

## Explicitly Correlated R12/F12 Methods for Electronic Structure

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### CONTENTS

1. Introduction	75	6.3. [2] <sub>R12</sub>	100
2. Electron Correlation in Atoms and Molecules	76	6.4. CASPT2-F12 and MRCI-F12	100
2.1. What Is "Electron Correlation"?	76	6.5. G-CASSCF	101
2.2. Portrait of Electron Correlation in a Two-Electron Atom	77	6.6. MR CABS Singles Correction	101
2.3. Configuration Interaction Wave Functions for Two-Electron Atoms	79	6.7. Comparison of MR-R12 Methods	101
2.4. Symmetries of Two-Electron Wave Functions	82	6.8. Summary	103
2.5. Cusp Conditions	83	7. Conclusion	103
2.6. Motivation for Explicitly Correlated Wave Functions	84	Appendix: Notation	104
3. Explicitly Correlated Methods: Historical Perspective	85	Author Information	104
3.1. Explicitly Correlated Wave Functions for Two-Electron Systems	86	Biographies	104
3.2. Explicitly Correlated Wave Functions for <i>n</i> -Electron Systems	86	Acknowledgment	105
3.2.1. Hylleraas-CI Method	87	References	105
3.2.2. Explicitly Correlated Gaussian Methods	87		
3.2.3. Many-Body Gaussian Geminal Methods	87		
3.2.4. Transcorrelated Method	88		
4. Core Technology of Modern R12 Methods	88		
4.1. Derivation of MP2-R12 Equations	88		
4.2. Approximate Treatments of Many-Electron Integrals	90		
4.3. Evaluation of the Fock Matrix in the Geminal Basis	91		
4.4. Geminal Amplitudes Can Be Determined by the Cusp Conditions	92		
4.5. Correction of the Basis Set Error of the Reference Wave Function	92		
5. Coupled-Cluster R12 Methods	93		
5.1. The CC-R12 Formalism	93		
5.2. Approximate CC-R12 Methods	95		
5.2.1. CC-R12 in Standard Approximation	95		
5.2.2. CC-R12 Using Cusp Conditions	95		
5.2.3. Perturbative Approximations to CC-R12	96		
5.2.4. The CCSD(R12) Method	97		
5.2.5. The CCSD-F12x Methods	97		
5.2.6. Comparison of the CC-R12 Methods	98		
6. Multireference R12 Methods	98		
6.1. R <sub>12</sub> -MRCI	99		
6.2. MRMP2-F12	100		

### 1. INTRODUCTION

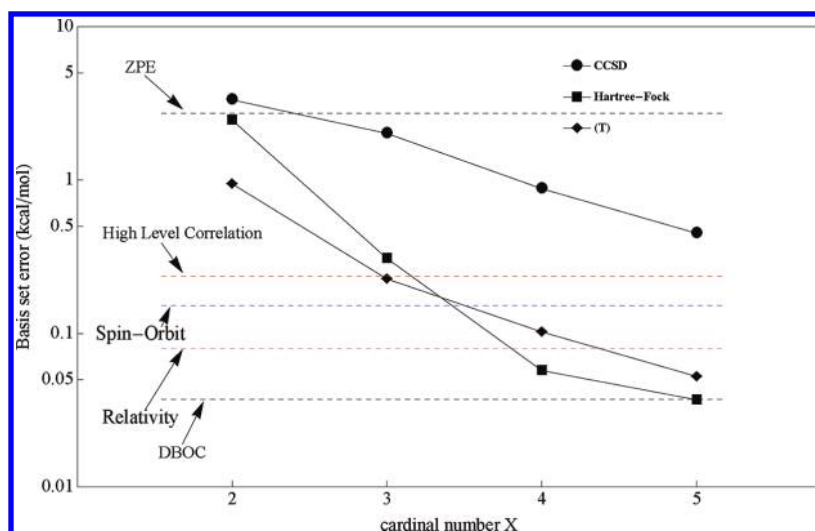
Electronic structure methods based on wave functions, or other many-electron quantities (Greens function, reduced *n*-particle density matrices), are the most versatile tools in quantum chemistry's toolkit. Despite much progress in the past 80 years, many types of queries of chemical relevance are still exceedingly difficult to answer with the wave function methods. The prediction of chemical equilibria and reaction rates, for example, requires computation of energies of involved species accurate to  $kT$ , or 2.5 kJ mol<sup>-1</sup> at room temperature (this level of accuracy in energy, rounded up to 1 kcal mol<sup>-1</sup>, is commonly referred to as chemical accuracy). To control and systematically eliminate the error to below this threshold is exceedingly difficult. For example, the density functional theory (DFT) model chemistries are efficient and accurate for many needs, but they do not permit error control because the error of a given DFT computation can only be estimated statistically, by benchmarking against large sets of data. High-end wave function models, such as the coupled-cluster singles and doubles augmented by perturbative treatment of triples, CCSD(T), can approach the chemical accuracy threshold for ground states of well-behaved molecules, but their computational cost is very high. Last, to truly control the error, many other contributions to the energy must be considered.

To illustrate how difficult it is to reach the chemical accuracy, consider Figure 1. It displays the magnitude of various contributions to the heats of formation for the core test set of the HEAT computational thermochemistry method.<sup>1,2</sup> The HEAT model defines the energy of a compound as the "exact" CCSD(T) energy plus contributions from higher-order electron correlation effects not included in CCSD(T), as well as relativistic, zero-point

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**Figure 1.** The mean absolute basis set errors of the components of the CCSD(T) contribution relative to that of various “small” contributions to the heats of formation for the core testset of the HEAT computational thermochemistry method.<sup>1,2</sup> Cardinal numbers  $X = 2, 3, 4, 5$  correspond to the aug-cc-pCVYZ basis sets<sup>3–5</sup> with  $Y = D, T, Q, 5$ , respectively.

vibrational, post-Born–Oppenheimer, and spin–orbit effects. The magnitude of each type of contribution past CCSD(T) is compared to the mean absolute basis set error of the components of the CCSD(T) energy. There are two conclusions: (1) the basis set error of CCSD is the largest individual contributor to the total basis set error of CCSD(T), and (2) it is larger than most “other” contributions to the energy. Clearly, the basis set error of the CCSD correlation energy is a major factor that determines the overall error of the compound’s heat of formation.

The fact that the basis set limit of correlation energy is difficult to compute precisely has been known for a long time. The origin for this problem is that the conventional methods like CCSD use antisymmetrized products of one-particle orbitals (Slater determinants) to construct two-electron and higher-rank basis sets. Slater determinants fail to model the exact wave functions at short interelectronic distances. To solve this problem, the wave function should be modeled explicitly in terms of the interelectronic distances. The advantages of such explicitly correlated wave functions have been known for a long time, but they have become ready for use by chemists only since the emergence of a particular group of explicitly correlated methods called R12 methods (also referred to by most developers as F12 methods in their recent uses to reflect the difference in the form of the two-electron basis; we will use these terms interchangeably here because both terms refer to exactly the same formalism).

The recent developments in R12/F12 methods are the focus of this Review. We will start the narrative with an introduction to the electron correlation from the perspective of many-electron wave functions (section 2). We will then briefly recap the history of explicitly correlated methods (section 3), followed by an introduction to the central ideas of R12 methods (section 4). The two recent thrusts of development of R12 methods, in the single-reference (coupled-cluster) and multireference (perturbation theory and configuration interaction) frameworks, will be covered in sections 5 and 6, respectively. We will conclude with our thoughts on the present status of the R12 methodology and speculate on its future. The notation is described in its own section in the Appendix.

We attempted to make this Review present a “big picture” of the field and be accessible to graduate students and postdocs in

the field of electronic structure. The technical nature of R12 technology made it sometimes difficult to balance the needs of the less advanced readers with that of advanced practitioners of the theory. The advanced readers are, of course, referred to the original articles for the complete technical details.

The intense activity in the field has resulted in several recent review articles<sup>6,7</sup> and book chapters.<sup>8,9</sup> The recent book on the subject<sup>10</sup> is a recommended read for the readers interested in the field of explicitly correlated wave functions (not just R12 methods).

## 2. ELECTRON CORRELATION IN ATOMS AND MOLECULES

This Review focuses on the influence of the basis set on the electron correlation energy. It is, therefore, imperative to start out with a discussion of the electron correlation as it applies to atoms and molecules.

### 2.1. What is “Electron Correlation”?

“Electron correlation” in the statistical sense exists if there is a difference between the ordinary,  $\rho(\mathbf{r})$ , and conditional,  $\rho(\mathbf{r}|\mathbf{r}')$ , probability densities of finding an electron at a particular point  $\mathbf{r}$ . The ordinary probability density is defined as the diagonal of the density operator averaged over  $n - 1$  electrons:

$$\rho(\mathbf{r}) = \frac{1}{n} \sum_{i=1}^n \rho_i(\mathbf{r}) \quad (1)$$

$$\rho_i(\mathbf{r}) = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_n \quad (2)$$

(Integration over all spin degrees of freedom is implied.) Extension of this concept to two electrons yields the pair probability density:

$$\rho(\mathbf{r}, \mathbf{r}') = \frac{1}{n(n-1)} \sum_{i \neq j}^n \rho_{ij}(\mathbf{r}, \mathbf{r}') \quad (3)$$

$$\rho_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_{i-1} d\mathbf{r}_{i+1} \dots d\mathbf{r}_{j-1} d\mathbf{r}_{j+1} \dots d\mathbf{r}_n \quad (4)$$

In the absence of correlation, the pair probability density is expressed as a product of the ordinary probability density:

$$\rho(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}') \quad (5)$$

In other words, the conditional probability density, defined as

$$\rho(\mathbf{r}|\mathbf{r}') \equiv \frac{\rho(\mathbf{r}, \mathbf{r}')}{\rho(\mathbf{r}')} \quad (6)$$

does not differ from the ordinary probability density in the absence of correlation:

$$\text{no correlation: } \rho(\mathbf{r}|\mathbf{r}') = \rho(\mathbf{r}) \quad (7)$$

$$\text{with correlation: } \rho(\mathbf{r}|\mathbf{r}') \neq \rho(\mathbf{r}) \quad (8)$$

The conditional density depends parametrically on  $\mathbf{r}'$ , indicated by the use of the vertical line in eq 6.

The origin of electron correlation is identified with two effects:

- (1) Electrons are indistinguishable and obey Fermi statistics, which mandates the change of the wave function sign under a permutation of labels of any two electrons; this is known as the Fermi correlation.
- (2) There is a Coulomb interaction between the electrons that generally decreases the probability of finding two electrons (of any spin) close to each other; this is known as the Coulomb correlation.

These definitions are, unfortunately, imprecise, and their use may lead to confusion. For example, the phenomenon of shell structure, the foundation of the Periodic Table and all of chemistry, can be understood as a consequence of Fermi correlation that limits the orbital occupation numbers at two and the Coulomb interaction that differentiates the energetics of  $l$  subshells in the same  $n$  shell. Both of these effects cause statistical correlation in the sense of eq 8; neither effect, however, is considered part of “electron correlation” of electronic structure theory.

The Fermi correlation is taken into account automatically by using Slater determinants, that is, fully antisymmetrized products of orbitals. The traditional starting point for the electronic structure is the Hartree–Fock (HF) method, in which the wave function is written as a single Slater determinant. The Hartree–Fock for the ground state of a two-electron atom, one of the central characters of this chapter, is expressed as

$$\begin{aligned} \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) &= |\phi(\mathbf{r}_1)\alpha_1\phi(\mathbf{r}_2)\beta_2\rangle \\ &= \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \alpha_2\beta_1) \end{aligned} \quad (9)$$

It is straightforward to see that conditions 5 and 7 are satisfied, and therefore this wave function is not correlated:

$$\rho(\mathbf{r}) = |\phi(\mathbf{r})|^2 \quad (10)$$

$$\rho(\mathbf{r}, \mathbf{r}') = |\phi(\mathbf{r})|^2|\phi(\mathbf{r}')|^2 \quad (11)$$

$$\rho(\mathbf{r}|\mathbf{r}') = |\phi(\mathbf{r})|^2 \quad (12)$$

For the  $M_S = 1$  component of the lowest-energy triplet state, however:

$$\begin{aligned} \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) &= |\phi_1(\mathbf{r}_1)\alpha_1\phi_2(\mathbf{r}_2)\alpha_2\rangle \\ &= \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1))\alpha_1\alpha_2 \end{aligned} \quad (13)$$

conditions 5 and 7 do not hold, and the wave function is correlated in that sense. The same can be said for any system with more than two electrons. Thus, even a general Hartree–Fock wave function is correlated in the statistical sense.

The traditional meaning of “electron correlation” in quantum chemistry is what the Hartree–Fock wave function fails to model. Following Löwdin,<sup>11</sup> the electron correlation energy is defined as the difference between the Hartree–Fock energy and the “exact” nonrelativistic Born–Oppenheimer energy:

$$E_{\text{corr}} \equiv E_{\text{exact}} - E_{\text{HF}} \leq 0 \quad (14)$$

Because the HF wave function includes Fermi correlation, the term “electron correlation” as used by quantum chemists refers primarily to Coulomb correlation.

Electron correlation can be described in several ways: (1) density functional theory (DFT) includes this effect via a density-dependent (and, recently, orbital-dependent) modification of the effective one-electron potential; (2) quantum Monte Carlo (QMC) methods explicitly compute averages over approximate or exact  $n$ -electron wave functions by stochastic sampling; (3) wave function theory (WFT) also involves the  $n$ -electron wave functions with known analytic form; the expectation values of such wave functions are computed explicitly, without sampling. This Review focuses exclusively on the wave function methods and their use in solving the electronic Schrödinger equation with high accuracy.

## 2.2. Portrait of Electron Correlation in a Two-Electron Atom

To understand how electron correlation affects the electronic wave functions in atoms, let us consider the ground state of the helium atom. It is a simple example of correlation between two electrons that orbit the same nucleus and span identical spatial scales. As shown above, the Hartree–Fock wave function for this state is statistically uncorrelated. The exact wave function can, therefore, be written as

$$\Psi_{\text{exact}}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2) + \Psi_{\text{corr}}(\mathbf{r}_1, \mathbf{r}_2) \quad (15)$$

where  $\Psi_{\text{corr}}$  is orthogonal to  $\Psi_{\text{HF}}$  and encapsulates all electron correlation not captured at the Hartree–Fock level (although some authors refer to  $\Psi_{\text{corr}}$  as Coulomb hole, this term was originally given a different meaning by Coulson and Neilson<sup>12</sup>). The exact wave function written in this form has the intermediate normalization:

$$\langle \Psi_{\text{HF}} | \Psi_{\text{exact}} \rangle = 1 \quad (16)$$

which is particularly convenient for working with many-body expansions.

To develop an intuitive picture of changes in the wave function due to electron correlation, consider Figure 2. It shows plots of the conditional  $\Psi_{\text{corr}}$ , defined as

$$\Psi_{\text{corr}}(\mathbf{r}_2|\mathbf{r}_1) \equiv \Psi_{\text{corr}}(\mathbf{r}_1, \mathbf{r}_2)/\phi(\mathbf{r}_1) \quad (17)$$

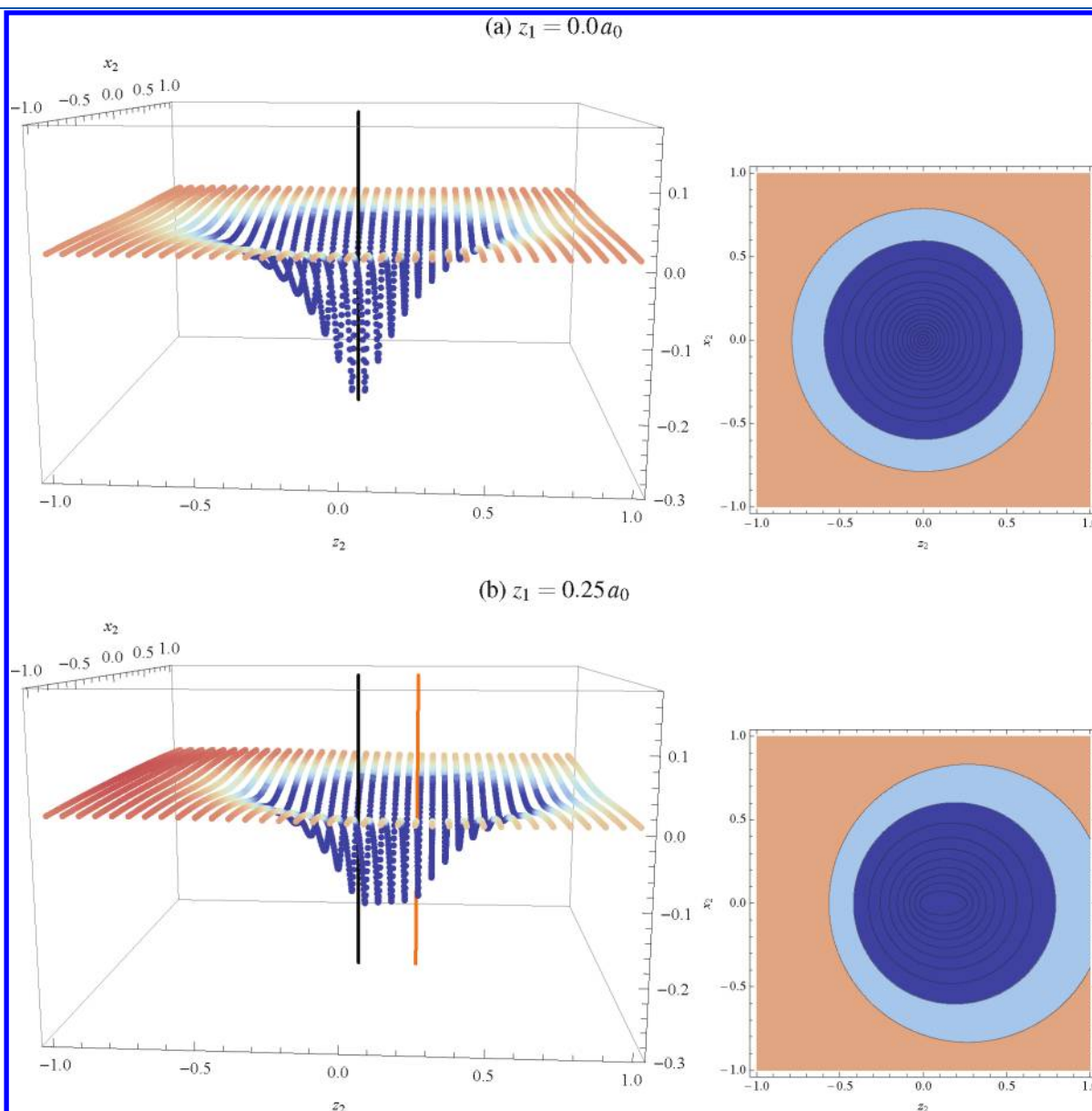
as a function of the position of electron 2 in the  $xz$ -plane parametrically dependent on the position of electron 1 fixed at a particular point on the  $z$  axis. Note that  $\Psi_{\text{corr}}(\mathbf{r}_2|\mathbf{r}_1)$  is the wave function counterpart of the conditional pair density in eq 6. The

reason to plot the conditional  $\Psi_{\text{corr}}$  is to account for the decreasing probability of finding an electron further away from the nucleus: indeed, the magnitude of  $\Psi_{\text{corr}}(\mathbf{r}_2|\mathbf{r}_1)$  is roughly constant (on the order of 0.1) for the entire range of  $z_1$ .

As is clearly seen from Figure 2, the shape of  $\Psi_{\text{corr}}$  changes qualitatively as electron 1 moves away from the nucleus. For small values of  $r_1$ , electron correlation “pushes” electron 2 away from the nucleus ( $\Psi_{\text{corr}}$  is negative near the nucleus and positive at  $r_2 > 1a_0$ ). This type of correlation is often referred to as in–out correlation: when one electron is inside the sphere of radius  $\langle r \rangle$ , the other is more likely to be found outside that sphere. As  $r_1$  increases,  $\Psi_{\text{corr}}$  becomes more asymmetrical, and for  $r_1 \approx 0.75a_0$ , there is a significant increase of probability on the opposite side of the nucleus. This type of correlation is known as angular correlation: electrons are more likely to be found on

the opposite sides of the nucleus than on the same side. When electron 1 is far away from the nucleus, electron correlation coalesces electron 2 near the nucleus, as expected.

The dominant feature of  $\Psi_{\text{corr}}$  is the Coulomb “hole” in the vicinity of the electron punctuated by the cusp at its bottom. As we discussed above, the structure of the wave function in this region is determined primarily by the electron–electron cusp condition. Two other features are the Coulomb “heap”<sup>13</sup> where the probability is increased due to the correlation, and the cusp at the position of the nucleus. Whereas the existence of Coulomb holes and heaps is not unexpected, the existence of the cusp in  $\Psi_{\text{corr}}$  at the position of the nucleus appears counterintuitive. Its existence becomes obvious, however, once we realize that the nucleus–electron cusps in  $\Psi$  and  $\Psi_{\text{HF}}$  do not cancel out exactly due to the difference in the wave function values at the nucleus–electron coalescence. Thus nuclei



**Figure 2.** Visualization of the changes induced in the ground-state wave function of He atom by Coulomb correlation. On the left are plots of the  $\Psi_{\text{corr}}(\mathbf{r}_1, \mathbf{r}_2) / \phi(\mathbf{r}_1)$  with electron 1 fixed at  $\{0, 0, z_1\}$  (indicated by the orange vertical line) and electron 2 constrained to the  $xz$  plane; the location of the nucleus,  $\{0, 0, 0\}$ , is indicated with the black vertical line. The corresponding contour plots are on the right. The correlation wave function was computed using a Hylleraas-type expansion (eq 56) with  $\zeta = 1.8109$  and all terms with  $k + l + m \leq 6$ .

