}$ term, which is not required

for the new \hat{S}_2^{\dagger} , by contracting the $\tilde{\Gamma}$'s in eqs 27–29 with the appropriate \hat{T}_2 amplitudes from the Hamiltonian terms,

$$\tilde{\Gamma}_{ij}^{ab} = \frac{1}{2} \tilde{\Gamma}_{cd}^{ab} t_{ij}^{cd} - \tilde{\Gamma}_{ej}^{mb} t_{im}^{ae} + \frac{1}{2} \tilde{\Gamma}_{ij}^{kl} t_{kl}^{ab} \quad (30)$$

The new energy expression can be written as

$$E_{\text{QCCD}} = E_0 + \gamma \mathbf{f} + \mathbf{\Gamma} \mathbf{\Gamma} \quad (31)$$

$$E_{\text{QCCD}} = E_0 + \frac{1}{2} \gamma_i^j f_j^i + \frac{1}{2} \gamma_a^b f_b^a + \frac{1}{4} \Gamma_{ij}^{kl} \langle ij || kl \rangle + \frac{1}{2} \Gamma_{ij}^{ab} \langle ij || ab \rangle + \frac{1}{2} \Gamma_{aj}^{ib} \langle aj || ib \rangle + \frac{1}{4} \Gamma_{ab}^{cd} \langle ab || cd \rangle \quad (32)$$

where E_0 is the reference energy and the Γ 's are the additions of the Γ_{CCD} from Table 4 and the QCCD $\tilde{\Gamma}$'s from eqs 27–30. The QCCD energy converges as the product of the error in t_{ij}^{ab} and the error in s_{ab}^{ij} .

An efficient implementation of the derivatives of the QCCD energy with respect to the \hat{T}_2 and \hat{S}_2^{\dagger} amplitudes (eqs 15 and 21) utilizes the repetition of many of the intermediates. Our algorithm for the calculation of the QCCD amplitude gradients and energy follows:

(1) Calculate the dressed Hamiltonian elements and u intermediates.

(2) Determine the new CCD amplitudes (eqs 9 and 13) from the above intermediates.

(3) Construct the other intermediates as needed, increment the t_{ij}^{ab} and s_{ij}^{ab} amplitudes, and then remove the intermediates from the disk, making it necessary to store only a few $O(N^4)$ quantities at any one time.

(4) Construct the full two-particle density matrices through the addition of Γ_{CCD} (Table 4) and $\tilde{\Gamma}_{\text{QCCD}}$ (eqs 27–30), and contract with the respective integrals to compute their contribution to the energy. Form the one-particle density matrices, and with the Fock elements, complete the determination of the correlation energy. Adding in the reference energy E_0 will yield the total QCCD energy. If convergence criteria are not met, return to step 1.

C. QCCD Orbital Rotation Gradients. The problem of determining the optimized orbitals that minimize the standard CCD energy has been considered in detail previously.^{12,13} In a manner similar to that utilized in ref 12, we compute the set of molecular orbitals ($C_{\mu p}[\theta]$) that minimize the QCCD energy by variationally optimizing the set of orbital rotation angles θ ,

$$C_{\mu p}(\theta) = C_{\mu q}^o U_{qp}(\theta) \quad (33)$$

where $U(\theta)$ is a unitary matrix consisting of the product of the set of Jacobi rotation matrices corresponding to orbital mixings that affect the energy. The energy minimization can be written as the following stationary condition:

$$\frac{\partial E}{\partial \theta} = \frac{\partial E}{\partial \mathbf{U}} \frac{\partial \mathbf{U}}{\partial \theta} = 0 \quad (34)$$

If we assume that the QCCD energy (eq 32) is stationary with respect to changes in the \hat{T}_2 and \hat{S}_2^{\dagger} amplitudes, then the gradient follows from the limited Hellmann–Feynmann theorem as in ref 12.

