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Citation: J. Chem. Phys. 136, 054114 (2012); doi: 10.1063/1.3680560
View online: http://dx.doi.org/10.1063/1.3680560
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v136/i5
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Quasi-variational coupled cluster theory

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(Received 10 November 2011; accepted 10 January 2012; published online 6 February 2012)

We extend our previous work on the construction of new approximations of the variational coupled cluster method. By combining several linked pair functional transformations in such a way as to give appropriately balanced infinite-order contributions, in order to approximate \( \langle \hat{e}^{2} \hat{H} \rangle_{L} \) well at all orders, we formulate a new quantum chemical method, which we name quasi-variational coupled cluster. We demonstrate this method to be particularly robust in the regime of strong static electron correlation, improving significantly on our earlier approximate variational coupled cluster approach.

I. INTRODUCTION

The ab initio calculation of molecular electronic structure has become, in recent years, an indispensable tool for the investigation of molecular phenomena. Typical calculations begin by making the Hartree–Fock (HF) approximation, in which it is assumed that the ground-state electronic structure is well described by a single-determinantal wavefunction, which corresponds to a mean-field treatment of the Coulomb and exchange interactions between electrons. The effects of the correlated motion of the electrons may be computed through corrections to this approximation, such as through Möller–Plesset perturbation theory. Unfortunately, the convergence of the perturbation series is often an issue, and so other approaches, such as configuration interaction (CI), the coupled electron pair approximation (CEPA), the linear coupled pair many electron theory (LCPMET), the coupled pair functional, and traditional coupled cluster (TCC) theory, are often used. Of all the approaches, TCC has become the most widespread due to its numerous beneficial methodological properties, such as rigorous extensivity (correct scaling of the energy with system size) and exactness (equivalence to full CI (FCI)) in the limit of a complete cluster operator.

While the single-determinantal reference wavefunction approximation is often valid, it can break down if more than one determinant becomes equally important for the proper description of a system. This phenomenon is commonly termed “static correlation”. In situations exhibiting strong static correlation, the above methods can encounter difficulties or even fail catastrophically. In the case of TCC, which is most often performed at the singles and doubles level, these failures sometimes emerge as unphysical maxima in potential energy surfaces, followed by non-variational collapse to energies below FCI (Ref. 20). The standard routes to circumvent this are either to compute increasingly higher-order corrections (such as through the explicit inclusion of triple and higher excitations), or make use of a multi-determinant reference wavefunction from the outset, although other approaches to the treatment of non-dynamical correlation have been proposed, such as the active-space CC methods of Head–Gordon, \(^{21–23}\) and the spin–flip \(^{24–25}\) and double-ionization-potential \(^{26–27}\) Equation of Motion (EOM) methods.

However, we and others have shown \(^{20–33}\) that the poor performance of TCC limited to single and double excitations (CSD) in the strong static correlation regime is not necessarily the fault of the coupled cluster (CC) wavefunction ansatz, but can arise from the projective determination of the cluster amplitudes through the TCC equations. “Alternative” CC methods have been proposed, including extended coupled cluster \(^{34}\) (ECC), quadratic coupled cluster \(^{35}\) (QCC), improved coupled cluster \(^{36}\) (ICC), unitary coupled cluster \(^{37–40}\) (UCC), and variational coupled cluster \(^{41}\) (VCC), and a number of studies \(^{20–33}\) have confirmed the superiority of VCC and related approaches over TCC for the treatment of problems involving strong static correlation. This can be attributed to the upper bound property of VCC, which ensures that calculated VCC energies are always higher than FCI energies, which is not the case for TCC. However, all of these methods scale unfavourably in computational complexity relative to TCC, and the recent study of Evangelista \(^{42}\) confirmed that the additional accuracy of these methods is usually significantly outweighed by their increased computational cost. However, the search for superior CC-like methods with more similarity to VCC than TCC may still prove fruitful as long as these methods are constrained by the criterion that their computational complexity is restricted to be comparable to that of TCC.

We have shown previously \(^{43–44}\) that it is possible to construct approximate VCC theories that demonstrate more upper bound character than TCC within the same computational complexity, and without sacrificing important methodological properties, such as extensivity or an exact description of isolated 2-electron subsystems, and which have some superior properties to TCC, for example that they satisfy the generalized Hellmann–Feynman theorem. Here, we review our approach and extend it by improved amplitude transformations that preserve, by construction, the correct behaviour in the strong correlation limit.

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II. THEORY
A. Review of previous work

Throughout this work, we use the Einstein summation convention and a spin-orbital notation. The fundamental ansatz of coupled cluster theory is the exponential parameterization of the ground-state wavefunction in the basis of the Slater determinants that can be produced by substituting orbitals occupied in by the reference wavefunction, for which we use labels belonging to \( \{i, j, k, \ldots\} \), with those unoccupied in the reference wavefunction, for which we use labels belonging to \( \{a, b, c, \ldots\} \).

\[
|\Phi\rangle = e^{\hat{T}}|\Phi_0\rangle. \tag{1}
\]

This exponential parameterization ensures the extensivity of the CC methods and is distinct from, for example, CI, in which the exact wavefunction is instead expanded linearly as \( (1 + \hat{C})|\Phi_0\rangle \). Only in the limit of complete operators, \( \hat{C} \) and \( \hat{T} \), do the CI and CC wavefunctions agree; the methods are then referred to as full CI (FCI) or, less commonly, full CC (FCC).

In TCC theory, the CC ansatz is inserted into the Schrödinger equation, which is then premultiplied by \( e^{-\hat{T}} \). This has the effect of decoupling the amplitude equations from the energy,

\[
e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{TCC}|\Phi_0\rangle. \tag{2}
\]

Partitioning the cluster operator by excitation rank,

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \ldots, \tag{3}
\]

\[
\hat{T}_1|\Phi_0\rangle = T_{a}^i|\Phi_a^i\rangle, \tag{4}
\]

\[
\hat{T}_2|\Phi_0\rangle = \frac{1}{4} T_{ab}^{ij} |\Phi_{ab}^{ij}\rangle, \tag{5}
\]

the energy is determined by projection of Eq. (2) onto the reference determinant, and the amplitude equations are determined similarly by projection onto the singly, doubly and more highly excited manifolds, as applicable. In the case of truncation to \( \hat{T} = \hat{T}_1 + \hat{T}_2 \), the CCSD method is defined by the following relationships:

\[
\langle \Phi_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = E_{CCSD}, \tag{6}
\]

\[
\langle \Phi_i^e|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0, \tag{7}
\]

\[
\langle \Phi_{ij}^{e^{2}}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle = 0. \tag{8}
\]

The Campbell–Baker–Hausdorff formula ensures that the similarity-transformed Hamiltonian operator, \( \hat{H} = e^{-\hat{T}}\hat{H}e^{\hat{T}} \), terminates at the \( O(\hat{T}^2) \) terms, making CCSD computationally practical with \( O(\alpha^2\nu^4) \) complexity, where \( \alpha \) and \( \nu \) refer, respectively, to the number of occupied and virtual orbitals in the calculation.