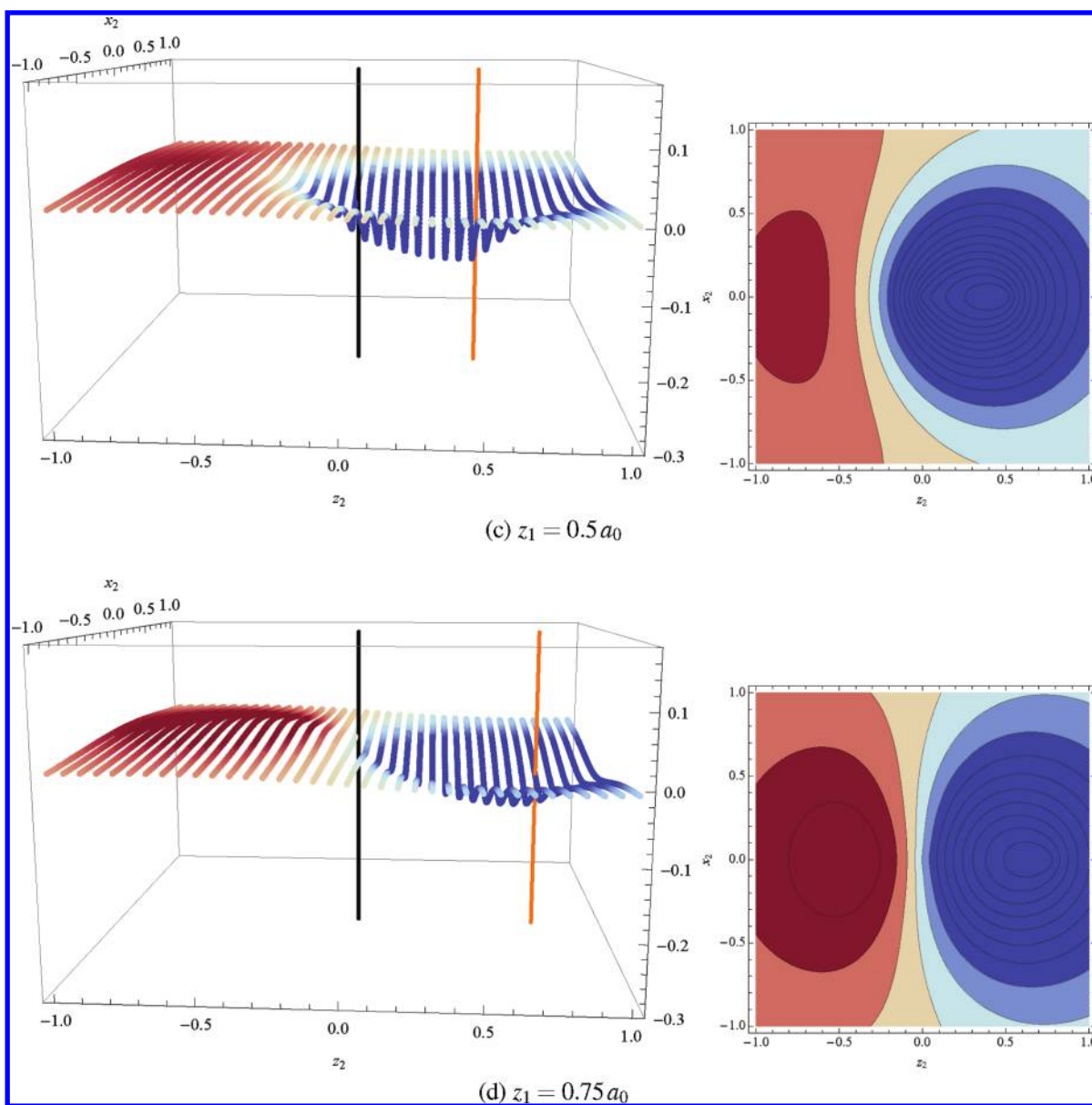


Figure 2. Continued

are important players in the electron correlation in atoms and molecules. Although the Coulomb correlation occurs due to the interelectronic repulsion of electrons only, its effect on the probability density depends on the electron–nucleus relative coordinates. This picture is in stark contrast to the idealized model of electrons in solids, the uniform electron gas, where the correlation effects are independent of position and thus can depend only on the coordinates of electrons relative to one another.

### 2.3. Configuration Interaction Wave Functions for Two-Electron Atoms

Configuration interaction (CI) expansion of an  $n$ -electron wave function is a linear combination of Slater determinants composed from a complete orthonormal set of orbitals  $\{\phi_i(\mathbf{r})\}$ . For example, the exact spin-free wave function for the ground state of helium can be expressed as:

$$\Psi_{\text{exact}}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij} C_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \quad (18)$$

where  $\phi_i$  are spin-free orbitals and therefore  $C_{ij} = C_{ji}$ . Without any loss of generality, we will assume that this set includes the Hartree–Fock orbital  $\phi(\mathbf{r})$ . It then is possible to represent  $\Psi_{\text{corr}}$  in a CI form:

$$\Psi_{\text{corr}}(\mathbf{r}_1, \mathbf{r}_2) = \sum'_{ij} C_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \quad (19)$$

where the  $ij$  sum excludes the Hartree–Fock product. The most important terms in this expansion can be deduced from the plots of  $\Psi_{\text{corr}}$  discussed above. With electron 1 fixed, the conditional correlation wave function becomes an orbital expansion:

$$\begin{aligned} \Psi_{\text{corr}}(\mathbf{r}_2|\mathbf{r}_1) &= \sum_{ij} C_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) / \phi(\mathbf{r}_1) \\ &\equiv \sum_{ij} D_{ij}(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \end{aligned} \quad (20)$$

For  $r_1 = 0$ , the only nonzero contributions to this sum will be

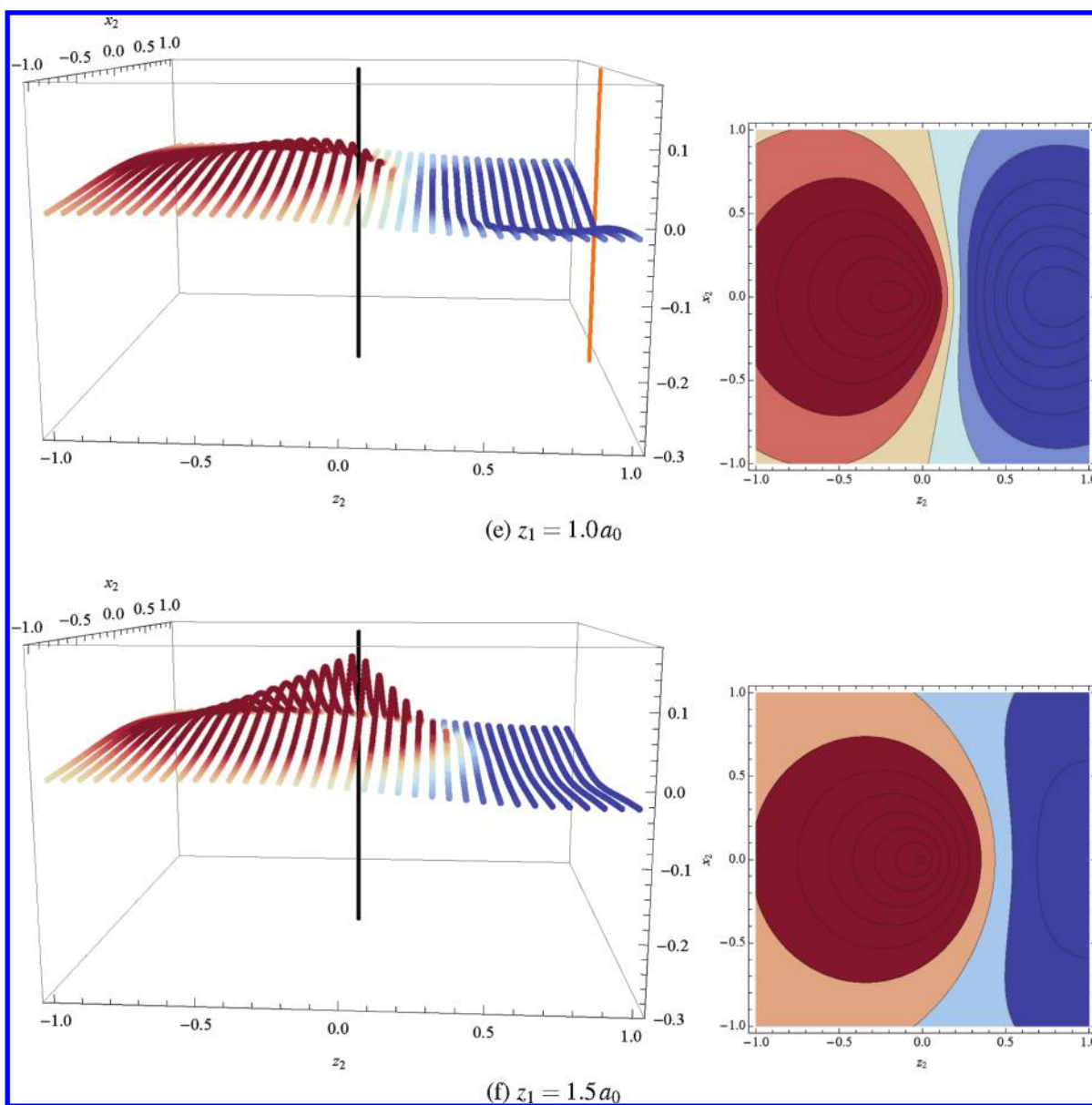


Figure 2. Continued

from *s*-type orbitals; the dominant contribution will come from an *s* orbital with one radial node, that is, a  $2s$ -like orbital (see Figure 2a). For  $r_1 = \{0,0,0.75a_0\}$  (Figure 2d), the dominant contribution to this sum will be from a  $2p_z$ -like orbital, and so on. To model  $\Psi_{\text{corr}}$  in a CI fashion, the basis therefore must include an extra set of *s* and *p* functions. It is exactly the composition of Dunning's smallest correlation-consistent basis set, cc-pVDZ,<sup>3</sup> for helium: in addition to one *s* function that models the Hartree–Fock orbital, it includes one *s* and one *p* set of functions, for a total of five functions per atom.

The structure of the Dunning base family of basis sets for He atom<sup>3</sup> bears strong similarity to the principal, or natural-orbital, expansion of the ground-state wave function first introduced by Löwdin and Shull.<sup>14,15</sup> They showed that the best (not in the sense of energy, but overlap!) CI approximation to the exact wave function of He is obtained in terms of natural orbitals (NO). NOs are defined as eigenfunctions of the exact one-

electron reduced density matrix (1-RDM):

$$\gamma(\mathbf{r}_1, \mathbf{r}_1') = \int \Psi^*(\mathbf{r}_1, \mathbf{r}_2) \Psi(\mathbf{r}_1', \mathbf{r}_2) d\mathbf{r}_2 \quad (21)$$

with the corresponding eigenvalues referred to as occupation numbers. Next, the following CI wave function composed of products of *r* NOs  $\{\tilde{\phi}_i\}$  with the highest occupation numbers:

$$\Psi_r(\mathbf{r}_1, \mathbf{r}_2) \equiv \sum_{i=1}^r \tilde{C}_i \tilde{\phi}_i(\mathbf{r}_1) \tilde{\phi}_i(\mathbf{r}_2) \quad (22)$$

is the optimal in the least-squares (overlap) sense. This result is, of course, related to the spectral theorem of functional analysis; for the finite-dimensional case, the result can be proved trivially via singular value decomposition<sup>16</sup> of the matrix of CI coefficients. Contrary to popular belief, it is not obvious that this result holds for systems with three and more electrons.

Although NOs prescribe a simple way to construct the “best” given-rank CI wave function, they do not guarantee optimality of the energy computed with such CI wave function. In practice, however, natural orbitals are believed to be close to optimal in the energy sense as well! Numerical computations of NOs for He found that the energy contribution from the  $\nu$ th NO with angular momentum quantum numbers<sup>17</sup>  $\{l, m\}$  follows the following empirical relationship:

$$\delta E_{\nu lm} \approx -\frac{1}{2} a_l \left( \nu + l - \frac{1}{2} \right)^{-6} \quad (23)$$

$$a_l = \begin{cases} 0.42, & l \geq 1 \\ 0.48, & l = 0 \end{cases} \quad (24)$$

Because the energy contribution depends on  $\nu + l \equiv n$ , the principal quantum number, it makes sense to use principal sets of NOs, by including all NOs with  $n \leq N$ . The minimal NO set ( $N = 1$ ) for helium would include one s function, the next smallest ( $N = 2$ ) would include two s functions and one p set, and so on:

$$\text{NO series: } 1s + 2s2p + 3s3p3d + 4s4p4d4f + \dots \quad (25)$$

The size of such a set:

$$\sum_{n=1}^N \sum_{l=0}^{n-1} \sum_{m=-l}^m 1 = \sum_{n=1}^N n^2 = \frac{N(N+1)(2N+1)}{6} \quad (26)$$

grows cubically with  $N$ . Equation 23 can then be used to estimate the error in the energy due to the finite NO set:

$$\begin{aligned} \Delta E_N &\equiv \sum_{n=N+1}^{\infty} \sum_{l=0}^{n-1} \sum_{m=-l}^m \delta E_{\nu lm} \\ &= -0.21 \sum_{n=N+1}^{\infty} \frac{n^2 + 0.14}{\left(n - \frac{1}{2}\right)^6} \\ &\sim -0.035\psi^{(3)}\left(N + \frac{1}{2}\right) + 0.0088\psi^{(4)}\left(N + \frac{1}{2}\right) \\ &\quad - 0.00068\psi^{(5)}\left(N + \frac{1}{2}\right) \end{aligned} \quad (27)$$

where  $\Psi^{(k)}(x)$  is the polygamma function of order  $k$ . Errors predicted by this formula are in a remarkable agreement with the basis set errors of CI energies computed with correlation-consistent basis sets (see Table 1). The agreement underlies strong similarities between the structure and function of the cc-pVXZ basis sets and the principal NO sets.

Medium-sized basis sets of NOs are sufficient for errors in the chemical accuracy range: for  $N = 4$ , eq 27 predicts the error of  $1.3 \text{ mE}_h = 0.8 \text{ kcal/mol}$ , in a near-perfect agreement with the actual error of the identical-size cc-pVQZ basis set (see Table 1). The real problem is the painfully slow asymptotic rate of convergence, easily obtained by the multipole expansion of eq 27:

$$\Delta E_N = -0.07N^{-3} - 0.053N^{-4} + \mathcal{O}(N^{-5}) \quad (28)$$

To decrease the error by a factor of 8, we must double  $N$ , and hence increase size of the NO set by a factor of 8 also! In other words, every digit of precision in correlation energy comes at the cost of

**Table 1. Basis Set Convergence of the Hartree–Fock and CI Energies (in  $E_h$ ) for the Ground-State Helium Atom<sup>a</sup>**

basis set <sup>3</sup>	$L_{\max}$	$n_{\text{bf}}$	$E(\text{HF})$	$E(\text{CI})$	$\Delta E(\text{CI})$	$\Delta E_N$
cc-pVDZ	1	5	-2.855160	-2.887595	0.016129	0.010977
cc-pVTZ	2	14	-2.861153	-2.900232	0.003492	0.003115
cc-pVQZ	3	30	-2.861514	-2.902411	0.001313	0.001271
cc-pV5Z	4	55	-2.861625	-2.903152	0.000572	0.000645
cc-pV6Z	5	91	-2.861673	-2.903432	0.000292	0.000361
				:		
complete	$\infty$	$\infty$	-2.86168 <sup>b</sup>	-2.903724377	0	0

<sup>a</sup> Each cc-pVXZ correlation-consistent basis set includes  $n_{\text{bf}}$  basis functions with angular momentum up to  $L_{\max}$  and corresponds to the natural orbital expansion set with  $N = L_{\max} + 1$ . The two rightmost columns compare the basis set error of CI energies with the values predicted for the NO sets by eq 27. <sup>b</sup> Reference 18.

increasing the size of the basis set by a factor of 10. For the two-electron atom, the length of NO-basis CI expansion (and hence its computational complexity) grows linearly with the basis set size, and hence this means roughly an order of magnitude increase in cost. Yet for general  $n$ -electron systems, an order of magnitude increase in orbital basis size means a steep (potentially, factorial) increase in computational complexity of the CI expansion as well as high-order polynomial increase in the computational cost of the matrix elements of the Hamiltonian. The resulting increase in computational complexity will in general be many orders of magnitude.

Another way to construct a CI-type wave function in a two-electron atom is a partial-wave (PW) expansion. It can be thought of as an expansion in sets of functions saturated to each angular momentum up to  $L$ :

$$\text{PW series: } 1s2s3s\dots + 2p3p4p\dots + 3d4d5d\dots + 4f5f6f\dots + \dots \quad (29)$$

PW expansion can be defined, however, without any need to specify basis sets. Consider the exact wave function for any S state of helium. It can be expressed in terms of  $r_1$ ,  $r_2$ , and  $\theta_{12}$ ,<sup>19</sup> with  $\theta_{12}$  the angle between vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , as a Legendre series:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \equiv \Psi(r_1, r_2, \theta_{12}) = \sum_{l=0}^{\infty} P_l(\cos \theta_{12}) \psi_l(r_1, r_2) \quad (30)$$

This expansion can be rewritten in a CI form by expanding the radial functions  $\Psi_l$  in terms of products of radial basis functions  $\rho$  and invoking the spherical harmonics addition theorem:

$$\begin{aligned} &\Psi(\mathbf{r}_1, \mathbf{r}_2) \\ &= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} \sum_{m=-l}^l (-1)^m \sum_{ij} C_{ij} \rho_i(r_1) Y_{l,-m}(\theta_1, \phi_1) \rho_j(r_2) Y_{lm}(\theta_2, \phi_2) \end{aligned} \quad (31)$$

The partial wave expansion of the exact wave function leads to the corresponding partial wave expansion of the energy:

$$E = \sum_{l=0}^{\infty} \delta E_l \quad (32)$$

The partial-wave expansion is exact only if a complete (infinite) set of radial functions is used. In practice, the convergence to the complete radial basis set limit for a given  $l$  value is fast in an appropriate basis. However, the  $l$  sums in eqs 31 and 32 are very slowly convergent. We can roughly estimate the asymptotic

behavior of partial-wave energy increments in eq 32 using eq 23:

$$\begin{aligned}\delta E_l &= \sum_{v=1}^{\infty} \sum_{m=-l}^l \delta E_{vlm} \approx -0.21(2l+1) \sum_{n=l+1}^{\infty} \left(n - \frac{1}{2}\right)^{-6} \\ &= -0.0035 \left(l + \frac{1}{2}\right) \psi^{(5)} \left(l + \frac{1}{2}\right) \\ &\sim -0.084 \left(l + \frac{1}{2}\right)^{-4} + \mathcal{O} \left(\left(l + \frac{1}{2}\right)^{-5}\right)\end{aligned}\quad (33)$$

The asymptotic error due to truncation of the  $l$  sum at some finite  $L$  is then:

$$\begin{aligned}\Delta E_L &\equiv \sum_{l=L+1}^{\infty} \delta E_l \approx -0.084 \sum_{l=L+1}^{\infty} \left(l + \frac{1}{2}\right)^{-4} \\ &\approx -0.028(L+1)^{-3} + \mathcal{O}((L+1)^{-4})\end{aligned}\quad (34)$$

Again, the error approaches zero very slowly: its reduction by an order of magnitude demands doubling the angular momentum to which the partial-wave expansion is computed.

Partial-wave expansions for atomic wave functions and properties can be computed numerically or analytically. In 1962, Schwartz derived the following asymptotic formula for the PW increment to the second-order energy in  $1/Z$  perturbation theory of ground-state He:<sup>20,21</sup>

$$\delta E_l^{(2)} = \frac{45}{256} \left(l + \frac{1}{2}\right)^{-4} \left\{ 1 - \frac{5}{4} \left(l + \frac{1}{2}\right)^{-2} + \mathcal{O} \left(\left(l + \frac{1}{2}\right)^{-4}\right) \right\}\quad (35)$$

Note that only even powers of  $(l + 1/2)$  appear. Kutzelnigg and Morgan generalized this result to any state of a two-electron atom.<sup>24</sup> For all natural-parity singlet states (see section 2.4), the leading order in the asymptotic expansion  $\delta E_l^{(2)}$  is  $(l + 1/2)^{-4}$ , with the coefficient determined by an appropriate integral of the zeroth-order wave function. Similarly, for triplet states the leading-order contribution is sixth order in  $1/(l + 1/2)$ ; for unnatural-parity singlet states, it is eighth order. Analogous asymptotic results hold for MP2 energies of atoms with any number of electrons. For the third-order  $1/Z$  energy, the PW increments converge faster with  $l$ : for natural-parity singlet, triplet, and unnatural-parity singlet states, the leading-order asymptotic terms are proportional to  $(l + 1)^{-5}$ ,  $(l + 1)^{-7}$ , and  $(l + 1)^{-9}$ , respectively.

For variational and exact wave functions of two-electron atoms, similar asymptotic expressions have been found. In 1965, Lakin studied<sup>22</sup> the exact ground-state wave function of He and its relationship with Coulomb singularities in the Hamiltonian to argue that the PW increment of the exact energy is proportional to  $(l + 1/2)^{-4}$ , a result in agreement with the earlier findings of Schwartz for the second-order  $1/Z$  energy (eq 35). In 1979 Carroll, Silverstone, and Metzger used sequences of CI computations that included functions up to  $l = 11$  to arrive at a numerical asymptotic expression of the PW increment to the CI energy:<sup>17</sup>

$$\delta E_L = C_1 \left(L + \frac{1}{2}\right)^{-4} + C_2 \left(L + \frac{1}{2}\right)^{-5} + \mathcal{O} \left[\left(L + \frac{1}{2}\right)^{-6}\right]\quad (36)$$

where  $C_1 = -0.074$ ,  $C_2 = -0.031$ . Later, Hill showed how to express the coefficients in eq 36 as radial integrals of the exact ground-state wave function:<sup>23</sup>

$$C_1 = 6\pi^2 \int_0^\infty |\Psi(r, r, 0)|^2 r^5 dr\quad (37)$$

$$C_2 = \frac{48\pi}{5} \int_0^\infty |\Psi(r, r, 0)|^2 r^6 dr\quad (38)$$

where  $\Psi$  is the wave function expressed in terms of  $r_1$ ,  $r_2$ , and  $\theta_{12}$  (see eq 30). Hill's findings were generalized to atomic states by Kutzelnigg and Morgan in 1992.<sup>24</sup>

The main lesson of this section is this: the manner in which a CI expansion is constructed does not matter as far as the basis set incompleteness is concerned. Whether it is an NO expansion, that is optimal in the least-squares sense, or a partial-wave expansion, that lends itself to rigorous analysis, the fact remains that the error of the CI expansion converges slowly with the basis set size, at least for "normal" singlet states. The origin of this slow convergence will be discussed in section 2.5. To prepare for that discussion, we must now elaborate on the manner in which spin/orbital angular momenta of the two electrons couple and how it affects the behavior of the wave function at short interelectronic distance.

#### 2.4. Symmetries of Two-Electron Wave Functions

Consider an arbitrary state of a two-electron atom, with wave function  $\Psi_{L, M_L, S, M_S}^{n_1, l_1, n_2, l_2}(\mathbf{r}_1, \mathbf{r}_2)$ , characterized by the total orbital and spin angular momentum quantum numbers  $L, M_L, S, M_S$  and whose zeroth-order description places electrons into  $n_1 l_1$  and  $n_2 l_2$  hydrogenic orbitals. We will focus on two fundamental symmetries of such a state: (1) parity, that is, symmetry under inversion of the coordinate system, and (2) particle exchange. Our discussion will largely follow that of Morgan and Kutzelnigg.<sup>25</sup>

The parity of a hydrogenic orbital is  $(-1)^l$ , and hence the parity of the wave function is  $(-1)^{l_1+l_2}$ :

$$\Psi_{L, M_L, S, M_S}^{n_1, l_1, n_2, l_2}(-\mathbf{r}_1, -\mathbf{r}_2) = (-1)^{l_1+l_2} \Psi_{L, M_L, S, M_S}^{n_1, l_1, n_2, l_2}(\mathbf{r}_1, \mathbf{r}_2)\quad (39)$$

The two-electron state is said to have natural parity if its parity is the same as for a one-electron state with orbital angular momentum  $L$ , that is,  $(-1)^{l_1+l_2} = (-1)^L$ , or  $L - l_1 - l_2$  is even. Otherwise the state is said to have unnatural parity. For example, the 2p3p configuration produces S, P, and D atomic terms, all with the same parity (+1, i.e., gerade). The S/D terms have natural parity (same as an s/d atomic orbital), whereas the P term has unnatural parity (opposite to that of a p atomic orbital).

