

# Spin-Restriction in Explicitly Correlated Coupled Cluster Theory: The Z-Averaged CCSD(2) $\overline{\text{R12}}$ Approach

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**S** Supporting Information

**ABSTRACT:** R12 methods have now been established to improve both the efficiency and accuracy of wave function-based theories. While closed-shell and spin-orbital methodologies for coupled cluster theory are well-studied, R12 corrections based on an open-shell, spin-restricted formalism have not been well developed. We present an efficient spin-restricted R12 method based on the symmetric exchange or Z-averaged approach that reduces the number of variational parameters. The current formalism reduces spin contamination relative to unrestricted methods but remains rigorously size consistent in contrast to other spin-adapted formulations. The theory is derived entirely in spin-orbital quantities, but Z-averaged symmetries are exploited to minimize the computational work in the residual equations. R12 corrections are formulated in a perturbative manner and are therefore obtained with little extra cost relative to the standard coupled cluster problem. R12 results with only a triple- $\zeta$  basis are competitive with conventional aug-cc-pV5Z and aug-cc-pV6Z results, demonstrating the utility of the method in thermochemical problems for high-spin open-shell systems.

## 1. INTRODUCTION

With only modestly sized basis sets, explicitly correlated methods can achieve remarkable accuracy, providing superior results for molecular energies,<sup>1–6</sup> geometries,<sup>7,8</sup> vibrational frequencies,<sup>9,10</sup> and other properties.<sup>11–13</sup> Approaches based on one-particle basis sets are unable to accurately treat the coalescence region between two electrons, which requires a cusp and a surrounding depletion of electron density (Coulomb hole) near  $r_{12} = 0$ .<sup>14–17</sup> In many extrapolation schemes<sup>18,19</sup> the error decreases as  $n^{-3}$  in the cardinal number of a Dunning correlation consistent (cc-pVnZ) basis set.<sup>20</sup> For methods with an  $N^4$  basis set dependence, the correlation energy error only converges as  $t^{-1/4}$  in the computational time!<sup>21,22</sup> Supplementing the orbital basis with pair functions depending explicitly on the interelectronic distance,  $r_{12}$ , directly includes the correct Coulomb hole shape, rapidly accelerating basis set convergence. Inclusion of  $r_{12}$ -dependent terms leads to a large number of difficult three- and four-electron integrals,<sup>23–25</sup> which originally restricted application to small molecules. R12 methods avoid these difficult integrals through a resolution of the identity (RI) approximation,<sup>26–28</sup> factoring the numerous many-electron integrals into products of simple two-electron integrals. Closed-shell coupled-cluster singles and doubles CCSD-R12 and unrestricted CCSD-R12 based methods are now well established, and the R12 corrections add little extra cost relative to the conventional computation.

While spin restriction is trivially imposed in closed-shell coupled cluster methods, extending R12 corrections to spin-restricted and multireference methods presents several new challenges. While the concepts of normal ordering and similarity transformation are trivially formulated in a spin-free manner in closed-shell problems, open-shell problems are much more difficult since the singly occupied orbitals can correspond to both hole (occupied) and particle (unoccupied) indices. While much

focus has been given recently to multireference coupled cluster theory,<sup>29</sup> even the single-reference, high-spin problem for open shells is nontrivial. This is clearly illustrated by the numerous high-spin open-shell approaches introduced for coupled cluster, including spin-orbital restricted open-shell Hartree–Fock (ROHF-CCSD),<sup>30</sup> partially spin-adapted (PSA-CCSD),<sup>31–33</sup> spin-restricted (SR-CCSD),<sup>34</sup> and spin-adapted (SA-CCSD)<sup>35</sup> coupled cluster methods. Although ROHF references spin-project correlation energy,<sup>36–38</sup> they do not necessarily eliminate spin contamination in the actual wave function. Important progress was made on state specific, rigorously spin-adapted methods for high-spin open-shell problems by Li and Paldus<sup>39,40</sup> and Bartlett and Nooijen.<sup>41</sup> The normal-ordered exponential and Hausdorff expansion that forms the basis of closed-shell coupled cluster was generalized in an elegant manner but lost the simplicity of the conventional Hausdorff expansion. The majority of high-spin open-shell applications therefore still employs a spin-orbital framework even if the cluster operator is expanded in CSFs.<sup>32,34,35</sup> In R12 methods, the Hausdorff expansion is central to simplifying approximations which ignore particular commutators,<sup>42</sup> making some rigorously spin-adapted approaches incompatible with current R12 methods. A spin-orbital approach which uses spin restriction to both reduce computational cost and spin contamination therefore presents the most tractable framework for developing efficient coupled cluster R12 methods, especially in extending the treatment beyond CCSD.

Beyond the theoretical simplifications, spin-orbital methods can even improve accuracy in some cases. Specifically in symmetry-breaking problems, unrestricted Hartree–Fock (UHF)-like solutions that break orbital symmetries often provide

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superior results, most notably for vibrational frequencies.<sup>43</sup> In particular, there has recently been renewed interest in unrestricted methods combined with spin constraints,<sup>44</sup> exploiting the physical picture of spin polarization while still avoiding the problematic spin contamination inherent in UHF.<sup>45</sup> For symmetry breaking problems, Brueckner methods can also improve results, but even for ROHF, references will break  $\alpha, \beta$  symmetry when reoptimizing the orbitals.<sup>46,47</sup> Due to the unrestricted nature of the orbitals and the need to recompute integrals on each iteration, however, tractable open-shell R12 extensions for Brueckner methods have not yet been proposed.

An “ideal” R12 coupled cluster formulation would therefore be spin restricted in nature, even in orbital-optimized approaches, like Brueckner theory, reducing computational cost and spin contamination while still maintaining a spin–orbital framework to make the R12 corrections tractable. This compromise is achieved in the Z-averaged approach of Lee and Jayatilaka<sup>48–51</sup> which employs symmetric spin functions:

$$\sigma^+ = \frac{1}{\sqrt{2}}(\alpha + \beta) \quad (1)$$

$$\sigma^- = \frac{1}{\sqrt{2}}(\alpha - \beta) \quad (2)$$

in the singly occupied space, ensuring that the open-shell exchange is symmetric for  $\alpha$  and  $\beta$  orbitals. Proceeding in an unrestricted formalism with no a priori assumptions, amplitude symmetry relations are automatically obtained similar to the closed-shell case which drastically reduce the computational cost. By spin-averaging exchange, ZA-CCSD can also be extended to a Brueckner theory which does not break orbital symmetries, drastically reducing the number of integrals that need to be recomputed. As an initial investigation of ZA-CCSD in explicitly correlated coupled cluster theory, we therefore present a partially spin-adapted formulation of ZA-CCSD for high-spin open-shell systems. R12 corrections are obtained based on the CCSD(2)<sub>RTZ</sub> ansatz of Valeev,<sup>52–54</sup> which provides a noniterative, perturbative R12 correction to the conventional CCSD energy. In previous formulations<sup>51</sup> based on symmetric spin functions, the theory was greatly complicated by the presence of  $\alpha, \beta$ -exchange excitations that do not conserve  $M_S$ . We make important simplifications regarding the  $\alpha, \beta$ -exchange excitations which both increase computational efficiency and actually decrease spin contamination. Excellent basis set convergence is observed for a set of atomization energies, rivaling conventional aug-cc-pVSZ and aug-cc-pV6Z computations with only an aug-cc-pVTZ orbital basis set. The new ZA-CCSD(2)<sub>RTZ</sub> theory therefore maximizes efficiency through accelerated basis set convergence, reduction in the number of amplitudes and residuals, and use of a determinantal formalism.

## 2. THEORETICAL BACKGROUND

**2.1. Notation.** In the current discussion, the following notation is used to distinguish orbital subspaces:

$i, j, k, l, \dots$	DOCC	doubly occupied orbitals
$a, b, c, d, \dots$	VIR	virtual orbitals
$s, t, \dots$	SOCC	singly occupied orbitals
$p, q, \dots$	ORB	computational orbital basis

Subspaces specific to R12 methods are also needed:

$x, y, \dots$		geminal space
$p', q', \dots$	CABS	external orbitals
$\alpha, \beta, \dots$	CBS	complete basis set
$p', q', \dots$	RI	resolution of the identity

The RI space approximates the complete basis obtained within a finite computational basis. The complementary auxiliary basis set (CABS) space represents those orbitals in the RI that are orthogonal to the orbital basis set. The indices  $\alpha, \beta$  denote orbitals in a formally complete basis but which never enter the programmable equations.