Drawing from ref 12, we use the one- and two-particle density matrices to compute the orbital rotation gradients, as seen in

TABLE 3: Optimized Orbital Gradient Equations^a

$$\begin{aligned}
\frac{\partial E}{\partial U_i^{p'}} &= 2f_i^{p'} + 2\gamma_k^i \langle j p^o | | k i' \rangle + 2\gamma_b^a \langle a p^o | | b i' \rangle \\
\frac{\partial E}{\partial U_i^p} &= 2f_i^{p'} + 2\Gamma_{ij}^{ab} \langle p^o j | | a b \rangle + 2\gamma_i^j f_j^{p'} + 2\gamma_k^j \langle j p^o | | k i \rangle + 2\gamma_b^a \langle a p^o | | b i \rangle \\
&\quad + 4\Gamma_{ij}^{kl} \langle p^o j | | k l \rangle + 2\Gamma_{ib}^{aj} \langle p^o a | | j b \rangle \\
\frac{\partial E}{\partial U_p^a} &= 2\Gamma_{ij}^{ab} \langle i j | | p^o b \rangle + 2\gamma_b^a f_{p'}^b + 4\Gamma_{cd}^{ab} \langle p^o b | | c d \rangle + 2\Gamma_{bi}^{ja} \langle i p^o | | j b \rangle \\
\frac{\partial E}{\partial U_p^{a'}} &= 0
\end{aligned}$$

^a All repeated indices are summed over.

TABLE 4: CCD One- and Two-Particle Density Matrices^a

$$\begin{aligned}
\gamma_a^b &= \frac{1}{4} P(a/b) s_{ac}^{ij} t_{ij}^{bc} \quad \gamma_i^j = -\frac{1}{4} P(i/j) s_{ab}^{jk} t_{ik}^{ab} \\
\Gamma_{ab}^{cd} &= \frac{1}{16} P(ab/cd) s_{ab}^{ij} t_{ij}^{cd} \quad \Gamma_{ij}^{kl} = \frac{1}{16} P(ij/kl) s_{ab}^{kl} t_{ij}^{ab} \quad \Gamma_{bj}^{ia} = -\frac{1}{2} P(ib/ja) s_{bc}^{ik} t_{jk}^{ac} \\
\Gamma_{ij}^{ab} &= \frac{1}{4} s_{ab}^{ij} + \frac{1}{4} t_{ij}^{ab} + \frac{1}{16} \gamma_{ij}^{ab} + \frac{1}{4} P(i/j) x_{ij}^{ab} - \frac{1}{8} P(a/b) u_{d'ij}^{ad} - \frac{1}{8} P(i/j) u_{ijl}^{l'ab}
\end{aligned}$$

^a All repeated indices are summed over.

Table 3. Note that the CCD one-particle and most of the two-particle density matrices in Table 4 are extremely similar to the u intermediates in eq 10. To include the effects of the additional terms from QCCD, one must modify the OD two-particle density matrices in Table 4 by including contributions from the $\tilde{\Gamma}$'s computed as the intermediates for the second part of the updating of \hat{S}_2^{\dagger} (eqs 27–30). Therefore, the same $\tilde{\Gamma}$'s used for the evaluation of the QCCD energy also may be used in the determination of the orbital gradient, making the evaluation of the gradient essentially free. To include the orbital rotations in the computational algorithm, one must recompute the molecular orbital coefficients $C_{\mu p}(\theta)$ for each iteration of \hat{T}_2 and \hat{S}_2^{\dagger} (step 3). This requires a transformation of the one- and two-electron integrals to the new molecular orbital basis, after which, if convergence is not reached, one returns to step 1 in the above algorithm with the new integrals. It should be emphasized that the QCCD algorithm involves concurrent iterations in both θ and amplitude space. Convergence is accelerated through the use of Pulay's direct inversion of the iterative subspace (DIIS)²² on each of the t_{ij}^{ab} , s_{ab}^{ij} , and θ vectors.