To understand how the parity affects the form of the wave function at short interelectronic distances, let us express the wave function in terms of center of mass and relative coordinates of the electron pair:

$$\mathbf{R}_{12} \equiv \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\quad (40)$$

$$\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2\quad (41)$$

In spherical polar coordinates,  $\mathbf{R}_{12} = \{R_{12}, \Theta_{12}, \Phi_{12}\}$  and  $\mathbf{r}_{12} = \{r_{12}, \theta_{12}, \phi_{12}\}$ . The kinetic energy and interelectronic repulsion separate in these coordinates, but the nuclear-electron attraction potential does not, except at infinitesimal interelectronic distances. Hence, the wave function can be expanded in a



Clebsch–Gordan series that is expected to converge quickly at short  $r_{12}$ :

$$\Psi_{L, M_L, S, M_S}^{n_1, l_1, n_2, l_2}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\lambda, \mu, l, m} \mathcal{R}_{\lambda, l}(R_{12}, r_{12}) Y_{\lambda, \mu}(\Theta_{12}, \Phi_{12}) Y_{l, m}(\theta_{12}, \phi_{12}) \begin{pmatrix} \lambda & l & L \\ \mu & m & M_L \end{pmatrix} \quad (42)$$

in which  $\lambda, \mu$  label orbital angular momentum of the electron pair moving as a whole about the nucleus, and  $l, m$  label orbital angular momentum of the internal motion within the electron pair. The parity of each term in the sum is  $(-1)^{\lambda+l}$  and must be equal to the parity of the state,  $(-1)^{l_1+l_2}$ . For the natural parity states  $(-1)^{\lambda+l} = (-1)^L$ , or  $L - \lambda - l$  is even; for the unnatural parity counterparts  $(-1)^{\lambda+l} = (-1)^{L+1}$ , or  $L - \lambda - l$  is odd.

The electronic wave function must satisfy Fermi statistics, that is, be antisymmetric with respect to the exchange of electronic labels “1” and “2”. Because singlet/triplet ( $S = 0/1$ ) spin wave functions are antisymmetric/symmetric, the spatial part of the wave function must be symmetric/antisymmetric. Yet particle exchange transforms  $\{r_{12}, \theta_{12}, \phi_{12}\}$  to  $\{r_{12}, \pi - \theta_{12}, \pi + \phi_{12}\}$ , and thus changes the sign of  $Y_{l, m}(\theta_{12}, \phi_{12})$  by  $(-1)^l$ . Therefore, to conform to Fermi statistics,  $l$  must be even/odd for singlet/triplet states.

It is now straightforward to show that the interplay between the angular momentum coupling rules, parity requirements, and particle exchange determines the short  $r_{12}$  behavior of the wave function.

- For singlet states  $l$  must be even; hence for natural parity singlet states  $L - \lambda$  must also be even. Angular momentum coupling of  $\lambda$  and  $l$  can produce  $L$  for any value of  $l$ : for  $l = 0$ ,  $\lambda$  must equal  $L$ ; for  $l = 2$ ,  $\lambda$  can be  $L, L + 2$ , or  $L - 2$ , etc.
- For unnatural parity singlet states  $l$  must be even and  $L - \lambda$  must be odd. Angular momentum coupling rules exclude the possibility of  $l = 0$ :  $\lambda$  would then have to equal  $L$ , but that contradicts the condition that  $L - \lambda$  is odd. All even  $l \geq 2$  are allowed; however, for  $l = 2$ ,  $\lambda$  can be  $L + 1$  or  $L - 1$ , etc.
- For triplet states  $l$  must be odd; hence for natural parity triplet states  $L - \lambda$  must be also odd. Any odd value of  $l \geq 1$  is allowed for such states: for  $l = 1$ ,  $\lambda$  can be  $L + 1$  or  $L - 1$ , etc.
- For unnatural parity triplet states  $l$  must be odd and  $L - \lambda$  must be even. Angular momentum coupling rules allow any odd  $l \geq 1$ : for  $l = 1$ ,  $\lambda$  must equal  $L$ ; for  $l = 3$ ,  $\lambda$  can be  $L, L + 2$ , or  $L - 2$ , etc.

Having determined the leading term (in  $l$ ) in eq 42, we can also understand short- $r_{12}$  behavior as a function of spin and parity. The solution to the radial Schrödinger equation for two electrons at short  $r_{12}$ :

$$\left( -\frac{1}{2r_{12}^2} \frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}} + \frac{l(l+1)}{2r_{12}^2} + \frac{1}{r_{12}} + \mathcal{O}(r_{12}^0) \right) \mathcal{R}_{\lambda, l}(R_{12}, r_{12}) = 0 \quad (43)$$

goes as  $r_{12}^l$ , in complete analogy to the standard hydrogen atom analysis.<sup>26</sup> Thus, at  $r_{12} = 0$  (the coalescence point), the natural parity singlet wave function does not vanish, the triplet wave function vanishes as  $r_{12}$ , and the unnatural parity singlet wave function vanishes as  $r_{12}^2$ . The first two facts are well-known; in fact, the often-cited motivation for first Hund’s rule is that triplet states have a Fermi hole around the coalescence point, which makes triplet states lower in energy than the corresponding singlet. The fact that there are singlet states that exhibit a feature analogous to the Fermi hole is not well-known. Morgan and Kutzelnigg modified Hund’s rules to account for the effects of

parity<sup>25</sup> (such modifications had been known as the alternating rule<sup>27</sup>) and were able to explain some notable failures of the original Hund’s rules, such as the ground state of Ce, as well as apply the new rules to explain energetic ordering of excited states.

Generalization of these results to molecules is simple: parity is no longer a good quantum number; hence singlet states will be characterized by eq 42 with even  $l \geq 0$ , and nonvanishing wave function at  $r_{12} = 0$ . Triplet states will be characterized by eq 42 with odd  $l \geq 1$ , and wave function vanishing at the coalescence point as  $r_{12}$ .

As we are about to see, the short- $r_{12}$  behavior of two-electron wave functions also has important consequences for the electron correlation.

## 2.5. Cusp Conditions

Kato, while exploring properties of the many-particle Schrödinger equation, showed that discrete-spectrum wave functions are continuous and have bounded continuous first derivatives, except at the Coulomb singularities.<sup>28</sup> He also showed that such discontinuity at the coalescence point of electrons  $i$  and  $j$  can be expressed as

$$\lim_{r_{ij} \rightarrow 0} \left( \frac{\partial \Psi^{\text{sph}}(\dots \mathbf{r}_i, \dots \mathbf{r}_j, \dots)}{r_{ij}} \right) = \frac{1}{2} \Psi \left( \dots \frac{\mathbf{r}_i + \mathbf{r}_j}{2}, \dots \frac{\mathbf{r}_i + \mathbf{r}_j}{2}, \dots \right) \quad (44)$$

where sph denotes spherical averaging over the hypersphere  $r_{ij} = \text{const}$ ,  $\mathbf{r}_i + \mathbf{r}_j = \text{const}$ . Similar conditions hold for other types of Coulomb singularities, such as at the electron–nucleus coalescence point. This result, known as the cusp condition, is rather technical, and it deservedly bears Kato’s name.

The cusp condition can be obtained much more easily, albeit without proofs of continuity, following the results of section 2.4. Considering, without any loss of generality, the behavior near the coalescence point of electrons 1 and 2, the exact solution to Schrödinger equation can be represented (see eq 43) in terms of  $\mathbf{r}_{12}$  as a spherical harmonic  $Y_{lm}$ , with  $l$  determined by particle exchange and/or other symmetries, times the radial part with the  $r_{12}^l$  leading term:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \approx \sum_{m=-l}^l r_{12}^l (c_0 + c_1 r_{12} + \mathcal{O}(r_{12}^2)) Y_{lm}(\theta_{12}, \phi_{12}) \Phi_m(\mathbf{R}_{12}, \dots) \quad (45)$$

where  $\Phi_m$  is the part of the wave function that depends on the center of mass of the electron pair and on the positions of other electrons in the system. By substitution into eq 43, we can show that  $c_1 = c_0/(2(l+1))$ , hence:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \approx r_{12}^l \sum_{m=-l}^l \left( 1 + \frac{r_{12}}{2(l+1)} + \mathcal{O}(r_{12}^2) \right) Y_{lm}(\theta_{12}, \phi_{12}) \Phi_m(\mathbf{R}_{12}, \dots) \quad (46)$$

In the absence of particle exchange or other symmetries,  $l = 0$  and this condition:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \approx \left( 1 + \frac{1}{2} r_{12} + \mathcal{O}(r_{12}^2) \right) \Phi_0(\mathbf{R}_{12}, \dots) \quad (47)$$

is equivalent to Kato's result. In this form, it is easy to see why eq 47 is called the cusp condition: regardless of the direction in which we approach the  $\mathbf{r}_{12} = 0$  point, the derivative of the wave function with respect to  $r_{12}$  is the same; hence crossing the coalescence point changes the sign of the first derivative. For electrons whose spins are coupled to triplet,  $l = 1$  and the cusp condition is significantly different:

$$\begin{aligned} & \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \\ & \approx r_{12} \sum_{m=-1}^1 \left( 1 + \frac{1}{4} r_{12} + \mathcal{O}(r_{12}^2) \right) Y_{1m}(\theta_{12}, \phi_{12}) \Phi_m(\mathbf{R}_{12}, \dots) \end{aligned} \quad (48)$$

The first derivative at the coalescence point is continuous for the triplet case because the first-order spherical harmonic is an odd function. For the case of an atomic unnatural-parity singlet state  $l = 2$ :

$$\begin{aligned} & \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots) \\ & \approx r_{12}^2 \sum_{m=-2}^2 \left( 1 + \frac{1}{6} r_{12} + \mathcal{O}(r_{12}^2) \right) Y_{2m}(\theta_{12}, \phi_{12}) \Phi_m(\mathbf{R}_{12}, \dots) \end{aligned} \quad (49)$$

The above approach was first pursued by Pack and Byers Brown in 1966<sup>29</sup> to eliminate the need for spherical averaging and expressed Kato cusp condition in a form including  $l = 0$  and  $l = 1$ . Kutzelnigg and Morgan in 1992 were first to formulate the cusp condition for atomic unnatural parity singlet states.<sup>24</sup> Last, Tew pursued this approach to derive higher-order terms in the partial-wave expansion around the cusp: the leading-order cusp condition is universal, that is, system-independent, whereas the second-order cusp condition includes system-dependent coefficients.<sup>30</sup>

Kato's groundbreaking achievement was to establish, for the first time, properties of the exact wave function near Coulomb singularities. Specifically, the structure of the wave function's first derivative can be universally described in terms of the interparticle coordinates. Although it was already known that wave functions that depend on the interelectronic coordinates are very efficient,<sup>31–33</sup> Kato's finding was not a mere rationalization of such wave function, but a constructive suggestion that "it is quite natural to expect that trial functions with the same type of singularity would give a better approximation than functions with different type of singularities".<sup>28</sup> As we shall see in section 4.4, modern explicitly correlated wave function can directly use Kato's cusp conditions to reduce the number of adjustable wave function parameters.

## 2.6. Motivation for Explicitly Correlated Wave Functions

At the time of Kato's discovery of cusp conditions in 1957, there were strong hints that interelectronic distances are universally useful for constructing efficient wave functions. The original motivation for the use of interelectronic distances, however, was not a result of rigorous analysis of mathematicians. In 1927, Slater attempted to construct a wave function for a two-electron atom that satisfied both the Rydberg limit, in which one electron is very far from the nucleus, and the "core" limit in which both electrons are close to the nucleus. In the Rydberg limit, the wave function should behave as  $\sim e^{-r_1} e^{-2r_2}$  (in the absence of penetration corrections), whereas near the core his analysis suggested a simple form  $\sim e^{-2(r_1+r_2) + r_{12}}$  that matches the Rydberg limit. A similar wave function that included the  $r_{12}$

coordinate:

$$\Psi(r_1, r_2, r_{12}) = e^{-2(r_1 + r_2) + r_{12}/2} \quad (50)$$

turned out to be an even better approximation overall and yielded a remarkably good approximation to the energy,  $\sim -2.856 E_h$ .<sup>34</sup> Slater published<sup>35</sup> this analysis in 1928 and followed up later in the same year with an application of the wave function in eq 50, piecewise connected to another Rydberg-limit wave function, to prediction of properties of helium, such as its diamagnetic susceptibility.<sup>36</sup>

At around the same time, Hylleraas was pondering how to refine his breakthrough variational wave function for the helium ground state, in error by a mere 0.1 eV.<sup>37</sup> He realized that his wave function, expressed in terms of  $r_1$ ,  $r_2$ , and  $\cos \theta_{12}$ , included even and odd powers of  $r_1$  and  $r_2$  but only even powers of  $r_{12}$  as can be seen from:

$$r_{12}^2 = (\mathbf{r}_1 - \mathbf{r}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2) = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12} \quad (51)$$

Almost miraculously, a very compact wave function with linear dependence on  $r_{12}$  produced the energy of  $E = -2.902431 E_h$ , in error from the exact Born–Oppenheimer nonrelativistic result by  $1.3 \text{ mE}_h \approx 0.035 \text{ eV}$ :<sup>31</sup>

$$\begin{aligned} \Psi(r_1, r_2, r_{12}) = & N(1 + c_1(r_1 - r_2)^2 \\ & + c_2 r_{12}) e^{-\alpha(r_1 + r_2)} \end{aligned} \quad (52)$$

where parameters  $\alpha$ ,  $c_1$ , and  $c_2$  were determined variationally ( $\alpha = -1.81607$ ,  $c_1 = 0.130815$ ,  $c_2 = 0.291786$ ; the corresponding normalization constant is 1.330839). The error can be reduced further by incorporating higher powers of  $r_1 \pm r_2$  and  $r_{12}$ .<sup>38</sup>

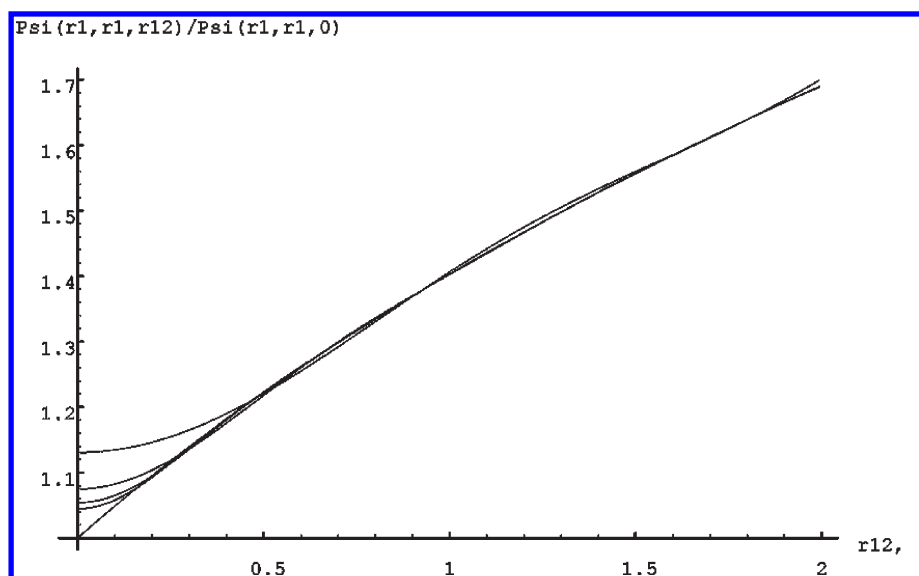
The Hylleraas expansions can be easily generalized for the two-electron atom by including higher powers of  $r_{12}$  and  $r_1 \pm r_2$ . One example is to restrict the sum of the powers:

$$\begin{aligned} \Psi_N(r_1, r_2, r_{12}) = & e^{-\alpha(r_1 + r_2)} \sum_i c_i (r_1 + r_2)^{n_i} (r_1 - r_2)^{l_i} r_{12}^{m_i}, \\ & n_i + l_i + m_i \leq N \end{aligned} \quad (53)$$

The resulting wave function sequence converges very rapidly with  $N$  (see Figure 3).

The rapid asymptotic convergence of the Hylleraas wave functions relative to the slow convergence of the CI-type expansions can be attributed to the presence of linear and other odd powers of  $r_{12}$ , as can be seen in Figure 3. CI-type wave functions only contain even powers of  $r_{12}$  (see eqs 30 and 51) and thus suffer from slow convergence near the cusp. Strictly speaking, it is CI's lack of odd powers of  $r_{12}$  combined with the global support of Slater determinants that causes the slow convergence; wave functions with local support could be used to mimic the local feature such as the cusp efficiently even without the odd-power terms.

One should not make the mistake of attributing the spectacular success of the three-term Hylleraas wave function (eq 52) to the inclusion of the linear  $r_{12}$  term alone as it is often implied. We have experimented with eq 52 by considering its generalization as a correlation prefactor times the uncorrelated orbital product:



**Figure 3.** Convergence of the configuration interaction wave functions for the ground state of helium. Plotted are 1 au  $\Psi(r,r,0)$  set to 0.032406. From top to bottom as seen near the origin: (1) a 56-term CI expansion; (2) a 286-term CI expansion; (3) an 816-term CI expansion; (4) a 1540-term CI expansion; and (5) a 346-term Hylleraas expansion. See footnotes to Figure 4 for the description of the wave functions.

**Table 2.** Comparison of the Three-Term Wave Function of Hylleraas with its Analogues Reveals the Importance of the  $(r_1 - r_2)^2$  Term and Relative Insensitivity to the Form of the  $r_{12}$ -Dependent Term<sup>a</sup>

$\Psi$	$E_{\Psi}, E_{\text{H}}$
$e^{-\alpha(r_1+r_2)}$	-2.847656
$(1 + c_1(r_1 - r_2)^2)e^{-\alpha(r_1+r_2)}$	-2.876675
$(1 + c_2r_{12})e^{-\alpha(r_1+r_2)}$	-2.891120
$(1 + c_1(r_1 - r_2)^2 + c_2r_{12})e^{-\alpha(r_1+r_2)}$	-2.902431
$(1 + c_1(r_1 - r_2)^2 + c_2e^{-\gamma r_{12}})e^{-\alpha(r_1+r_2)}$	-2.902592
$(1 + c_1(r_1 - r_2)^2 + c_2r_{12}e^{-\gamma r_{12}})e^{-\alpha(r_1+r_2)}$	-2.902585
exact	-2.903724

<sup>a</sup>All nonlinear as well as nonlinear parameters were fully optimized in each case.

$$\Psi(r_1, r_2, r_{12}) = N(1 + c_1(r_1 - r_2)^2 + c_2f(r_{12}))\Phi(r_1, r_2) \quad (54)$$

$$\Phi(r_1, r_2) \equiv \phi(r_1)\phi(r_2) \quad (55)$$

Here,  $f(r_{12})$  is a function of  $r_{12}$  whose Taylor expansion includes linear terms, and  $\phi(r)$  is a spherically symmetric orbital. The results of these experiments are collected in Tables 2 and 3 and can be summarized as follows:

- Neither the  $r_{12}$  nor the  $(r_1 - r_2)^2$  term by itself is sufficient for high precision. Inclusion of both terms is essential.
- Reoptimization of the orbital shape is also crucial for high precision. The use of Hartree–Fock orbitals, in single-exponential or exact form, produces very poor wave functions. The optimal orbitals for multiplicative account of correlation are more compact than the Hartree–Fock orbitals. This can be qualitatively rationalized as follows: in the presence of correlation factors, the electrons can get closer to

**Table 3.** Effect of the Orbital Form ( $\phi$  in Eq 54) on the Effectiveness of the Three-Term Wave Function of Hylleraas

$\phi$	$E_{\Phi}$	$E_{\Psi}$
$e^{-1.68750r}$	-2.847655	-2.892624
$e^{-1.81607r}$	-2.831126	-2.902431
Hartree–Fock	-2.861680	-2.883707
optimal	-2.833417	-2.902619

the nucleus while minimizing their repulsion by staying on the opposite sides of the nucleus. Similar findings, that the bare-nucleus Hamiltonian orbitals are more appropriate for recovery of correlation, were pointed out by Kutzelnigg for He-like atoms<sup>39</sup> and by Röhse et al. for  $\text{H}_2$  and  $\text{H}_3^+$ .<sup>40</sup>

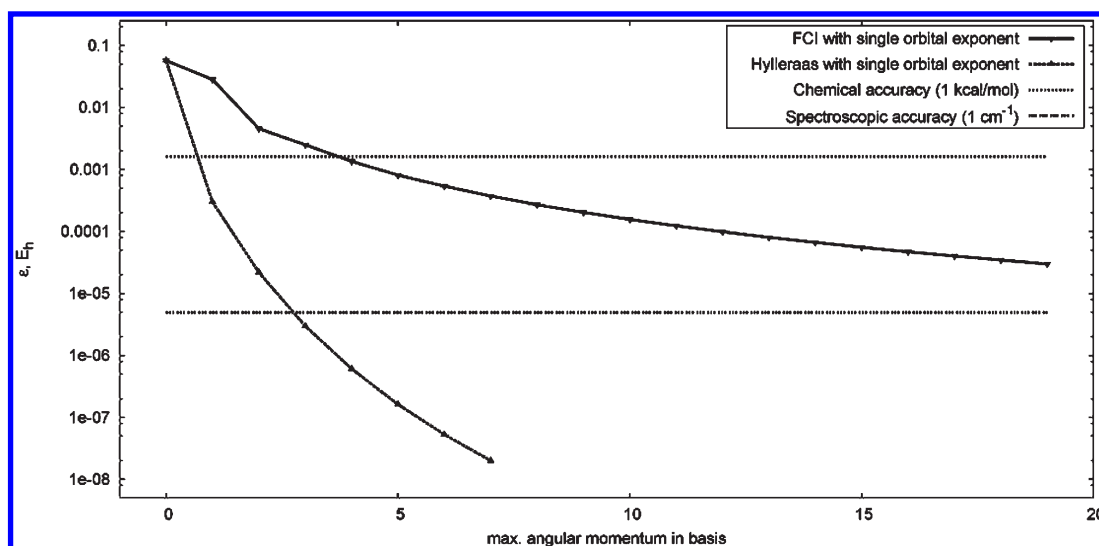
- The exact manner of dependence on  $r_{12}$  does not seem to matter much as long as the Taylor expansion includes terms linear in  $r_{12}$ . For example, linear and exponential forms seem to work equally well.

These findings suggest that to produce most compact wave functions the use of  $r_{12}$  terms is necessary, but not sufficient.

The case for the use of explicitly correlated wave functions is clear-cut: appropriate account for the cusps of the electronic wave function is essential for rapid decay of the basis set errors of many-electron wave functions. It is the high dimensionality of the integrals that accompany the use of the interelectronic distances  $r_{ij}$  that prevented a realization of the idea of Slater and Hylleraas in practical methods. Turning that idea into a generally applicable tool required finding clever ways to evaluate such integrals efficiently. In the next section, we briefly review the history of such developments.