**2.2. Z-averaged Coupled Cluster.** For closed-shell coupled cluster, the amplitudes are related by

$$T_{i\alpha j\alpha}^{a\alpha b\alpha} = T_{i\alpha j\beta}^{a\alpha b\beta} - T_{j\alpha i\beta}^{a\alpha b\beta} \quad (3)$$

which guarantees that even if the individual determinants in the  $N$ -particle basis are not spin eigenfunctions, the total wave function will be. For open-shell cases using a truncated model space, such as CCSD or CISD, the determinantal basis does not automatically produce a spin eigenfunction even if a restricted open-shell Hartree–Fock (ROHF) reference is chosen. Due to asymmetric exchange of  $\alpha$  and  $\beta$  orbital subspaces, the amplitude symmetry in eq 3 is broken, resulting in unrestricted  $T_{i\alpha j\alpha}^{a\alpha b\alpha}$ ,  $T_{i\alpha j\beta}^{a\alpha b\beta}$ , and  $T_{i\beta j\beta}^{a\beta b\beta}$  amplitudes. Furthermore, the projection manifold usually includes only configurations in the Møller–Plesset (MP2) first-order interacting space so that connected pseudo-triple excitations:

$$\Phi_{i\alpha j\beta s\alpha}^{a\alpha b\alpha s\beta} \quad (4)$$

are neglected despite being necessary for an exact spin eigenfunction. This presents both an efficiency concern due to the extra amplitudes and an accuracy concern due to spin contamination in the wave function. Practically speaking, for high-spin open-shell CCSD with ROHF or UHF references, spin contamination is very small<sup>34,55</sup> except for molecules, such as NO<sub>2</sub>, which have severely spin-contaminated UHF reference functions. The model space for CCSD therefore seems to be complete enough that Schrödinger projection:

$$\langle \Phi_{ij}^{ab} | \bar{H} | 0 \rangle = 0 \quad (5)$$

is enough to eliminate much of the spin contamination.

Generally speaking, the most common approach is the unrestricted coupled cluster with restricted orbitals scheme (ROHF-CCSD) described above.<sup>30,56,57</sup> The coupled cluster equations are derived in a purely spin–orbital form, and separate amplitudes are allowed for each spin case. No efficiency is gained relative to UHF-based methods except that only a single set of integrals is required. Many methods were therefore developed to overcome the “unrestricted” problem of ROHF-based coupled cluster. Janssen and Schaefer<sup>33</sup> proposed a spin-adapted formulation employing the unitary group generators. For singly occupied orbitals, the unitary group operators contain both excitation and de-excitation operators with respect to the ROHF reference. The commutativity of the individual terms in  $\hat{T}$  is then no longer guaranteed, and the Hausdorff expansion does not truncate at quadruply nested commutators. Despite having fewer independent amplitudes than the unrestricted approach, the theory does not seem to provide a major efficiency advantage. Similar problems are encountered in the approach of Li and

Table 1. Doublet CSFs Used in SR-CCSD

$$\begin{aligned}
D\tilde{\Phi}_i^a(1) &= \frac{1}{\sqrt{2}}(\Phi_{ia}^{a\alpha} + \Phi_{i\beta}^{a\beta}) \\
D\tilde{\Phi}_i^a(2) &= \frac{1}{\sqrt{6}}(\Phi_{ia}^{a\alpha} - \Phi_{i\beta}^{a\beta} - 2\Phi_{sa i\beta}^{a\alpha s\beta}) \\
D\tilde{\Phi}_s^a(1) &= \Phi_{sa}^{a\alpha} \\
D\tilde{\Phi}_i^s(1) &= \Phi_{i\beta}^{s\beta} \\
D\tilde{\Phi}_{ij}^{ab}(1) &= \frac{1}{2\sqrt{3}}(2\Phi_{iaja}^{a\alpha b\alpha} + 2\Phi_{i\beta j\beta}^{a\beta b\beta} + \Phi_{iaj\beta}^{a\alpha b\beta} - \Phi_{ja i\beta}^{a\alpha b\beta} + \Phi_{i\beta ja}^{a\beta b\alpha} - \Phi_{j\beta ia}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{ij}^{ab}(2) &= \frac{1}{2}(\Phi_{iaj\beta}^{a\alpha b\beta} + \Phi_{ja i\beta}^{a\alpha b\beta} + \Phi_{i\beta ja}^{a\beta b\alpha} + \Phi_{j\beta ia}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{si}^{ab}(1) &= \frac{1}{\sqrt{6}}(2\Phi_{saia}^{a\alpha b\alpha} + \Phi_{sa i\beta}^{a\alpha b\beta} - \Phi_{sa i\beta}^{b\alpha a\beta}) \\
D\tilde{\Phi}_{si}^{ab}(2) &= \frac{1}{\sqrt{2}}(\Phi_{sa i\beta}^{a\alpha b\beta} + \Phi_{sa i\beta}^{b\alpha a\beta}) \\
D\tilde{\Phi}_{ij}^{as}(1) &= \frac{1}{\sqrt{6}}(2\Phi_{i\beta j\beta}^{a\beta s\beta} - \Phi_{iaj\beta}^{a\alpha s\beta} + \Phi_{ja i\beta}^{a\alpha s\beta}) \\
D\tilde{\Phi}_{ij}^{as}(2) &= \frac{1}{\sqrt{2}}(\Phi_{iaj\beta}^{a\alpha s\beta} + \Phi_{ja i\beta}^{a\alpha s\beta})
\end{aligned}$$

Paldus.<sup>39,40</sup> A simpler partially spin-adapted (PSA-CCSD) approach was therefore proposed by Janssen,<sup>33</sup> Werner,<sup>32,58</sup> and Neogrady,<sup>31,59,60</sup> who employed spin-adapted  $\hat{T}$  operators for connected excitations resulting in spin adaptation of the linear terms. A reduction in the number of independent amplitudes is achieved, but no de-excitations are included in the cluster operator, restoring the conventional Hausdorff expansion. The independent amplitudes are determined from configuration state function (CSF) projections, producing a minimal number of residual equations. For the doublet case, CSFs are listed in Tables 1 and 2 with doublet configurations denoted by  $D$  and the external configurations denoted by  $Q$ , following the notation of Gauss and Szalay.<sup>34</sup> While the approach is almost entirely free of spin contamination, the spin expectation value is not rigorously, for example, 0.75 for doublet states, since the wave function is only spin adapted in the linear excitations.

This partial spin adaptation was extended by Gauss and Szalay<sup>34,35,61,62</sup> in SR-CCSD. The Schrödinger projections (eq 5) for CSFs of the desired spin are supplemented by spin constraints on the external configurations:

$$\langle Q\tilde{\Phi}_{ij}^{ab} | \exp(-\hat{T})\hat{S}_N^2 \exp(\hat{T}) | 0 \rangle = 0 \quad (6)$$

Here subscript  $N$  denotes normal ordering with respect to the Hartree–Fock reference. The spin projections add almost no extra computational cost relative to the Schrödinger projections, and the SR-CCSD method is therefore similar in computational cost to the PSA-CCSD method. For SR-CCSD, the expectation value  $\langle \hat{S}^2 \rangle$  computed from differentiation of the CCSD Lagrangian is rigorously  $S(S+1)$  for a given multiplicity. We must emphasize, however, that the coupled cluster wave function is not a spin eigenfunction unless the spin constraints are extended to all configurations in the full configuration interaction (FCI) wave function. Efforts along these lines were pursued by Heckert et al.,<sup>35</sup> leading to the SA-CCSD approach. Gauss and Szalay suggested only including spin constraints for those configurations in the first-order interacting space, limiting the cluster operator to connected double excitations.<sup>34</sup> For accurate treatment of certain