In VCC, on the other hand, the CC wavefunction is instead inserted into the quantum mechanical energy expectation value and the ground-state energy calculated as the minimum of this functional with respect to the set, \( \{T_{a}^i\} \cup \{T_{ab}^{ij}\} \cup \ldots \), of cluster amplitudes,

\[
E_{VCC} = \frac{\langle \Phi_0|e^{\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle}{\langle \Phi_0|e^{\hat{T}}|\Phi_0\rangle} = \langle \Phi_0|\hat{H}e^{\hat{T}}|\Phi_0\rangle_L. \tag{9}
\]

Our current interest remains an accurate approximation of VCC, and numerous attempts have been made towards this goal by other authors, with varying degrees of success. The simplest such approximations rely on simply truncating the exponential operator, \( e^{\hat{T}} \), to 1 + \( \hat{T} \) in one of the two forms of the VCC functional given above, resulting in either variational CI,

\[
E_{CI} = \langle \hat{H} \rangle + \frac{2\langle \hat{H} \hat{T} \rangle + \langle \hat{T}^{\dagger}\hat{H}\hat{T} \rangle}{1 + \langle \hat{T}^{\dagger}\hat{T} \rangle}, \tag{10}
\]

which is known not to be extensive for a truncated cluster operator, or CEPA(0),

\[
E_{CEPA(0)} = \langle (1 + \hat{T})^{\dagger}\hat{H}(1 + \hat{T}) \rangle_L = \langle \hat{H} \rangle + 2\langle \hat{H} \hat{T} \rangle + \langle \hat{T}^{\dagger}(\hat{H} - \langle \hat{H} \rangle) \hat{T} \rangle_L, \tag{11}
\]

which is not exact even for a complete cluster operator.

These problems can be understood more generally; in VCC, the unlinked terms in the numerator cancel exactly with the entire denominator, leaving only the linked terms in the numerator. This is why the VCC functional may be written in one of the two forms given in Eq. (9). The truncation of the exponential in the first form destroys this cancellation, which results in the inclusion of unlinked terms and thus the loss of extensivity. After performing the cancellation of the VCC denominator with the unlinked parts of the VCC numerator, un-cancelled exclusion-principle-violating terms remain, so that \( \langle e^{\hat{T}}\hat{H}e^{\hat{T}}\rangle_L \) does not naturally truncate at the number of electrons; it is always an infinite expression. Any finite approximation to this infinite expression is then necessarily incorrect even when the cluster operator is itself complete. Thus, simply including more of the Maclaurin series of \( e^{\hat{T}} \) does not resolve these problems.

Asymmetric expectation value expressions derived from a VCC starting point have also been proposed, such as extended coupled cluster.\(^{34}\)

\[
E_{ECC} = \langle \Phi_0|e^{\hat{\Sigma}}e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle. \tag{12}
\]

Here, the functional is minimized with respect to both \( \hat{T} \) and \( \hat{\Sigma} \) independently. Truncation of the operator \( e^{\hat{\Sigma}} \) yields a hierarchy of methods stepping from the TCC functional, corresponding to the truncation \( 1 + \hat{\Sigma} \), to VCC for no truncation. The quadratic coupled cluster\(^{35}\) method, which represents the first step above TCC in this hierarchy, corresponds to truncation of the operator to \( 1 + \hat{\Sigma} + \frac{1}{2}\hat{\Sigma}^2 \). Unfortunately, while it offers increased accuracy over CCD, the QCDD method
TABLE 1. Linked $O(T^3)$ contributions to VCCD, where $\eta = \frac{1}{2} T_{ab}^{ij} T_{ij}^{ab}$, and where $ee$ and $hh$ label the two spinorbitals occupied and unoccupied in the reference wavefunction, respectively.

<table>
<thead>
<tr>
<th>Diagram</th>
<th>$\frac{1}{2} (T_{ij}^a \hat{H}^a_{ij})_{L}$ Diagram</th>
<th>$2 \frac{1}{2} (T_{ij}^a \hat{H}^a_{ij})_{L}$ Contribution</th>
<th>Two electrons</th>
<th>Two holes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$\frac{1}{2} T_{ij}^{ae} T_{kl}^{eb} T_{ij}^{ab} (ij</td>
<td></td>
<td>ab) = -T_{ij}^{ae} \delta_e^b (ij</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$\frac{1}{2} T_{ik}^{ab} T_{kl}^{cd} T_{ij}^{cd} (ij</td>
<td></td>
<td>ab) = -T_{ik}^{ab} \eta_{ij} (ij</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>$\frac{1}{2} T_{kl}^{ab} T_{ij}^{cd} T_{ij}^{cd} (ij</td>
<td></td>
<td>ab) = \frac{1}{2} T_{ij}^{ab} \eta_{ij}^e (ij</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>$T_{ij}^{ae} T_{kl}^{eb} T_{ij}^{ab} (ij</td>
<td></td>
<td>ab) = T_{ik}^{ab} \eta_{ij} (ij</td>
<td></td>
</tr>
</tbody>
</table>

requires an expensive $O(v^b)$ step in the iterative procedure. The improved coupled cluster hierarchy has the same requirement.

The method that underpins our current approximations is the linked pair functional (LPF), or LPFD, making explicit the doubles-only nature of the theory. Here, the effect of the exponential operator is replaced by closed-form geometric series of the cluster amplitudes, and these series are tuned such that certain VCC doubles (VCCD) terms are reproduced exactly through all orders. The LPFD energy functional,

$$E_{LPFD} = \langle \hat{H} \rangle + 2\langle \hat{H}^2 \rangle + \langle \hat{T}^2 \rangle (\hat{H} - \langle \hat{H} \rangle),$$

is defined through transformed cluster operators,

$$qT_{ij}^{ab} = \frac{1}{4} qT_{ij}^{ab} (\Phi_{ij}^{ab}),$$

$$qT_{ij}^{ab} = (qU^{e \nu} T)_{ab}^{ij} = \frac{1}{2} (qU^{e \nu} T)_{kl}^{ij} T_{ab}^{kl},$$

$$qU_{kl}^{ij} = \delta_{kl} + qS_u \Delta_{kl}^{ij}.$$  \hspace{1cm} (16)

where $\tau_{ij}$ permutes the labels $i, j$ in what follows it, and the transformation matrix is, in turn, defined in terms of the following density matrices:

$$\eta_{kl}^{ij} = \langle \hat{T}^2 \rangle (\hat{H}^2)_{kl}^{ij} = \frac{1}{2} T_{ij}^{ab} T_{ab}^{ij},$$

$$\eta_{ij}^{ij} = \langle \hat{T}^2 \rangle (\hat{H}^2)_{ij}^{ij} = \frac{1}{2} T_{ij}^{ab} T_{ab}^{ij} \equiv \eta_{ij}^{ij}.$$  \hspace{1cm} (18)