### 3. EXPLICITLY CORRELATED METHODS: HISTORICAL PERSPECTIVE

Extension of the idea of Hylleraas to general systems is straightforward but technically challenging. The crucial obstacle



**Figure 4.** The error of the helium ground-state energy computed with the Hylleraas expansion and a conventional CI wave function. The Hylleraas wave function (eq S6) with all terms  $k + l + m \leq 2L_{\max}$  included. The orbital exponent  $\zeta$  was fixed at 1.8149, the optimal value for the original 3-term Hylleraas wave function in eq S2.<sup>37</sup> CI expansions were computed<sup>44</sup> with the method of Brown and Fontana<sup>45</sup> utilizing one-particle basis sets of modified hydrogenic orbitals with angular momentum up to  $L_{\max}$  and principal quantum number up to  $L_{\max} + 1$ , parametrized by a single orbital exponent that was nonlinearly optimized for each wave function.<sup>45</sup>

is the high dimension of the required integrals. Therefore, the explicitly correlated wave functions have been primarily used in high-precision atomic and molecular physics. Only with the recent developments of R12 methods have explicitly correlated methods become applicable to general molecules. While the R12 methods are the primary focus of this Review, we will start with a brief historical tour of the explicitly correlated methodology; for an in-depth exposé, interested readers are referred to a recent book.<sup>10</sup>

### 3.1. Explicitly Correlated Wave Functions for Two-Electron Systems

The wave functions of Hylleraas for helium atom that we discussed in section 2.6 can be easily generalized to attain high precision. A general Hylleraas-type wave function for an S state of a two-electron atom is expanded linearly in terms of nonnegative integer powers of  $r_{12}$ ,  $(r_1 + r_2)$ , and  $(r_1 - r_2)$ , with the orbital exponent as the only nonlinear parameter:

$$\Psi(r_1, r_2, r_{12}) = \sum_{klm} c_{klm} e^{-\zeta(r_1 + r_2)} (r_1 + r_2)^k (r_1 - r_2)^l r_{12}^m \quad (56)$$

where  $l$  must be even/odd for singlet/triplet states. Schwartz generalized eq 56 to include half-integer values of  $k$  and  $m$ ,<sup>41,42</sup> and Kinoshita extended it to allow negative integer values of  $k$  and  $m$ .<sup>33,43</sup> Nanohartree accuracy with Kinoshita expansion can be easily achieved using a few hundred terms. All Hylleraas-type expansions converge very rapidly as higher values of  $klm$  are included; this convergence is much more rapid than that of CI wave functions, which can be represented in the form of eq 56 with even values of  $m$  only. This is clearly illustrated in Figure 4 that compares the error of the Hylleraas expansion in eq 56 relative to that of a conventional CI wave function.

The error of Hylleraas expansion, especially for excited states, can be further decreased by introducing several orbital exponents.<sup>46,47</sup> The Hylleraas approach is also a precursor to

related, even more compact expansions by Pekeris,<sup>48</sup> Thakkar,<sup>49</sup> and others. Last, we should note that the best estimate of He ground-state energy at the moment,  $-2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,404\,446\,696\,924$ , was obtained with the explicitly correlated free Iterative-Complement-Interaction (ICI) wave function of Nakatsuji et al.,<sup>50</sup> which can be viewed as a wave function composed of terms that are produced by repeatedly applying the Hamiltonian to a small trial wave function, and regularizing each term.

The explicit dependence of the wave function on the inter-electronic distance was also key to early accurate wave functions for the hydrogen molecule by James and Coolidge. They used a 13-term explicitly correlated expansion to compute the ground-state energy accurate to 1 mE<sub>h</sub>.<sup>32</sup> The James–Coolidge wave function does not, however, describe the wave function correctly in the dissociation limit; it was later generalized by Kołos and Wolniewicz<sup>51</sup> to yield some of the most accurate expansions known for the hydrogen molecule, capable of nanohartree accuracy.<sup>52</sup>

### 3.2. Explicitly Correlated Wave Functions for $n$ -Electron Systems

Application of explicitly correlated techniques to molecular systems with more than two electrons faces one basic challenge: the need to evaluate numerous and expensive many-electron integrals. Even if we restrict each  $n$ -electron basis function to depend on one of the interelectronic distances only, up to four-electron integrals are necessary. Dealing with these integrals is the central technical challenge in working with the explicitly correlated wave functions. Over the years, the following methods have been pursued:

- exact evaluation of integrals is possible for atoms or for certain types of explicitly correlated basis functions; for example, explicitly correlated Gaussian functions allow analytic evaluation of integrals for molecules with any number of electrons.<sup>53</sup>

- similarity transformation of the Hamiltonian to eliminate the Coulomb singularities analytically (transcorrelated method);<sup>54,55</sup> the resulting Hamiltonian is more complicated and includes three-electron terms, but its wave functions are cusp-less and thus can be represented efficiently by Slater determinants.
- weak orthogonality functionals of Szalewicz et al. can be used to avoid some high-dimensional integrals.<sup>56,57</sup>
- stochastic evaluation is used in variational Quantum Monte Carlo (QMC) methods to evaluate  $n$ -electron integrals; somewhat related to variational QMC are diffusion or other “true” QMC methods,<sup>58</sup> and Nakatsuji’s local Schrödinger equation (LSE) method.<sup>59</sup>
- resolution-of-the-identity (RI) is used in R12 methods<sup>39</sup> to reduce three- and four-electron integrals to two-electron integrals only.

In this section, we will highlight how some of these methods were employed in historical predecessors of R12 methods. The use of RI in R12 methods will be discussed in section 4.2.

**3.2.1. Hylleraas-CI Method** The Hylleraas-CI wave function<sup>60</sup> is expanded as a linear combination of  $n$ -electron basis functions composed from a set of  $M$  standard Slater determinants (or CSFs)  $\Phi_m$  premultiplied by a nonnegative integer power of  $r_{ij}$ :

$$\Psi = \sum_{k=0}^{k_{\max}} \sum_m^M c_{m,k} \sum_{i < j}^n r_{ij}^k \Phi_m \quad (57)$$

For  $k_{\max} = 0$ , the Hylleraas-CI wave function is equivalent to the conventional CI. Terms with  $k = 1$  introduce electron–electron cusps and are most important after  $k = 0$ . Thus, setting  $k_{\max} = 1$  can already produce a reasonable wave function and was often used in practice.

At most, only one  $r_{ij}$  appears in individual term in eq 57, whereas the most straightforward generalization of the Hylleraas wave function to  $n$ -electron systems would introduce linked products  $r_{ij}r_{jk}$ ,  $r_{ij}r_{jk}r_{kl}$ , etc. The resulting matrix elements in the Hylleraas-CI method include up to four-electron integrals only, which is a significant improvement over  $n$ -electron integrals of the generalized Hylleraas method. More importantly, these integrals can be computed analytically for atoms and numerically for molecules. The number of such integrals and their expense are dramatically greater than in conventional CI calculations.

The Hylleraas-CI method has been applied successfully to systems with as many as 10 electrons.<sup>61</sup> Most applications, however, have been limited to extremely accurate computations on few-electron atoms (He,<sup>62</sup> Li,<sup>63</sup> Be<sup>64</sup>), because the expense of numerical integration in molecules with three and more electrons seemingly outweighs possible benefits.<sup>65</sup>

**3.2.2. Explicitly Correlated Gaussian Methods.** Boys<sup>66</sup> and Singer<sup>67</sup> noted that the use of Gaussian explicitly correlated basis functions (known as Gaussian geminals for two electrons) leads to many-electron integrals, which can be evaluated analytically for molecules.<sup>53</sup> A primitive spherical Gaussian geminal:

$$g_k(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\alpha_{1k}|\mathbf{r}_1 - \mathbf{A}_k|^2 - \alpha_{2k}|\mathbf{r}_2 - \mathbf{B}_k|^2 - \gamma_k r_{12}^2) \quad (58)$$

can be viewed as a product of two s-type Gaussians and a Gaussian correlation factor  $\exp(-\gamma_k r_{12}^2)$ . Although Gaussian geminals do not satisfy the cusp condition (eq 44), a linear combination of Gaussian geminals can efficiently approximate the shape of the electronic wave function near the electron cusp due

to the explicit dependence on the interelectronic distance; this is similar to how contracted one-electron Gaussian functions approximate cusped orbital shapes near the nuclei. The Gaussian geminal is a special (two-electron) case of the Exponentially Correlated Gaussian (ECG) function, whose spatial part in Boys form<sup>66</sup> reads:

$$\Phi_k(\mathbf{r}_1 \dots \mathbf{r}_n) = \exp\left(-\sum_{i=1}^n \alpha_{k,i} |\mathbf{r}_i - \mathbf{C}_{k,i}|^2 - \sum_{i < j} \gamma_{k,ij} |\mathbf{r}_i - \mathbf{r}_j|^2\right) \quad (59)$$

Modern variational calculations on systems with more than four electrons usually restrict each  $n$ -electron basis function to at most one  $r_{ij}$ ,<sup>68</sup> in complete analogy to Hylleraas-CI (i.e., for a given  $k$  only one  $\gamma_{k,ij}$  in eq 59 is nonzero). The resulting matrix elements include up to four-electron integrals only. Nonfactorizable  $n$ -electron integrals must be computed in the absence of such restrictions, which is expensive but possible.<sup>69</sup>

ECGs have been traditionally used in accurate variational computations on two- to four-electron systems.<sup>70</sup> For example, a 2400-term ECG wave function for the helium dimer produced the energy accurate to 0.1  $\mu E_h$ . The main difficulty with ECG wave functions is the need to optimize not only the linear expansion coefficient but also the nonlinear parameters of each  $\Phi_k$  ( $\alpha_{k,i}$ ,  $\mathbf{C}_{k,i}$ , and  $\gamma_{k,ij}$ , a total of  $n(n+7)/2$  parameters for a molecule without special symmetry).<sup>49,71</sup>

ECGs can also be used to represent molecular wave functions.<sup>69</sup> Using explicitly correlated basis functions is essential in such computations because the molecular wave function must be invariant (up a phase factor) with respect to translations; therefore, basis functions should depend exclusively on distances between the particles.

**3.2.3. Many-Body Gaussian Geminal Methods.** Explicitly correlated Gaussians have been also used in accurate many-body computations. Consider the standard coupled-cluster ansatz:

$$|\Psi\rangle = e^{\hat{T}}|0\rangle \quad (60)$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_k \quad (61)$$

$$\hat{T}_1 = \sum_i^n \hat{t}_1(\mathbf{r}_i) \quad (62)$$

$$\hat{T}_2 = \sum_{i < j}^n \hat{t}_2(\mathbf{r}_i, \mathbf{r}_j), \text{ etc.} \quad (63)$$

Cluster operators  $\hat{t}_1, \hat{t}_2$  are defined in terms of cluster functions  $\tau_i, \tau_{ij}$ :

$$\begin{aligned} \hat{t}_1(\mathbf{r}) &\equiv |\tau_i(\mathbf{r})\rangle\langle\phi_i(\mathbf{r})| \\ \hat{t}_2(\mathbf{r}, \mathbf{r}') &\equiv |\tau_{ij}(\mathbf{r}, \mathbf{r}')\rangle\langle\phi_i(\mathbf{r})\phi_j(\mathbf{r}')|, \text{ etc.} \end{aligned} \quad (64)$$

For example, the effect of  $\hat{t}_1$  is to substitute orbital  $\phi_i$  occupied in the reference wave function  $|0\rangle$  with one-particle cluster function  $\tau_i$ . In the coupled-cluster singles and doubles (CCSD) model, only  $\hat{T}_1$  and  $\hat{T}_2$  are included.

In the conventional CCSD method, each cluster function is expanded in terms of products of virtual orbitals (i.e., orbitals not present and orthogonal to the occupied orbitals in  $|0\rangle$ ):

$$|\tau_i\rangle = \sum_a t_a^i |\phi_a\rangle \quad (65)$$

$$|\tau_{ij}\rangle = \sum_{a < b} t_{ab}^{ij} |\phi_a\phi_b\rangle \quad (66)$$

where  $t_a^i$  and  $t_{ab}^{ij}$  are undetermined singles and doubles amplitudes. In Gaussian geminal-based coupled-cluster methods, two-electron cluster functions  $\tau_{ij}$  are expanded:

$$|\tau_{ij}(\mathbf{r}_1, \mathbf{r}_2)\rangle = \hat{Q}(1, 2) \sum_k^K t_k^{ij} |g_{ijk}(\mathbf{r}_1, \mathbf{r}_2)\rangle \quad (67)$$

where  $g_{ijk}$  are geminal basis functions specified by eq 58,  $K$  is the number of geminals  $g_{ijk}$  per pair function  $\tau_{ij}$ , and  $t_k^{ij}$  are undetermined geminal amplitudes. The role of the projector  $\hat{Q}(1, 2)$  is to make sure that  $\tau_{ij}$  is strongly orthogonal to products of occupied orbitals:

$$\hat{Q}(1, 2) = (1 - \hat{O}(1))(1 - \hat{O}(2)) \quad (68)$$

$$\hat{O}(1) = \sum_i^n |\phi_i\rangle\langle\phi_i| \quad (69)$$

The strong orthogonality condition ensures that  $\hat{t}_2$  produces “true” two-electron excitations relative to the reference wave function and not simply one-electron excitations coupled with some rotation of occupied orbitals.

Note that the Gaussian geminal coupled-cluster wave function formally includes in its exponential expansion terms that depend on several, up to  $n/2$ , interelectronic distances via terms like  $g_i(\mathbf{r}_1\mathbf{r}_2)g_j(\mathbf{r}_3\mathbf{r}_4)$ , etc. (terms like  $g_i(\mathbf{r}_1\mathbf{r}_2)g_j(\mathbf{r}_2\mathbf{r}_3)$  do not appear). Using a linear expansion in terms of ECGs that depend on up to  $n/2$  interelectronic distances would require evaluation of up to  $n$ -electron integrals. In the CC framework, however, only five-electron integrals appear in the CCSD version of the method (only four-electron integrals are necessary to compute MP2 energy with this approach). This is a substantial simplification and allows one to extend coupled-cluster Gaussian geminal framework to systems with more than four electrons.

The need to evaluate four- and five-electron integrals and to perform nonlinear optimization of geminal parameters are significant challenges. Several workarounds have been explored. The weak orthogonality approach, proposed by Szalewicz et al.,<sup>56,57</sup> reduced the dimensionality of the prerequisite integrals by relaxing the strong orthogonality requirement on the geminal functions at the cost of including a penalty function in the Hylleraas functional of MP2 energy or the CCSD Lagrangian. There is some evidence that in the context of R12-like methods modified weak orthogonality functionals of Tew et al. should be used.<sup>72</sup>

To reduce the cost and improve robustness of the optimization procedure for nonlinear parameters, a variety of approaches have been tried.<sup>73,74</sup> Despite the substantial progress, the high computational cost of nonlinear optimization and integral evaluation has prevented applications to molecules with more than 10 electrons;<sup>75</sup> most benchmark applications were for systems with up to four electrons (He, H<sub>2</sub>, Be, LiH).<sup>76</sup>

**3.2.4. Transcorrelated Method.** The idea of the transcorrelated method of Boys and Handy<sup>54,55</sup> is to use similarity transformation to produce a Hamiltonian free of electron–electron singularities:

$$\hat{H}_G = e^{-\hat{G}}\hat{H}e^{\hat{G}} \quad (70)$$

$$\hat{G} = \sum_{i < j} f(\mathbf{r}_i, \mathbf{r}_j) \quad (71)$$

where  $f_{ij} \equiv f(\mathbf{r}_i, \mathbf{r}_j)$  can be a very general function.<sup>77</sup> The Hausdorff expansion of the non-Hermitian  $\bar{H}$ :

$$\bar{H} = \hat{H} + [\hat{T}, \hat{G}] + \frac{1}{2!}[[\hat{T}, \hat{G}], \hat{G}] + \dots \quad (72)$$

truncates exactly after the second term due to the multiplicative nature of  $\hat{G}$ . Therefore,  $\bar{H}$  contains only up to three-electron terms, of type  $(\nabla_i f_{ij}) \cdot (\nabla_i f_{ik})$ .

Handy chose the following form for  $f_{ij}$ :<sup>78</sup>

$$f_{ij} = \sum_k c_k g_k(\mathbf{r}_i, \mathbf{r}_j) + \sum_\mu d_\mu \phi_\mu(\mathbf{r}_i) \quad (73)$$

where  $g_k$  is a Gaussian geminal of eq 58, and  $\phi_\mu$  is an atomic orbital. The energy is obtained from

$$E = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle \quad (74)$$

where  $\Phi_0$  is a Slater determinant of MOs, which are also optimized. Handy was able to apply the transcorrelated method to several small systems (as large as H<sub>2</sub>O) and obtain good results using a very small number of parameters.<sup>78</sup>

Ten-no has applied the transcorrelated method setting  $\hat{G}$  to a linear combination of Gaussian Geminals.<sup>79</sup>  $\hat{G}$  was optimized to cancel electron repulsion in the vicinity of the coalescence point. Initial applications to small systems (Ne, H<sub>2</sub>O) were promising but highlighted the challenge of choosing a universal operator  $\hat{G}$  and the growing importance of three-body terms in the transformed Hamiltonian.<sup>79,80</sup> A recent report by Luo et al. suggests that it may be possible to obtain high-quality results with the transcorrelated method.<sup>81</sup>

## 4. CORE TECHNOLOGY OF MODERN R12 METHODS

The groundbreaking idea of Kutzelnigg that led to modern R12 methods was to factorize all of the difficult many-electron integrals into one- and two-electron integrals by inserting the resolution of the identity (RI), and use the partial wave analysis to show how to do this accurately.<sup>39</sup> Starting with the MP2-R12 method, Kutzelnigg, Klopper, and co-workers have systematically introduced the “original” R12 technology into all mainstream wave function methods. Unfortunately, the original technology required the use of large basis sets and was not scalable to larger systems. Thus, the attention of researchers between 2002 and 2006 focused on making the R12 technology more practical. The plethora of improvements that were introduced during this period are not easy to navigate, even for a specialist; thankfully, some consolidation of ideas has occurred. Although there is still some variation in formalisms and nomenclature used by different developers of R12 methods, a consensus set of formalisms, what we will call the modern R12 technology, has mostly crystallized.<sup>82–85</sup>

In this section, we will describe the essential features of the modern R12 technology using the MP2-R12 method as an example. The same basic technology will apply to coupled-cluster methods (section 5) and multiconfiguration R12 wave functions (section 6).

### 4.1. Derivation of MP2-R12 Equations

The first-order Møller–Plesset wave function is obtained by minimizing Hylleraas functional for the second-order

MP energy:

$$H^{(2)}(\psi^{(1)}) = \langle \psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \psi^{(1)} \rangle + 2 \langle \psi^{(1)} | \hat{H}^{(1)} | \psi^{(0)} \rangle \quad (75)$$

where the intermediate normalization was assumed. The zeroth-order MP Hamiltonian is the Fock operator. The principal difference between the standard MP2 and MP2-R12 methods is the form of the first-order wave function; the former includes only conventional doubly excited determinants:<sup>86</sup>

$$|\psi_{\text{MP}}^{(1)}\rangle = \sum_{i < j, a < b} t_{ab}^{ij} |ij\rangle \quad (76)$$

The MP1-R12 wave function also includes explicitly correlated (geminal) functions:

$$|\psi_{\text{MP-R12}}^{(1)}\rangle = |\psi_{\text{MP}}^{(1)}\rangle + \sum_{i < j, x < y} t_{xy}^{ij} |ij\rangle^{xy} \quad (77)$$

The geminal basis functions are quasi-double excitations with respect to the reference:

$$|ij\rangle^{xy} = \frac{1}{2} \bar{R}_{\alpha\beta}^{xy} \tilde{a}_{ij}^{\alpha\beta} |\psi^{(0)}\rangle \quad (78)$$

where  $\bar{R}_{\alpha\beta}^{xy}$  are matrix elements of the explicitly correlated geminal factor  $f(r_{12})$  projected by  $\hat{Q}_{12}$ :

$$R_{\alpha\beta}^{xy} = \langle \alpha\beta | \hat{Q}_{12} f(r_{12}) | xy \rangle \quad (79)$$

The purpose of the projector  $\hat{Q}_{12}$  is to enforce strong orthogonality of geminal functions  $|ij\rangle^{xy}$ , that is, their orthogonality to any single excitations; usually  $\hat{Q}_{12}$  also ensures orthogonality to the standard doubly excited determinants  $|ij\rangle^{ab}$ . The most common choice<sup>83</sup> is

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1 \hat{V}_2 \quad (80)$$

but other  $\hat{Q}_{12}$  values have also been considered.<sup>87,88</sup> We also note that the geminal-generating orbitals  $x$  and  $y$  are typically the (active) occupied orbitals, but other choices have been considered.<sup>89,90</sup>

Because many readers will be familiar with the standard MP2 formalism that involves one-step inversion of the zeroth-order Hamiltonian, we will first consider how to obtain the MP2-R12 energy in the same manner. The Hylleraas functional is formally minimized by the following first-order wave function:

$$|\psi^{(1)}\rangle = -\hat{P}^{(1)}(\hat{H}^{(0)} - E^{(0)})^{-1}\hat{P}^{(1)}\hat{H}^{(1)}|\psi^{(0)}\rangle \quad (81)$$

where  $\hat{P}^{(1)}$  projects on the first-order interacting space: in the case of MP method, it includes doubly excited determinants  $|ij\rangle^{ab}$  only, whereas in the case of MP-R12, it also includes the geminal functions  $|ij\rangle^{xy}$ . Consider the matrix representation of eq 81 in the MP2-R12 method:

$$\begin{pmatrix} T_D \\ T_R \end{pmatrix} = - \begin{pmatrix} \mathbf{H}_{DD}^{(0)} & \mathbf{H}_{DR}^{(0)} \\ \mathbf{H}_{RD}^{(0)} & \mathbf{H}_{RR}^{(0)} \end{pmatrix}^{-1} \begin{pmatrix} \mathbf{H}_D^{(1)} \\ \mathbf{H}_R^{(1)} \end{pmatrix} \quad (82)$$

where  $T_D$  and  $T_R$  are first-order coefficients of conventional doubly excited determinants and their geminal counterparts

defined in eqs 76 and 77, respectively. Whereas  $\mathbf{H}_{DD}^{(0)}$  is diagonal in canonical orbitals and is easily inverted in MP2 method, the zeroth-order matrix in MP2-R12 cannot be directly inverted because  $\mathbf{H}_{DR}^{(0)} = (\mathbf{H}_{RD}^{(0)})^\dagger$  is nonzero; its inversion by block-diagonalization is possible as follows.