Table 2. External Quartet and Sextet CSFs Used in SR-CCSD

$$\begin{aligned}
Q\tilde{\Phi}_i^a(1) &= \frac{1}{\sqrt{3}}(\Phi_{ia}^{a\alpha} - \Phi_{i\beta}^{a\beta} + \Phi_{sa i\beta}^{a\alpha s\beta}) \\
Q\tilde{\Phi}_{ij}^{ab}(1) &= \frac{1}{2\sqrt{3}}(2\Phi_{iaja}^{a\alpha b\alpha} - 2\Phi_{i\beta j\beta}^{a\beta b\beta} + \Phi_{iaj\beta}^{a\alpha b\beta} + \Phi_{j\beta ia}^{a\alpha b\beta} - \Phi_{ja i\beta}^{a\alpha b\beta} - \Phi_{i\beta ja}^{a\beta b\alpha}) \\
Q\tilde{\Phi}_{ij}^{ab}(2) &= \frac{1}{2}(\Phi_{i\beta ja}^{a\beta b\alpha} + \Phi_{j\beta ia}^{a\beta b\alpha} - \Phi_{iaj\beta}^{a\alpha b\beta} - \Phi_{ja i\beta}^{a\alpha b\beta}) \\
Q\tilde{\Phi}_{ij}^{ab}(3) &= \frac{1}{\sqrt{6}}(\Phi_{iaja}^{a\alpha b\alpha} + \Phi_{i\beta j\beta}^{a\beta b\beta} - \Phi_{iaj\beta}^{a\alpha b\beta} - \Phi_{j\beta ia}^{a\alpha b\beta} + \Phi_{ja i\beta}^{a\alpha b\beta} + \Phi_{i\beta ja}^{a\beta b\alpha}) \\
Q\tilde{\Phi}_{ij}^{ab}(4) &= \frac{1}{\sqrt{6}}(\Phi_{iaja}^{a\alpha b\alpha} - \Phi_{i\beta j\beta}^{a\beta b\beta} - \Phi_{iaj\beta}^{a\alpha b\beta} + \Phi_{j\beta ia}^{a\alpha b\beta} - \Phi_{ja i\beta}^{a\alpha b\beta} + \Phi_{i\beta ja}^{a\beta b\alpha}) \\
Q\tilde{\Phi}_{si}^{ab}(1) &= \frac{1}{\sqrt{3}}(\Phi_{saia}^{a\alpha b\alpha} - \Phi_{sa i\beta}^{a\alpha b\beta} + \Phi_{sa i\beta}^{b\alpha a\beta}) \\
Q\tilde{\Phi}_{ij}^{as}(1) &= \frac{1}{\sqrt{3}}(\Phi_{i\beta j\beta}^{a\beta s\beta} + \Phi_{iaj\beta}^{a\alpha s\beta} - \Phi_{ja i\beta}^{a\alpha s\beta})
\end{aligned}$$

excited states in the equation-of-motion (EOM) method, pseudotriple excitations were also important,<sup>61</sup> and the method was further extended through SR-CCSDT.<sup>62</sup>

A fundamentally different approach to reducing the number of independent parameters was given by Lee and Jayatilaka<sup>50,51</sup> by introducing a symmetric spin basis:

$$\sigma^+ = \frac{1}{\sqrt{2}}(\alpha + \beta) \quad (7)$$

$$\sigma^- = \frac{1}{\sqrt{2}}(\alpha - \beta) \quad (8)$$

for the singly occupied orbitals. This technique was denoted either open-shell CCSD (OCCSD) or Z-averaged perturbation theory (ZAPT).<sup>48,49</sup> We here choose the name Z-averaged CCSD (ZA-CCSD) to emphasize that symmetry relations among the amplitudes are introduced by Z-averaging the SOCC space against the DOCC space. The exchange operator, however, no longer conserves  $M_S$  in the DOCC space, producing nonzero spin–exchange excitations:

$$K_{i\alpha}^{a\beta} = \frac{1}{2} \sum_s \langle si | as \rangle \quad (9)$$

which couple  $\alpha$  and  $\beta$  subspaces via the symmetric spin orbitals. The ZA-CCSD generalization of eq 3 is therefore

$$T_{iaja}^{a\alpha b\alpha} + T_{iaja}^{a\beta b\beta} = T_{iaj\beta}^{a\alpha b\beta} - T_{ja i\beta}^{a\alpha b\beta} \quad (10)$$

where an additional set of independent amplitudes  $T_{iaja}^{a\alpha b\beta}$  is nonzero. The ZA-CCSD approach can be greatly simplified by noting from second-order perturbation theory that  $\alpha$ ,  $\beta$ -exchange amplitudes are not included in the first-order interacting space and might be neglected in the cluster operator as higher-order excitations. We therefore proceed by ignoring these  $\alpha$ ,  $\beta$ -exchange terms.

In practice, CSF residuals are usually computed as linear combinations of single determinant projections rather than directly computed from spin-adapted matrix elements. The single CSF residual:

$$\begin{aligned}
\langle D\tilde{\Phi}_{ij}^{ab}(1) | \bar{H} | 0 \rangle &= \frac{1}{2\sqrt{3}}(2R_{iaja}^{a\alpha b\alpha} + 2R_{i\beta j\beta}^{a\beta b\beta} + R_{iaj\beta}^{a\alpha b\beta} \\
&\quad - R_{ja i\beta}^{a\alpha b\beta} + R_{i\beta ja}^{a\beta b\alpha} - R_{j\beta ia}^{a\beta b\alpha}) \quad (11)
\end{aligned}$$



$$R_{iaja}^{a\alpha b\alpha} = \langle \Phi_{iaja}^{a\alpha b\alpha} | \bar{H} | 0 \rangle \quad (12)$$

would therefore require three separate spin cases to be computed. Because of the extra ZA-CCSD symmetry in eq 10, the CSF projection in eq 11 only requires the spin–orbital residuals  $R_{ia\beta}^{a\alpha b\beta}$  and  $R_{ia\alpha}^{a\beta b\beta}$  (although the amplitudes  $T_{ia\alpha}^{a\beta b\beta}$  are chosen zero, the corresponding residuals are not). The computational cost of  $R_{ia\alpha}^{a\beta b\beta}$  is negligible, only requiring terms of the form:

$$R_{ia\alpha}^{a\beta b\beta} \leftarrow g_{c\beta d\beta}^{a\beta b\beta} T_{ia}^{c\beta} T_{ja}^{d\beta} \quad (13)$$

$$R_{ia\alpha}^{a\beta b\beta} \leftarrow g_{s-t}^{a\beta b\beta} T_{iaja}^{s-t} \quad (14)$$

which involve either a  $T_1$  contraction or a SOCC index, and therefore only  $N^5$  work. Only a single  $N^6$  spin–orbital residual  $R_{ia\beta}^{a\alpha b\beta}$  must therefore be computed, drastically reducing the computational cost. The ZA-CCSD approach therefore imposes useful amplitude symmetries via the symmetric spin basis, and residuals are computed entirely in terms of determinantal rather than CSF projections.

**2.3. Brueckner and CCSD(T) Extensions.** The spin-restricted formalism in ZA-CCSD provides the foundation for two important, cost-saving extensions. First, Brueckner theory can be reformulated such that the orbitals are not spin polarized, drastically reducing the computational cost by maintaining spin restriction in the integral transformation on each iteration. In general, Brueckner theory reformulates the cluster operator:

$$\exp(\hat{T}) = \exp(\hat{T}_2 + \hat{T}_3 + \dots) \exp(\hat{T}_1 - \hat{T}_1^\dagger) \quad (15)$$

such that  $\hat{T}_1$  now introduces a unitary transformation. In ZA-CCSD we have two separate components: a conventional  $\hat{T}_1$  which preserves  $M_S$  and a  $\hat{T}_1^{\alpha\beta}$  which introduces the spin–exchange excitations. We can redefine the Brueckner cluster operator in ZA-CCSD as

$$\exp(\hat{T}) = \exp(\hat{T}_1^{\alpha\beta} + \hat{T}_2 + \hat{T}_3 + \dots) \exp(\hat{T}_1 - \hat{T}_1^\dagger) \quad (16)$$

with only the conventional  $\hat{T}_1$  generating a unitary transformation. Because ZA-CCSD has the amplitude symmetry:

$$T_{ia}^{a\alpha} = T_{i\beta}^{a\beta} \quad (17)$$

the orbital transformation maintains equivalent  $\alpha$  and  $\beta$  orbitals. This partitioning of  $\hat{T}_1$  is consistent with the perturbative analysis of Lee and Jayatilaka who argue that the excitation rank of the operator should include not only the number of orbital substitutions but also the number of spin flips. In this regard, even though  $\hat{T}_1^{\alpha\beta}$  corresponds to a single *substitution*, it should be considered a double *excitation*. We therefore consider  $\hat{T}_1^{\alpha\beta}$  to be of rank two. Initial attempts along these lines were attempted by Crawford et al.<sup>47</sup> and yielded promising results, particularly for vibrational frequencies of difficult radicals like NO<sub>3</sub>. Rigorous benchmarking of these Brueckner approximations, however, is not included in this work, as we are here only concerned with validating the R12 approximations described above within the basic Z-averaged formalism.