The values of the parameters $qS_u$ and $qP_u$ (but not $\lambda$) are determined uniquely by the requirement that the method is exact, here meaning that it becomes equivalent to Configuration Interaction with double excitations (CID), in the limiting case of two electrons,

$$qS_u = 1,$$

$$qP_u = -q \frac{1}{2},$$

The two transformed cluster operators, denoted $qT$ for $q \in \{1, 2\}$, introduce, through the matrix powers in Eq. (15), division by the parts of a CID-like denominator that are coupled to the correlation of a given pair of reference-state orbitals. In the limit of isolated electron pairs, the transformation matrix becomes diagonal and this results in the re-introduction of CID denominators for each pair, such that the functional becomes exact. However, since the transformation generates only linked terms, the method is also rigorously extensive, unlike CID. Through the binomial series of a power of the matrix,

$$qU^{e \nu} = (1 + qS_u \Delta)^{e \nu} = 1 + qS_u qP_u \Delta + \ldots ,$$

LPFD generates VCCD-like terms to infinite-order in the cluster amplitudes, and the particular subset of terms present in VCCD that is captured, along with the weighting of each term, is controlled by the value of the parameter $\lambda$. Accordingly, we proposed the notation LPFD($\lambda$), should specificity be required. The exactness of LPFD in the limit of two electrons may also be understood from this infinite series perspective; the VCCD functional possesses an internal mathematical structure that, in this limiting case, results in the mutual cancellation of numerous terms through all orders of the cluster amplitudes. For example, at $O(T^3)$, the lowest order at which LPFD and VCCD differ, for which the contributing terms are given in Table 1, the following relationships hold in the 2-electron limit:

$$A + D = 0,$$

$$B + 2C = 0.\hspace{1cm} (21)$$
So, in this case of two electrons, the VCCD terms, \( A + B + C + D \), may be reproduced in infinitely many ways corresponding to the continuously adjustable weightings of the \( B \) and \( C \) terms, controlled by the parameter \( \lambda \),

\[
A + B + C + D = \frac{1 - \lambda}{2} B - \lambda C. \tag{22}
\]

These are precisely the terms generated at \( \mathcal{O}(T^3) \) in LPFD(\( \lambda \)), and this behaviour persists to higher orders also. Clearly, the choice \( \lambda = -1 \) leads to the most desirable VCCD approximation, since then the terms are present as \( B + C \), exactly as they appear in VCCD.

Given the possible values of \( q \), the existence of the negative and non-integer powers of the transformation matrix needs to be considered carefully. Only if the matrix is positive-definite (meaning that all eigenvalues of the matrix are strictly positive), for all possible values of the cluster amplitudes, will the LPFD method be robustly applicable to a wide range of chemical systems. In particular, LPFD(\(-1\)) is ruled out by this positivity constraint, and only the choice \( \lambda = +1 \) leads to a matrix that is guaranteed to be positive-definite, since then \( \Delta \) is Gramian, making it positive-semidefinite.

We also recognized\(^44\) that a positive-definite matrix indexed by electrons, rather than electron pairs, could be constructed and used to perform the transformations with no impairment of the methodological properties.

\[
qT_{ij}^{ab} = (qU^{Pc}a V^{Pc});(1 - \tau_{ij})(qU^{Pc})^{\dagger} k T_{ij}^{ab}, \tag{23}
\]

\[
qU_j^{\dagger} = \delta_j + qS_a \Delta_j^{\dagger}, \tag{24}
\]

\[
\Delta_j^{\dagger} = \eta_j^{\dagger}. \tag{25}
\]

This approximates LPFD(0) correctly to \( \mathcal{O}(T^4) \), and we continue to refer to this approximate theory simply as LPFD(0) unless otherwise specified. Since, for systems with many electrons, the number of electrons is very much less than the number of electron pairs, this matrix is significantly simpler to handle computationally, and we saw no reason not to prefer this theory over LPFD(+1).

Using LPFD(0) to account for the infinite-order behaviour, we then devised a scheme to improve the approximation of VCCD at low orders,\(^44\) which we named approximate variational coupled cluster (AVCCD). We proposed multiplicatively compounding the original transformation with further matrices; the AVCCD method is defined by the same functional, but new density matrices are introduced,

\[
\eta_{ij}^{ab} = (T^a)^{jk} b a i \hat{T} \equiv T_{jk}^{ac} T_{ij}^{bc}, \tag{26a}
\]

\[
\eta_{ij}^{ab} = (T^a)^{jk} b a \hat{T} = \frac{1}{2} T_{ij}^{ac} T_{ij}^{bc} \equiv \eta_{ij}^{ab}, \tag{26b}
\]

so that two new transformations can be defined. The \( W \) transformation,

\[
(qW^{Pc}a V^{Pc})^{ij} = \frac{1}{2} (qW^{Pc})^{ij}_{kl} T_{kl}^{ab}, \tag{27}
\]

\[
qW^{ij}_{kl} = \delta^{ij}_{kl} + qS_a \Omega_{kl}^{ij}, \tag{28}
\]

adds the terms \( \frac{1}{2} B + C \), and the \( V \) transformation,

\[
(qV^{Pc}a V^{Pc})_{ij}^{kl} = \frac{1}{4} (1 - \tau_{ij})(1 - \tau_{ab}) (qV^{Pc})_{ak}^{ic} T_{ck}^{ij}, \tag{29}
\]

\[
qV^{ib}_{aj} + \delta_{aj} qS_a \Gamma^{ib}_{aj}, \tag{30}
\]

\[
\Gamma^{ib}_{aj} = 2(\delta^i_j \eta^{ib}_a - \eta^{ib}_j \delta^i_a), \tag{31}
\]

\[
\Omega_{kl}^{ij} = \eta_{kl}^{ij} - \frac{1}{2} (1 - \tau_{ij})(1 - \tau_{ab}) \delta_{kl}^{ij}, \tag{32}
\]

\[
\Omega_{kl}^{ij} = \eta_{kl}^{ij} - \frac{1}{2} \eta_{kl}^{ij}, \tag{33}
\]

\[
\Omega_{kl}^{ij} = \eta_{kl}^{ij} - \frac{1}{2}, \tag{34}
\]

\[
\Omega_{kl}^{ij} = \eta_{kl}^{ij} - \frac{1}{2}, \tag{35}
\]

\[
\Omega_{kl}^{ij} = \eta_{kl}^{ij} - \frac{1}{2}, \tag{36}
\]

Of course, this means no new VCCD terms are generated to infinite-order except through coupling with the LPFD(0) terms already present.

At \( \mathcal{O}(T^3) \), AVCCD possesses the terms \( A + B + C + D \), so is equivalent to VCCD to this order. In addition, if the Hamiltonian is partitioned into its 1-electron and 2-electron components, \( \hat{H} = \hat{F} + \hat{V} \), the Fock operator and fluctuation potential, respectively, then the constraints given so far are also sufficient to ensure that AVCCD contains \((1/2!)^2 (\hat{T}_{2}^2)^2 \hat{T}_{2}^2 \) correctly. This is important for consistency, since this term enters together with \((\hat{T}_{2}^1 \hat{V} \hat{T}_{2}^2 \) at fourth-order in perturbation theory.

**B. A comparison of the positive-definite LPFD methods**

Our goal in this work is to determine if superior definitions of the transformed amplitudes exist. Since LPFD(0) and LPFD(+1) are both feasible choices to provide the infinite-order contributions for an approximate VCCD theory, and since we have so far given no convincing theoretical argument to prefer either, other than the pragmatic consideration...
of computational cost, we begin with a more rigorous comparison of the two in terms of their mathematical and numerical properties.

