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# Breaking Multiple Covalent Bonds with Hartree-Fock-based Quantum Chemistry: Quasi-Variational Coupled Cluster Theory with Perturbative Treatment of Triple Excitations

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**We enhance the recently proposed Optimized-orbital Quasi-Variational Coupled Cluster Doubles (OQVCCD) method for the calculation of ground-state molecular electronic structure by augmenting it with the standard perturbative (T) correction for the effects of connected triple excitations. We demonstrate the OQVCCD(T) ansatz to be outstandingly robust and accurate in the description of the breaking of the triple bond in diatomic nitrogen, N<sub>2</sub>, where traditional CCSD and CCSD(T) completely fail, yet with a computational cost that is nearly the same as that of CCSD(T). This result provides insight into the failure of CCSD(T) and related methods and how it may be overcome.**

It is the electronic structure of a molecule that primarily determines its physical and chemical properties, and the construction of new algorithms for its efficient and accurate computational calculation continues to be a very active area of research. One of the key challenges in obtaining sufficient accuracy for reliable and quantitative prediction of empirical phenomena is to obtain the energy associated with the correlation of the electrons sufficiently completely. The Coupled Cluster<sup>1-3</sup> (CC) method has emerged as the standard approach to the treatment of this problem, sometimes replaced by, or combined with, perturbative approximations. The usual approach is to model the wavefunction as the action of an exponential operator on a reference wavefunction consisting of a single Slater determinant, then to project Schrödinger's equation onto the appropriate manifold of excited determinants and iteratively solve the resulting equations to determine the cluster operator. This projective approach is sometimes called Traditional Coupled Cluster (TCC). TCC calculations are most commonly performed with a cluster operator that generates only single and double excitations of the reference, typically Hartree-Fock (HF), wavefunction, and this is termed CCSD. The TCC energy is rigorously extensive, even for a truncated cluster operator, and exactly equivalent to Full Configuration Interaction (FCI) when the cluster operator is complete. In addition, the Campbell-Baker-Hausdorff expansion<sup>4</sup> of the similarity-transformed Hamiltonian naturally truncates at the fourth power of the cluster operators, ensuring that the compu-

tational effort of a TCC calculation is always of polynomial, as opposed to factorial, complexity.

However, some aspects of the TCC formalism are problematic; the similarity-transformed Hamiltonian is not Hermitian, which complicates the calculation of both ground- and excited-state properties, and calculated TCC energies are not upper bounds on the exact ground-state Schrödinger energy eigenvalue. In contrast, fully variational methods have the advantage that the error in the minimized energy is second order in remaining errors in the wavefunction or parameterisation. Historically, this property led to the use of variational configuration interaction (CI) for introducing electron correlation, but in recent decades, the importance of the guaranteed energy extensivity of TCC has led to a decline in the use of CI.

Furthermore, in many situations the single-determinantal reference wavefunction approximation breaks down and becomes a poor approximation to the ground-state electronic structure, and then there are questions as to whether at a finite truncation level (e.g. CCSD) TCC can describe phenomena such as dissociating molecules or excited states faithfully. An alternative approach in these circumstances is to adopt a reference wavefunction consisting of multiple determinants, for example multireference CI (MRCI)<sup>5,6</sup>, and related formulations that correct approximately for the size-extensivity error of variational MRCI<sup>7-9</sup>. However, such methods are difficult to deploy on large molecules and in a general prescriptive way, and often lead to both a high scaling of computational effort and problems arising from the lack of rigorous extensivity of the energy.

A number of studies<sup>10-17</sup> have established that the poor performance of single-reference CCSD in the bond-breaking regime is not necessarily the fault of the single-reference CC wavefunction ansatz, and have confirmed the utility of Variational Coupled Cluster<sup>18</sup> (VCC) and related approximations in overcoming this difficulty. In VCC, the same exponentially-generated wavefunction is used, but it is optimized through minimization of the energy expectation value rather than by projection. Unfortunately, VCC remains very rarely used since its factorial computational complexity, even in the case of a double-excitation cluster operator (VCCD), renders it prohibitively difficult to perform for all but the smallest of molecular systems.