The ZA-CCSD formalism can also be further extended to a spin-restricted CCSD(T) for open-shells.<sup>63</sup> The CCSD(T) formalism requires the full Hamiltonian to be partitioned into a diagonal  $\hat{H}_0$  and a perturbation  $\hat{V}$ . For ROHF references,  $\hat{H}_0$  is usually constructed by semicanonicalization of the orbitals, diagonalizing the Fock operator separately within the occupied and the virtual subspaces. The mixed occupied–virtual terms,  $f_i^a$ ,

are neglected in  $\hat{H}_0$  instead being included in the perturbation. Because of asymmetric exchange, however, the orbital canonicalization breaks  $\alpha$ ,  $\beta$ -symmetry requiring several different spin cases to be treated. In contrast, diagonalization of the symmetric-exchange Fock operator in ZA-CCSD maintains equivalent orbitals and eigenvalues for  $\alpha$  and  $\beta$  subspaces, requiring only a single spin case to be treated. Additionally, in line with the Brueckner arguments given above for  $T_1$ , for ZA-CCSD canonical orbitals, the matrix elements  $f_{ia}^{a\alpha}$  are rigorously zero. Unlike most ROHF-based theories, ZA-CCSD therefore has a pseudo-Brillouin condition similar to the closed-shell case, and only the off-diagonal Fock matrix elements  $f_{ia}^{a\beta}$  must be included in the perturbation. Again, we delay a complete discussion of the CCSD(T) extension and focus here on the R12 treatment.

**2.4. Explicitly Correlated CCSD.** To illustrate the essential concepts in R12 theory, we first briefly review the MP2 equations.<sup>16,26,64–66</sup> In MP2-R12, the conventional residual equations are generalized to

$$R_{ab}^{ij} = f_a^c T_{cb}^{ij} + f_b^c T_{ac}^{ij} - f_k^i T_{ab}^{kj} - f_k^j T_{ab}^{ik} + C_{ab}^{xy} T_{xy}^{ij} + g_{ab}^{ij} \quad (18)$$

where  $f_p^a$  are Fock matrix elements and the  $T_{xy}^{ij}$  are explicit amplitudes associated with the pair correlations:

$$|ij\rangle \rightarrow \hat{Q}_{12} F(r_{12}) |xy\rangle \quad (19)$$

with  $x, y$  the geminal generating space, usually taken to be occupied orbitals. The correlation factor,  $F(r_{12})$ , is usually of Slater-type<sup>11,67–70</sup> and approximated as a sum of Gaussian geminals:

$$F(r_{12}) = \exp(-\gamma r_{12}) \approx \sum_n c_n \exp(-\alpha_n r_{12}^2) \quad (20)$$

The projection operator,  $\hat{Q}_{12}$ , is included to ensure the explicit geminals are orthogonal to the reference function,  $\hat{o}$ , and virtual pairs,  $\hat{v}$

$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1 \hat{v}_2) \quad (21)$$

We enforce in the current work that the R12 terms contribute to the manifold of doubly excited configurations only and do not directly contribute to the singles correlation energy. Schemes have been developed for including R12 terms to correct the one-particle contribution, and we refer the reader to refs 71–73. The standard MP2 expression is augmented by the coupling matrix between conventional and R12 terms:

$$C_{ab}^{xy} = \langle ab | (\hat{f}_1 + \hat{f}_2) \hat{Q}_{12} F(r_{12}) | xy \rangle \quad (22)$$

For the explicit amplitudes, we must solve

$$R_{xy}^{ij} = V_{xy}^{ij} + B_{xy}^{wz} T_{wz}^{ij} - X_{xy}^{wz} (f_k^i T_{wz}^{kj} + f_k^j T_{wz}^{ik}) + C_{xy}^{ab} T_{ab}^{ij} \quad (23)$$

Here  $V_{xy}^{ij}$  is the R12 generalization of the electron repulsion integral:

$$V_{xy}^{ij} = \left\langle xy \left| F(r_{12}) \hat{Q}_{12} \frac{1}{r_{12}} \right| ij \right\rangle \quad (24)$$

where the conventional pair correlation function is replaced by the R12 geminal.  $B_{xy}^{wz}$  is the generalization of the energy denominator:

$$B_{xy}^{wz} = \langle xy | F(r_{12}) \hat{Q}_{12} (\hat{f}_1 + \hat{f}_2) \hat{Q}_{12} F(r_{12}) | wz \rangle \quad (25)$$

and  $X_{xy}^{wz}$  is the geminal overlap matrix:

$$X_{xy}^{wz} = \langle xy | F(r_{12}) \hat{Q}_{12} F(r_{12}) | wz \rangle \quad (26)$$

For further details, we refer the reader to refs 26, 64, or 65.

Rigorous development of the CCSD-R12<sup>74–77</sup> model with RI approximations leads to new, difficult R12 intermediates with a severe auxiliary basis set dependence<sup>78</sup> which are absent in MP2. The CCSD(2)<sub>RTZ</sub><sup>52–54</sup> approach formulates the R12 terms as a perturbative correction to the conventional CCSD wave function. Performing a Löwdin partitioning of the similarity transformed Hamiltonian:

$$\bar{H} = \begin{pmatrix} \bar{H}_{PP} & \bar{H}_{PQ} \\ \bar{H}_{QP} & \bar{H}_{QQ} \end{pmatrix} \quad (27)$$

The R12 geminal excitations are given as an external space,  $Q$ , while the conventional CCSD determinants comprise the reference space,  $P$ . The Hamiltonian is partitioned into zeroth- and first-order parts as

$$\bar{H}^{(0)} = \begin{pmatrix} \bar{H}_{PP} & 0 \\ 0 & \bar{H}_{QQ}^{(0)} \end{pmatrix} \quad (28)$$

$$\bar{H}^{(1)} = \begin{pmatrix} 0 & \bar{H}_{PQ} \\ \bar{H}_{QP} & \bar{H}_{QQ}^{(1)} \end{pmatrix} \quad (29)$$

Similar approximations are followed in CCSD(F12)<sup>79–82</sup> and CCSD-F12a,b approaches which<sup>4,83</sup> directly include R12 geminal excitations:

$$\hat{T}'_2 = T_{xy}^{ij} F_{\alpha\beta}^{xy} a_{ij}^{\alpha\beta} \quad (30)$$

$$F_{\alpha\beta}^{xy} = \langle \alpha\beta | \hat{Q}_{12} F(r_{12}) | xy \rangle \quad (31)$$

in the cluster operator but approximate R12 commutators as

$$[\hat{H}, \hat{T}'_2] \approx [\hat{J}, \hat{T}'_2] \quad (32)$$

neglecting contractions between  $\hat{T}'_2$  and the fluctuation potential. By partitioning the Hamiltonian for R12 terms, the basis set dependence of R12 matrix elements is drastically reduced, and MP2-R12 codes can be straightforwardly generalized for CCSD. Although all CCSD-R12 approaches are essentially equivalent in cost to a conventional CCSD computation, the approach of Valeev has the extra theoretical appeal of being noniterative and generated automatically by the underlying CCSD wave function. In this regard, the CCSD(2)<sub>RTZ</sub> correction is more easily generalized to spin-restricted open-shell techniques or multireference coupled cluster ansätze and has therefore been called an “universally explicitly correlated coupled cluster.”<sup>84</sup>

While the zeroth-order  $H_{QQ}^{(0)}$  is trivially selected as the Fock operator for closed-shell molecules, the exact definition of  $\hat{H}_0$  is greatly complicated for ROHF references by the nonzero occupied virtual block  $f_{ia}$  of the Fock operator. The ROHF reference function is not an eigenfunction of the Fock operator, requiring a new partition of the Hamiltonian. Numerous ROHF-based perturbation theories have therefore been developed,<sup>49,85,86</sup> including open-shell perturbation theory (OPT1 and OPT2),<sup>86–88</sup> invariant open-shell perturbation theory (IOPT),<sup>89</sup> restricted open-shell Møller-Plesset (ROMP),<sup>90</sup> restricted Møller-Plesset (RMP),<sup>37,91</sup> and Z-averaged perturbation

theory (ZAPT).<sup>48–51</sup> The most straightforward perturbation theory, RMP, currently forms the basis for the CCSD(F12), CCSD-F12a,b, and CCSD(2)<sub>RTZ</sub> methods. Projection operators eliminate the undesired  $f_{ia}$  terms:

$$\hat{H}_0 = \hat{o}\hat{f}\hat{o} + \hat{v}\hat{f}\hat{v} \quad (33)$$

Asymmetric exchange in  $\hat{f}$ , however, breaks the spin restriction for  $\alpha$  and  $\beta$  orbitals and is therefore not appropriate for the spin-restricted CCSD methods developed here. In ZA-CCSD we choose for DOCC and VIR orbitals:

$$\hat{H}_0 = \hat{h} + \hat{J} - \hat{K}_c - \frac{1}{2}\hat{K}_o \quad (34)$$

which Z-averages the open-shell exchange

$$K_o^{pq} = \sum_{s \in \text{SOCC}} \langle sp | qs \rangle \quad (35)$$

Here  $\hat{h}$  is the core Hamiltonian,  $\hat{J}$  is the Coulomb operator, and  $\hat{K}_c$  is the closed-shell exchange:

$$K_c^{pq} = \sum_{i \in \text{DOCC}} \langle ip | qi \rangle \quad (36)$$

This is conceptually equivalent to using  $\sigma^+$  and  $\sigma^-$  orbitals within the SOCC space. For occupied SOCC orbitals:

$$\hat{H}_0 = \hat{h} + \hat{J} - \hat{K}_c - \hat{K}_o \quad (37)$$

and for unoccupied SOCC orbitals:

$$\hat{H}_0 = \hat{h} + \hat{J} - \hat{K}_c \quad (38)$$

The partition enforces  $\alpha, \beta$  symmetry in the DOCC space. However, in contrast to other ROHF-based partitions,<sup>86–89</sup> an eigenvalue splitting is introduced between  $\sigma^+$  and  $\sigma^-$  orbitals. Compared to other choices of partition,<sup>37,88,91</sup> the Z-averaged Fock operator here is therefore unique in maintaining  $\alpha, \beta$  spin-restriction without unphysically treating occupied and virtual orbitals within the SOCC space equivalently. We emphasize again that the difference choices of  $\hat{H}_0$  are only relevant for open-shell molecules. For closed shell, the ZA-CCSD(2)<sub>RTZ</sub> method becomes equivalent to the original CCSD(2)<sub>RTZ</sub> method of Valeev.<sup>52</sup>

Applying Rayleigh–Schrödinger perturbation theory through second order, the energy correction is given as

$$E_2 = \bar{H}_{PQ} (\bar{H}_{QQ}^{(0)} - S_{QQ} E_0)^{-1} \bar{H}_{QP} \quad (39)$$

For the R12 correction in CCSD, the  $P$  space can be partitioned into the reference determinant  $\Phi_0$  and the set of excited determinants  $\{\Phi_i^a\}$  and  $\{\Phi_{ij}^{ab}\}$ . The external space  $Q$  is the set of R12 configurations:

$$|\Phi_{ij}^{xy}\rangle = \Phi_{ij}^{\alpha\beta} F_{\alpha\beta}^{xy} \quad (40)$$

This leads to the matrix elements:

$$\langle \Phi_0 | \bar{H} | \Phi_{ij}^{xy} \rangle = V_{ij}^{xy} \quad (41)$$

$$T_k^a \langle \Phi_a^k | \bar{H} | \Phi_{ij}^{xy} \rangle = T_i^a V_{aj}^{xy} \quad (42)$$

$$T_{kl}^{ab} \langle \Phi_{ab}^{kl} | \bar{H} | \Phi_{ij}^{xy} \rangle = V_{ij}^{xy} + P(ij) V_{aj}^{xy} T_i^a + \frac{1}{2} V_{ab}^{xy} \tau_{ij}^{ab} + P(ij) F_{ap'}^{xy} \tau_{jb}^{p'k} T_{ik}^{ab} + \dots \quad (43)$$

where RI indices have been substituted for CBS indices and

$$\tau_{ij}^{ab} = T_{ij}^{ab} + T_i^a T_j^b - T_i^b T_j^a \quad (44)$$

Following Valeev,<sup>54</sup> two important approximations are made. First, to be consistent with our perturbative approach, cluster products, such as  $\hat{T}_1^2$ , are neglected as higher order, resulting in the replacement of  $T_{ij}^{ab}$  for  $\tau_{ij}^{ab}$ . For closed shell,  $\hat{T}_1$  terms could also be neglected. However, for consistency with ROHF references, in contrast to the original formulation of Valeev,<sup>52</sup> we include these terms even for closed-shell molecules following the spirit of the CCSD(T) correction.<sup>92,93</sup> The more important approximation is the neglect of the term:

$$F_{ap'}^{xy} \delta_{jb}^{p'k} T_{ik}^{ab} \quad (45)$$

Under the original R12 standard approximation,<sup>16</sup> the projection operator annihilates  $a, p''$  virtual-CABS pairs. Although the favored projection operator for MP2 applications would not annihilate this term, the current work and the work of Valeev<sup>53,54</sup> demonstrate that neglecting this term still yields excellent results. Following similar arguments, we find

$$\langle \Phi_{xy}^j | \bar{H} | \Phi_0 \rangle \approx V_{xy}^{ij} + T_a^i V_{xy}^{aj} + \frac{1}{2} V_{xy}^{ab} T_{ab}^{ij} \quad (46)$$

The final amplitudes are solved from the residuals equation:

$$R_{xy}^{ij} = B_{xy}^{wz} T_{wz}^{ij} - T_{wz}^{ij} X_{xy}^{wz} (f_k^i T_{xy}^{kj} + f_k^j T_{xy}^{ik}) + \tilde{V}_{xy}^{ij} \quad (47)$$

where the MP2 matrix element  $V_{xy}^{ij}$  is replaced by the intermediate:

$$\tilde{V}_{ij}^{xy} = V_{ij}^{xy} + P(ij) V_{aj}^{xy} T_i^a + \frac{1}{2} V_{xy}^{ab} T_{ab}^{ij} \quad (48)$$

which incorporates the first interference terms between conventional CCSD terms and the R12 geminals. Details of computing ZAPT matrix elements have been given previously.<sup>65</sup>

Only the diagonal R12 amplitudes  $T_{ij}^{ij}$  are necessary to satisfy the cusp condition and may be fixed at their asymptotic cusp values of 1/2 and 1/4 for singlet and triplet pairs, respectively.<sup>94–98</sup> Using the rational generator of Ten-no,<sup>99–101</sup> a pair correlation can be asymptotically represented in spin–orbital form:

$$|ij\rangle \rightarrow \frac{3}{8} |ij\rangle + \frac{1}{8} p(12) |ij\rangle \quad (49)$$

where  $p(12)$  is a permutation operator that permutes the spatial orbitals but not the spins. For closed shells, this leads, for example, to the pair correlation:

$$|i_\alpha j_\beta\rangle \rightarrow \frac{3}{8} |i_\alpha j_\beta\rangle + \frac{1}{8} |j_\alpha i_\beta\rangle \quad (50)$$

while for the case of ZAPT in the symmetric spin basis we have<sup>65</sup>

$$|i_\alpha s_+\rangle \rightarrow \frac{3}{8} |i_\alpha s_+\rangle + \frac{1}{8} |s_\alpha i_+\rangle \quad (51)$$

The fixed amplitude ansatz leads to a severe dependence of the energy on the geminal exponent,  $\gamma$ .<sup>82,83</sup> It is therefore necessary to define a second-order Lagrangian (Hylleraas functional in the case of MP2), to soften the dependence of the correlation energy on the “error” associated with fixed amplitudes. Following approximations similar to those adopted by Tew in CCSD-(F12),<sup>82</sup> a Lagrangian energy functional can be constructed for

the CCSD(2)<sub>RT2</sub> approach:<sup>54</sup>

$$E_2^{R12} = 2\tilde{V}_{ij}^{xy} T_{xy}^{ij} + T_{ij}^{wz} B_{wz}^{xy} T_{xy}^{ij} - T_{ij}^{wz} X_{wz}^{xy} (f_k^i T_{xy}^{kj} + f_k^j T_{xy}^{ik}) \quad (52)$$

A similar approach is followed by Werner and Adler,<sup>4,83</sup> although the explicit residual is approximated by the MP2 residual (CCSD-F12a) or additional terms from CEPA-0 (CCSD-F12b). Superior results are usually obtained within the diagonal approximation due to the absence of geminal basis set superposition errors.<sup>17,66</sup>