Analogously to the limiting case of two electrons, one can examine the case of two holes, or two unoccupied spinor-bits in the reference wavefunction. This situation would not arise in any molecular example, but approximates certain strong-correlation situations such as in the C$_2$ molecule, where the $1\pi_g^*$ reference is strongly coupled to the $1\pi_u^* 3\sigma_g^*$ configuration. Examining the case of the $O(T^3)$ VCCD terms, given in Table I, reveals the following relationships hold in this limit:

$$B + D = 0,$$
$$A + 2C = 0.$$  \hspace{1cm} (37)

Just as in the 2-electron case, the VCCD contribution may be captured in infinitely many ways, which we choose to enumerate with the real and continuously adjustable parameter $\mu$,

$$A + B + C + D = \frac{1 - \mu}{2} A - \mu C.$$  \hspace{1cm} (38)

It can be seen that by making the choice $\lambda = \mu = 1$, $-C$ is obtained in both the 2-electron and 2-hole limiting cases, and no other choices of $\lambda$ and $\mu$ can give the correct contribution for both cases. This is not a coincidence that occurs at $O(T^3)$, but is, in fact, a consequence of hole-particle symmetry that persists at all orders. In short, LPFD(+1) is exact for both two electrons and two holes, and a proof of this statement is given as an appendix. This result initially led us to consider a modified AVCCD$^{44}$ theory based on LPFD(+1),

$$qT_{ab}^{ij} = (qU^{q/2})T_{ab}^{ij} - \frac{q}{2}(qU^{q/4} - (1/2)) \Gamma qU^{q/4} - (1/2) T_{ab}^{ij} + q(\rho qU^{q/4} - (1/2)) \Omega qU^{q/4} - (1/2) T_{ab}^{ij}.$$  \hspace{1cm} (39)

Here, we are using the notation in Eq. (34), where it is understood that, for example, $(\Gamma \Gamma)$ means to apply the transformation of Eq. (30) with the matrix defined in Eq. (32). The additional factor of 2 on the $\Omega$ contribution adds $B + 2C$ instead of $\frac{1}{2} B + C$, correcting the $-C$ acquired by LPFD(+1) at $O(T^3)$ to $B + C$. The corrective transformations not only continue to vanish for two electrons, but also mutually cancel for two holes, so both the 2-electron and 2-hole limiting cases remain correct. The dressing of the corrective transformations with $\rho qU$ matrices ensures that the size of the transformed amplitudes remains comparable to that of the untransformed amplitudes if the latter grow large.

Unfortunately, our investigations have shown that both LPFD(0) and LPFD(+1) diverge in numerous examples where VCCD performs exceptionally well, such as for N$_2$. The theoretical superiority of LPFD(+1), as outlined above, is of little help in this regard. This can be understood by recognizing that each of LPFD(0) and LPFD(+1) contain just one class of VCCD term, albeit to infinite-order; LPFD(0) contains only the $B$-like terms and LPFD(+1) contains only the $C$-like terms. The VCCD terms omitted by these methods are of no less importance than those included, and a balance of the terms at all orders can be expected to overcome the problem. In fact, LPFD(-1) provides direct evidence for this, since it contains a balance of $B$-like and $C$-like terms at all orders and is often more stable than either LPFD(0) or LPFD(+1).

Furthermore, this presents a problem for both AVCCD and the hypothetical theory above; these methods employ only a finite-order correction of the infinite-order LPFD(0) and LPFD(+1) theories, respectively; if the underlying infinite-order theory becomes qualitatively incorrect, then it is impossible to recover completely with only a finite-order correction.

Thus, we are motivated to find a theory in the spirit of LPFD, with balanced contributions to infinite-order, as in LPFD(-1), while also embracing hole-particle symmetry, and using only positive-definite transformations.

**C. Quasi-variational coupled cluster theory**

In order to propagate each type of $O(T^3)$ term to infinite-order so that balance between the terms is maintained in our approximation to VCCD, we can look back at our definitions of the density matrices, now labelling each with the letter corresponding to the term it is responsible for generating at $O(T^3)$,

$$\alpha U_{ab}^a = (\hat{\xi} a \bar{b} \bar{a} \hat{\xi}) = \frac{1}{2} T_{bc}^{ij} T_{ij}^{ac},$$  \hspace{1cm} (40)

$$\beta U_{ij}^i = (\hat{\xi} j \bar{i} \bar{i} \hat{\xi}) = \frac{1}{2} T_{ab}^{ij} T_{ij}^{ab},$$  \hspace{1cm} (41)

$$\gamma U_{kl}^i = (\hat{\xi} k \bar{l} \bar{j} \hat{\xi}) = \frac{1}{2} T_{ab}^{ij} T_{ij}^{kl},$$  \hspace{1cm} (42)

$$\delta U_{ab}^{ij} = (\hat{\xi} \bar{b} \bar{a} \hat{\xi}) = T_{ab}^{ij} T_{ij}^{bc}.$$  \hspace{1cm} (43)

It is apparent that each of these matrices is positive-semidefinite, since each is Gramian. Therefore, we propose a new ansatz for the transformed amplitudes that is a linear combination of the individual transformations,

$$qT_{ab}^{ij} = \alpha \left[ \frac{1}{2} (1 - \tau_{ab}) (\alpha U_{ab}^a) T_{ij}^{ab} \right] + \beta \left[ \frac{1}{2} (1 - \tau_{ij}) (\alpha U_{ij}^i) T_{ij}^{kl} \right] + \gamma \left[ \frac{1}{2} (\alpha U_{kl}^i) T_{ij}^{kl} \right] + \delta \left[ \frac{1}{4} (1 - \tau_{ij}) (\alpha U_{ab}^a) T_{ij}^{bc} \right],$$  \hspace{1cm} (44)

$$\alpha U_{ab}^a = \delta_{b}^a + \alpha' \omega_{ab}^a, \quad \beta U_{ij}^i = \delta_{ij}^i + \gamma' \omega_{ij}^i, \quad \gamma U_{kl}^i = \delta_{kl}^i + \gamma' \omega_{ij}^i.$$

This formulation avoids the difficulty encountered earlier that linear combinations of $\alpha U, \beta U, \gamma U$, and $\delta U$ are not positive definite. The parameters must then be carefully chosen to satisfy the constraints that the theory is exact for two electrons and two holes, as well as correct to $O(T^3)$ in VCCD. First, since the leading-order contribution to each transformation is
the identity, for correct behaviour to \( \mathcal{O}(T^2) \), we have the following constraint:

\[
\alpha + \beta + \gamma + \delta = 1. \tag{45}
\]

In the 2-electron limit, both \( \mathcal{U} \) and \( \mathcal{J} \) become diagonal and can therefore combine to induce division by the CID denominator, whereas \( \mathcal{J} \) and \( \mathcal{J} \) cannot, but can cancel. In order for correct behaviour for two electrons, we hence demand the following:

\[
\beta(\delta + \beta' \eta)^{P_b} + \gamma(\delta + \gamma' \eta) = (1 + \langle \hat{T}_2 \rangle^2)^{q \over 2}, \tag{46}
\]

\[
\alpha(\delta + \alpha' \eta)^{P_d} + \delta(\delta + \delta' \eta)^{P_a} = 0. \tag{47}
\]

By expanding the left and right sides of both equations as binomial series, requiring that the left and right sides of each equation match at all orders, and ignoring the trivial case \( \alpha = \delta = 0 \), which would completely switch off the \( \mathcal{J} \) and \( \mathcal{J} \) contributions, we derive the following constraints:

\[
\begin{align*}
P_b &= P_e = -q \over 2 \quad \alpha' - \delta' = 0 \\
P_a - P_d &= 0 \quad \beta + \gamma = 1 \\
\beta' &= \gamma' = 1 \quad \alpha + \delta = 0.
\end{align*} \tag{48}
\]