We have recently proposed several new approximations to

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VCCD<sup>19–21</sup>, of which the most recent, Quasi-Variational Coupled Cluster (QVCC)<sup>21</sup>, shows very promising behaviour. We have demonstrated that this single-reference method, which makes use of an extensive and Hermitian energy functional that is exact for any number of isolated 2-electron subsystems, and, by construction, approximates parts of VCCD through all orders, is often more robust than TCCD when the superposition of two or more reference states should be required for a qualitatively correct description of the electronic wavefunction, that is, when static (or non-dynamic) correlation effects are strong.

It is well known that in order to achieve chemical accuracy from single-reference calculations, the effects of at least triple excitations must be included, and the correction to CCSD based on perturbation theory, CCSD(T)<sup>22</sup>, is extremely widely used and successful in predicting the structure and properties of molecules near their equilibrium geometry. To remedy the failure of CCSD(T) to describe bond-breaking situations<sup>23</sup>, several authors have proposed alternatives, such as the  $\Lambda$  methods of Bartlett et al.<sup>24</sup>, the CCSD(2) method<sup>25</sup> and the Completely Renormalized CC (CR-CC(2,3)) method of Piecuch et al.<sup>26</sup>.

In this communication, we investigate instead the application of a standard perturbative triples correction<sup>22,27</sup> to Quasi-Variational Coupled Cluster, exploring the hypothesis that the near-variational character of this ansatz captures the essential physics of strong static correlation, and that remaining dynamic correlation effects can legitimately be included perturbatively. We note at the outset that it is not clear whether this supposition will be valid, since, as chemical bonds break, the energy gap between the highest occupied and lowest unoccupied molecular orbitals reduces, thereby amplifying the perturbed wavefunction and potentially overestimating the remaining correlation energy.

Using the Einstein summation convention and a spin-orbital notation in which we take labels belonging to  $\{i, j, k, \dots\}$  to denote orbitals occupied in the single-determinantal reference wavefunction,  $|\Phi_0\rangle$ , and labels belonging to  $\{a, b, c, \dots\}$  to denote those unoccupied, the CCSD cluster operator is

$$\hat{T} = \hat{T}_1 + \hat{T}_2 \quad (1)$$

$$\hat{T}_1|\Phi_0\rangle = T_a^i a^\dagger i|\Phi_0\rangle \quad (2)$$

$$\hat{T}_2|\Phi_0\rangle = \frac{1}{4} T_{ab}^{ij} b^\dagger j a^\dagger i|\Phi_0\rangle. \quad (3)$$

The VCCSD ground-state energy then corresponds to the minimum of the following functional with respect to the set of cluster amplitudes,  $\{T_a^i\} \cup \{T_{ab}^{ij}\}$ .

$$E_{\text{VCCSD}} = \frac{\langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi_0 \rangle} = \langle \Phi_0 | e^{\hat{T}^\dagger} \hat{H} e^{\hat{T}} | \Phi_0 \rangle_L \quad (4)$$

The  $L$  subscript indicates that the expression is restricted to include linked terms only.

In the LPFD<sup>19</sup>, AVCCD<sup>20</sup> and QVCCD<sup>21</sup> methods, one computes the ground-state energy analogously to VCC, by variational minimization of the functional,

$$E = \langle \Phi_0 | \hat{H} (1 + 2 \hat{T}) | \Phi_0 \rangle + \langle \Phi_0 | {}_1\hat{T}^\dagger \hat{H} {}_1\hat{T} | \Phi_0 \rangle_L \quad (5)$$

with respect to the doubles-only cluster amplitudes. The effects of single excitations are taken into account through either minimization of the functional also with respect to the orbitals<sup>28</sup>, which defines OLPFD, OAVCCD and OQVCCD respectively, or by introducing the Brueckner condition<sup>29,30</sup>, defining the BLPFD, BAVCCD and BQVCCD methods respectively. The  ${}_q\hat{T}$  operators are, in the case of QVCCD,