Let us introduce a matrix:

$$\mathbf{Y} = -(\mathbf{H}_{DD}^{(0)})^{-1}\mathbf{H}_{DR}^{(0)} \quad (83)$$

It is easy to verify that the transformation matrix:

$$\begin{pmatrix} \mathbf{1} & \mathbf{Y} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \quad (84)$$

block-diagonalizes the zeroth-order Hamiltonian matrix in eq 82:

$$\begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{Y}^\dagger & \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{H}_{DD}^{(0)} & \mathbf{H}_{DR}^{(0)} \\ \mathbf{H}_{RD}^{(0)} & \mathbf{H}_{RR}^{(0)} \end{pmatrix} \begin{pmatrix} \mathbf{1} & \mathbf{Y} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} = \begin{pmatrix} \mathbf{H}_{DD}^{(0)} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{B}} \end{pmatrix} \quad (85)$$

where

$$\bar{\mathbf{B}} \equiv \mathbf{H}_{RR}^{(0)} - \mathbf{Y}^\dagger \mathbf{H}_{DD}^{(0)} \mathbf{Y} = \mathbf{H}_{RR}^{(0)} - \mathbf{H}_{RD}^{(0)} (\mathbf{H}_{DD}^{(0)})^{-1} \mathbf{H}_{DR}^{(0)} \quad (86)$$

Transforming eq 82 yields

$$\begin{pmatrix} T_D \\ T_R \end{pmatrix} = - \begin{pmatrix} \mathbf{1} & \mathbf{Y} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \begin{pmatrix} (\mathbf{H}_{DD}^{(0)})^{-1} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{B}}^{-1} \end{pmatrix} \begin{pmatrix} \mathbf{H}_D^{(1)} \\ \bar{\mathbf{V}} \end{pmatrix} \quad (87)$$

where

$$\bar{\mathbf{V}} \equiv \mathbf{H}_R^{(1)} - \mathbf{Y}^\dagger \mathbf{H}_D^{(1)} = \mathbf{H}_R^{(1)} - \mathbf{H}_{RD}^{(0)} (\mathbf{H}_{DD}^{(0)})^{-1} \mathbf{H}_D^{(1)} \quad (88)$$

Matrix  $\mathbf{H}_{DD}^{(0)}$  is diagonal and trivial to invert, whereas  $\bar{\mathbf{B}}$  is block-diagonal and can be inverted. In practice, the inversion is avoided in favor of solving a linear system, directly or iteratively. This linear system is often poorly conditioned and/or near-singular (e.g., see ref 91). Thus, it is best to avoid the geminal coefficient optimization altogether and use the SP ansatz of Ten-no (also known as the diagonal orbital-invariant) that is discussed in section 4.4.

The final first-order MP-R12 wave function is expressed as a sum of conventional, R12, and ‘‘coupling’’ terms, respectively:

$$\begin{pmatrix} T_D \\ T_R \end{pmatrix} = - \begin{pmatrix} (\mathbf{H}_{DD}^{(0)})^{-1} \mathbf{H}_D^{(1)} \\ \mathbf{0} \end{pmatrix} - \begin{pmatrix} \mathbf{0} \\ \bar{\mathbf{B}}^{-1} \bar{\mathbf{V}} \end{pmatrix} + \begin{pmatrix} \mathbf{Y} \bar{\mathbf{B}}^{-1} \bar{\mathbf{V}} \\ \mathbf{0} \end{pmatrix} \quad (89)$$

Although the standard doubles and geminal functions are orthogonal to one another, their coefficients are coupled via the off-diagonal  $\mathbf{H}_{DR}^{(0)}$  block of the zeroth-order Hamiltonian. This zeroth-order coupling is relatively weak and quickly vanishes as the basis set is enlarged.

The second-order energy is represented as a sum of the conventional MP2 energy and the R12 correction term:

$$E_{\text{MP} - \text{R12}}^{(2)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(1)} \rangle = \begin{pmatrix} \mathbf{H}_D^{(1)} \\ \mathbf{H}_R^{(1)} \end{pmatrix}^{\dagger} \begin{pmatrix} \mathbf{T}_D \\ \mathbf{T}_R \end{pmatrix} \\ = -(\mathbf{H}_D^{(1)})^{\dagger} (\mathbf{H}_{DD}^{(0)})^{-1} \mathbf{H}_D^{(1)} - \bar{\mathbf{V}}^{\dagger} \bar{\mathbf{B}}^{-1} \bar{\mathbf{V}} = E_{\text{MP2}}^{(2)} + E_{\text{R12}}^{(2)} \quad (90)$$

Equation 90 is exact. As compared to the conventional MP2 method, it involves new matrices:

$$\mathbf{H}_R^{(1)} : \langle ij | \hat{H}^{(1)} | \psi^{(0)} \rangle \equiv V_{ij}^{xy} \quad (91)$$

$$\mathbf{H}_{RR}^{(0)} : \langle xy | \hat{H}^{(0)} - E^{(0)} | ij^{wz} \rangle = \langle xy | \hat{H}^{(0)} | ij^{wz} \rangle - E^{(0)} \langle xy | ij^{wz} \rangle \\ \equiv B_{xy}^{wz} - (F_i^x + F_j^y) X_{xy}^{wz} \equiv (\tilde{B}^{(ij)})_{xy}^{wz} \quad (92)$$

$$\mathbf{H}_{RD}^{(0)} : \langle xy | \hat{H}^{(0)} - E^{(0)} | ij^{ab} \rangle = \langle xy | \hat{H}^{(0)} | ij^{ab} \rangle \equiv C_{xy}^{ab} \quad (93)$$

which are formulated in terms of four special intermediates of R12 theory, arranged in the order of difficulty:

$$B_{xy}^{ow} \equiv \langle xy | \hat{\gamma}_{12} \hat{F}_{12} \hat{\gamma}_{12} | ow \rangle \quad (94)$$

$$X_{xy}^{ow} \equiv \langle xy | \hat{\gamma}_{12}^{\dagger} \hat{\gamma}_{12} | ow \rangle \quad (95)$$

$$V_{ij}^{xy} \equiv \langle ij | \frac{1}{r_{12}} \hat{\gamma}_{12} | xy \rangle \quad (96)$$

$$C_{xy}^{ab} \equiv \langle xy | \hat{\gamma}_{12} \hat{F}_{12} | ab \rangle \quad (97)$$

where

$$\hat{\gamma}_{12} \equiv \hat{Q}_{12} f(r_{12}) \quad (98)$$

Intermediate *B* involves up to four-electron integrals, intermediates *X* and *V* up to three-electron integrals, and *C* is a two-electron integral. These integrals can be evaluated analytically if the correlation factor is Gaussian. This is the approach of Persson and Taylor,<sup>92</sup> who also used the Weak Orthogonality Functional (WOF) to avoid four-electron integrals. The computational complexity of such calculations is high.<sup>93</sup> In the next two sections, we will consider how the R12 technology makes possible fast and accurate evaluation of these intermediates.

#### 4.2. Approximate Treatments of Many-Electron Integrals

Let us consider matrix *V* expressed in opposite-spin orbitals (same-spin expressions can be obtained by antisymmetrization of the bra or the ket). By expanding the strong-orthogonality projector, we obtain

$$V_{ij}^{xy} = \langle ij | \frac{1}{r_{12}} (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1 \hat{V}_2) f(r_{12}) | xy \rangle \\ = \langle ij | \frac{f(r_{12})}{r_{12}} | xy \rangle - \langle ij | \frac{1}{r_{12}} \hat{O}_1 f(r_{12}) | xy \rangle - \langle ij | \frac{1}{r_{12}} \hat{O}_2 f(r_{12}) | xy \rangle \\ + \langle ij | \frac{1}{r_{12}} \hat{O}_1 \hat{O}_2 f(r_{12}) | xy \rangle - \langle ij | \frac{1}{r_{12}} \hat{V}_1 \hat{V}_2 f(r_{12}) | xy \rangle \quad (99)$$

$$+ \langle ij | \frac{1}{r_{12}} \hat{O}_1 \hat{O}_2 f(r_{12}) | xy \rangle - \langle ij | \frac{1}{r_{12}} \hat{V}_1 \hat{V}_2 f(r_{12}) | xy \rangle \quad (100)$$

The first term is a two-electron integral that can be evaluated in Gaussian basis sets using standard technologies developed for the electron repulsion integrals. Each of the last two terms is a finite sum of products of two-electron integrals, for example:

$$\langle ij | \frac{1}{r_{12}} \hat{V}_1 \hat{V}_2 f(r_{12}) | xy \rangle \\ = \sum_{ab} \langle ij | \frac{1}{r_{12}} | ab \rangle \langle ab | f(r_{12}) | xy \rangle = g_{ij}^{ab} r_{ab}^{xy} \quad (101)$$

However, the second and third terms involve sums of three-electron integrals:

$$\langle ij | \frac{1}{r_{12}} \hat{O}_1 f(r_{12}) | xy \rangle = \sum_m \langle ij m | \frac{1}{r_{12}} f(r_{23}) | myx \rangle \quad (102)$$

$$\langle ij | \frac{1}{r_{12}} \hat{O}_2 f(r_{12}) | xy \rangle = \sum_m \langle ij m | \frac{1}{r_{12}} f(r_{13}) | xmy \rangle \quad (103)$$

These expensive integrals can be reduced to sums of products of two-electron integrals by inserting the approximate resolution of the identity:

$$1 \approx \hat{P}' = \sum_{p'} | p' \rangle \langle p' | \quad (104)$$

into each integral:

$$\langle ij | \frac{1}{r_{12}} \hat{O}_1 f(r_{12}) | xy \rangle \stackrel{\text{RI}}{\approx} \langle ij | \frac{1}{r_{12}} \hat{O}_1 \hat{P}'_2 f(r_{12}) | xy \rangle \quad (105)$$

$$= \sum_{mp'} \langle ij | \frac{1}{r_{12}} | mp' \rangle \langle mp' | f(r_{12}) | xy \rangle \quad (106)$$

$$= g_{ij}^{mp'} r_{mp'}^{xy} \quad (107)$$

Approximation 107 becomes exact in atoms when the RI basis  $\{|p'\rangle\}$  is saturated up to angular momentum  $3L_{\text{occ}}$ , with  $L_{\text{occ}}$  the maximum angular momentum of the occupied orbitals. Although this statement cannot be extended to molecules due to the lack of spherical symmetry, in practice the same guidelines for the RI basis set may be used.

As a note of caution, the use of RI approximation in R12 method does not mean that all terms can be treated by RI. For example, the integral of  $f(r_{12})/r_{12}$  operator in the *V* intermediate must be evaluated in closed form, without RI, because its finite partial-wave expansion has a  $\mathcal{O}(L+1)^{-3}$  error and approximating it via RI would defeat the purpose of the R12 method. All special intermediates of R12 theory, except *C*, include at least one such integral.

Most implementations of R12 methods use Gaussian basis sets for the resolution of the identity. In the early work expansion, eq 104 utilized the orthonormal orbitals of the orbital basis set (OBS);<sup>82</sup> Klopper and Samson later introduced a separate auxiliary basis set (ABS) for this purpose.<sup>88</sup> The ABS basis must, however, include OBS for the RI approximation to be accurate.<sup>83</sup> This issue is avoided in the complementary ABS (CABS)



approach,<sup>83</sup> in which  $\hat{Q}_{12}$  of eq 80 is rewritten as<sup>83</sup>

$$\hat{Q}_{12} = 1 - \hat{O}_1 \hat{P}_2'' - \hat{P}_1'' \hat{O}_2 - \hat{P}_1 \hat{P}_2 \quad (108)$$

where  $\hat{P}'' \equiv 1 - \hat{P}$  is the projector onto the orthogonal complement to OBS. Instead of approximating the identity via eq 104, CABS is used to approximate the  $\hat{P}''$  projector directly:

$$\hat{P}'' \stackrel{\text{CABS}}{\approx} \sum_{a'} |a'\rangle\langle a'| \quad (109)$$

Thus, the  $V$  matrix in CABS approximation becomes

$$V_{ij}^{xy} = \langle ij | \frac{1}{r_{12}} (1 - \hat{O}_1 \hat{P}_2'' - \hat{P}_1'' \hat{O}_2 - \hat{P}_1 \hat{P}_2) f(r_{12}) | xy \rangle \quad (110)$$

$$\stackrel{\text{CABS}}{\approx} (gr)_{ij}^{xy} - g_{ij}^{ma'} r_{ma'}^{xy} - g_{ij}^{a'm} r_{a'm}^{xy} - g_{ij}^{pq} r_{pq}^{xy} \quad (111)$$

Just like the straight RI approximation, the CABS approximation also becomes exact for atoms when CABS is saturated to  $3L_{\text{occ}}$ .

Atom-centered RI basis sets are convenient and not too burdensome for p-elements, but require very high angular momenta for heavy elements: to cover the entire Periodic Table, functions of angular momentum 9 will be required. The angular momentum requirement could be relaxed somewhat by a clever rearrangement of the three-electron integrals prior to the RI application, as suggested by Ten-no and Manby:<sup>94</sup>

$$\begin{aligned} & \langle ij | \frac{1}{r_{12}} f(r_{23}) | mlk \rangle \\ & \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_m^*(\mathbf{r}_3) \frac{1}{r_{12}} f(r_{23}) \phi_m(\mathbf{r}_1) \phi_l(\mathbf{r}_2) \phi_k(\mathbf{r}_3) \\ & \stackrel{\text{RI}}{\approx} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \phi_i^*(\mathbf{r}_1) \phi_m(\mathbf{r}_1) \frac{1}{r_{12}} \hat{P}' f(r_{23}) \phi_j^*(\mathbf{r}_2) \phi_l(\mathbf{r}_2) \phi_m^*(\mathbf{r}_3) \phi_k(\mathbf{r}_3) \\ & = \sum_{p'} \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_m^*(\mathbf{r}_1) \phi_m(\mathbf{r}_1) \frac{1}{r_{12}} \phi_{p'}(\mathbf{r}_2) \\ & \quad \times \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_m^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \phi_{p'}^*(\mathbf{r}_2) f(r_{12}) \phi_k(\mathbf{r}_1) \phi_l(\mathbf{r}_2) \\ & \equiv \sum_{p'} g_{mj}^{1p'} r_{m(jp')}^{kl} \quad (112) \end{aligned}$$

Perhaps the most promising approach is to evaluate the three-electron integrals by numerical quadratures (QD).<sup>95,96</sup> The QD approach resembles the RI approximation, eq 104, formulated in the basis set of grid points (delta functions). QD applied to eq 107 yields:

$$\begin{aligned} & \langle ij | \frac{1}{r_{12}} \hat{O}_1 f(r_{12}) | kl \rangle \\ & \stackrel{\text{QD}}{\approx} \sum_{m,g} \langle ij | \frac{1}{r_{12}} | m \delta(\mathbf{r}_2 - \mathbf{r}_g) \rangle w_g \langle m \delta(\mathbf{r}_2 - \mathbf{r}_g) | f(r_{12}) | kl \rangle \quad (113) \\ & = \sum_{m,g} \langle i | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_g|} | m \rangle \phi_j^*(\mathbf{r}_g) w_g \phi_l(\mathbf{r}_g) \langle m | f(|\mathbf{r}_1 - \mathbf{r}_g|) | k \rangle \quad (114) \end{aligned}$$

where  $g$  indexes grid points, with position  $\mathbf{r}_g$  and weight  $w_g$ . Whereas RI reduces the three-electron integrals in matrix  $V$  to four-center two-electron integrals, only three-center one-electron integrals appear in its QD formulation. The same efficient technology of 3-D grid construction from the molecular density-functional theory methods can be used here; its

drawback, however, is the number of grid points per atom is  $\mathcal{O}(10^4)$ . Significant optimizations along the lines of the pseudospectral method<sup>97</sup> should be possible. Another issue with the QD technology is that more complicated many-electron integrals of the R12 methods either require six-dimensional quadrature (hence computationally expensive) or must be combined with the CABS or RI approximation in an atom-centered basis.<sup>96</sup>

Matrices  $B$ ,  $X$ , and  $C$  can be treated in a similar spirit. The simplest of these is the zeroth-order “coupling” matrix  $C$ , which in CABS approximation becomes:

$$C_{ij}^{ab} \stackrel{\text{CABS}}{\equiv} r_{aa'}^{ij} F_b^{a'} + r_{a'b}^{ij} F_a^{a'} \quad (115)$$

Evaluation of  $X$  is essentially identical to that of  $V$ . The most complex intermediate is  $B$ , in which one encounters four-electron and other difficult three-electron integrals; its evaluation deserves its own section.

### 4.3. Evaluation of the Fock Matrix in the Geminal Basis

Currently there are two main approaches to evaluation of the  $B$  intermediate. These approaches, labeled B and C, are closely related and produce similar results. The main difference between the two is that approach B involves analytic evaluation of single commutators of the kinetic energy operators with the correlation factor, whereas approach C implicitly treats these terms by the resolution of the identity. Although there are reasons to prefer the numerical properties of approach B (approach C, for example, involves differences of two large terms which can cause loss of numerical precision), all available evidence suggests that approach C is technically somewhat simpler and as reliable as approach B.

Consider the following two integrals that occur in intermediate  $B$  upon expansion of the strong orthogonality projectors:

$$\langle pq | \hat{F}_1 f(r_{12}) | ow \rangle \quad (116)$$

$$\langle xy | f(r_{12}) \hat{T}_1 f(r_{12}) | ow \rangle \quad (117)$$

The first integral can be evaluated via the direct RI insertion (approach C):<sup>85</sup>

$$\begin{aligned} & \langle pq | \hat{F}_1 f(r_{12}) | ow \rangle \stackrel{\text{RI}}{\approx} \langle pq | \hat{F}_1 \hat{P}'_1 f(r_{12}) | ow \rangle \\ & = \sum_{p'} \langle p | \hat{F}_1 | p' \rangle \langle p' q | f(r_{12}) | ow \rangle = F_p^{p'} r_{p'q}^{ow} \quad (118) \end{aligned}$$

or using RI and the commutator trick (approach B):<sup>82,88</sup>

$$\begin{aligned} & \langle pq | \hat{F}_1 f(r_{12}) | ow \rangle \\ & = \langle pq | [\hat{F}_1, f(r_{12})] | ow \rangle + \langle pq | f(r_{12}) \hat{F}_1 | ow \rangle \\ & = \langle pq | [\hat{T}_1, f(r_{12})] | ow \rangle - \langle pq | [\hat{K}_1, f(r_{12})] | ow \rangle \\ & \quad + \langle pq | f(r_{12}) \hat{F}_1 | ow \rangle \\ & \stackrel{\text{RI}}{\approx} \langle pq | [\hat{T}_1, f(r_{12})] | ow \rangle - \langle pq | [\hat{K}_1, f(r_{12})] | ow \rangle \\ & \quad + \sum_{p'} \langle pq | f(r_{12}) | p' w \rangle \langle p' | \hat{F}_1 | o \rangle \\ & = [T, r]_{pq}^{ow} - [K, r]_{pq}^{ow} + r_{pq}^{p'w} F_p^o \quad (119) \end{aligned}$$

Note that the only parts of the (nonrelativistic) Fock operator that do not commute with  $f(r_{12})$  are the kinetic energy and exchange. Integrals of  $[\hat{T}_i, f(r_{12})]$  are evaluated analytically in approach B, whereas the exchange commutators are evaluated via the RI approximation.

Integral (eq 117) in both approaches is evaluated via a combination of analytic and RI methods:

$$\begin{aligned} & \langle xy|f(r_{12})\hat{T}_1 f(r_{12})|ow\rangle \\ &= \frac{1}{2}\langle xy|[f(r_{12}), [T_1, f(r_{12})]]|ow\rangle \\ &+ \frac{1}{2}\langle xy|f(r_{12})^2\hat{T}_1|ow\rangle + \frac{1}{2}\langle xy|\hat{T}_1 f(r_{12})^2|ow\rangle \\ &\approx \frac{1}{2}\langle xy|[f(r_{12}), [T_1, f(r_{12})]]|ow\rangle \\ &+ \frac{1}{2}\sum_{p'}\langle xy|f(r_{12})^2|p'w\rangle\langle p'|T_1|o\rangle \\ &+ \frac{1}{2}\sum_{p'}\langle x|\hat{T}_1|p'\rangle\langle p'y|f(r_{12})^2|ow\rangle \end{aligned} \quad (120)$$

The double commutator integrals and the  $f(r_{12})^2$  integrals are evaluated in closed form (without RI) in both approaches B and C.

For completeness, we also give the complete expression for intermediate *B* in approach C:

$$\begin{aligned} B_{xy}^{B^{ow}} &= [r, [T, r]]_{xy}^{ow} + \hat{S}_{xy, ow}[(\hat{r}^2)_{xy}^{p'w}(F + K)_{p'}^o \\ &+ (\hat{r}^2)_{xy}^{op'}(F + K)_{p'}^o] - \hat{r}_{xy}^{p'q}K_{p'}^{r'q'} - \hat{r}_{xy}^{p'm}F_{p'}^{r'm} - \hat{r}_{xy}^{ow} \\ &+ \hat{r}_{xy}^{mb'}F_{m'}^{nb'} - \hat{r}_{xy}^{pb}F_{p'}^{rb} - 2\hat{S}_{xy, ow}(\hat{r}_{xy}^{mb'}F_{m'}^{p'b'} + \hat{r}_{xy}^{a'b}F_{a'}^{qb}) \end{aligned} \quad (121)$$

In addition to standard Coulomb integrals, MP2-R12 and other R12 methods involve analytic integrals of the following two-electron operators:  $f(r_{12}), f(r_{12})/r_{12}, (f(r_{12}))^2, [f(r_{12}), [\hat{T}_1, f(r_{12})]]$ , and, in approach B,  $[T_1, f(r_{12})]$ . Higher-order R12 methods (e.g., CC-R12) will also require integrals of the  $(f(r_{12}))^2/r_{12}$  operator. Note that integrals over multiple distinct orbital spaces are involved; thus management of the MO-basis integrals is more complicated in R12 methods than in their non-R12 counterparts.

The basic R12 technology as described here can also be used to evaluate geminal matrix elements of other types of one- and two-electron operators, such as those found in relativistic methods<sup>98,99</sup> or in property computations.<sup>100</sup>

#### 4.4. Geminal Amplitudes Can Be Determined by the Cusp Conditions

The behavior of the exact wave function at the cusp is known analytically and can be used to predetermine the asymptotic values the geminal amplitudes. Near the cusp the behavior of the exact pair functions is linear in  $r_{12}$  and completely determined by the value at the coalescence and the relative angular momentum of the two electrons; the first-order wave function can be written for (natural-parity) singlet pairs and triplet pairs, respectively:

$$\psi_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}r_{12}\psi_{ij}^{(0)}(\mathbf{r}, \mathbf{r}) + \mathcal{O}(r_{12}^2) \quad (122)$$

$$\begin{aligned} \psi_{ij}^{(1)}(\mathbf{r}_1, \mathbf{r}_2) &= \frac{1}{4}r_{12}\sum_{m=-1}^1|Y_{1m}(\Omega_{12})\rangle\langle Y_{1m}(\Omega_{12})|\psi_{ij}^{(0)}(\mathbf{r}, \mathbf{r}) \\ &+ \mathcal{O}(r_{12}^2) \end{aligned} \quad (123)$$

These conditions are satisfied automatically by making the correlation factor depend on spin:

$$|ij\rangle = \frac{1}{2}\bar{\mathcal{C}}_{\alpha\beta}^{ij}\tilde{\alpha}^{\alpha\beta}|\psi^{(0)}\rangle \quad (124)$$

where

$$\mathcal{R}_{\alpha\beta}^{ij} \equiv \langle\alpha\beta|\hat{Q}_{12}f(r_{12})(\frac{1}{2}\hat{P}_0 + \frac{1}{4}\hat{P}_1)|ij\rangle \quad (125)$$

Projectors  $\hat{P}_0$  and  $\hat{P}_1$  project onto  $S = 0$  and  $S = 1$  spin-pair states:

$$\hat{P}_0 = |\alpha\beta\rangle_0\langle\alpha\beta|_0 \quad (126)$$

$$\hat{P}_1 = |\beta\beta\rangle\langle\beta\beta| + |\alpha\beta\rangle_1\langle\alpha\beta|_1 + |\alpha\alpha\rangle\langle\alpha\alpha| \quad (127)$$

with

$$|\alpha\beta\rangle_0 = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

$$|\alpha\beta\rangle_1 = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}$$

Note that each pair function now includes only one geminal function (compare eq 124 to eq 78).