Similarly, in the limiting case of two holes, it is instead \( \mathcal{J} \) and \( \mathcal{J} \) that can combine to produce the CID denominator. In the case of \( \mathcal{J} \), this is a result of the fact that the powered \( \mathcal{J} \) transformation generates an identical infinite series to a hypothetical \( \mathcal{J} \)-like matrix indexed by hole pairs rather than electron pairs, as shown in the appendix. Hence, we demand the following:

\[
\begin{align*}
\alpha(\delta + \alpha' \eta)^{P_a} + \gamma(\delta + \gamma' \eta) = (1 + \langle \hat{T}_2 \rangle^2)^{q \over 2}, \tag{49}
\end{align*}
\]

\[
\beta(\delta + \beta' \eta)^{P_d} + \delta(\delta + \delta' \eta)^{P_b} = 0, \tag{50}
\]

imposing the constraints below,

\[
\begin{align*}
P_e &= P_c = -q \over 2 \quad \beta' - \delta' = 0 \\
P_b - P_d &= 0 \quad \alpha + \gamma = 1 \\
\alpha' &= \gamma' = 1 \quad \beta + \delta = 0.
\end{align*} \tag{51}
\]

We now combine all of the discovered constraints, noting that some are equivalent,

\[
\begin{align*}
P_a &= P_b = P_e = P_d = -q \over 2, \tag{52}
\end{align*}
\]

\[
\begin{align*}
\alpha' &= \beta' = \gamma' = \delta' = 1, \tag{53}
\end{align*}
\]

\[
\begin{align*}
\alpha + \beta + \gamma + \delta = 1, \tag{54}
\end{align*}
\]

\[
\begin{align*}
\beta + \gamma = 1, \tag{55}
\end{align*}
\]

\[
\begin{align*}
\alpha + \gamma = 1. \tag{56}
\end{align*}
\]

Three unique constraints are insufficient to uniquely determine the four variables \( \alpha, \beta, \gamma \) and \( \delta \). A final constraint enters from the requirement that this method matches VCCD to \( \mathcal{O}(T^3) \). We first notice that choosing \( \gamma = +1 \) above implies \( \alpha = \beta = \delta = 0 \), consistent with the fact that LPFD(+1) is correct to \( \mathcal{O}(T^2) \), and is exact for both two electrons and two holes. However, since LPFD(+1) yields \(-\mathcal{C}\) at \( \mathcal{O}(T^3) \), whereas \(+\mathcal{C}\) is the correct VCCD term, we must have

\[
\gamma = -1, \tag{57}
\]

which acts as the final constraint, and the remaining parameters are then determined uniquely,

\[
\begin{align*}
\alpha &= +2, \tag{58}
\beta &= +2, \tag{59}
\delta &= -2. \tag{60}
\end{align*}
\]

Each of the above values is exactly consistent with the required factors on each of the transformations in order to get the the remaining \( \mathcal{O}(T^3) \) terms correct. Note that, as before, the constraints imposed so far are also sufficient to get \( \langle \hat{T}_2 \rangle^2 \mathcal{F} \hat{T}_2 \rangle \) correct, important for consistency at fourth-order in perturbation theory.

Hence, we can unambiguously write

\[
\begin{align*}
q T_{ab}^{ij} &= 2 \left[ \frac{1}{2} (1 - t_{ab}) \left( \mathcal{J}^{-q \over 2} \right)^c \hat{T}_{ab} \right]
+ 2 \left[ \frac{1}{2} (1 - t_{ij}) \left( \mathcal{J}^{-q \over 2} \right)^i \hat{T}_{ab} \right]
- 1 \left[ \frac{1}{2} \left( \mathcal{J}^{-q \over 2} \right)^d \hat{T}_{ab} \right]
- 2 \left[ \frac{1}{4} (1 - t_{ij})(1 - t_{ab}) \left( \mathcal{J}^{-q \over 2} \right)^{i \over c} \hat{T}_{ab} \right].
\end{align*}
\]

and when these amplitudes are inserted into a functional of the form given in Eq. (13), we name the corresponding method, “quasi-variational coupled cluster” (QVCC) or QVCCD, since we are currently discussing a theory involving double excitations only. Neither this definition of the transformed amplitudes, nor the functional contain any arbitrary parameters, and hence, distinct from both LPFD and AVCCD, the QVCCD method is unique.

Although the QVCCD method does not yield an upper bound on the exact ground-state Schrödinger energy eigenvalue, the QVCCD ground-state energy corresponds, analogously to VCCD, to the minimum of the functional given in Eq. (13). This minimum is defined by the vanishing of the derivatives of the energy with respect to the set of untransformed cluster amplitudes,

\[
dE = \frac{1}{4} \frac{\partial E}{\partial T_{ab}^{ij}} dT_{ab}^{ij} = 0 \tag{62}
\]
the corresponding vector of eigenvalues. The LPFD, A VCCD and QVCCD coupled-pair functionals has been discussed extensively by Kollmar and Heßelmann. The use of orbital optimization for minimization of the energy with respect to the orbitals, in ad-
notation of Ref. 48, as follows:

$$d \left( U^{\nu} \right)_{ij} = x \sum_{k=1}^{N} X_{ik} X_{jk} \epsilon_{k}^{-1} \sum_{m,n=1}^{N} X_{mk} dU_{mn} X_{nk}$$

$$+ \sum_{k,l=1, l \neq k}^{N} \epsilon_{k}^{x} - \epsilon_{l}^{x} X_{il} X_{jk} \sum_{m,n=1}^{N} X_{ml} dU_{mn} X_{nk},$$

where the columns of $X$ are the eigenvectors of $U$, and $\epsilon$ is the corresponding vector of eigenvalues.

The small effects of single excitations may be treated by minimization of the energy with respect to the orbitals, in addition to the minimization with respect to the doubles amplitudes, as discussed above. The use of orbital optimization for coupled-pair functionals has been discussed extensively by Kollmar and Heßelmann. The LPFD, AVCCD and QVCCD orbital gradients, $f_{ab}$, may be specified, in the spin-adapted notation of Ref. 48, as follows:

$$f_{a}^{i} = F_{a}^{i} - T_{j}^{i} F_{j}^{i} - T_{b}^{i} F_{b}^{i}$$

$$- T_{a}^{i} \left[ 2 \langle i | l | a k \rangle - \langle i | l | a k \rangle \right]$$

$$+ T_{a}^{i} \left[ 2 \langle d | a c \rangle - \langle d | a c \rangle \right]$$

$$+ T_{a}^{i} \left[ 2 \langle d | a c \rangle - \langle d | a c \rangle \right]$$

$$+ T_{a}^{i} \left[ 2 \langle d | a c \rangle - \langle d | a c \rangle \right]$$

$$+ T_{a}^{i} \left[ 2 \langle d | a c \rangle - \langle d | a c \rangle \right]$$

$$+ T_{a}^{i} \left[ 2 \langle d | a c \rangle - \langle d | a c \rangle \right]$$

with the following definitions of the involved quantities:

$$q_{ab}^{ij} = 2q_{ab}^{ij} - q_{ba}^{ij},$$

$$T_{a}^{i} = \tilde{T}_{a}^{i},$$

$$T_{a}^{b} = \tilde{T}_{a}^{b},$$

$$F_{a}^{p} = h_{a}^{p} + 2 \langle p | i | q \rangle - \langle p | i | q \rangle,$$

$$h_{r}^{p} = \int \psi_{r}^{*}(\mathbf{r}) \left( -\frac{1}{2} \nabla^{2} + V(\mathbf{r}) \right) \psi_{r}(\mathbf{r}) d^{3}\mathbf{r},$$

$$\langle pq | rs \rangle = \int \psi_{p}^{*}(\mathbf{r}) \psi_{q}^{*}(\mathbf{r}) \left( \frac{1}{| \mathbf{r}_{1} - \mathbf{r}_{2} |} \psi_{r}(\mathbf{r}_{1}) \psi_{s}(\mathbf{r}_{2}) d^{3}\mathbf{r}_{1} d^{3}\mathbf{r}_{2}. $$

The condition for stationarity of the energy with respect to the orbitals is, of course, $f_{ab} = 0$. When orbital optimization is employed, we refer to the methods LPFD, AVCCD and QVCCD, respectively, as OLPFD, OAVCCD and OQVCCD.