As first proposed in ref 13, with the introduction of optimized orbitals it becomes possible to apply the coupled-cluster \hat{T}_2 and \hat{S}_2^{\dagger} operators to a limited subset of orbitals, known as an active space. By choosing the active space to include either the full valence or the 1:1 perfect pairing space, we can make an approximation to CASSCF and describe the nondynamical (static) correlation energy. Within the QCCD framework, we define this process as the valence quadratic coupled-cluster doubles (VQCCD) method. Limiting the orbital space over which the QCCD operators act also increases the applicable range of molecules that can be studied. By reducing the size of the active virtual orbital space through the definition of a valence space, we greatly reduce the importance of the limiting $O(V^6)$ step introduced by the quadratic term in eq 27. Table 3 already contains the components necessary to determine the active/inactive orbital rotation gradients. The only change required in

the calculation of the new amplitudes is to limit the orbitals summed over to those contained within the active space. Factoring in these small changes, we find that the algorithm stated above remains valid.

III. Equilibrium Geometries with the Perfect Pairing Active Space

Although there are various possible applications for the QCCD method, one of the most promising serves as an approximation to the complete active space SCF (CASSCF) method, which has polynomial rather than factorial scaling with the number of active orbitals. This approximation will permit all valence electrons to be included in the active space for small and medium-sized molecules. It could then be a useful complement to CASSCF as a check on the effect of expanding the active space from just a few orbitals toward the full valence space. CASSCF is often employed to predict equilibrium or transition structures for problems where significant multireference effects are expected or encountered.

A prerequisite for such VQCCD applications is to establish the accuracy that can be expected with the full valence space for equilibrium geometries of simple polyatomic molecules. We address this issue here using the perfect pairing (PP) active space (one correlating orbital for each occupied valence orbital). This permits direct comparison against results obtained with the generalized valence bond (GVB) method in the PP approximation. GVB-PP has been applied to the prediction of equilibrium geometries using the 6-31G* basis previously.¹⁸ GVB-PP in coupled-cluster language^{23–25} is a strong local correlation approximation where only a linear number of the full quartic number of double excitations are retained. Comparing VQCCD with no local correlation approximation against GVB-PP in the same active space will allow us to judge the effects of the GVB-PP local truncation.

We used the standard 6-31G* and 6-31+G(2df,p) Pople basis sets for Hartree–Fock (HF), Møller–Plesset (MP2), generalized valence bond (GVB),²⁶ and valence quadratic coupled-cluster doubles (VQCCD) calculations.^{27–30} Whereas all orbitals are optimized in the two valence space methods, electron correlation effects are treated only in the perfect pairing active space. In the MP2 calculations, all electrons (core and valence) were correlated in the full space of all orbitals. Amplitudes for all wave functions were converged to 10^{-7} or better, whereas orbital gradients were converged to 10^{-6} or better. GVB/6-31G* results are from the work of Wang and Poirier.¹⁸ All calculations performed in this study used the experimental geometries as initial starting points and then were allowed to relax free of constraints using their respective analytic gradients. All calculations were carried out with the QCHEM 2.0 program package.³¹

The 22 closed-shell molecules used in this study are a sample of the cases studied at the GVB/6-31G* level in the work of Wang and Poirier.¹⁸ In this set of AH_nBH_m molecules, there are 22 r_{A-B} bonds and 11 r_{A-H} bonds. We inspect the mean errors, standard deviations, and maximum errors verses experiment for the r_{all} , r_{A-H} , and r_{A-B} distances. The molecules range from single-, double-, and triple-bond diatomics to assorted tri- and polyatomic molecules.