Ten-no was first to propose this formulation under the name ‘‘SP ansatz’’.<sup>84</sup> It is relatively straightforward to incorporate the spin-projectors into the formulas for the R12 intermediates. It should be noted that the implementation of this approach for open-shell MP2-R12 with spin-unrestricted references leads to unusual integrals whose counterparts do not appear in the standard UMP2 method,<sup>101,102</sup> such as  $\langle I_{\alpha}\beta|f(r_{12})|J_{\beta}I_{\alpha}\rangle$  (where  $\alpha$  and  $\beta$  specify which spatial orbital is used; no spin functions are included).

#### 4.5. Correction of the Basis Set Error of the Reference Wave Function

In single reference methods (typically with the Hartree–Fock determinant as the reference), the total electronic energy separates into two components: the reference energy  $E_{\text{HF}}$  and the correlation energy  $E_{\text{corr}}$ . The error due to the finite basis set,  $\Delta E^{\text{BSIE}}$ , can also be split into two corresponding parts:  $\Delta E_{\text{HF}}^{\text{BSIE}}$  and  $\Delta E_{\text{corr}}^{\text{BSIE}}$ . The R12 methods have been very effective in reducing  $\Delta E_{\text{corr}}^{\text{BSIE}}$  by introducing the interelectronic distance into the wave function expansion. With  $E_{\text{corr}}$  quickly converging to CBS limits in R12 methods,  $\Delta E_{\text{HF}}^{\text{BSIE}}$  becomes the dominant source of error. Therefore, it becomes necessary to reduce  $\Delta E_{\text{HF}}^{\text{BSIE}}$  to achieve balanced accuracies.

In principle, a straightforward approach to decrease  $E_{\text{HF}}$  is to employ a large basis set that is used to expand occupied orbitals only. However, with ABS introduced in R12 methods, introducing yet another basis for the purpose of  $\Delta E_{\text{HF}}^{\text{BSIE}}$  would further complicate the already-complex method. The pragmatic solution is to utilize the ABS to account for the basis incompleteness of  $E_{\text{HF}}$  perturbatively. This approach has proven to be very effective and comes under the name ‘‘CABS singles’’<sup>8,103–108</sup> (for a generalization to multireference theory, see section 6.6). Related approaches developed in different contexts include dual-basis methods and alike.<sup>109–113</sup>

The Hartree–Fock method minimizes the reference energy by rotating orbitals between occupied and virtual spaces. Conceptually (with CABS approximating the missing virtual space with respect to CBS), we can attribute the source of  $\Delta E_{\text{HF}}^{\text{BSIE}}$  in a finite OBS to the missing rotation between occupied space and CABS. We can take the effect of the missing rotation, represented by the Fock operator  $F_{a'}^i a_i^a + hc$  ( $hc$  = hermitian conjugate), as the perturbation  $\hat{H}^{(1)}$ . To define a single set of equations for RHF, UHF, and ROHF references and to be consistent with standard

ROHF-MBPT,  $(F_a^i a_i^a + hc)$  is also included in  $\hat{H}^{(1)}$ . Thus, we have

$$\hat{H}^{(0)} = \begin{pmatrix} F_j^i & 0 & 0 \\ 0 & F_b^a & F_b^{a'} \\ 0 & F_b^a & F_b^{a'} \end{pmatrix}, \hat{H}^{(1)} = \begin{pmatrix} 0 & F_i^a & F_i^{a'} \\ F_a^j & 0 & 0 \\ F_b^j & 0 & 0 \end{pmatrix}$$

Applying the Rayleigh–Schrödinger perturbation procedure, with the Hartree–Fock determinant as the zeroth order function, yields the CABS singles energy correction. For UHF and RHF references, although  $F_a^i = F_i^{a'} = 0$ , the second-order correction will include contributions from the (OBS) virtual space due to the coupling blocks  $F_b^a$  and  $F_b^{a'}$  present in  $\hat{H}^{(0)}$ . If the coupling blocks are included in  $\hat{H}^{(1)}$  instead of  $\hat{H}^{(0)}$ , then at second-order, the energy correction simplifies and only includes contributions from CABS:  $-\sum_{a',i} |F_i^{a'}|^2 / (e_{a'} - e_i)$ .<sup>103–105</sup> However, the former treatment is more robust, especially for small basis sets. The CABS singles approach incurs negligible cost in the context of the MP2-R12 (without hybrid approximation)<sup>114</sup> and CC-R12 methods.

## 5. COUPLED-CLUSTER R12 METHODS

The technology of R12 methods described in the previous section can be straightforwardly applied to extend any method. Although the early development of R12 methods was within the MP2-R12 framework, the MP2-R12 has very limited chemical applicability. To reach its full potential, the R12 technology must be applied in combination with highly accurate methods, such as coupled-cluster methods that include at least triple excitations.

Although the first implementation of the CCSD-R12 method utilizing the standard approximation appeared within 5 years of MP2-R12, a full implementation of CC-R12 in the modern R12 framework is rather complicated and only appeared recently.<sup>115,156</sup> Because of its high computational complexity, rigorous (i.e., not using any approximations other than the RI) CCSD-R12 is not suitable for general applications. Thus, much recent activity has focused on the development of practical approximations to CCSD-R12.

This section is split into two parts. The first part will cover the full CC-R12 method, whereas approximate CC-R12 methods will be discussed in the second part.

### 5.1. The CC-R12 Formalism

Noga et al.<sup>117,118</sup> introduced the CC-R12 wave function ansatz by extending the standard CC cluster operator with the additional R12 (geminal) operator that takes care of the electron cusp. For example, the CCSD-R12 wave function is parametrized as

$$|\Psi\rangle = e^{\hat{T}}|0\rangle \quad (128)$$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{R} \quad (129)$$

where  $|0\rangle$  is the reference wave function, usually of the Hartree–Fock kind. Operators

$$\hat{T}_1 = t_a^i \tilde{a}_i^a \quad (130)$$

$$\hat{T}_2 = \frac{1}{(2!)^2} t_{ab}^{ij} \tilde{a}_{ij}^{ab} \quad (131)$$

are the standard single- and double-excitation CC cluster operators parametrized by the corresponding amplitudes,  $t_a^i$  and  $t_{ab}^{ij}$ , in the given orbital basis set. The difference between CCSD and

CCSD-R12 is due to the presence of the geminal operator:

$$\hat{R} = \frac{1}{(2!)^3} t_{xy}^{ij} \bar{R}_{\alpha\beta}^{xy} \tilde{a}_{ij}^{\alpha\beta} \quad (132)$$

One way to interpret the geminal operator is to put it in the form of eq 131:

$$\hat{R} = \frac{1}{(2!)^2} \tilde{t}_{\alpha\beta}^{ij} \tilde{a}_{ij}^{\alpha\beta} \quad (133)$$

where we introduced effective amplitudes:

$$\tilde{t}_{\alpha\beta}^{ij} = \frac{1}{2!} t_{xy}^{ij} \bar{R}_{\alpha\beta}^{xy} \quad (134)$$

that are analogous to the standard  $t_{ab}^{ij}$  amplitudes in eq 131. The  $\hat{T}_1$  and  $\hat{T}_2$  operators alone are not sufficient to obtain the “exact” CCSD wave function because the cluster operators are limited to excitations within the finite set of unoccupied orbitals  $\{a\}$ . The “exact” cluster operators must include excitations into the formally complete set of virtuals:

$$\hat{\mathcal{T}}_1 = t_a^i \tilde{a}_i^a \quad (135)$$

$$\hat{\mathcal{T}}_2 = \frac{1}{(2!)^2} t_{\alpha\beta}^{ij} \tilde{a}_{ij}^{\alpha\beta} \quad (136)$$

In practice, one cannot construct operators  $\hat{\mathcal{T}}_1$  and  $\hat{\mathcal{T}}_2$  because the  $\{\alpha\}$  set of orbitals is infinite in size. Equation 133 portrays  $\hat{R}$  as an operator that produces two-electron excitations into the formal complete virtual space  $\{\alpha\}$  and thereby complements the standard  $\hat{T}_2$  operator by accounting for the portion of  $\hat{\mathcal{T}}_2$  that is missing in  $\hat{T}_2$ .

Unlike  $\hat{\mathcal{T}}_2$  that is parametrized by an infinite number of parameters  $t_{\alpha\beta}^{ij}$ ,  $\hat{R}$  is parametrized by a finite set of coefficients  $t_{xy}^{ij}$  in combination with a formally infinite number of matrix elements  $R_{\alpha\beta}^{xy}$  of the correlation factor  $f(r_{12})$ . For example, the so-called diagonal R12 ansatz sets  $xy = ij$ , and the entire set of effective amplitudes  $\tilde{t}$  is parametrized by a single coefficient,  $t_{ij}^{ij}$ . The reason that the entire infinite set of amplitudes  $\tilde{t}$  can be parametrized by few coefficients is because the two-electron excitations missing in  $\hat{T}_2$  but present in  $\hat{\mathcal{T}}_2$  are high-energy and primarily describe the wave function at short interelectronic distances. As we saw in section 2, the analytic structure of the wave function in that region is universally described by cusp conditions. Thus, very compact parametrizations of  $\hat{R}$  are possible by using correlation factors that model the cusp region of the wave function.

Yet another way to represent the geminal cluster operator is a linear combination:

$$\hat{R} = \frac{1}{(2!)^2} t_{xy}^{ij} \tilde{\gamma}_{ij}^{xy} \quad (137)$$

where  $\tilde{\gamma}$  are elementary geminal excitation operators:

$$\tilde{\gamma}_{ij}^{xy} = \frac{1}{2!} \bar{R}_{\alpha\beta}^{xy} \tilde{a}_{ij}^{\alpha\beta} \quad (138)$$

The geminal excitation operator  $\tilde{\gamma}_{ij}^{xy}$  is directly analogous to the standard excitation operator  $\tilde{a}_{ij}^{ab}$ : the latter replaces the orbital pair  $|ij\rangle$  with the orbital pair  $|ab\rangle$ , whereas the former produces an  $r_{12}$ -dependent geminal:

$$\tilde{\gamma}_{ij}^{xy} |ij\rangle = \hat{Q}_{12} f(r_{12}) |xy\rangle \quad (139)$$

The traditional CCSD-R12 method is obtained by substituting the CCSD-R12 wave function (eq 128) into the time-independent

Schrödinger equation and multiplying on the left by the  $e^{-\hat{T}}$  operator:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}|0\rangle \equiv \bar{H}|0\rangle = Ee^{-\hat{T}}e^{\hat{T}}|0\rangle = E|0\rangle \quad (140)$$

where we introduced the similarity-transformed coupled-cluster Hamiltonian  $\bar{H}$ . The energy is computed by left-projecting the coupled-cluster Schrödinger equation with the reference wave function:

$$\begin{aligned} E_{\text{CC-R12}} &= \langle 0|\bar{H}|0\rangle = \langle 0|\hat{H}|0\rangle + \langle 0|[\hat{F}, \hat{T}]|0\rangle \\ &+ \langle 0|[\hat{W}, \hat{T}]|0\rangle + \langle 0|\frac{1}{2}[[\hat{W}, \hat{T}], \hat{T}]|0\rangle \\ &= E_0 + t_a^i F_i^a + \frac{1}{4} t_{ab}^{ij} \bar{g}_{ij}^{ab} + \frac{1}{8} t_{xy}^{ij} \bar{R}_{\alpha\beta}^{xy} \bar{g}_{ij}^{\alpha\beta} + \frac{1}{2} t_a^i t_b^j \bar{g}_{ij}^{ab} \\ &= E_0 + t_a^i F_i^a + \frac{1}{4} t_{ab}^{ij} \bar{g}_{ij}^{ab} + \frac{1}{4} t_{xy}^{ij} V_{ij}^{xy} + \frac{1}{2} t_a^i t_b^j \bar{g}_{ij}^{ab} \quad (141) \end{aligned}$$

where  $\hat{F}$  and  $\hat{W} \equiv \hat{H} - \hat{F}$  are the Fock and fluctuation operators, respectively, and  $V$  is the intermediate we encountered in the MP2-R12 method (section 4).

Corresponding projections onto conventional singly and doubly excited determinants:

$$|i^a\rangle \equiv \tilde{a}_i^a |0\rangle \quad (142)$$

$$|ij^{ab}\rangle \equiv \tilde{a}_{ij}^{ab} |0\rangle \quad (143)$$

etc., as well as the geminal functions produced by the geminal generators (eq 138):

$$|ij^{xy}\rangle \equiv \tilde{\gamma}_{ij}^{xy} |0\rangle \quad (144)$$

determine the conventional amplitudes:

$$0 = \langle i^a|\bar{H}|0\rangle \quad (145)$$

$$0 = \langle ij^{ab}|\bar{H}|0\rangle \quad (146)$$

etc., and the geminal cluster amplitudes:

$$0 = \langle ij^{xy}|\bar{H}|0\rangle \quad (147)$$

Equations 141, 145, and 146 are analogous to those that define the standard (non-R12) CCSD method, whereas eq 147 does not appear in CCSD. Although the rank of the additional amplitude equations is small ( $\mathcal{O}(o^4)$ ), the implementation and computational complexities of the CCSD-R12 are vastly greater than that of CCSD and MP2-R12. First, in addition to the “special”  $V$ ,  $B$ ,  $X$ , and  $C$  intermediates that appeared in MP2-R12 method:

$$V_{xy}^{pq} = \frac{1}{2} \bar{g}_{\alpha\beta}^{pq} \bar{R}_{xy}^{\alpha\beta} \quad (148)$$

$$X_{xy}^{ow} = \frac{1}{2} \bar{R}_{\alpha\beta}^{ow} \bar{R}_{xy}^{\alpha\beta} \quad (149)$$

$$B_{xy}^{ow} = \bar{R}_{\alpha\gamma}^{ow} t_{\beta}^{\alpha} \bar{R}_{xy}^{\beta\gamma} \quad (150)$$

$$C_{ab}^{xy} = \bar{R}_{a\alpha}^{xy} f_b^{\alpha} \quad (151)$$

CCSD-R12 requires two new special intermediates:

$$P_{xy}^{ow} = \frac{1}{4} \bar{R}_{\alpha\beta}^{ow} \bar{g}_{\gamma\delta}^{\alpha\beta} \bar{R}_{xy}^{\gamma\delta} \quad (152)$$

$$Z_{xy;m}^{ow;p} = \bar{R}_{\alpha\gamma}^{ow} \bar{g}_{\beta m}^{\alpha p} \bar{R}_{xy}^{\beta\gamma} \quad (153)$$

where  $ow;p$  indicates antisymmetry with respect to permutation of  $o$  and  $w$  only. Evaluation of intermediates  $V$ ,  $X$ ,  $B$ , and  $C$  was discussed in section 4; here we focus only on the last two intermediates. Their evaluation must utilize analytic evaluation to prevent slowly convergent expansions in terms of atomic basis functions. An expression for  $P$  in the CABS approach is obtained as follows:<sup>115,119</sup>

$$\begin{aligned} P_{xy}^{ow} &= \frac{1}{4} \bar{R}_{\alpha\beta}^{ow} \bar{g}_{\gamma\delta}^{\alpha\beta} \bar{R}_{xy}^{\gamma\delta} = \frac{1}{2} V_{\gamma\delta}^{ow} \bar{R}_{xy}^{\gamma\delta} \\ &= \frac{1}{2} ((\bar{g}^r)^{ow}_{\gamma\delta} - \frac{1}{2} \bar{g}_{\gamma\delta}^{rs} \bar{r}_{rs}^{ow} - \bar{g}_{\gamma\delta}^{m\alpha'} \bar{r}_{m\alpha'}^{ow}) \bar{R}_{xy}^{\gamma\delta} \quad (154) \end{aligned}$$

$$= \frac{1}{2} (\bar{g}^r)^{ow}_{\gamma\delta} \bar{R}_{xy}^{\gamma\delta} - \frac{1}{2} V_{xy}^{rs} \bar{r}_{rs}^{ow} - V_{xy}^{m\alpha'} \bar{r}_{m\alpha'}^{ow} \quad (155)$$

$$\begin{aligned} &= \frac{1}{2} (\bar{g}^r)^{ow}_{\kappa\lambda} \bar{r}_{xy}^{\kappa\lambda} - \frac{1}{2} (\bar{g}^r)^{ow}_{rs} \bar{r}_{xy}^{rs} - (\bar{g}^r)^{ow}_{m\alpha'} \bar{r}_{m\alpha'}^{ow} \\ &- \frac{1}{2} V_{xy}^{rs} \bar{r}_{rs}^{ow} - V_{xy}^{m\alpha'} \bar{r}_{m\alpha'}^{ow} \quad (156) \end{aligned}$$

$$= (\bar{g}^r)^{ow}_{xy} - \frac{1}{2} (\bar{g}^r)^{ow}_{rs} \bar{r}_{xy}^{rs} - (\bar{g}^r)^{ow}_{m\alpha'} \bar{r}_{m\alpha'}^{ow} - \frac{1}{2} V_{xy}^{rs} \bar{r}_{rs}^{ow} - V_{xy}^{m\alpha'} \bar{r}_{m\alpha'}^{ow} \quad (157)$$

Its computational and storage costs are similar to that of the  $B$  intermediate. Evaluation of the  $Z$  intermediate is more laborious:<sup>116</sup>

$$\begin{aligned} Z_{xy;m}^{ow;p} &\stackrel{\text{CABS}}{=} \frac{1}{2} [\hat{\mathcal{L}}_{ow}(\bar{r}^2)_{xy}^{p'w} \mathcal{G}_{p'm}^{op} \\ &+ \hat{\mathcal{L}}_{xy}(\bar{r}^2)_{p'y}^{ow} \mathcal{G}_{xm}^{p'p}] - \bar{r}_{qs}^{ow} \mathcal{G}_{qm}^{qp} \bar{r}_{xy}^{rs} - \bar{r}_{a'n}^{ow} \mathcal{G}_{b'm}^{ap} \bar{r}_{xy}^{b'n} - \bar{r}_{a's}^{ow} \mathcal{G}_{m}^{ap} \bar{r}_{xy}^{rs} \\ &- \bar{r}_{qs}^{ow} \mathcal{G}_{a'm}^{qp} \bar{r}_{xy}^{a's} - \bar{r}_{na'}^{ow} \mathcal{G}_{p'm}^{np} \bar{r}_{xy}^{p'a'} - \bar{r}_{p'a'}^{ow} \mathcal{G}_{nm}^{p'p} \bar{r}_{xy}^{na'} + \bar{r}_{na'}^{ow} \mathcal{G}_{km}^{np} \bar{r}_{xy}^{ka'} \\ &- (\bar{r}_{a'c}^{ow} \mathcal{G}_{b'm}^{pa'} \bar{r}_{xy}^{b'c'} + \bar{r}_{a'c}^{ow} \mathcal{G}_{b'm}^{pa'} \bar{r}_{xy}^{b'c'} + \bar{r}_{ac'}^{ow} \mathcal{G}_{bm}^{pa} \bar{r}_{xy}^{bc'}) \\ &+ \bar{r}_{a'c'}^{ow} \mathcal{G}_{bm}^{pa'} \bar{r}_{xy}^{bc'} + \bar{r}_{ac'}^{ow} \mathcal{G}_{b'm}^{pa} \bar{r}_{xy}^{b'c'}) \quad (158) \end{aligned}$$

Precomputing intermediate  $Z$  requires  $\mathcal{O}(N^8)$  operations and  $\mathcal{O}(N^6)$  storage, which is a dramatic increase with respect to standard CCSD. Direct computation of  $Z$  every iteration decreases the cost to  $\mathcal{O}(N^6)$  and avoids its storage, albeit at the increased computational expense.

Besides the special intermediates necessary for CCSD-R12, the sheer number of terms that appear in amplitude equations is staggering. Thus, the pioneering work of Noga, Kutzelnigg, and Klopper<sup>117,118,120</sup> on the CC-R12 method utilized the so-called standard approximation (SA)<sup>82</sup> to dramatically simplify the equations and the expressions for special intermediates; the standard approximation can be viewed as an approximation to the state-of-the-art R12 technology of today, and therefore we will discuss Noga et al.'s work along with other approximate CC-R12 methods in section 5.2. The modern (unabridged) formulation of CC-R12 became possible only through automated

equation derivation and implementation. Shiozaki et al. were the first to implement CCSD-R12 using automated compiler smith<sup>115,121</sup> and documented its performance for Ne, H<sub>2</sub>O, and F<sub>2</sub>. Their comparison of CCSD-R12 to the CCSD(R12) and CCSD(2)<sub>R12</sub> methods reviewed below showed that the latter two methods differed from the CCSD-R12 result by less than the residual basis set incompleteness in a given basis, and therefore their approximations were robust. Note that their implementation included all terms but evaluated the *Z* intermediate via RI insertion and thus evaluated the integral of  $f(r_{12})^2$  (see the first two terms on the right-hand side of eq 158) by RI approximation. Later, Köhn et al. implemented the CCSD-R12 method using GECKO program with the *Z* intermediate evaluated via eq 158; their results showed significantly reduced errors due to the RI approximation and underscored the importance of proper evaluation of the *Z* intermediate.

The automated approach also allowed Shiozaki et al. to implement higher-rank CC-R12 methods, such as CCSDT-R12 and CCSDTQ-R12,<sup>122</sup> without any approximations other than the RI. Although the R12 terms greatly reduced the error due to the basis set incompleteness of the two-electron basis, the basis set error of three- and four-electron bases was effectively unchanged. These findings called for the use of explicitly correlated terms in higher-rank basis functions as well.<sup>123,124</sup>

The geminal amplitude equation of CCSD-R12 involves  $o^3v^3$  operations, whereas the cost of CCSD is  $o^2v^4$ . Thus, the computational cost of CCSD-R12 scales asymptotically as the sixth power of the system size, similar to CCSD. Despite the same scaling, the absolute computational complexity of CCSD-R12 in terms of operations and storage is significantly greater than that of CCSD. Thus, the primary utility of the full CCSD-R12 method is to provide benchmarks for developing approximate CCSD-R12 methods. For higher-rank CC-R12 methods, these approximations are not as critical. For example, the computational complexity of the CCSDT-R12 and CCSDTQ-R12 methods scales with the system size in the same manner as their respective non-R12 counterparts,<sup>121</sup> as the 8th and 10th power of the system size.