Some comment is necessary on the nature of spin–exchange terms, such as  $V_{i_\alpha j_\beta}^{x_\alpha y_\alpha}$ .<sup>65</sup> Such terms will be nonzero by virtue of contraction with spin–exchange amplitudes  $t_{i_\alpha}^{a_\beta}$ . Clearly, the R12 correction should not be generating correlations of the form

$$|i_\alpha j_\beta\rangle \rightarrow |a_\alpha b_\alpha\rangle \quad (53)$$

as our chosen ZA-CCSD model enforces these to be zero in the basis set limit. As has been discussed previously,<sup>65</sup> the correlation factor is spinless and cannot produce spin–exchange configurations. We can consider the projection of the pair correlation function onto a formally complete virtual space:

$$(1 - \hat{o}_1)(1 - \hat{o}_2)F(r_{12})|xy\rangle = \sum_{\kappa\nu} |\kappa\nu\rangle \langle \kappa\nu | F(r_{12}) | xy \rangle \quad (54)$$

where the sum runs over all virtual orbitals  $\kappa, \nu$ . Clearly, projections of the form:

$$\langle \kappa_\alpha \nu_\alpha | F(r_{12}) | x_\alpha y_\beta \rangle \quad (55)$$

are zero so that  $\alpha, \beta$  spin exchanges are not generated by the correlation factor. However, virtual pairs of the form:

$$\langle \kappa_\alpha s_- | F(r_{12}) | x_\alpha y_\beta \rangle \quad (56)$$

$$\langle s_- t_- | F(r_{12}) | x_\alpha y_\beta \rangle \quad (57)$$

are nonzero due to the symmetric spin basis, allowing nonzero spin–exchange terms  $V_{i_\alpha j_\beta}^{x_\alpha y_\alpha}$  from the contraction:

$$V_{i_\alpha j_\beta}^{x_\alpha y_\alpha} \leftarrow \delta_{i_\alpha j_\beta}^{\kappa_\alpha s_-} F_{\kappa_\alpha s_-}^{x_\alpha y_\alpha} \quad (58)$$

No true  $\alpha, \beta$  spin exchanges are included, and the correlation factor is actually generating SOCC pairs. These terms are actually not included in the context of the diagonal ansatz anyway but will be important for other ansätze, such as those employed in response theory.<sup>12</sup> For the diagonal terms, by virtue of the amplitude symmetries in the conventional CCSD amplitudes, the spin-restriction symmetry, viz.:

$$\tilde{V}_{i_\alpha j_\alpha}^{i_\alpha j_\alpha} = \tilde{V}_{i_\alpha j_\beta}^{i_\alpha j_\beta} - \tilde{V}_{j_\alpha i_\beta}^{i_\alpha j_\beta} \quad (59)$$

therefore automatically extends to R12 matrix elements.

**2.5. Spin Contamination.** To assess spin contamination,<sup>55</sup> we compute expectation values as energy derivatives:

$$\hat{H}(\lambda) = \hat{H} + \lambda \hat{S}^2 \quad (60)$$

$$\langle \hat{S}^2 \rangle = \frac{dE(\lambda)}{d\lambda} \Big|_{\lambda=0} \quad (61)$$

The CCSD energy functional must therefore be replaced by the Lagrangian:

$$L = \langle 0 | (1 + \hat{\Lambda}) \bar{H} | 0 \rangle \quad (62)$$

Table 3. Doublet CSFs Used in ZA-CCSD

$$\begin{aligned}
D\tilde{\Phi}_i^a(1) &= \Phi_{i\alpha}^{a\alpha}, \Phi_{i\beta}^{a\beta} \\
D\tilde{\Phi}_i^a(2) &= \Phi_{i\alpha}^{a\beta}, \Phi_{i\beta}^{a\alpha} \\
D\tilde{\Phi}_s^a(1) &= \Phi_{s+}^{a\alpha}, \Phi_{s+}^{a\beta} \\
D\tilde{\Phi}_i^s(1) &= \Phi_{i\alpha}^{t-}, \Phi_{i\beta}^{s-} \\
D\tilde{\Phi}_{ij}^{ab}(1) &= \frac{1}{2\sqrt{3}}(2\Phi_{i\alpha j\alpha}^{a\alpha b\alpha} + 2\Phi_{i\beta j\beta}^{a\beta b\beta} + \Phi_{i\alpha j\beta}^{a\alpha b\beta} - \Phi_{i\alpha j\beta}^{a\beta b\alpha} + \Phi_{i\beta j\alpha}^{a\alpha b\alpha} - \Phi_{i\beta j\alpha}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{ij}^{ab}(2) &= \frac{1}{2}(\Phi_{i\alpha j\beta}^{a\alpha b\beta} + \Phi_{i\alpha j\beta}^{a\beta b\alpha} + \Phi_{i\beta j\alpha}^{a\alpha b\alpha} + \Phi_{i\beta j\alpha}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{si}^{ab}(1) &= \frac{1}{2\sqrt{3}}(2\Phi_{s+ i\alpha}^{a\alpha b\alpha} + 2\Phi_{s+ i\beta}^{a\beta b\beta} + \Phi_{s+ i\beta}^{a\alpha b\beta} - \Phi_{s+ i\beta}^{a\beta b\alpha} + \Phi_{s+ i\alpha}^{a\alpha b\alpha} - \Phi_{s+ i\alpha}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{si}^{ab}(2) &= \frac{1}{2}(\Phi_{s+ i\beta}^{a\alpha b\beta} + \Phi_{s+ i\beta}^{a\beta b\alpha} + \Phi_{s+ i\alpha}^{a\alpha b\alpha} + \Phi_{s+ i\alpha}^{a\beta b\alpha}) \\
D\tilde{\Phi}_{ij}^{as}(1) &= \frac{1}{2\sqrt{3}}(2\Phi_{i\alpha j\alpha}^{a\alpha s-} - 2\Phi_{i\beta j\beta}^{a\beta s-} + \Phi_{i\beta j\alpha}^{a\beta s-} - \Phi_{i\beta j\alpha}^{a\alpha s-} - \Phi_{i\alpha j\beta}^{a\alpha s-} + \Phi_{i\alpha j\beta}^{a\beta s-}) \\
D\tilde{\Phi}_{ij}^{as}(2) &= \frac{1}{2}(\Phi_{i\beta j\alpha}^{a\beta s-} + \Phi_{i\beta j\alpha}^{a\alpha s-} - \Phi_{i\alpha j\beta}^{a\alpha s-} - \Phi_{i\alpha j\beta}^{a\beta s-}) \\
D\tilde{\Phi}_{si}^{at}(1) &= \Phi_{s+ i\alpha}^{a\alpha t-}, \Phi_{s+ i\alpha}^{a\beta t-}, \Phi_{s+ i\alpha}^{a\alpha t-}, \Phi_{s+ i\beta}^{a\beta t-}
\end{aligned}$$

$$\langle 0 | \hat{\Lambda} = \lambda_i^a \langle \Phi_i^a | + \lambda_{ij}^{ab} \langle \Phi_{ij}^{ab} | \quad (63)$$

where the  $\lambda_i^a$  and  $\lambda_{ij}^{ab}$  are the Lagrange multipliers. In ZA-CCSD, individual Lagrange multipliers are associated with projection by the CSFs given in Table 3. The  $\lambda_{ij}^{ab}$  amplitudes therefore have the same Z-averaged symmetries as the  $T_{ij}^{ab}$  amplitudes. Defining density matrix elements as

$$\gamma_r^p = \langle 0 | (1 + \hat{\Lambda}) \exp(-\hat{T}) a_r^p \exp(\hat{T}) | 0 \rangle \quad (64)$$

$$\gamma_{rs}^{pq} = \langle 0 | (1 + \hat{\Lambda}) \exp(-\hat{T}) a_{rs}^{pq} \exp(\hat{T}) | 0 \rangle \quad (65)$$

the spin expectation value can be computed. The density matrices are not Hermitian and are therefore symmetrized in the actual implementation. Further details can be found in refs 55 and 102.