Tables 5 and 6 summarize the HF, MP2, GVB, and VQCCD results with the 6-31G* and 6-31+G(2df,p) basis sets. For all methods, increasing the basis set size decreases the bond lengths on average (Table 7). Because HF theory underestimates bond lengths, the HF/6-31G* results are actually slightly better overall than the HF/6-31+G(2df,p) results, although basis set extension effects are small. By contrast, MP2 theory performs significantly

TABLE 5: HF and MP2 Equilibrium Bond Lengths (Å) for AH_mBH_n Molecules with the 6-31G* and 6-31+G(2df,p) Basis Sets Compared to Experiment^a

molecule	bond	HF/ 6-31G*	MP2/ 6-31G*	HF/ 6-31+G(2df,p)	MP2/ 6-31+G(2df,p)	expt
Li ₂ (<i>D_{∞h}</i>)	LiLi	2.807	2.773	2.810	2.710	2.673
N ₂ (<i>D_{∞h}</i>)	NN	1.078	1.130	1.072	1.118	1.098
F ₂ (<i>D_{∞h}</i>)	FF	1.345	1.421	1.331	1.407	1.412
CO (<i>C_{∞v}</i>)	CO	1.114	1.150	1.106	1.137	1.128
CS (<i>C_{∞v}</i>)	CS	1.520	1.544	1.515	1.540	1.535
NP (<i>C_{∞v}</i>)	NP	1.455	1.536	1.451	1.522	1.491
P ₂ (<i>D_{∞h}</i>)	PP	1.859	1.932	1.856	1.920	1.893
NaF (<i>C_{∞v}</i>)	NaF	1.885	1.898	1.926	1.922	1.926
ClF (<i>C_{∞v}</i>)	ClF	1.612	1.659	1.596	1.643	1.628
Cl ₂ (<i>D_{∞h}</i>)	ClCl	1.989	2.015	1.980	1.989	1.988
HCN (<i>C_{∞v}</i>)	CN	1.132	1.169	1.129	1.168	1.153
	HC	1.059	1.069	1.059	1.065	1.065
HNC (<i>C_{∞v}</i>)	NC	1.154	1.186	1.148	1.175	1.169
	HN	0.985	1.002	0.983	0.997	0.994
HCP (<i>C_{∞v}</i>)	CP	1.515	1.560	1.512	1.553	1.540
	HC	1.063	1.076	1.063	1.072	1.069
HNO (<i>C_s</i>)	NO	1.175	1.236	1.168	1.221	1.212
	HN	1.032	1.058	1.031	1.050	1.063
HPO (<i>C_s</i>)	PO	1.461	1.517	1.450	1.499	1.512
	HP	1.431	1.453	1.441	1.449	
HOF (<i>C_s</i>)	OF	1.376	1.444	1.363	1.430	1.442
	HO	0.952	0.979	0.947	0.969	0.966
HOCl (<i>C_s</i>)	OCl	1.670	1.715	1.652	1.693	1.690
	HO	0.951	0.978	0.945	0.968	0.975
H ₂ CO (<i>C_{2v}</i>)	CO	1.184	1.220	1.179	1.210	1.208
	CH	1.092	1.104	1.094	1.101	1.116
H ₂ CS (<i>C_{2v}</i>)	CS	1.597	1.616	1.593	1.610	1.611
	CH	1.078	1.090	1.079	1.088	1.093
H ₂ O ₂ (<i>C₂</i>)	OO	1.396	1.468	1.386	1.452	1.452
	OH	0.949	0.976	0.944	0.966	0.965
H ₂ S ₂ (<i>C₂</i>)	SS	2.063	2.069	2.058	2.053	2.058
	SH	1.327	1.344	1.329	1.338	1.345
N ₂ H ₂ (<i>C_{2h}</i>)	NN	1.216	1.266	1.212	1.257	1.252
	NH	1.014	1.036	1.013	1.029	1.028

^a Reference 18.

better in the larger basis set, consistent with the known requirement of large basis sets for wave function-based treatments of dynamic correlation. For HF, the maximum error for both basis sets is due to Li₂ (Table 7), whereas the F₂ molecule is the most underestimated bond. These are both well-known to be cases that are strongly affected by electron correlation.