## 5.2. Approximate CC-R12 Methods

A variety of practical approximations for CCSD-R12 exist. They can be broadly divided into two categories, iterative and noniterative. The iterative group of approaches is characterized by doubles and/or singles amplitude equations that are different from those of CCSD; noniterative approaches depart from the standard CCSD equations and introduce the geminal terms perturbatively. Both types of approaches can be further simplified by the use of cusp conditions to fix the values of geminal amplitudes, as described in section 4.4; this simplification could be viewed as a separate CC-R12 ansatz rather than as a way to approximate eq 132.

**5.2.1. CC-R12 in Standard Approximation.** The starting point for our discussion is the original implementation of CC-R12 by Noga, Kutzelnigg, and Klopper within the standard approximation. Standard approximation is characterized by the use of the orbital basis set for the RI approximation. Hence, the SA CC-R12 method can be obtained from the modern formulation by dropping all terms that include sums over CABS indices. For example, the *V* intermediate in standard approximations can be obtained from eq 110 by dropping the second and third terms on its right-hand side:

$$V_{xy}^{pq} \stackrel{\text{SA}}{=} (\bar{g}^r)_{xy}^{pq} - \bar{g}_{rs}^{pq} r_{xy}^{rs} \quad (159)$$

Noga et al. implemented SA CCSD-R12,<sup>117,125</sup> CCSD[T]-R12,<sup>117,126</sup> and CCSD(T)<sup>126</sup> using linear correlation factor; they also discussed the formalism of CCSDT-R12.<sup>118</sup> SA CCSD(T)-R12 was recently reimplemented with nonlinear (Slater-type) correlation factor in a simplified manner by utilizing the cusp conditions to fix the values of geminal amplitudes (see sections 4.4 and 5.2.2).<sup>127</sup>

The simplifications due to SA come at a steep price: the need for extended primitive atomic basis sets nearly saturated to at least  $3L_{\text{occ}}$ , where  $L_{\text{occ}}$  is the maximum angular momentum of the occupied atomic orbitals. Therefore, practical applications of SA CC-R12 are limited mostly to highly accurate studies of atoms and small molecules. Nevertheless, SA CC-R12 methods were a crucial milestone for R12 methodology.

**5.2.2. CC-R12 Using Cusp Conditions.** A drastic simplification of the CC-R12 method is possible by taking advantage of Ten-no's idea<sup>84</sup> that coefficients of geminal terms in the wave function can be simply prescribed by the cusp conditions. Using fixed geminal amplitudes eliminates the need to solve the poorly conditioned geminal amplitude equations,<sup>120,128</sup> reduces the overall computational expense, and eliminates the geminal superposition error.<sup>129</sup> Therefore, the use of fixed amplitudes is the standard practice in most practical applications.

The simplest way to use the fixed geminal amplitudes in CCSD-R12 is to solve the singles and doubles amplitude equations, and evaluate the energy via eq 141. However, this method yields the error in the energy that is linear with respect to the error in the geminal amplitudes introduced by using the cusp conditions. The error can be made quadratic by using the variational (Lagrangian) formulation of the traditional coupled-cluster method. Consider the CCSD-R12 Lagrangian:

$$L_{\text{CCSD-R12}}(\{\lambda\}, \{t\}) = E_{\text{CC-R12}} + \lambda_i^a \langle i | \bar{H} | 0 \rangle + \lambda_{ij}^{ab} \langle ij | \bar{H} | 0 \rangle + \lambda_{ij}^{xy} \langle ij | \bar{H} | 0 \rangle \equiv \langle 0 | (1 + \hat{\Lambda}) \bar{H} | 0 \rangle \quad (160)$$

where the CC-R12 energy is given by eq 141. The CCSD-R12 lambda operator  $\hat{\Lambda}$  introduced in eq 160 is defined similarly to the cluster operator  $\hat{T}$ :

$$\hat{\Lambda} = \hat{\Lambda}_1 + \hat{\Lambda}_2 + \hat{L} \quad (161)$$

$$\hat{\Lambda}_1 = \lambda_i^a \tilde{a}_a^i \quad (162)$$

$$\hat{\Lambda}_2 = \frac{1}{(2!)^2} \lambda_{ij}^{ab} \tilde{a}_{ab}^{ij} \quad (163)$$

$$\hat{L} = \frac{1}{(2!)^2} \lambda_{ij}^{xy} (\tilde{v}_{ij}^{xy})^\dagger \quad (164)$$

Making Lagrangian stationary with respect to both parameter sets,  $\lambda$  and  $t$  renders its value equal to the CCSD-R12 energy computed with fully optimized  $t$  amplitudes via eq 141. If these parameters are not fully optimized (hence, some or all  $t$  amplitudes are not optimal), the value of the Lagrangian deviates from the exact CCSD-R12 energy quadratically with the deviation of the  $t$  amplitudes. In practice, only approximately quadratic error can be expected because geminal lambda amplitudes are approximated also in the same manner as the geminal  $t$  amplitudes. Nevertheless, the difference between the optimized and fixed-amplitude approaches rapidly decreases with the basis set.

Although the use of fixed geminal amplitudes eliminates the need to solve the associated equations, the use of the Lagrangian formalism requires evaluation of the  $\langle \mathcal{L} | \bar{H} | 0 \rangle$  residual once. The evaluation of this residual is expensive in the unabridged CCSD-R12 method. Therefore, this residual is usually approximated further, as we discuss below.

**5.2.3. Perturbative Approximations to CC-R12.** Although the perturbative CC-R12 framework of Valeev et al.<sup>130</sup> was not the first post-SA iterative approximation,<sup>131</sup> it is more natural to discuss the perturbative approaches first because perturbation theory arguments support all iterative CC-R12 approximations as well.

To develop a perturbative expansion of the CC-R12 energy and wave function, we must choose the zeroth-order state and the corresponding Hamiltonian. Among the infinite set of possibilities, the following two choices stand out:

- the MBPT $n$  (or MP $n$ ) framework, in which the zeroth-order state is the standard single-determinant reference (Hartree–Fock),  $|0\rangle$ , and the Fock operator (in finite-basis or otherwise)<sup>132</sup> plays the role of the zeroth-order Hamiltonian.
- the CC( $n$ ) framework,<sup>133</sup> in which the zeroth-order state is the standard CC wave function (e.g., CCSD), and the zeroth-order Hamiltonian is obtained by Löwdin partitioning<sup>134</sup> of the similarity-transformed Hamiltonian.

Both approaches have been productively used in the past to analyze and construct approximations to high-rank CC wave functions.<sup>135–141</sup> For example, the successful CCSD(T) method<sup>132</sup> in which the CCSD energy is perturbatively corrected for the effect of connected triples was initially motivated by arguments based on the MBPT analysis of the CCSDT energy. Later, Stanton and Gauss<sup>142,143</sup> pointed out that the (T) correction can be viewed as an approximation to the second-order energy computed within the CC( $n$ ) framework in which the CCSD wave function and Hamiltonian were chosen as zeroth-order. The relative simplicity of this “derivation” of the CCSD(T) method suggests that the CC( $n$ ) framework might be preferred over the MBPT $n$  framework in terms of consistency. The CC( $n$ ) approach also allows one to construct perturbative expansions of energies but also wave functions.

These considerations prompted Valeev to develop a CC( $n$ )-type perturbation expansion of the CCSD-R12 energy and wave function.<sup>130</sup> Consider the CCSD-R12 Lagrangian (eq 160). It can be rewritten in matrix form as

$$L_{\text{CCSD-R12}}(\{\lambda\}, \{t\}) = \mathbf{L}^+ \bar{\mathbf{H}} \mathbf{R} \quad (165)$$

where  $\bar{\mathbf{H}}$  is the matrix representation of similarity-transformed CCSD-R12 Hamiltonian in the basis that includes reference determinant  $0 \equiv |0\rangle$ , singles  $S \equiv \{|i^a\rangle\}$ , doubles  $D \equiv \{|ij^ab\rangle\}$ , and the explicitly correlated geminal substitutions  $\Gamma \equiv \{|ij^{xy}\rangle\}$ .  $\mathbf{L}$  and  $\mathbf{R}$  are column vectors that represent the ground-state left- and right-hand eigenstates of the CCSD-R12 Hamiltonian, that is, the  $(1 + \Lambda)^+ |0\rangle$  and  $|0\rangle$  states. To construct a perturbative expansion of the CCSD-R12 Lagrangian around the CCSD state ( $t_{ij}^{xy} = 0$ ,  $\lambda_{ij}^{xy} = 0$ ), it is convenient to partition the  $O \oplus S \oplus D \oplus \Gamma$  space into reference space,  $P \equiv O \oplus S \oplus D$ , and the external space,  $Q \equiv \Gamma$ . The matrix representation of the CCSD Hamiltonian,  $\bar{H} = e^{-\bar{T}_1 - \bar{T}_2} \bar{H}_e \bar{T}_1 + \bar{T}_2$ , in these spaces:

$$\bar{\mathbf{H}} = \begin{pmatrix} \bar{\mathbf{H}}_{PP} & \bar{\mathbf{H}}_{PQ} \\ \bar{\mathbf{H}}_{QP} & \bar{\mathbf{H}}_{QQ} \end{pmatrix} \quad (166)$$

can be straightforwardly used to develop a Löwdin-type perturbation expansion.<sup>134</sup> Such an expansion can be defined in a

number of ways; one possibility is to partition the Hamiltonian as:

$$\bar{\mathbf{H}}^{(0)} = \begin{pmatrix} \bar{\mathbf{H}}_{PP} & 0 \\ 0 & \bar{\mathbf{H}}_{QQ}^{(0)} \end{pmatrix} \quad (167)$$

$$\bar{\mathbf{H}}^{(1)} = \begin{pmatrix} 0 & \bar{\mathbf{H}}_{PQ} \\ \bar{\mathbf{H}}_{QP} & \bar{\mathbf{H}}_{QQ}^{(1)} \end{pmatrix} \quad (168)$$

where  $\bar{\mathbf{H}}_{QQ} = \bar{\mathbf{H}}_{QQ}^{(0)} + \bar{\mathbf{H}}_{QQ}^{(1)}$ . The zeroth-order vectors  $L$  and  $R$  are defined in terms of the ground-state CCSD eigenvectors,  $\mathcal{L}$  and  $\mathcal{R}$ , as

$$\mathbf{L}^{(0)} = \begin{pmatrix} \mathcal{L} \\ \mathbf{0} \end{pmatrix} \quad (169)$$

$$\mathbf{R}^{(0)} = \begin{pmatrix} \mathcal{R} \\ \mathbf{0} \end{pmatrix} \quad (170)$$

The zeroth-order Lagrangian,  $(\mathbf{L}^{(0)})^+ \bar{\mathbf{H}}^{(0)} \mathbf{R}^{(0)}$ , then equals the ground-state CCSD energy, the first-order Lagrangian vanishes, and the second-order contribution takes the following form:<sup>144</sup>

$$L^{(2)}(\mathbf{L}_Q^{(1)}, \mathbf{R}_Q^{(1)}) = \mathcal{L}^+ \bar{\mathbf{H}}_{PQ} \mathbf{R}_Q^{(1)} + (\mathbf{L}_Q^{(1)})^+ H_{QP} \mathcal{R} + (\mathbf{L}_Q^{(1)})^+ (\bar{\mathbf{H}}_{QQ}^{(0)} - E^{(0)} \mathbf{S}_{QQ}) \mathbf{R}_Q^{(1)} \quad (171)$$

where the overlap matrix for space  $Q$  appears because the geminal functions as defined in eq 144 are not orthonormal. The second-order energy is obtained by extremization of this Lagrangian, or by plugging in the geminal amplitudes fixed by the cusp conditions (section 5.2.2). Choosing the Fock operator as  $\bar{\mathbf{H}}_{QQ}^{(0)}$  makes the correction maximally similar to that of the MP2-R12 method. However, the main difference is the asymmetric character of the CC correction due to its dependence on two sets of geminal amplitudes ( $\mathbf{L}_Q^{(1)}$  and  $\mathbf{R}_Q^{(1)}$ ), rather than one set in MP2-R12. The asymmetric character of the correction is a consequence of the non-Hermitian character of the coupled-cluster Hamiltonian and, therefore, naturally appears in perturbative CC approaches. Also note that the correction requires knowledge of not only  $t$  CCSD amplitudes, but also the  $\lambda$  CCSD amplitudes. That is also a known feature of CC( $n$ ) approaches: see, for example, the asymmetric,<sup>145</sup> or  $\Lambda$ ,<sup>146</sup> (T) correction to CCSD.

The second-order Lagrangian in eq 171 requires evaluation of the same types of special intermediates that already appear in the MP2-R12 method; its implementation by Shiozaki, Hirata, and Valeev will be documented soon. Valeev et al. implemented a simplified version of the theory, dubbed CCSD(2) $_{\text{R12}}$ , by employing what they called screening approximations (ScrA).<sup>130,147,148</sup> The screening approximations make it possible to formulate a Hylleraas-type second-order functional for the R12 correction of CCSD(2) $_{\text{R12}}$  that does not require CCSD  $\lambda$  amplitudes for its evaluation. The (2) $_{\text{R12}}$  Lagrangian is expressed as:

$$L_{(2)_{\text{R12}}}(\{t_{xy}^{ij}\}) = \frac{1}{2} \bar{V}_{ij}^{xy} t_{ij}^{xy} + \frac{1}{8} t_{ij}^{ow} (\bar{B}^{(ij)})_{ow}^{xy} t_{ij}^{xy} \quad (172)$$

The second term also appears in the MP2-R12 Lagrangian; the only difference is in the first term, where the standard  $V_{ij}^{xy}$

intermediate of MP2-R12 is replaced with its counterpart<sup>149</sup>

$$\bar{V}_{xy}^{ij} \equiv V_{xy}^{ij} + \frac{1}{2}(V_{xy}^{ab} + C_{xy}^{ab})t_{ab}^{ij} + \hat{\mathcal{L}}_{i,j}V_{xy}^{aj}t_a^i \quad (173)$$

“dressed” by the CCSD amplitudes  $t_a^i$  and  $t_{ab}^{ij}$ . The original implementation of CCSD(2) $_{\overline{\text{R12}}}$  also discarded the terms that include  $C$  and  $t_a^i$ . As pointed out by Hättig et al., the  $C$ -including term is important, especially for small basis sets.<sup>150</sup>

The  $t$ -dependent terms in eq 176 account for the entire difference between the R12 correction of MP2-R12 and CCSD(2) $_{\overline{\text{R12}}}$ . This difference can therefore be identified with the observed empirical connection between the size of the basis set error and the type of the electron correlation model, also known as the basis set “interference” effect.<sup>151</sup> It is empirically known that the basis set error of MP2 energy is larger than that of higher-level CC and CI correlation models, and in practice the MP2-R12 correction is larger than that of CCSD(2) $_{\overline{\text{R12}}}$ .

It is also straightforward to include the effects of triples and higher-rank excitations using the approach outlined here, by including the appropriate determinants into  $Q$ . In the most important case, geminals and triples are included:  $Q \equiv \Gamma \oplus T$ . Valeev and Crawford argued<sup>148</sup> that the smallness of the coupling between the geminal and triples suggests using the simplest zeroth-order Hamiltonian, the Fock operator, in which the effect of geminals and triples is completely decoupled. Thus, the energy of the CCSD(T) $_{\overline{\text{R12}}}$  method is defined as:

$$E_{\text{CCSD(T)}_{\overline{\text{R12}}}} = E_{\text{CCSD}} + E_{(T)} + E_{(2)_{\overline{\text{R12}}}} \quad (174)$$

The CC( $n$ ) perturbative framework has also been extended by Shiozaki et al. to include the effects of high-rank conventional excitations, including up to second- and third-order terms in energy, into the CCSD-R12 and CCSDT-R12 methods with exact and approximate (R12) treatment of geminal functions.<sup>152</sup> Their findings confirmed that the R12 terms only correct the basis set incompleteness of the two-electron part of the wave function, that is, that attributed to doubles.

The (2) $_{\overline{\text{R12}}}$  approach is an excellent approximation to the “exact” CCSD-R12: the differences between the CCSD(2) $_{\overline{\text{R12}}}$  and CCSD-R12 correlation energies (absolute and relative) are significantly smaller than the residual basis set error of CCSD-R12.<sup>122,150</sup> The perturbative CC-R12 methods are very easy to implement because the standard coupled-cluster amplitude equations are not modified. The (2) $_{\overline{\text{R12}}}$  method is currently available to the scientific community in the free open-source MPQC package.<sup>153</sup>

**5.2.4. The CCSD(R12) Method.** To make the CCSD-R12 method affordable without the use of SA, Klopper and coworkers proposed the CCSD(R12) method.<sup>131,154,155</sup> The “(R12)” approximation (1) retains the terms that are at most linear in geminal amplitudes, and (2) additionally omits the  $[\hat{W}, \hat{R}]$  term from the geminal amplitude equation. While the singles equation (eq 145) is the same as in the CCSD-R12 method, the doubles and geminal amplitude equations (eqs 146 and 147) take the following simpler form in CCSD(R12):<sup>131</sup>

$$\langle ij | \bar{H}_{\text{SD}} + [\bar{H}_{\text{SD}}, \hat{R}] | 0 \rangle = 0 \quad (175)$$

$$\langle ij | \bar{H}_{\text{SD}} + [\bar{F}_{\text{SD}}, \hat{R}] | 0 \rangle = 0 \quad (176)$$

where the “SD” subscript denotes similarity-transformation with singles and doubles cluster operators only:

$$\begin{aligned} \bar{H}_{\text{SD}} &\equiv e^{-\hat{T}_1 - \hat{T}_2} \hat{H} e^{\hat{T}_1 + \hat{T}_2} \\ &= e^{-\hat{T}_1 - \hat{T}_2} \hat{F} e^{\hat{T}_1 + \hat{T}_2} + e^{-\hat{T}_1 - \hat{T}_2} \hat{W} e^{\hat{T}_1 + \hat{T}_2} \\ &\equiv \bar{F}_{\text{SD}} + \bar{W}_{\text{SD}} \end{aligned} \quad (177)$$

The (R12) approximation can also be similarly formulated for higher-rank CC-R12 methods, as was done by Shiozaki et al.<sup>122</sup>

The (R12) approximation can be rationalized from a perturbation theory viewpoint that assumes the smallness of geminal amplitudes and is reminiscent of the CC2 and CC3 methods<sup>156,157</sup> as well as, for example, of the CCSDT-1 method.<sup>158</sup> These approximations dramatically reduce the computational complexity of the method relative to the CCSD-R12. For example, approximation (2) allows one to avoid  $P$  and  $Z$  intermediates completely; Köhn et al. found that this assumption decreased the cost significantly but at the cost of insignificant deterioration of the error with respect to the full CCSD-R12.<sup>116</sup> The (R12) simplification in the equations allows CCSD(R12) to be implemented by a modest extension of the computational elements developed in the MP2-R12 implementations.

The CCSD(R12) method was found to be an excellent approximation to CCSD-R12 (the difference between the two methods is typically much smaller than the residual basis set error of CCSD-R12).<sup>115,116</sup> The method is straightforward to utilize with the fixed geminal amplitudes (see section 5.2.2).<sup>159</sup> The (R12) approximation is also amenable for formulation of response and excited-state CC-R12 methods.<sup>160–163</sup>

Recently, Hättig et al. proposed additional simplifications of the (R12) approach, dubbed CCSD[F12] and CCSD(F12\*).<sup>150</sup> These simplifications are obtained from CCSD(F12) by further perturbative screening of the amplitude equations and are reminiscent of the simplifications involved in the CCSD-F12x (5.2.5) and CCSD(2) $_{\overline{\text{R12}}}$  methods (section 5.2.3). These methods seem to perform as well as CCSD(F12), at the cost approaching that of CCSD. Recently, Köhn and Tew further extended the perturbation theory analysis that led to the [F12] and (F12\*) approximations.<sup>164</sup>

The CCSD(R12) method is widely available to the scientific community in the TURBOMOLE package. It is also implemented in programs of the Ten-no group (GELLAN) and Köhn group (GECKO), as well as the MPQC package.

**5.2.5. The CCSD-F12x Methods.** In 2007, Adler et al. proposed a family of iterative approximations to CCSD-R12, dubbed CCSD-F12x ( $x = a, b$ ),<sup>104,106</sup> that can be viewed as a further simplification of CCSD(R12). First, the geminal amplitudes in these methods are always fixed by cusp conditions or, optionally, at their MP2-R12 values. Second, the same singles amplitude equations are used as in CCSD-R12 and CCSD(R12) (eq 148), whereas the doubles equations differ from CCSD(R12) by the omission of the  $[[\hat{W}, \hat{T}_2], \hat{R}]$  term. Third, all summations over CABS indices, except those appearing in special intermediates  $V, X, B$ , and  $C$  of MP2-R12, are omitted. For example, the  $V_{xy}^{ij}$  intermediate is evaluated using eq 110, but the  $V_{xy}^{ab}$  intermediate that appears, for example, in the  $\langle ij | [\hat{W}, \hat{R}] | 0 \rangle$  term is evaluated as

$$V_{xy}^{ab \text{ F12x}} \equiv (\bar{g}r)_{xy}^{ab} - \bar{g}_{rs}^{ab-rs} r_{xy} \quad (178)$$

This expression is equivalent to standard approximation (eq 159); thus, CCSD-F12x can be viewed as CCSD-R12 with some terms dropped and SA applied to terms that do not appear in MP2-R12.

Because the geminal amplitudes are fixed in CCSD-F12x, the energy is evaluated via the CC Lagrangian (eq 160). Both singles and doubles amplitude equations are solved exactly; therefore, the terms including singles and doubles lambda amplitudes can be dropped. Further, the geminal lambda amplitudes are set to the same values as the geminal  $t$  amplitudes, and the geminal residual is approximated. The CCSD-F12b energy expression becomes:

$$E_{\text{CCSD-F12x}} = E_{\text{CC-R12}} + (t_{xy}^{ij})^\dagger \langle xy | [\hat{F}, \hat{T}_2] + \hat{W} + [\hat{H}, \hat{R}] | 0 \rangle$$

In CCSD-F12a, the geminal residual is further approximated by replacing  $[\hat{H}, \hat{R}]$  with  $[\hat{F}, \hat{R}]$ . The computational complexity of CCSD-F12x methods is essentially similar to that of CCSD (the additional cost of MP2-R12 computation can be usually neglected).

In practice, the CCSD-F12x method in either variant involves approximations that are more severe than CCSD(R12), but considering its low computational cost it is an excellent compromise. The implementation of CCSD-F12x methods in the MOLPRO package makes them widely available to the chemistry community.

**5.2.6. Comparison of the CC-R12 Methods.** To highlight the relative performance of the various CC-R12 methods, we present results of comparison of several CC-R12 methods recently published in Hättig, Tew, and Köhn.<sup>150</sup> Table 4 includes the results of statistical analyses of basis set errors of correlation energies (per valence electron) for two data sets: (1) the atomization energies of 30 small molecules containing the elements H, C, N, O and F, and (2) the energies of decomposition reactions for a 25-molecule subset into the molecules H<sub>2</sub>, F<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, and CO. The performance on the second set can be considered representative for heats of formation. All computations utilized cc-pVXZ-F12 basis sets<sup>165,166</sup> and the SP ansatz<sup>84</sup> of Ten-no (see section 4.4).