Alternatively, single excitations may be taken into account by minimization of the functional with respect to the doubles amplitudes only, if an additional Brueckner constraint is satisfied,

$$\langle \Phi_{a}^{i} | \hat{H} \langle 1 + i \tilde{T}_{2} | \Phi_{0} = 0, $$

which defines the BLPFD, BAVCCD and BQVCCD methods, respectively. These methods are computationally less expensive than energy optimization, but expected to be less reliable. The above equations defining both the orbital optimization procedure and the Brueckner condition require no modification for different definitions of the transformed amplitudes, and are thus equally applicable to any of the LPFD, AVCCD or QVCCD methods.

### Table III. Calculated barrier heights (in milliHartrees, $mE_h$) with the cc-pVTZ basis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>OAVCCD</th>
<th>QOVCDD</th>
<th>CISD+Q</th>
<th>LCPMET</th>
<th>CCSD</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}^{-} + \text{CH}_3\text{Cl} \rightarrow \text{FCH}_3 + \text{Cl}^{-}$</td>
<td>2.037</td>
<td>2.035</td>
<td>1.832</td>
<td>-2.180</td>
<td>1.682</td>
<td>-0.369</td>
</tr>
<tr>
<td>$\text{Cl}^{-} + \text{CH}_3\text{Cl} \rightarrow \text{CICH}_3 + \text{Cl}^{-}$</td>
<td>22.898</td>
<td>22.897</td>
<td>23.054</td>
<td>18.193</td>
<td>22.517</td>
<td>19.807</td>
</tr>
<tr>
<td>$\text{OH}^{-} + \text{CH}_3\text{F} \rightarrow \text{HOCH}_3 + \text{F}^{-}$</td>
<td>-14.683</td>
<td>-14.627</td>
<td>-3.881</td>
<td>-21.508</td>
<td>-15.363</td>
<td>-20.276</td>
</tr>
<tr>
<td>HCN $\rightarrow$ HNC</td>
<td>77.046</td>
<td>76.983</td>
<td>76.239</td>
<td>71.506</td>
<td>76.752</td>
<td>76.076</td>
</tr>
</tbody>
</table>
TABLE IV. Comparison of equilibrium bond lengths and spectroscopic constants for some diatomic molecules. Basis set: cc-pVQZ, with correlation energy $x^{-3}$-extrapolated using cc-pVTZ and cc-pVQZ.

<table>
<thead>
<tr>
<th>System</th>
<th>Method</th>
<th>$R_e$/Å</th>
<th>$\omega_e$/cm$^{-1}$</th>
<th>$\omega_{exe}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>CCSD</td>
<td>0.913</td>
<td>4203.5</td>
<td>89.1</td>
</tr>
<tr>
<td></td>
<td>OA VCCD</td>
<td>0.913</td>
<td>4209.2</td>
<td>86.8</td>
</tr>
<tr>
<td></td>
<td>OQVCCD</td>
<td>0.913</td>
<td>4210.7</td>
<td>87.2</td>
</tr>
<tr>
<td></td>
<td>Empirical$^{63}$</td>
<td>0.917</td>
<td>4138.3</td>
<td>89.9</td>
</tr>
<tr>
<td>F$_2$</td>
<td>CCSD</td>
<td>1.389</td>
<td>1020.5</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>OA VCCD</td>
<td>1.386</td>
<td>1034.9</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td>OQVCCD</td>
<td>1.386</td>
<td>1030.3</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>Empirical</td>
<td>1.412</td>
<td>916.6</td>
<td>11.2</td>
</tr>
<tr>
<td>N$_2$</td>
<td>CCSD</td>
<td>1.092</td>
<td>2445.3</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>OA VCCD</td>
<td>1.091</td>
<td>2456.4</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>OQVCCD</td>
<td>1.090</td>
<td>2461.0</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>Empirical</td>
<td>1.098</td>
<td>2358.6</td>
<td>14.3</td>
</tr>
</tbody>
</table>

III. NUMERICAL RESULTS

The QVCCD, OQVCCD and BQVCCD methods have been implemented in the closed-shell CCSD program$^{50}$ of the MOLPRO$^{55}$ quantum chemistry software package. When it is desirable to benchmark CCD, A VCCD and QVCCD, against VCCD and FCI results directly, we choose the minimal STO-3G basis set. When larger basis sets, such as the correlation-consistent basis sets$^{56}$, $cc$-$pV_xZ$ with $x \in \{D, T, Q, \ldots\}$, possibly augmented by additional diffuse functions$^{57}$, aug-$cc$-$pV_xZ$, are used, we instead compare CCSD, OA VCCD and OQVCCD against CCSD(T)$^{58}$ or internally contracted multi-reference configuration interaction$^{59}$ with the Davidson correction$^{60}$ to account for the lack of extensivity (MRCI+Q).

We begin by confirming that, like OA VCCD, OQVCCD results are of at least CCSD quality for general calculations. An examination of the valence-shell correlation energies for the singlet ground states of some first- and second-row atoms, for which data are given in Table II, reveals that the differences between OQVCCD and CCSD are small. In every case, we see that OQVCCD performs similarly to the earlier OA VCCD method.

Next, we computed the forward barrier heights for the following closed-shell reactions:

\[
\begin{align*}
F^- + CH_3Cl & \rightarrow FCH_3 + Cl^- \\
Cl^- + CH_3Cl & \rightarrow CICH_3 + Cl^- \\
OH^- + CH_3F & \rightarrow HOCH_3 + F^- \\
HCN & \rightarrow HNC.
\end{align*}
\]

Truhlar and co-workers$^{61,62}$ have used this class of calculation as a systematic test of ground-state electronic structure methods. Our results are given in Table III. We also give calculated spectroscopic constants for a selection of diatomic molecules in Table IV. These two sets of data yield the same conclusion; the OA VCCD and OQVCCD methods perform similarly, with only small differences from the CCSD values.

Next we test a simple bond-breaking example, the abstraction of a single hydrogen from CH$_4$ in the cc-pVDZ basis, for which a plot of calculated potential energy curves is given in Fig. 1. In this system, where only one chemical bond is being broken, the CCSD and OQVCCD methods are indistinguishable, although it is also clear that OQVCCD is an improvement on the earlier OA VCCD method.

A system that exemplifies potentially strong variations in the performance of single-reference correlation methods is CuF, for which it was demonstrated$^{64}$ that the QCISD$^{65}$ method predicts very poor dipole moments, in comparison to CCSD. We include a plot of the dipole moment curves predicted by the various methods, calculated by finite difference differentiation, in Fig. 2. The large error of QCISD relative to CCSD is obvious, but the CCSD, OA VCCD and OQVCCD methods all perform similarly.