$${}_q\hat{T}|\Phi_0\rangle = \frac{1}{4} {}_qT_{ab}^{ij} b^\dagger j a^\dagger i|\Phi_0\rangle \quad (6)$$

$$\begin{aligned} {}_qT_{ab}^{ij} = & (1 - \tau_{ab}) ({}_a\mathbf{U}^{-\frac{q}{2}})_c T_{cb}^{ij} \\ & + (1 - \tau_{ij}) ({}_b\mathbf{U}^{-\frac{q}{2}})_k T_{ab}^{kj} \\ & - \frac{1}{2} ({}_c\mathbf{U}^{-\frac{q}{2}})_{kl} T_{ab}^{kl} \\ & - \frac{1}{2} (1 - \tau_{ij}) (1 - \tau_{ab}) ({}_d\mathbf{U}^{-\frac{q}{2}})_{ac} T_{cb}^{kj} \end{aligned} \quad (7)$$

$$\begin{aligned} {}_aU_b^a = & \delta_b^a + \frac{1}{2} T_{bc}^{ij} T_{ij}^{ac} & {}_cU_{kl}^{ij} = & \delta_{kl}^{ij} + \frac{1}{2} T_{ab}^{ij} T_{kl}^{ab} \\ {}_bU_j^i = & \delta_j^i + \frac{1}{2} T_{ab}^{ik} T_{jk}^{ab} & {}_dU_{aj}^{ib} = & \delta_{aj}^{ib} + T_{ac}^{ik} T_{jk}^{bc} \end{aligned} \quad (8)$$

where  $\tau_{pq}$  permutes the labels  $p, q$  in what follows. The essential point of this construction is that the transformations introduce partial local normalisation of the cluster amplitudes, and in such a way that, by design, the energy functional contains VCCD-like terms to all orders in  $\hat{T}$ , and such that the functional agrees with VCCD at low orders, yet possessing a limiting computational complexity identical with that of CCSD. For a more detailed discussion of the theoretical principles at work in this method, we refer the reader to our earlier papers<sup>19–21</sup>.

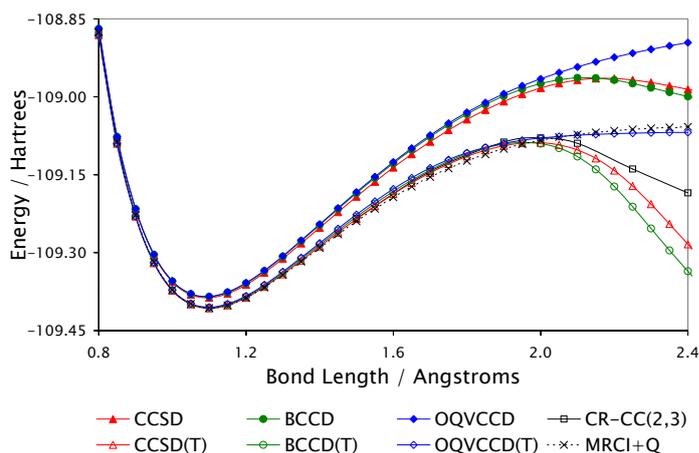
The OQVCCD method is already correct to third-order in Møller-Plesset perturbation theory<sup>31</sup> and correctly constructs the terms  $\langle \hat{T}_2^\dagger \hat{V} \hat{T}_2^2 \rangle_L$  and  $(\frac{1}{2!})^2 \langle (\hat{T}_2^\dagger)^2 \hat{F} \hat{T}_2^2 \rangle_L$  that enter at fourth-order, but omits those containing connected triple excitations. This is the same position as CCSD, and mutual cancellation between the VCCD terms at this order ensures that the standard [T] correction<sup>27</sup> remains valid for OQVCCD, making it correct to fourth-order in Møller-Plesset theory. Since, in OQVCCD, the effects of single excitations are introduced through orbital optimization, [T] and (T)<sup>22</sup> are identical. This defines the OQVCCD(T) method.