Turning to the two perfect pairing valence space methods, we see that GVB-PP yields slightly longer bonds on average than does MP2, regardless of the basis set. There is only a slight reduction in the RMS deviation in the larger basis set, consistent with the fact that the valence-only correlation is much less sensitive to the basis set than is correlation in the full space (as in MP2 theory, which is substantially improved in the larger basis). The overall performance is clearly superior to that of HF theory but does not surpass the performance of MP2 theory for these straightforward closed-shell cases. VQCCD yields slightly superior statistical performance to that of the GVB-PP method, as should be expected because the latter can be viewed as an approximation to the former. However, the overall performance difference is modest and suggests that most of the remaining errors are associated with correlation effects that lie outside the active space. We shall comment more on this question below.

There are some particular cases where the comparison between the various theories deserves further comment. Let us begin with several cases where VQCCD clearly improves upon the performance of GVB-PP. Perhaps the most striking is the F₂ molecule, where VQCCD substantially improves upon the GVB-PP result. Other single bonds to halogen atoms, such as in HOF, HOCl, and FCl, are also significantly improved by VQCCD. In these cases, the leading errors in GVB-PP are

TABLE 6: GVB and VQCCD Equilibrium Bond Lengths (Å) for AH_mBH_n Molecules with the 6-31G* and 6-31+G(2df,p) Basis Sets Compared to Experiment^a

molecule	bond	GVB/ 6-31G*	VQCCD/ 6-31G*	GVB/ 6-31+G(2df,p)	VQCCD/ 6-31+G(2df,p)	expt
Li ₂ (<i>D_{∞h}</i>)	LiLi	2.717	2.717	2.723	2.723	2.673
N ₂ (<i>D_{∞h}</i>)	NN	1.103	1.114	1.096	1.107	1.098
F ₂ (<i>D_{∞h}</i>)	FF	1.492	1.422	1.494	1.411	1.412
CO (<i>C_{∞v}</i>)	CO	1.131	1.140	1.120	1.133	1.128
CS (<i>C_{∞v}</i>)	CS	1.537	1.549	1.528	1.542	1.535
NP (<i>C_{∞v}</i>)	NP	1.501	1.506	1.494	1.500	1.491
P ₂ (<i>D_{∞h}</i>)	PP	1.916	1.921	1.910	1.926	1.893
NaF (<i>C_{∞v}</i>)	NaF	1.894	1.899	1.938	1.955	1.926
ClF (<i>C_{∞v}</i>)	ClF	1.693	1.651	1.666	1.638	1.628
Cl ₂ (<i>D_{∞h}</i>)	ClCl	2.071	2.045	2.029	2.039	1.988
HCN (<i>C_{∞v}</i>)	CN	1.157	1.169	1.153	1.164	1.153
	HC	1.073	1.079	1.072	1.078	1.065
HNC (<i>C_{∞v}</i>)	NC	1.173	1.183	1.164	1.176	1.169
	HN	0.999	1.006	0.996	1.004	0.994
HCP (<i>C_{∞v}</i>)	CP	1.553	1.561	1.548	1.556	1.540
	HC	1.079	1.086	1.078	1.085	1.069
HNO (<i>C_s</i>)	NO	1.220	1.219	1.210	1.212	1.212
	HN	1.050	1.067	1.046	1.064	1.063
HPO (<i>C_s</i>)	PO	1.509	1.497	1.481	1.486	1.512
	HP	1.452	1.471	1.458	1.475	
HOF (<i>C_s</i>)	OF	1.491	1.440	1.473	1.429	1.442
	HO	0.971	0.978	0.966	0.973	0.966
HOCl (<i>C_s</i>)	OCl	1.761	^b	1.727	1.700	1.690
	HO	0.972	^b	0.963	0.970	0.975
H ₂ CO (<i>C_{2v}</i>)	CO	1.215	1.215	1.206	1.210	1.208
	CH	1.106	1.117	1.106	1.118	1.116
H ₂ CS (<i>C_{2v}</i>)	CS	1.634	1.636	1.628	1.630	1.611
	CH	1.094	1.103	1.095	1.104	1.093
H ₂ O ₂ (<i>C₂</i>)	OO	1.499	1.461	1.480	1.452	1.452
	OH	0.969	0.974	0.962	0.969	0.965
H ₂ S ₂ (<i>C₂</i>)	SS	2.108	^b	2.092	^b	2.058
	SH	1.350	^b	1.350	^b	1.345
N ₂ H ₂ (<i>C_{2h}</i>)	NN	1.249	1.260	1.247	1.255	1.252
	NH	1.032	1.042	1.030	1.039	1.028