Given the above results, we can be reasonably confident that OQVCCD treats dynamic correlation effects with a similar quality as the CCSD method. Now we turn to some examples that involve strong static correlation, where qualitative differences between CCD and VCCD emerge. In the literature,$^{66}$ a standard example of this is the H$_8$ model system; here, hydrogen atoms are arranged at the vertices of a regular octagon of side length 1.06 Å. Two opposite sides of the octagon are symmetrically moved away from each other by a total distance of 2R. We give calculated potential energy curves with the STO-3G basis in Fig. 3, where we began...
the calculation with $R = -0.12 \text{ Å}$, and tested values up to $R = +0.12 \text{ Å}$. In this test, AVCCD performs poorly; it quickly becomes too high in energy from about 0.2 Å. Additionally, CCD exhibits its lack of upper bound character, going below the FCI curve beyond about 0.1 Å. VCCD is somewhat higher than FCI, and is faithfully reproduced by the approximate QVCCD. We also give $H_8$ results with the cc-pVTZ basis in Fig. 4. Since the relative positionings of the curves have changed very little, it seems we can trust the minimal basis results and expect that OQVCCD represents a better approximation to VCCSD than CCSD. The OA VCCD curve is still clearly wrong, and we infer that OQVCCD is significantly more robust.

Similar behaviour is observed for the dissociation of $N_2$. When restricted to the manifold of double excitations, this is a difficult system for most methods to treat. VCCD is known to perform extremely well here, whereas, in the case of traditional coupled cluster, it has been demonstrated elsewhere that quadruple excitations are required for a proper description of the dissociation. This can be understood in light of the analyses of Kutzelnigg and others; TCC does not begin to converge towards VCC until the inclusion of quadruples. A significantly less expensive option may be to use a method with more upper bound character from the outset. Figure 5 shows that in the STO-3G basis, QVCCD is very close to VCCD, which in turn is close to FCI; AVCCD has significant errors, and, as previously observed, CCD predicts very low non-variational energies at long bond lengths. With the cc-pVQZ basis, illustrated in Fig. 6, the minimal basis behaviours persist, and we find that the CCSD method continues to predict an unphysical maximum around 2.1 Å, whereas, OQVCCD remains qualitatively correct throughout. Again, OQVCCD does better than OA VCCD also, which performs no better than CCSD in this case. We have also compared CCSD and OQVCCD with QCCSD, for which results were obtained from Kállay’s MRCC program, in Table V. These results are as expected; QCCSD is more accurate than OQVCCD overall and does not collapse in a non-variational fashion as the bond is stretched. However, this is achieved by the addition of terms that improve TCCSD towards VCCSD, which, as was noted earlier, comes at the cost of a very expensive $O(v^6)$ step in the QCCSD iterative procedure.

Next, we consider $C_2$, for which STO-3G results are given in Fig. 7. The CCD curve, again, predicts an unphysical maximum at approximately 2.0 Å, although this is significantly more shallow than in $N_2$. It then crosses the FCI curve at approximately 2.2 Å. VCCD encounters conver-
gence difficulties around 2.0 Å, and this problem seems also to be inherited by QVCCD, but we are still able to stretch the bond sufficiently far to see that QVCCD follows the VCCD curve beyond the point at which CCD begins to plateau. On the other hand, AVCCD encounters these difficulties well before the equilibrium bond length, and hence it is not illustrated on the plot.

The aug-cc-pVQZ basis results for C2 are given in Fig. 8. The CCSD curve predicts a bond that is, apparently, fully broken from about 2.6 Å, at odds with the MRCI+Q curve. The curve is also very slightly negative in slope from 3.1 Å, indicating that the unphysical maximum still exists. However, the behaviour of OQVCCD mimics that of VCCD evident in the minimal basis results.

Finally, we examine one of the example calculations performed in Ref. 32; the distortion of H4. In this system, four hydrogen atoms are arranged in a rectangle that can be specified by 2 parameters. The parameter R, measured in angstroms, controls the distance of each H atom from the centre of the rectangular arrangement. The parameter \( \theta \), measured in degrees, is the angle subtended at the centre of mass by radii to two neighbouring H nuclei, and controls the distortion from square, corresponding to \( \theta = 90^\circ \), to rectangular geometry. We have varied \( \theta \) with R fixed at 1.738 Å; cc-pVDZ results, for which, in this small system, comparisons with VCCSD and FCI can be made, are given in Fig. 9. Instead of benchmarking the doubles-only methods, as we have done previously, we have chosen to compare the methods including the effects of singles here, which are quite important in this case. Results with cc-pVQZ are given in Fig. 10.

It is clear in both plots that all the single-reference methods predict an unphysical cusp in the potential energy surface; only FCI and MRCI+Q are smooth at \( \theta = 90^\circ \). However, the difference between the cusps predicted by the CCSD and VCCSD methods is easily seen, and it is clear that, of the single-reference methods, VCCSD performs best. The OQVCCD points are almost coincident with the VCCSD points in the cc-pVDZ plot, whereas the OAVCCD points are shifted to higher energies, giving a sharper cusp, which is yet another indication of the superior approximation of VCCSD inherent to OQVCCD relative to both OAVCCD and CCSD. All trends persist into the larger basis, where if constrained to a single-reference method of \( O(\alpha^3 \beta^3) \) complexity, OQVCCD is the method of choice here. Unfortunately, however, higher excitations are required to remove the cusps from the single-reference curves completely.

---

**TABLE V.** Errors relative to FCI (in milliHartrees, mEh) for a selection of bond lengths (in angstroms) for N2 with the cc-pVDZ basis set (d functions omitted). The FCI energies are quoted (in Hartrees) for completeness.

<table>
<thead>
<tr>
<th>R</th>
<th>CCSD</th>
<th>QCCSD</th>
<th>OQVCCD</th>
<th>FCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.96</td>
<td>5.01</td>
<td>6.59</td>
<td>−109.0210</td>
</tr>
<tr>
<td>1.1</td>
<td>8.29</td>
<td>6.90</td>
<td>9.44</td>
<td>−109.0729</td>
</tr>
<tr>
<td>1.2</td>
<td>11.39</td>
<td>9.32</td>
<td>13.34</td>
<td>−109.0648</td>
</tr>
<tr>
<td>1.3</td>
<td>15.39</td>
<td>12.28</td>
<td>18.44</td>
<td>−109.0304</td>
</tr>
<tr>
<td>1.4</td>
<td>20.29</td>
<td>15.68</td>
<td>24.65</td>
<td>−108.9883</td>
</tr>
<tr>
<td>1.5</td>
<td>25.83</td>
<td>19.31</td>
<td>31.38</td>
<td>−108.9475</td>
</tr>
<tr>
<td>1.6</td>
<td>31.32</td>
<td>22.81</td>
<td>37.35</td>
<td>−108.9120</td>
</tr>
<tr>
<td>1.7</td>
<td>35.12</td>
<td>27.43</td>
<td>41.00</td>
<td>−108.8833</td>
</tr>
<tr>
<td>1.8</td>
<td>33.51</td>
<td>25.65</td>
<td>42.30</td>
<td>−108.8617</td>
</tr>
<tr>
<td>1.9</td>
<td>19.50</td>
<td>28.77</td>
<td>42.98</td>
<td>−108.8467</td>
</tr>
<tr>
<td>2.0</td>
<td>−11.80</td>
<td></td>
<td></td>
<td>−108.8369</td>
</tr>
</tbody>
</table>
IV. CONCLUDING REMARKS

We have constructed a new quantum chemical method, QVCCD, with a strong theoretical relationship to VCCD, which appears to be more robust than CCD when a single-reference wavefunction becomes a poor approximation to the ground-state electronic structure of a system. Furthermore, we have shown that the viability of the LPFD-type approximations of VCCD is strongly dependent on the choice of transformed amplitudes, since it is important to balance sufficiently many classes of VCCD terms to infinite-order to maintain VCCD-like upper bound character across a wide range of systems. The QVCCD results demonstrate that this is indeed possible to achieve. We have included the effects of single excitations through either orbital optimization or the use of a Brueckner condition, and the resulting method is extremely theoretically attractive, given its numerous advantageous methodological properties, listed below.