### 3. THEORETICAL METHODS

The ZA-CCSD-R12 method was implemented within the MPQC<sup>103,104</sup> and the PSI3<sup>105</sup> packages for a Slater-type correlation factor with exponent 1.4 approximated as a sum of 6 Gaussian geminals.<sup>67</sup> Only valence electrons were correlated. R12 intermediates were computed within approximation C so that kinetic energy commutator integrals were not necessary.<sup>106</sup> All R12 results are computed with fixed amplitudes, extended Brillouin condition (EBC), and hybrid RI approximation as described in greater detail in ref 65. Integrals were implemented in the CINTS/LIBINT<sup>107</sup> package within MPQC through a modification of the Obara–Saika scheme.<sup>69,108–110</sup> Conventional ZA-CCSD computations were performed with the Dunning aug-cc-pVnZ<sup>20,111</sup> family of basis sets (denoted aVnZ). The basis set limit is estimated from an aVSZ–aV6Z extrapolation using an  $n^{-3}$  extrapolation.<sup>19</sup> All R12 computations use the Peterson F12<sup>112</sup> and F12-RI basis sets<sup>113</sup> (hereafter denoted R12-XZ). All molecules in the current work were optimized at the CCSD(T)/cc-pVQZ level using the ACESII package.<sup>114–118</sup>

Table 4. Comparison of Total Energy (Hartree)<sup>a</sup> and  $\hat{S}^2$  Values for Open-Shell CCSD Methods Computed with cc-pVTZ Basis

Method	Energy	$\langle \hat{S}^2 \rangle$
CH ( <sup>2</sup> Π)		
ROHF-CCSD	−38.41802	0.750111
PSA-CCSD <sup>b</sup>	−38.41788	0.750000
SR-CCSD <sup>b</sup>	−38.41788	0.750000
ZA-CCSD	−38.41789	0.750006
CN ( <sup>2</sup> Σ <sup>+</sup> )		
ROHF-CCSD	−92.57190	0.754327
PSA-CCSD	−92.57115	0.750004
SR-CCSD	−92.57147	0.750000
ZA-CCSD	−92.57116	0.750038
NO ( <sup>2</sup> Π)		
ROHF-CCSD	−129.72282	0.750371
PSA-CCSD	−129.72232	0.750001
SR-CCSD	−129.72234	0.750000
ZA-CCSD	−129.72232	0.750010
NO <sub>2</sub> ( <sup>2</sup> A <sub>2</sub> )		
ROHF-CCSD	−204.72711	0.768465
PSA-CCSD	−204.72447	0.750000
SR-CCSD	−204.72440	0.750000
ZA-CCSD	−204.72467	0.751310
HCCO ( <sup>2</sup> Π)		
ROHF-CCSD	−151.69353	0.751820
PSA-CCSD	−151.69257	0.750020
SR-CCSD	−151.69274	0.750000
ZA-CCSD	−151.69262	0.750145

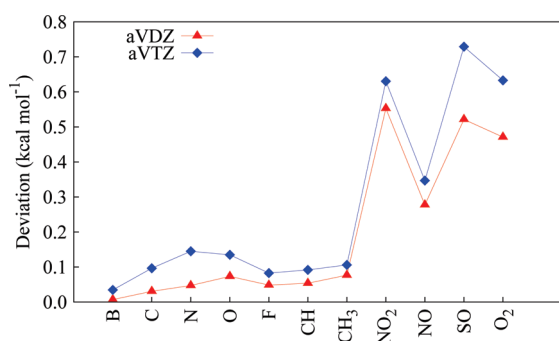
<sup>a</sup> Geometries from ref 34. <sup>b</sup> PSA-CCSD and SR-CCSD values from ref 34.

All ROHF-CCSD and PSA-CCSD results were computed using the Molpro2006.1 package.<sup>119</sup> Spin contamination values were computed by modification of the  $\lambda$  equation and the CCSD two-particle density codes within PSI3. See Supporting Information for a complete list of geometries, total energies, and ZA-CCSD correlation energies for all computed molecules.

### 4. RESULTS AND DISCUSSION

**4.1. Comparison of CCSD Methodologies.** Of primary concern is the performance of the newly proposed ZA-CCSD method with respect to previously established high-spin open-shell CCSD methodologies. For a series of atomic and molecular energies, the difference between the ZA-CCSD correlation energy from spin–orbital ROHF-CCSD is shown in Figure 1. Because the energy differences between the various CCSD methodologies are so small (less than 1 kcal mol<sup>−1</sup>), it is not possible to identify one as intrinsically more accurate. We therefore only assert that the ZA-CCSD method should perform similar to ROHF-CCSD, and the primary benefit for ZA-CCSD will therefore be a minimum number of  $N^6$  contractions. For the hydrocarbon radicals CH and CH<sub>3</sub>, the difference is only 0.1 kcal mol<sup>−1</sup>. However, for CN, NO<sub>2</sub>, and NO with much greater spin contamination, deviations are as large as 0.7 kcal mol<sup>−1</sup>, which is





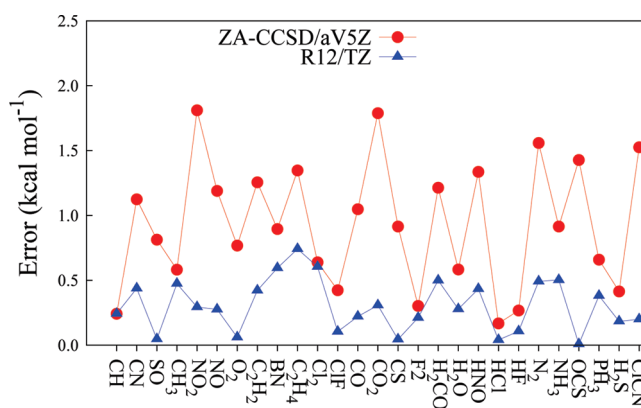
**Figure 1.** Correlation energy difference of Z-averaged CCSD from spin-orbital ROHF-CCSD for aug-cc-pVXZ (aVXZ) basis sets.

consistent with the partial spin-restrictions imposed. The difference is similar to that observed previously for PSA-CCSD and SR-CCSD.<sup>34</sup> A more subtle effect is observed for higher spin multiplicities, which generally show greater deviations than doublets as seen for nitrogen, oxygen, SO, and O<sub>2</sub>. The  $\alpha$ ,  $\beta$  spin-exchange amplitudes occur through contractions involving symmetric spin orbitals. Since these spin-exchange terms are neglected in the current treatment, larger deviations from ROHF-CCSD will occur as the number of singly occupied orbitals is increased.

For a series of model systems considered in previous work,<sup>34</sup> we have also computed  $\langle \hat{S}^2 \rangle$ . For CH, CN, NO, and HCCO, the ZA-CCSD results are essentially equivalent to PSA-CCSD, both of which demonstrate significant reductions in spin contamination relative to ROHF-CCSD. Energies match PSA-CCSD within 0.1 mH and even SR-CCSD within 0.3 mH. The ZA-CCSD spin contamination is slightly greater than PSA-CCSD, consistent with ZA-CCSD imposing fewer spin constraints. For the severe case of NO<sub>2</sub>, ZA-CCSD deviates from SR-CCSD and PSA-CCSD but still exhibits a drastic reduction in spin contamination relative to ROHF-CCSD.

There is some ambiguity in separate trade-offs between the spin-restricted and unrestricted approaches. It has long been known that perturbation theories based on restricted reference functions converge much more quickly with respect to perturbation order than those based on unrestricted references.<sup>120–124</sup> One therefore anticipates that reduced spin contamination will accelerate convergence with respect to the coupled cluster CCSD, CCSDT, and CCSDTQ hierarchy. Conversely, for certain symmetry breaking problems, UHF or Brueckner solutions which break orbital symmetries may provide more accurate results at the truncated CCSD level.<sup>43,47,125,126</sup> Given the small energy differences observed here between the different methodologies, a discussion of which method is intrinsically more accurate by comparison to experiment would not be meaningful at the CCSD level. We therefore emphasize instead that the approximations made in the Z-averaged ansatz will not degrade the accuracy relative to other CCSD methods (indeed, spin-contamination is reduced!), but a great deal of efficiency is gained by minimizing the number of independent amplitudes and residuals. The theoretical three-fold speedup is intrinsic to the ZA-CCSD method regardless of the inclusion of R12 corrections.

**4.2. Size Consistency of Spin-Adapted Approaches.** The introduction of amplitude constraints in PSA-CCSD can actually introduce size-consistency errors when the cluster operator  $\hat{T}$  is truncated at double excitations. For example, the computed



**Figure 2.** Error of correlation energy increments ( $\delta[\text{CCSD}]$ , see text) to atomization energies for Z-averaged CCSD with aug-cc-pVSZ (ZA-CCSD/aVSZ) and ZA-CCSD(2)<sub>R12</sub>/TZ with cc-pVTZ-F12 (R12/TZ) basis set with respect to aVSZ/aV6Z extrapolation benchmark.