^a Reference 18. ^b Nonconvergent.

largely due to incomplete correlation treatment in the valence space rather than to an inadequate model space. These are structural consequences of the neglect of interpair correlation effects that is inherent in the GVB-PP wave function.²³ These errors may also be remedied by local correlation theories that incorporate just the leading part of such interactions^{24,25} rather than all doubles, as included in the VQCCD calculations.

We now move on to other cases where VQCCD does not substantially improve upon GVB-PP. There are perhaps three general possibilities for why improved agreement is not obtained. The first two are associated with the definition of the PP active space. First, it is possible that correlation effects that are dynamical in nature (i.e., involve excitations to higher virtual orbitals that are outside the PP space) may significantly affect the geometries in these cases. Second, it is possible that treating only the valence orbitals is insufficient within the perfect pairing model in some of these cases; it may be necessary to correlate some inner electrons also. Third, it is possible that correlation effects within the PP active space are not treated adequately by the QCCD method, which would be the case if, for instance, there are large contributions from connected triple, quadruple, or higher excitations because QCCD explicitly treats only doubles. In general, we expect that dynamical correlation is most likely to be the leading source of error. Whereas we cannot disentangle these factors fully, we shall now discuss the poorer VQCCD results in terms of these possibilities.

Upon inspecting the data in Table 6, we see that there appear to be two types of cases where large GVB-PP errors are not substantially improved by VQCCD. The first involves bonds to electropositive elements such as Li and Na, as seen in molecules such as Li₂ and NaF. The second involves a number of cases associated with other second-row elements such as P,

TABLE 7: Mean Error and Standard Deviation (Å) for HF, MP2, GVB, and VQCCD in the 6-31G* and the 6-31+G(2df,p) Basis Sets Relative to Experiment

	mean			standard deviation			maximum error
	r_{all}	$r_{\text{A-H}}$	$r_{\text{A-B}}$	r_{all}	$r_{\text{A-H}}$	$r_{\text{A-B}}$	
HF/6-31G*	-0.020	-0.016	-0.021	0.032	0.008	0.040	0.134
MP2/6-31G*	0.015	0.003	0.021	0.021	0.008	0.023	0.100
GVB/6-31G*	0.017	0.002	0.025	0.028	0.007	0.031	0.083
VQCCD/6-31G*	0.013	0.010	0.014	0.015	0.005	0.018	0.057
HF/6-31+G(2df,p)	-0.023	-0.017	-0.026	0.035	0.008	0.043	0.137
MP2/6-31+G(2df,p)	0.004	-0.003	0.007	0.012	0.006	0.013	0.037
GVB/6-31+G(2df,p)	0.010	-0.001	0.015	0.022	0.008	0.025	0.082
VQCCD/6-31+G(2df,p)	0.010	0.007	0.011	0.015	0.006	0.018	0.051

TABLE 8: Geometric Parameters (Å and deg) of *trans*-N₂H₂ in the cc-pVDZ Basis Set

	VQCCD (12,12)	VQCCD(12,10)	CASSCF (12,10) ^a
R_{HN}	1.048	1.052	1.053
R_{NN}	1.260	1.264	1.265
θ_{HNN}	105.78	105.08	105.05

^a Reference 19.

S, and Cl. These two cases account for all bond length deviations larger than 0.015 Å that are seen with VQCCD in the larger basis set. It appears that these two cases have different origins. The poor performance of VQCCD for bonds to electropositive elements is largely due to the neglect of core correlation on the electropositive elements, as can be inferred from the fact that MP2-optimized geometries with frozen cores for Li₂ and NaF are both longer by 0.07 Å than for MP2 with full correlation. By contrast, the poor bond lengths to P, S, Cl appear to be largely due to a dynamic correlation effect, as inferred by the fact that frozen-core MP2 geometries for Cl₂ and P₂ have bond lengths that are longer by only 0.006 and 0.009 Å, respectively than for MP2 with full correlation. This result appears to suggest that the perfect pairing active space is slightly less effective for second-row elements than for first-row elements.