We now apply the OQVCCD(T) ansatz to the breaking of the triple bond in the diatomic nitrogen molecule,  $\text{N}_2$ , a quintessential example of a system with strong multi-reference character that single-reference methods such as

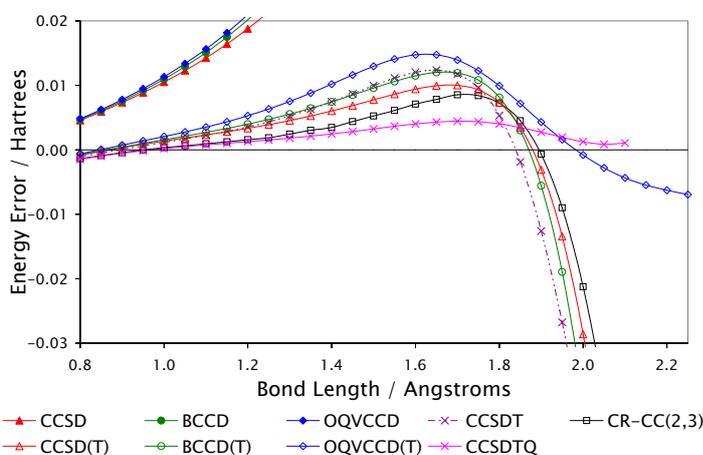
CCSD fail to model adequately<sup>23</sup>. Musial and Bartlett, for instance, have found that all of CCSD(T), CCSD(T<sub>q</sub>), CCSDT and their  $\Lambda$  variants fail here<sup>32</sup>. The CR-CC(2,3) method also fails for N<sub>2</sub>, and one must go to CCSDTQ before a qualitatively correct potential energy curve can be predicted by the single-reference TCC methods. We here compare the CCSD, CCSD(T), BCCD, BCCD(T)<sup>30</sup>, OQVCCD and OQVCCD(T) methods with the accurate standard of internally-contracted MRCI<sup>5,6</sup> using a complete active space reference wavefunction where the active space consists of the atomic valence orbitals. The approximate extensivity correction of Davidson<sup>33</sup> was additionally applied to the MRCI energy (MRCI+Q). These calculations were performed with the Molpro<sup>34,35</sup> quantum chemistry software package. In addition, we obtained CR-CC(2,3) results using the GAMESS package<sup>36</sup>.

In Fig. 1, we give calculated potential energy curves for N<sub>2</sub> using the aug-cc-pVQZ orbital basis set<sup>37</sup>. CCSD clearly provides an inadequate description of the bond breaking in this strongly-correlated example. However, we find that OQVCCD does not manifest the same unphysical maximum in the potential energy curve. When the (T) correction is added to CCSD, the problem is magnified. Even CR-CC(2,3), excellent for single-bond breaking<sup>38</sup>, collapses in a non-variational fashion to energies significantly below the MRCI+Q curve, whereas OQVCCD(T) is in outstanding agreement with MRCI+Q out to internuclear separations where the triple covalent bond is essentially broken. In Fig. 2, we show results in the smaller cc-pVDZ basis set<sup>39</sup>, in which it is possible also to perform CCSDT and CCSDTQ calculations using Kállay's MRCC program<sup>40</sup>. The results are presented as a plot of the errors relative to MRCI+Q. It is clearly seen that CCSDT also fails completely, but inclusion of the effects of connected quadruple excitations yields a qualitatively correct curve. The behaviour of OQVCCD(T) is quite exceptional, with this  $O(N^7)$ -scaling theory outperforming  $O(N^8)$  CCSDT, and rivalling  $O(N^{10})$  CCSDTQ. Even though one might expect the perturbative part of OQVCCD(T) to become unreliable as the highest occupied and lowest unoccupied molecular orbitals approach degeneracy, our present results challenge the conventional wisdom that a full, non-perturbative treatment of triple and quadruple excitations is required to correctly dissociate this system.