- It is exactly equivalent to FCI for the limiting cases of two electrons and two holes.
- The functional contains fully linked terms only, so is rigorously extensive.
- The energy is a scalar that is invariant to rotations in the underlying orbital spaces \{\psi_i\} and \{\psi_a\}.
- The doubles-only theory is equivalent to VCCD to \(O(T^3)\), and the one-electron \(O(T^4)\) terms are also constructed correctly.
- The energy is not an upper bound to the exact ground-state Schrödinger eigenvalue, but variational minimization of the functional gives a theory that satisfies the generalized Hellmann–Feynman theorem.\(^{45}\)
- Its computational complexity is \(O(o^2v^4)\), the same as CCSD.

From our numerical experience, we note that allowing the different transformations to mix typically has an energy-lowering effect. This is, of course, because some sets of higher-order VCCD terms can only be captured by a combination of more than one of the \(u\), \(u\), \(u\), \(u\) or \(u\) matrices. It may be that there are further transformations that can be found beyond those presented here, which sum additional VCCD diagrams to infinite order, and which may go some way to improving the treatment of correlation from CCD-like to VCCD-like quality.

It is worthwhile to note that if we were to relax the constraint on the computational complexity of QVCCD from \(O(o^2v^4)\) to \(O(o^6)\), our approximation of VCCD could be further improved from correct to \(O(T^3)\) to correct to \(O(T^4)\). We observe that QVQCCD already predicts potential energy curves for strongly-correlated systems such as \(N_2\) that are qualitatively similar to those of QCCSD without the inclusion of this expensive step.

Finally, we note that although QVCCD is computable within \(O(o^2v^4)\) time, the requirement of solving the eigen-problems for each of the matrices, particularly the large \(u\) matrix, makes QVCCD slightly more difficult than an equivalent CCD calculation, although with complexity \(O(o^3v^6)\), it is not the limiting step. Instead of calculating \(u\), it may be viable to consider a low-order approximation through the associated binomial series. As long as \(u\) is truncated to the same order, then the necessary cancellations will ensure that the method remains exact for two electrons. Although such truncations will mean that the method is then no longer exact for two holes, the error in the 2-hole limit should be small, given the untruncated behaviour, and can be systematically reduced by adding higher terms in the series. Only the \(B\)-like and \(C\)-like terms are then present at all orders through \(u\) and \(u\), and, although this remains superior to AVCCD or any approach that includes only one class of term, and is very much like LPFD(-1), it is unclear whether this allows for the inheritance of sufficient upper bound character from the parent VCCD theory to treat difficult problems such as \(N_2\); this remains to be investigated.

APPENDIX: PROOF THAT LPFD(+1) IS EXACT FOR 2 HOLES

Analogously to LPFD(+1), for which the transformation matrix is a scalar in the limit of two electrons, we could write down a definition for the transformed amplitudes that would lead to a theory equivalent to CID for a 2-hole system,

\[
T_{\alpha\beta} = \frac{1}{2} (\mathcal{U}^{-\frac{q}{2}})_{\alpha\beta} T^{ij}_{ij},
\]

\[
U_{\alpha\beta} = \delta_{\alpha\beta} + T^{cd}_{cd},
\]

\[
\eta_{\alpha\beta} = \frac{1}{2} T^{kl}_{kl} T^{ij}_{ij}.
\]

Now, consider the binomial expansions of the powered matrices in LPFD(+1); in this hypothetical theory,

\[
\frac{1}{2} (\mathcal{U}^{-\frac{q}{2}})_{kl} T^{kl}_{ab} = \frac{1}{2} \sum_{n=0}^{\infty} \left( -\frac{q}{2} \right)^n \left( \eta^n \right)_{kl} T^{kl}_{ab},
\]

\[
\frac{1}{2} (\mathcal{U}^{-\frac{q}{2}})_{cd} T^{ij}_{cd} = \frac{1}{2} \sum_{n=0}^{\infty} \left( -\frac{q}{2} \right)^n \left( \eta^n \right)_{cd} T^{ij}_{cd}.
\]

The following property,

\[
\left( \eta^n \right)_{kl} T^{kl}_{ab} = \left( \eta^n \right)_{cd} T^{ij}_{cd} \quad \forall n \in \mathbb{N}^0,
\]

is obviously true for \(n = 0\),

\[
\delta_{kl} T^{kl}_{ab} = \delta_{cd} T^{ij}_{cd} = T_{ab}.
\]

\[
T_{\alpha\beta} = \frac{1}{2} (\mathcal{U}^{-\frac{q}{2}})_{\alpha\beta} T^{ij}_{ij},
\]

\[
U_{\alpha\beta} = \delta_{\alpha\beta} + T^{cd}_{cd},
\]

\[
\eta_{\alpha\beta} = \frac{1}{2} T^{kl}_{kl} T^{ij}_{ij}.
\]

FIG. 10. Energies of the \(H_4\) system as a function of \(\theta\), with \(R\) fixed at 1.738 Å, with the cc-pVQZ basis set.
and \( n = 1 \),
\[
\eta_{kl}^{ij} T_{ab}^{kl} = \eta_{kl}^{cd} T_{cd}^{ij} = \frac{1}{2} \eta_{kl}^{ij} T_{cd}^{kl} T_{ab}^{cd},
\]
(A6)
and the general result follows by mathematical induction; if we assume the case of \((n - 1)\) holds, then \( n \) follows:
\[
(\eta^n)^{ij}_{kl} T_{ab}^{kl} = \frac{1}{2} \eta_{kl}^{ij} (\eta^{n-1})^{kl}_{mn} T_{mn}^{ij} = \frac{1}{4} \eta_{kl}^{ij} T_{cd}^{ij} (\eta^{n-1})^{kl}_{mn} T_{ab}^{mn} = \frac{1}{4} \eta_{kl}^{ij} T_{cd}^{ij} (\eta^{n-1})^{ef}_{ab} T_{ef}^{kl} = \frac{1}{2} \eta_{kl}^{ij} (\eta^{n-1})^{kl}_{ab} T_{cd}^{ef} = (\eta^n)_{ab}^{ij} T_{cd}^{ij}.
\]
(A7)

This result, coupled with the series expansions given in Eqs. (A2) and (A3), is sufficient to demonstrate that the series are identical and that we have the following:
\[
\frac{1}{2} (U^{-\frac{1}{2}}) T_{ab}^{ij} = \frac{1}{2} (U^{-\frac{1}{2}}) T_{cd}^{ij},
\]
(A8)

Hence, the hypothetical theory is identical to LPFD(+1) and we conclude that LPFD(+1) is exact for both two electrons and two holes.

2. V. Fock, Z. Phys. 61, 126 (1930).
3. C. Möller and M. S. Plesset, Phys. Rev. 46, 618 (1934).