IV. Transition Structure for Hydrogen + *trans*-Diazene

Although it is beyond our present scope to study the performance of VQCCD for transition structures in the same way that we have investigated equilibrium geometries, we performed test calculations on a single system that has been well-studied by CASSCF and single reference methods including coupled-cluster and density functional theory (DFT). This is the transition structure for the addition of hydrogen to *trans*-diazene, which has been examined in three recent studies.^{19–21} In particular, the transition structure with CASSCF has been optimized in the full valence space (13 electrons in 11 orbitals or (13, 11))¹⁹ as well as in a smaller space of 5 electrons in 6 orbitals (5, 6),²⁰ each in the cc-pVDZ basis.³² The popular DFT method, B3LYP, incorrectly predicts the reaction to be barrierless,²⁰ illustrating the limitations of DFT for saddle points at present (by contrast with their great success for equilibrium geometries). Finally, high-level single reference methods such as CCSD and CCSD(T) have been reported²¹ both in the cc-pVDZ and cc-pVTZ basis sets.

Before comparing CASSCF and VQCCD calculations of the transition structure, let us first compare their performance for the equilibrium geometry of *trans*-diazene itself. Such a comparison is presented in Table 8 using the full valence (12 electrons in 10 orbitals) active space in the cc-pVDZ basis. We also include the perfect pairing VQCCD results. The full valence active space comparison between CASSCF and VQCCD shows near-quantitative agreement between the two active space methods. Clearly for this problem VQCCD is an entirely

TABLE 9: Reaction Barrier Heights (kcal/mol) and Geometric Parameters (Å and deg) of the H + *trans*-N₂H₂ → H₂ + N₂H Reaction with the cc-pVDZ Basis Set

	VQCCD (5,6)	VQCCD (13,13)	VQCCD (13,11)	CASSCF (5,6) ^a	CASSCF (13,11) ^b
V^\ddagger		8.51	5.98		8.77
R_{NN}^\ddagger	1.227	1.051	1.055		1.056
$R_{\text{H}_1\text{N}}^\ddagger$	1.024	1.240	1.241		1.246
$R_{\text{H}_2\text{N}}^\ddagger$	1.212	1.168	1.177	1.20	1.165
$R_{\text{H}_2\text{H}_3}^\ddagger$	1.054	1.155	1.143	1.09	1.196
$\theta_{\text{H}_1\text{NN}}^\ddagger$	107.30	106.56	106.04		105.81
$\theta_{\text{NNH}_3}^\ddagger$	106.12	106.66	106.57		106.20
$\theta_{\text{NH}_2\text{H}_3}^\ddagger$	172.70	173.73	172.44		173.52

^a Reference 20. ^b Reference 19.

satisfactory replacement for CASSCF. Let us now turn to the more challenging problem of the transition structure for the addition of hydrogen to *trans*-diazene.

We have performed VQCCD calculations using the cc-pVDZ basis on the transition structure with the (5, 6) and (13, 11) active spaces for which CASSCF results are available as well as the (13, 13) perfect pairing active space. These results are compared in Table 9. There are three interesting comparisons that can be made from this Table. First is the level of agreement between the VQCCD and CASSCF results in a given active space, which will directly measure how well VQCCD approximates CASSCF. Inspection of the Table shows that the level of agreement achieved is not quantitative for all parameters. In particular, the nascent HH bond is underestimated by approximately 0.04 and 0.05 Å in the (5, 6) and (13, 11) active spaces, respectively. This difference must be attributed to an effect of higher-than-double excitations within the active space (but confusingly, our predicted barrier height is actually slightly lower than that of CASSCF in the (13, 11) active space). Other geometric parameters are in satisfactory agreement between VQCCD and CASSCF.