As a further example of multiple bond breaking, we consider cyclo-H<sub>8</sub>, in which eight hydrogen atoms are arranged at the vertices of a regular octagon, with edge length  $R$ . For  $R \approx 1 \text{ \AA}$ , the electronic structure is described approximately by two equally-weighted configurations corresponding to the two classical resonance forms, but with other configurations strongly mixed. As  $R$  is increased, the eight partial bonds break simultaneously, and, in terms of symmetry-adapted molecular orbitals, the exact singlet-coupled 8-hydrogen atom



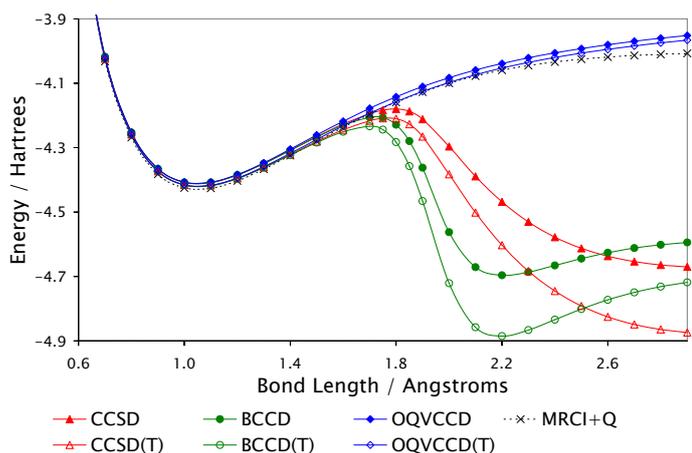
**Fig. 1** Calculated potential energy curves for N<sub>2</sub> with the aug-cc-pVQZ basis set<sup>37</sup>.



**Fig. 2** Errors relative to MRCI+Q for N<sub>2</sub> with the cc-pVDZ basis set<sup>39</sup>.

wavefunction is represented by a mixture of 48 determinants with coefficients  $\pm 1/4\sqrt{6}, \pm 1/2\sqrt{6}$ . The restricted Hartree-Fock approximation is thus poor for small  $R$ , and completely wrong at separation. Fig. 3 shows that despite this, CCSD and BCCD perform well up to  $R = 1.5 \text{ \AA}$ , but at larger separation have very large errors. The (T) correction to these methods exacerbates the problem further. In contrast, both OQVCCD and OQVCCD(T) are able to cope with the poor reference wavefunction and remain in excellent quantitative agreement with MRCI+Q throughout.

In conclusion, we have demonstrated that combining the OQVCCD approximation with the standard Møller-Plesset-based (T) perturbative introduction of connected triple excitations gives a very powerful and versatile new electronic structure ansatz. Able to achieve a physically correct and quantitatively accurate description of the bond breaking in extreme examples such as N<sub>2</sub>, the OQVCCD(T) method is significantly



**Fig. 3** Calculated potential energy curves for increasing the edge length of the regular octagonal  $H_8$  model with the cc-pVQZ basis<sup>39</sup>.

more robust than either CCSD(T) or BCCD(T). We emphasize that no improvements have been made to the (T) correction, which is exactly the same function of the cluster amplitudes in OQVCCD(T) as in BCCD(T). We conclude that not only does our functional inherit pseudo-variational character from its fully variational parent theory, VCCSD, but the use of the corresponding optimum cluster amplitudes to construct a perturbative correction indirectly improves the stability of that correction also. Conversely, the catastrophic performance of CCSD(T) in describing multiple bond dissociation can be attributed to defects in traditional projective CCSD, rather than arising from a breakdown of perturbation theory. This prompts the re-evaluation of the importance of the variational upper bound property, even if only approximately fulfilled, in computational methods for the calculation of molecular electronic structure.