energy of two fluorine atoms at infinite separation coupled to a triplet will not be exactly twice the energy of an isolated fluorine atom in its doublet ground state. The imposed spin constraints effectively introduce an infinite-range interaction between the monomers. For multiplicities of triplet or higher, PSA-CCSD employs the “semi-internal” triplet CSF:

$$T \tilde{\Phi}_{is}^{as} = \Phi_{ia}^{a\alpha} - \Phi_{i\beta}^{a\beta} - \frac{m+1}{m+2} \Phi_{sa\beta}^{a\alpha\beta} + \frac{1}{m+2} \sum_{t \neq s} \Phi_{ta\beta}^{a\alpha t\beta} \quad (66)$$

along with the spin-symmetric single excitation

$$T \tilde{\Phi}_i^a = \Phi_{ia}^{a\alpha} + \Phi_{i\beta}^{a\beta} \quad (67)$$

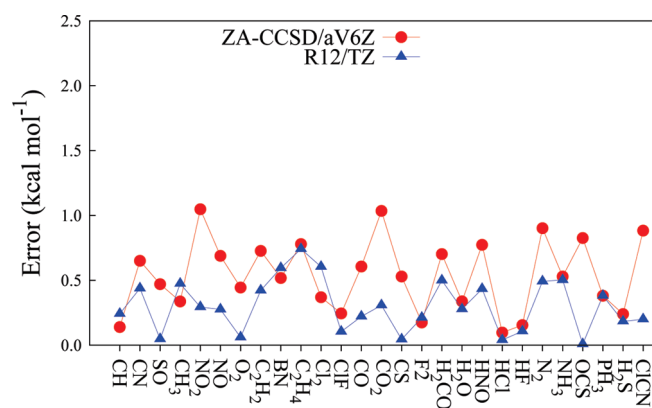
In this regard, semi-internal doubly excited determinants are coupled by spin constraints to singly excited determinants. Assuming localized orbitals for centers A and B, suppose we have orbitals  $i$ ,  $a$ ,  $s$  on center A and singly occupied orbital  $t$  on center B. Upon convergence, we will have nonzero spin-orbital amplitudes  $T_{ia}^{a\alpha}$  and  $T_{i\beta}^{a\beta}$  which by virtue of asymmetric exchange will be spin-polarized such that  $T_{ia}^{a\alpha} \neq T_{i\beta}^{a\beta}$ . To introduce spin polarization of the single amplitudes, we must have a nonzero  $T_{si}^{as}$  for the CSF in eq 66. By virtue of the spin constraints, we must have a nonzero amplitude  $T_{td\beta}^{a\alpha t\beta}$  where the *connected*  $T_2$  amplitude now contains mixed indices for centers A and B, leading to the size consistency error. The Z-averaged formalism only ensures  $T_{ia}^{a\alpha} = T_{i\beta}^{a\beta}$  and does not constrain the  $T_1$  amplitudes in any way relative to semi-internal doubly excited configurations. The numerical importance of this size-consistency error is probably negligible in many systems. For triplet fluorine dissociation the size consistency error is only 0.043 mH. Still, ZA-CCSD has the additional theoretical appeal of being rigorously size consistent at all levels of truncation in the cluster operator.

**4.3. R12 Corrections.** For simplicity, we here focus only on the correlation increment for the energy difference  $A \rightarrow B$

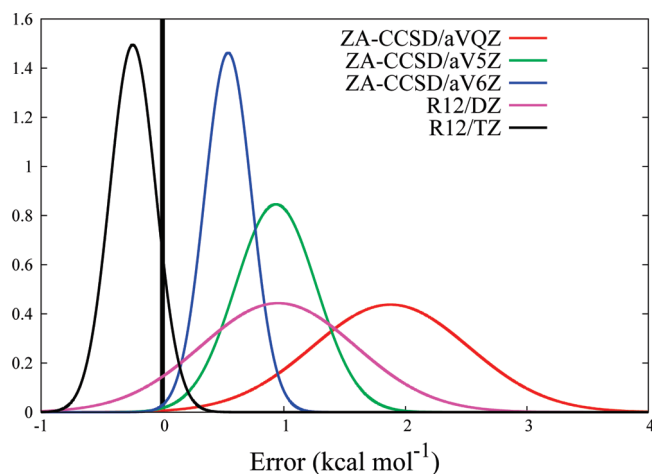
$$\delta[\text{CCSD}] = E_{\text{CCSD}}^{\text{corr}}(B) - E_{\text{CCSD}}^{\text{corr}}(A) \quad (68)$$

and neglect the basis set error associated with the Hartree–Fock reference. The accelerated basis set convergence of the CCSD-R12 corrections is demonstrated for a series of atomization energies with the CBS limit taken as an aVSZ-aV6Z extrapolation. Figure 2 clearly demonstrates that even with the cc-pVTZ-F12 basis, the method even outperforms the conventional aVSZ





**Figure 3.** Error of correlation energy increments ( $\delta[\text{CCSD}]$ , see text) to atomization energies for Z-averaged CCSD with aug-cc-pV6Z (ZA-CCSD/aV6Z) and ZA-CCSD(2) $_{\text{RT}2}$  with cc-pVTZ-F12 (R12/TZ) basis set with respect to aV5Z/aV6Z extrapolation benchmark.



**Figure 4.** Error distribution of correlation energy increments ( $\delta[\text{CCSD}]$ , see text) to atomization energies for Z-averaged CCSD with aug-cc-pVXZ (ZA-CCSD/aVXZ) and ZA-CCSD(2) $_{\text{RT}2}$  with cc-pVXZ-F12 (R12/XZ) basis sets with respect to aV5Z/aV6Z extrapolation benchmark.

basis. In Figure 3, the conventional aV6Z results are nearly equivalent to the TZ-R12 method but have a dramatically higher computational cost. The aV6Z basis is four times larger! The R12 results could be further improved by extending to the cc-pVQZ-F12 basis and performing a  $n^{-4}$   $T-Q$  extrapolation,<sup>112,127</sup> which has been demonstrated previously to yield excellent results for atomization energies.<sup>65</sup> The total correlation energies of individual molecules for the cc-pVTZ-F12 basis themselves should be converged to be better than 0.1 mH per valence electron. For example, for oxygen atom, the correlation energy difference between TZ-R12 and QZ-R12 computations is only 0.5 mH (see Supporting Information). Although cancellation of errors likely contributes in some fashion for the R12 corrections (as it does for the conventional methods), the observed basis set convergence results primarily from the intrinsic accuracy of the individual correlation energies.

The accuracy and precision of the results are summarized in Figure 4. The observed basis set convergence of the Z-averaged scheme closely parallels atomization energy results observed for

the RMP formulation of R12 matrix elements.<sup>66</sup> Although not explicitly used for atomization energies, formulations based on UHF have demonstrated excellent basis set convergence as well.<sup>100</sup> In this regard, the basis set convergence properties do not seem sensitive to the particular choice of  $\hat{H}_0$  used in computing R12 matrix elements. We therefore again emphasize that the primary advantage of the ZA-CCSD(2) $_{\text{RT}2}$  approach is greatly increased computational efficiency and reduced spin contamination from spin restriction in the wave function.

The success of the cc-pVTZ-F12 results is quite dramatic when all of the approximations involved are considered. For the R12 matrix elements, the EBC assumes the virtual space is closed under the action of the Fock operator. The virtual space is relatively more complete in describing the mean field correlation of the Fock operator than the cusp region, and the EBC is therefore nearly exact for basis sets of at least triple- $\zeta$  quality.<sup>24</sup> The R12 amplitudes themselves are also not optimized, being fixed at their asymptotic value. However, this fixed amplitude approach yields precise results provided a residuals correction is included via a Lagrangian functional. A Hermiticity simplification is further made on the left- and right-hand eigenvectors. However, to a first approximation (linearized coupled cluster), the left and right amplitudes are equal so that the symmetric amplitude assumption appears justified. All of the above approximations therefore seem appropriate for the desired level of accuracy.

## 5. CONCLUSION

The broad range of thermochemical and spectroscopic problems associated with high-spin, open-shell radicals clearly motivates maximizing the efficiency of current CCSD methods. The ZA-CCSD(2) $_{\text{RT}2}$  approach provides results competitive with CCSD/aV6Z with only a triple- $\zeta$  quality basis. For rigorous thermochemistry, a  $T-Q$  R12 extrapolation should therefore provide unrivaled accuracy in computing energies at the basis set limit. We have employed the Z-averaged ansatz to make two important simplifications. Z-averaged symmetries are exploited in the conventional CCSD equations to give spin-restricted amplitudes, yielding a theoretical 3-fold speedup over current open-shell R12 methods. The Z-averaged partitioning of the Hamiltonian is also employed in formulating perturbative R12 corrections, leading to greatly simplified, spin-restricted R12 intermediates. Beyond conventional singles and doubles, the Z-averaged approach also provides the basis for an improved Brueckner theory and a perturbative triples correction based on spin-restricted amplitudes. While some complications arise associated with  $\alpha$ ,  $\beta$ -exchange excitations, ZA-CCSD remains inherently simple in its spin-orbital form. Results are similar to existing CCSD methods, and ZA-CCSD therefore improves computational efficiency without any reduction in accuracy.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Supporting Information is available containing a complete list of geometries, total energies, and ZA-CCSD correlation energies for all computed molecules. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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