The second point of comparison is the effect of the active space size on the transition structure (within the chosen cc-pVDZ basis). Comparing the (5, 6) and (13, 11) and PP active spaces, we see that there is a significant change in the optimized geometries. The smaller active space leads to a later transition structure by significantly underestimating the nascent HH bond (by almost 0.1 Å via either VQCCD or CASSCF) and overestimating the breaking NH bond (by about 0.035 Å). The fact that these trends in the dependence of results on active space size are correctly captured by VQCCD is encouraging and indicates that it may well be a useful method to estimate the effects of increasing the active space size when such increases are beyond the feasible limit for CASSCF.

Finally, the third point of comparison is the effect of dynamic correlation. Comparison of VQCCD (in e.g., (13, 11) or (13, 13) active spaces) against CCSD and CCSD(T)²¹ suggests that

there are significant dynamical correlation effects on the transition structure, with dynamic correlation making the transition structure earlier in the reaction (i.e., the HH distance is longer by about 0.10 Å, and the breaking NH distance is shorter by about 0.07 Å).

If we combine the effect of dynamic correlation with the effect of beyond-doubles in the active space discussed above, we are left with a guess for the transition structure (in the small cc-pVDZ basis) that has an HH distance of about 2.29 Å and an NH distance of about 1.10 Å, which are not in particularly good agreement with any of the results reported in Table 9. It appears that the problem of predicting accurate transition structures for radical–neutral reactions remains a substantial challenge.

V. Conclusions

The recently proposed quadratic coupled-cluster doubles (QCCD) method¹⁵ is a potentially significant improvement upon the conventional CCD method because it is stable for multiple bond breaking. Additionally, a very promising second-order correction has also been defined for remaining correlation effects.³³ In this work, we have presented the amplitude equations for QCCD as well as the orbital gradient required for orbital optimization. Through the use of an intelligent choice of $O(N^4)$ intermediates, one can compute both the QCCD energy and gradient in $O(N^6)$ time. The limiting step in most calculations is the computation of several $O(V^4)$ size intermediates in $O(V^6)$ time.

These terms restrict the size of systems studied to approximately 80 to 100 active orbitals in our implementation, a vast improvement over the limit of 13 or 14 associated with CASSCF, although still small by the standards of conventional CCD. When used for highly correlated problems, the other limiting factor can be the number of orbital rotations required to minimize the QCCD energy. For well-behaved systems where all orbitals are correlated, the average number of iterations required is roughly 20. For more difficult molecules, the orbital rotations can take up to hundreds of iterations to converge with our present implementation. There is clearly room for improvement, but a wide variety of small-molecule problems can still be studied with the formulation given here.

As an application of VQCCD using the perfect pairing active space for all valence electrons, we optimized the geometries of 22 small closed-shell molecules with VQCCD and compared our results to experiment as well as to Hartree–Fock, MP2, and GVB–PP. We find that VQCCD yields generally satisfactory results, although bonds to electropositive elements (Li, Na) are poor, and some bonds to second-row elements are less accurately predicted than the corresponding bonds to first-row elements. Relative to the GVB–PP model, VQCCD with the same active space yields significantly improved results in some cases such as single bonds to halogens. This appears to set the stage for the use of VQCCD with the PP active space for studies of reactive processes, including transition structures.

As a preliminary example of this type, we report a test calculation on the transition structure for the addition of hydrogen to *trans*-diazene. We compare results in a limited active space used previously for VQCCD against CASSCF and find tolerable agreement. We also find tolerable agreement against CASSCF in the full valence space. Importantly, we find that the significant changes in structural parameters between the two active spaces are accurately described by VQCCD. This illustrates the potential for using VQCCD to test the effect of small active spaces on CASSCF geometries as well as permitting full valence calculations on larger systems. In this way, VQCCD

could be a valuable complement to the CASSCF method. Further studies will be needed to confirm the extent to which this is true across a range of problems.

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