## References

- 1 F. Coester and H. Kümmel, *Nucl. Phys.*, 1960, **17**, 477.
- 2 J. Čížek, *J. Chem. Phys.*, 1966, **45**, 4256.
- 3 R. J. Bartlett, *Ann. Rev. Phys. Chem.*, 1981, **32**, 359.
- 4 E. Merzbacher, *Quantum Mechanics*, Wiley, New York, 2nd edn., 1970.
- 5 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1988, **89**, 5803–5814.
- 6 P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.*, 1988, **145**, 514–522.
- 7 R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.*, 1988, **143**, 413.
- 8 P. G. Szalay and R. J. Bartlett, *Chem. Phys. Lett.*, 1993, **214**, 481.
- 9 H.-J. Werner and P. J. Knowles, *Theor. Chem. Acc.*, 1991, **78**, 175–187.
- 10 P.-D. Fan, K. Kowalski and P. Piecuch, *Molec. Phys.*, 2005, **103**, 2191–2213.
- 11 P.-D. Fan and P. Piecuch, *Adv. Quantum Chem.*, 2006, **51**, 1–57.
- 12 P. Piecuch, I. S. O. Pimenta, P.-D. Fan and K. Kowalski, *ACS symposium series*, 2007, **958**, 37–73.
- 13 P. Piecuch, K. Kowalski, P.-D. Fan and I. S. O. Pimenta, *Progress in Theoretical Chemistry and Physics*, 2010, **12**, 119–206.
- 14 T. Van Voorhis and M. Head-Gordon, *J. Chem. Phys.*, 2000, **113**, 8873.
- 15 P.-D. Fan, K. Kowalski and P. Piecuch, *Molec. Phys.*, 2005, **103**, 2191.
- 16 B. Cooper and P. J. Knowles, *J. Chem. Phys.*, 2010, **133**, 234102.
- 17 F. A. Evangelista, *J. Chem. Phys.*, 2011, **134**, 224102.
- 18 R. J. Bartlett and J. Noga, *Chem. Phys. Lett.*, 1988, **150**, 29.
- 19 P. J. Knowles and B. Cooper, *J. Chem. Phys.*, 2010, **133**, 224106.
- 20 J. B. Robinson and P. J. Knowles, *J. Chem. Phys.*, 2011, **135**, 044113.
- 21 J. B. Robinson and P. J. Knowles, *J. Chem. Phys.*, 2012, **136**, 054114.
- 22 K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479.
- 23 W. D. Laidig, P. Saxe and R. J. Bartlett, *J. Chem. Phys.*, 1987, **86**, 887.
- 24 A. Taube and R. Bartlett, *J. Chem. Phys.*, 2008, **128**, 044110.
- 25 S. R. Gwaltney and M. Head-Gordon, *Chem. Phys. Lett.*, 2000, **323**, 21–28.
- 26 P. Piecuch and M. Włoch, *J. Chem. Phys.*, 2005, **123**, 224105.
- 27 M. Urban, J. Noga, S. J. Cole and R. J. Bartlett, *J. Chem. Phys.*, 1985, **83**, 4041.
- 28 C. Kollmar and A. Heßelmann, *Theor. Chem. Acc.*, 2009, **127**, 311.
- 29 K. A. Brueckner, *Phys. Rev.*, 1954, **96**, 508.
- 30 N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari and G. W. Trucks, *Chem. Phys. Lett.*, 1989, **164**, 185.
- 31 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.
- 32 M. Musial and R. J. Bartlett, *J. Chem. Phys.*, 2010, **133**, 104102.
- 33 S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, 1974, **8**, 61–72.
- 34 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, *MOLPRO, version 2010.2, a package of ab initio programs*, 2011, see <http://www.molpro.net>.
- 35 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz, *WIREs Comput Mol Sci.*, 2012, **2**, 242–253.
- 36 M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery Jr, *J. Comput. Chem.*, 1993, **14**, 1347–1363.
- 37 R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806.
- 38 Y. Ge, M. Gordon and P. Piecuch, *J. Chem. Phys.*, 2007, **127**, 174106.
- 39 T. H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 40 M. Kállay and P. R. Surján, *J. Chem. Phys.*, 2001, **115**, 2945.