The last two methods, CCSD[F12] and CCSD(F12\*), were designed by Hättig et al.<sup>145</sup> by omitting certain terms in CCSD(F12) so that the overall performance is not compromised substantially. Their computational cost is lower than that of CCSD(F12) and is similar to that of CCSD-F12b. Therefore, all methods in Table 4, except (2) $\overline{\text{R12}}$ , are iterative approximations to CCSD-R12.

As expected, atomization energies suffer from larger basis set errors because there will be necessarily a number of electron pairs broken in the course of atomization, whereas in these reactions the number of pairs stays constant. Nevertheless, maximum errors can be just as large for reactions when the smallest double- $\zeta$  basis set is used. Therefore, it is imperative to consider maximum errors in evaluating the performance of these methods.

For reaction energies, the best performing of all listed methods is CCSD(F12). Only when the largest quadruple- $\zeta$  basis set is used can slightly smaller errors be obtained with the CCSD(2) $\overline{\text{R12}}$  method or the CCSD[F12] method. Its performance, however, is closely matched by that of CCSD(F12\*). CCSD[F12], a slight simplification of CCSD(F12\*), is also an excellent approximation to CCSD-F12. CCSD-F12x methods generally perform worse than the other iterative methods; keep in mind that they are, however, the cheapest iterative CC-R12 methods examined here. The noniterative CCSD(2) $\overline{\text{R12}}$  method is only slightly

**Table 4. Comparison of Various Approximate CCSD-R12 Methods<sup>a</sup>**

method	X	RE				AE			
		mean	$\sigma_N$	rms	max	mean	$\sigma_N$	rms	max
(F12)	D	-0.10	0.10	0.14	-0.32	-0.61	0.21	0.65	-1.05
	T	-0.01	0.01	0.02	-0.06	-0.08	0.08	0.11	-0.33
	Q	0.00	0.01	0.01	0.01	0.04	0.05	0.06	-0.13
(2) $\overline{\text{R12}}$	D	-0.13	0.15	0.20	-0.42	-0.72	0.44	0.85	-1.48
	T	-0.02	0.02	0.03	-0.08	-0.13	0.17	0.21	-0.53
	Q	0.00	0.00	0.00	0.01	0.04	0.08	0.09	-0.19
F12a	D	-0.14	0.20	0.25	-0.50	-0.37	0.27	0.46	-0.79
	T	-0.02	0.04	0.05	-0.11	0.19	0.09	0.21	0.58
	Q	0.00	0.01	0.01	0.02	0.27	0.06	0.28	0.45
F12b	D	-0.16	0.20	0.26	-0.53	-0.85	0.38	0.93	-1.54
	T	-0.03	0.05	0.06	-0.12	-0.16	0.12	0.20	-0.40
	Q	0.00	0.01	0.01	-0.03	0.05	0.06	0.07	0.14
[F12]	D	-0.09	0.11	0.14	-0.30	-0.32	0.23	0.39	-0.76
	T	-0.01	0.02	0.02	-0.05	0.05	0.09	0.10	-0.26
	Q	0.00	0.00	0.00	-0.01	0.10	0.05	0.11	0.17
(F12*)	D	-0.10	0.10	0.14	-0.32	-0.60	0.21	0.64	-1.04
	T	-0.01	0.01	0.02	-0.06	-0.08	0.08	0.11	-0.33
	Q	0.00	0.01	0.01	0.01	0.04	0.05	0.06	-0.13

<sup>a</sup>CCSD basis set error statistics for reaction energies (RE) and atomization energies (AE) computed using CCSD-F12 models and cc-pVXZ-F12 basis sets in kJ/mol per valence electron from Hättig et al. (see Table 1 in ref 150).

worse than CCSD(F12) for the double- and triple- $\zeta$  basis sets and is among the best performers with the quadruple- $\zeta$  basis set.

For atomization energies, the best performers with the double- $\zeta$  basis set are CCSD[F12] and, unexpectedly, CCSD-F12a. With the largest basis set, however, the best two methods are again CCSD(F12) and CCSD(F12\*), with F12b close behind. The performance of the lone noniterative CC-R12 approximation, CCSD(2) $\overline{\text{R12}}$ , is again comparable, but slightly worse than CCSD(F12).

It is difficult to pinpoint the reasons for a better or poorer performance of a particular approximations to CCSD-R12. The most thorough job to date has been done by Köhn and Tew.<sup>164</sup> Of course, all analyses of this type are largely empirical in nature. In practice, the differences between various approximations are rather small, and almost always will be smaller than the residual errors of the computation (such as those due to the lack of higher-order excitations, etc.). Therefore, pragmatically speaking, the current set of approximate CCSD-R12 methods is good enough, with some slight variation in performance, and the focus of R12 field is likely to shift to other, more pressing problems.

## 6. MULTIREFERENCE R12 METHODS

Major efforts of the R12 developers have been until recently focused on single reference methods, in which the Hartree–Fock determinant is assumed to provide a proper zeroth-order description of the electronic state. However, there are situations where the wave function has significant contributions from multiple configurations; for example, for stretched covalent bonds, electronically excited states, and transition metal compounds, there are often degenerate or nearly degenerate configurations. In those scenarios, multireference (MR) methods are mandated,



the ansätze of which explicitly take into account the multiconfigurational nature and often employ (but are not restricted to) a complete active space self-consistent-field (CASSCF) wave function as the reference function.

Because the cusp conditions dictate the behavior of the wave function at short interelectronic distances, regardless of the electronic state, and the conventional MR methods also employ the usual determinantal expansion in a one-particle basis, they also suffer the slow convergence of electronic (correlation) energies with respect to the basis. To accelerate the convergence, it is essential to incorporate terms directly dependent on the  $r_{12}$  into the wave function, especially considering the tremendous progress and already promising performance of single reference R12 (SR-R12) approaches. Evidently, the key technologies evolved from the development of SR-R12 methods, such as the RI, etc., will be also essential for the MR-R12 methods.

To ease further discussion, instead of using the strong-orthogonality two-particle projector  $\hat{Q}_{12}$  in eq 79, we will employ determinant-based state-specific many-electron projectors  $\hat{Q}$  (following the notation in ref 167), assuming that a reference state  $|0\rangle$  is predefined. These projectors simplify the formalism of MR-R12 methods by reducing the number of projection operators in the expressions.  $\hat{Q}_{\alpha\beta,ij}$  is defined as the projector onto the determinantal space  $\{a_{ij}^{\kappa\lambda}|0\rangle = |_{ij}^{\kappa\lambda}\rangle, \forall \kappa, \lambda, i, j\}$ ;  $\hat{Q}_{\kappa,i}$  is the projector onto the space  $\{a_i^{\kappa}|0\rangle = |_i^{\kappa}\rangle, \forall \kappa, i\}$ , etc. Notice that if  $|0\rangle$  is a single determinant, the determinants  $\{|_i^{\kappa}\rangle\}$  are orthonormal and thus  $\hat{Q}_{\kappa,i} = |_i^{\kappa}\rangle\langle_i^{\kappa}|$ ; in contrast, if  $|0\rangle$  is a multideterminantal function, the simple equality does not hold, because the configurations are in general neither orthogonal nor normalized. In that case, an explicit expression of  $\hat{Q}$  in terms of configurations will involve a metric matrix. The same situation applies to  $\hat{Q}_{\kappa\lambda,ij}$  etc. With the notation  $\hat{Q}$ , we purposely avoid the explicit expressions and implementations of the projectors (there may be multiple ways to express them) and use  $\hat{Q}$  to reformulate the theories under discussion at our convenience to unify them to some extent.

In the MR-R12 methods developed so far, the conventional wave function is augmented by an explicitly correlated component. Except the  $R_{12}$ -MRCI and  $R_{12}$ -MR-ACPF methods of Gdanitz, the explicitly correlated terms are introduced in a contracted manner; that is, given a multideterminantal reference function  $|0\rangle = \sum_R t_R |R\rangle$ , a universal R12 operator acts on  $|0\rangle$  as a whole to generate the explicitly correlated function:

$$\hat{Q} \left( \frac{1}{2} t_{kl}^{ij} r_{\kappa\lambda}^{kl} a_{ij}^{\kappa\lambda} \right) |0\rangle = \hat{Q} \left( \frac{1}{2} t_{kl}^{ij} r_{\kappa\lambda}^{kl} a_{ij}^{\kappa\lambda} \right) \sum_R t_R |R\rangle \quad (179)$$

$$= \hat{Q} \hat{R}_{12} |0\rangle \quad (180)$$

Here,  $\hat{R}_{12}$  produces a single explicitly correlated function from a general multideterminantal reference. In contrast, the earlier MR-R12 methods of Gdanitz generated many explicitly correlated functions from each individual reference determinant; optimization of the resulting large number of parameters posed a serious numerical problem. The idea of internal contraction in MR-R12 was first introduced by Ten-no in the development of MRMP-F12;<sup>84</sup> it leads to a dramatically more compact, yet robust, parametrization and alleviates the numerical challenges faced by the uncontracted ansätze, because now there is only one set of geminal amplitudes to be determined (or none in the SP

ansatz) and its number does not grow with the number of reference determinants. The numerical stability of MR-R12 was further enhanced by adopting the SP ansatz,<sup>84</sup> as was first realized in MRMP-F12 of Ten-no. The combination of internal contraction and SP ansatz in MR-R12 paved the way for developing efficient and numerically stable MR-R12 methods and was followed by all later MR-R12 developments.

These common features result in an R12 operator (generator of the explicitly correlated basis functions) of the following form:

$$\hat{R}_{12} = t_{kl}^{ij} r_{\kappa\lambda}^{kl} E_{ij}^{\kappa\lambda} = \tilde{r}_{\kappa\lambda}^{ij} E_{ij}^{\kappa\lambda} \quad (181)$$

where  $E$  is the spin-free substitution operator,  $t$  is fixed by the cusp condition, and  $\tilde{r}$  is introduced for convenience:

$$E_{ij}^{\kappa\lambda} = \sum_{u,v \in \{\alpha,\beta\}} a_{uv}^{\kappa\lambda} \quad (182)$$

$$t_{kl}^{ij} = \frac{3}{8} \delta_k^i \delta_l^j + \frac{1}{8} \delta_l^i \delta_k^j \quad (183)$$

$$\tilde{r}_{\kappa\lambda}^{ij} = \frac{3}{8} r_{\kappa\lambda}^{ij} + \frac{1}{8} r_{\kappa\lambda}^{ji} \quad (184)$$

### 6.1. $R_{12}$ -MRCI

The first MR-R12 method was formulated by Gdanitz<sup>168,169</sup> in the 1990s, where a linear correlation factor is used, that is,  $f(r_{12}) = r_{12}$ . In  $R_{12}$ -MRCI of Gdanitz, the conventional MRCI is augmented by an explicitly correlated component with coefficients to be optimized:

$$|\Psi\rangle = |\Psi_{\text{MRCI}}\rangle + \sum_I \hat{Q}^I t_{kl}^{ij}(I) r_{\kappa\lambda}^{kl} a_{ij}^{\kappa\lambda} |I\rangle \quad (185)$$

where  $I$  refers to any determinant in the reference space,  $i/j/k/l$  denote any internal orbitals. (If for some  $i/j$ , the orbitals are not occupied in  $I$ , the operator  $a_{ij}^{\kappa\lambda}$  will annihilate the reference determinant  $I$  and thus those terms will not contribute. Therefore, it is not necessary to confine  $i/j$  to orbitals occupied in  $I$ .) The uncontracted MRCI wave function is represented as

$$|\Psi_{\text{MRCI}}\rangle = \sum_I t_I |I\rangle + \sum_S \sum_a t_a^S |\Phi_S^a\rangle + \sum_P \sum_{a,b} t_{ab}^P |\Phi_P^{ab}\rangle \quad (186)$$

$a$  and  $b$  denote external orbitals (not occupied in any reference configurations), and  $S$  and  $P$  denote internal  $N - 1$  and  $N - 2$  electron hole states.  $|I\rangle$ ,  $|\Phi_S^a\rangle$ , and  $|\Phi_P^{ab}\rangle$  denote internal, singly external, and doubly external configurations, respectively.

The reference determinant dependent projector  $\hat{Q}^I$  (i.e., with  $|I\rangle$  as the reference function of the projector) ensures that the explicitly correlated functions are orthogonal to the conventional MRCI wave function, and it is defined as

$$\hat{Q}^I = \hat{Q}_{\kappa\lambda,ij}^I - \hat{Q}_{pq,ij}^I \quad (187)$$

To simplify the theory, the author suggested to restrict the orbital pair  $kl$  to few pairs selected by chemical arguments.<sup>169</sup> This restriction makes  $R_{12}$ -MRCI lose the orbital invariance. Along the same line, Gdanitz developed the explicitly correlated multi-reference averaged coupled-pair functional  $R_{12}$ -MR-ACPF. The methods were applied to the potential energy surfaces of  $\text{N}_2$ ,<sup>169,170</sup>  $\text{Be}_2$ ,<sup>171</sup>  $\text{He}_2$ ,<sup>174,173</sup>  $\text{Ne}_2$ ,<sup>174</sup>  $\text{HF}$ ,<sup>175</sup> the reaction  $\text{F}_2 + \text{H} \rightarrow \text{HF} + \text{H}$ ,<sup>176</sup> the atomic ground states and ionization

potentials,<sup>177</sup> electron affinities,<sup>178</sup> and the valence excited states of methylene.<sup>179</sup>

## 6.2. MRMP2-F12

Ten-no developed an R12 correction<sup>180</sup> in the framework of MRMP2 theory.<sup>181,182</sup> If the zeroth-order wave function is represented by  $|0\rangle$ , the R12 augmented first-order wave function is

$$|\Psi^{(1)}\rangle = |\Psi_{\text{MRMP}}^{(1)}\rangle + \hat{Q}\hat{R}_{12}|0\rangle = |\Psi_{\text{MRMP}}^{(1)}\rangle + |\Psi_{\text{R12}}^{(1)}\rangle \quad (188)$$

$\hat{R}_{12}$  is defined as in eq 181, where  $i/j$  refer to the internal orbitals. The projector  $\hat{Q}$  is chosen as  $(\hat{Q}_{\alpha\beta,ij} - \hat{Q}_{ab,ij})$ . The semi-internal excitations are excluded from the geminal operator, based on the analogy with atomic cases, where their contribution vanishes once OBS is saturated up to 3  $L_{\text{occ}}$  (“occ” refers to occupied orbitals in  $|0\rangle$ ). It was also demonstrated by the example of  $\text{O}_2$  that the semi-internal contribution to the correlation energy is rather insensitive to the basis set.

The second-order energy correction with R12 contribution is obtained from the minimization of the Hylleraas functional:

$$\mathcal{H}^{(2)} = 2\langle 0|\hat{H}^{(1)}|\Psi^{(1)}\rangle + \langle \Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle \quad (189)$$

and upon introducing further approximations, simplifies to an additive form:

$$\mathcal{H}^{(2)} = E_{\text{conv}}^{(2)} + E_{\text{R12}}^{(2)} \quad (190)$$

where  $E_{\text{R12}}^{(2)} = 2\langle 0|\hat{H}^{(1)}|\Psi_{\text{R12}}^{(1)}\rangle + \langle \Psi_{\text{R12}}^{(1)}|\hat{H}^{(0)}|\Psi_{\text{R12}}^{(1)}\rangle$ . The evaluation of the second term is further simplified by an approximate Fock operator along with the so-called approximation A. The Hylleraas functional reduces to the MP2-F12/A\*(SP) energy for a Hartree–Fock reference function.<sup>96</sup> MRMP2-F12 is applied to the excitation energy of carbon atom, the atomization energy of  $\text{CH}_2$ , and the potential energy curve of  $\text{O}_2$ .

## 6.3. $[2]_{\text{R12}}$

Torheyden and Valeev formulated a generally applicable second-order R12 correction, dubbed  $[2]_{\text{R12}}$ .<sup>147</sup> Given an arbitrary electronic state  $|0\rangle$ , the explicitly correlated function  $|\Psi^{(1)}\rangle$  is generated by the  $\hat{R}_{12}$  operator:

$$|\Psi^{(1)}\rangle = \hat{\Omega}^{(1)}|0\rangle = \hat{Q}\hat{R}_{12}|0\rangle \quad (191)$$

The projector is defined as  $(\hat{Q}_{\kappa\lambda,ij} - \hat{Q}_{pq,ij} - \hat{Q}_{\alpha'i})$ . Despite the apparent formal difference, the above simpler expression is an equivalent reformulation of the first-order wave function given in ref 147. Because only the orbital pairs  $pq$  from OBS are projected out from the double excitations, semi-internal excitations are included in  $|\Psi^{(1)}\rangle$ , and this was found to be important for  $[2]_{\text{R12}}$ . In addition, the singly excited configurations  $\{|i^{\alpha'}\rangle\}$  (a subset of the semi-internal excitations) are excluded via the projector  $\hat{Q}_{\alpha',i}$  because these determinants are considered as the source of one-particle incompleteness and will be taken care of independently.

The second-order energy correction is computed by evaluating the Hylleraas functional (see eq 189), with  $\hat{H}^{(0)} = \hat{F} = F_{\lambda}^{\kappa} a_{\kappa}^{\lambda}$ . Because of the existence of semi-internal contributions, the evaluation of the geminal–geminal block of  $\langle \Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle$  requires 4-RDM and is relatively complicated. Therefore, two additional approximations are introduced: (1) 3- and 4-RDM are approximated by 1- and 2-cumulants; and (2) in the spirit of screening approximations,<sup>183</sup> all diagrams are omitted, in which two  $r$  matrix elements or a  $r$  and a Coulomb ( $g$ ) matrix

elements are connected via a 2-cumulant. These further approximations lead to an approximate Hylleraas functional.

An important feature of  $[2]_{\text{R12}}$  is its general applicability: it applies to any electronic state as long as the 2-RDM is available. This was demonstrated by applying the correction to a MRCI wave function, that is,  $|0\rangle = |\Psi_{\text{MRCI}}\rangle$ . In that case, all orbitals in OBS are occupied orbitals. The potential energy surfaces of HF and  $\text{N}_2$  were studied.

With a MRCI wave function as the reference function,  $[2]_{\text{R12}}$  is relatively expensive. A much less expensive alternative is to correlate only the dominant contribution of  $|\Psi_{\text{MRCI}}\rangle$ . The simplest choice may be the CASSCF wave function, that is,  $|0\rangle = |\Psi_{\text{CASSCF}}\rangle$ . In addition, the original  $[2]_{\text{R12}}$  (termed as SO- $[2]_{\text{R12}}$  to distinguish from the spin-free version) is formulated in spin–orbital basis due to the use of a spin–orbital Fock operator. It will be advantageous to develop a spin-free  $[2]_{\text{R12}}$  to further reduce the cost and avoid biasing toward any particular spin components. This is achieved by using the spin-averaged Fock operator instead of the spin–orbital one. These extensions are incorporated in the development of SF- $[2]_{\text{R12}}$  by Kong and Valeev,<sup>184</sup> and the Hylleraas functional is expressed in terms of spin-free RDMs. In addition, a different approximation to the geminal–geminal block is introduced to partially avoid high-rank RDMs:

$$\langle \Psi^{(1)}|(\hat{H}^{(0)} - E^{(0)})\hat{\Omega}^{(1)}|\Psi^{(0)}\rangle \approx \langle \Psi^{(1)}|[\hat{H}^{(0)}, \hat{\Omega}^{(1)}]|\Psi^{(0)}\rangle \quad (192)$$

This approximation is valid in SR-R12 methods if we consider the Brillouin condition and assume the generalized Brillouin condition. With this approximation, only up to 3-RDM is required to evaluate the Hylleraas functional. The screening approximation and a spin-free cumulant approximation<sup>185</sup> are then invoked for further simplicity. The method was benchmarked with the bond-breaking of HF and  $\text{N}_2$  and the singlet–triplet separation of methylene.

## 6.4. CASPT2-F12 and MRCI-F12

Shiozaki and Werner developed the MR-R12 methods named CASPT2-F12<sup>167</sup> and MRCI-F12.<sup>186</sup> In CASPT2-F12, based on the methods of Werner and Knowles,<sup>187,188</sup> the conventional wave function is augmented by the explicitly correlated part:

$$|\Psi\rangle = (t_I|I\rangle + t_a^S|\Phi_a^S\rangle + t_{ij}^{pp}|\Phi_{ij}^{pp}\rangle) + \hat{Q}\hat{R}_{12}|0\rangle \quad (193)$$

( $p = \pm 1$  corresponds to singlet and triplet coupling of external electrons, respectively; the doubly excited configurations are internally contracted  $|\Phi_{ij}^{ab}\rangle = (1/2)(E_i^a E_j^b + p E_i^b E_j^a)|0\rangle$ .) The projector is chosen to be  $(\hat{Q}_{\kappa\lambda,ij} - \hat{Q}_{pq,ij})$ , which is equivalent to the projector defined by eq 4 in the original paper (they produce the same wave function when acting on  $\hat{R}_{12}|0\rangle$ ). Therefore, the semi-internal excitations are included, but the singly excited configurations are not projected out. Instead, the authors used normal ordered operators to approximately project out the singles:

$$\hat{R}_{12} = \tilde{r}_{\kappa\lambda}^{kl} \{E_{ij}^{\kappa\lambda}\} \quad (194)$$

where  $\{\}$  denotes normal order of Mukherjee and Kutzelnigg.<sup>189</sup> The current ansatz is essentially equivalent to the ones presented by the authors in ref 167, where the semi-internal component of the R12 function is further decomposed using explicit singles projectors for practical reasons. The Hylleraas functional (eq 189) is then minimized to determine the conventional amplitudes and the second-order energy, with  $\hat{H}^{(0)} = \hat{F}$ . In comparison

to MRMP-F12 and  $[2]_{R12}$ , the amplitudes of the conventional wave function are modified due to the coupling with the explicit correlation. CASPT2-F12 was applied to the singlet–triplet splitting of methylene, the dissociation energy of ozone, and low-lying excited states of pyrrole.

In MRCI-F12 of Shiozaki and Werner,<sup>186</sup> the ansatz reads:

$$|\Psi\rangle = |\Psi_{\text{MRCI}}\rangle + |\Psi_{R12}\rangle \\ = (t_I|I\rangle + t_a^S|\Phi_S^a\rangle + t_{ab}^{ijp}|\Phi_{ijp}^{ab}\rangle) + t_{F12}\hat{Q}\hat{R}_{12}|0\rangle \quad (195)$$

The ansatz is similar to CASPT2-F12, but a direct diagonalization procedure is taken instead of a perturbative treatment. One additional parameter  $t_{F12}$  is introduced to allow for more flexibility (if  $t_{F12}$  is set to 1, the ansatz is called the FIX ansatz; it is called the SFIX ansatz if  $t_{F12}$  is optimized). The projector is defined as  $(\hat{Q}_{\kappa\lambda,ij} - \hat{Q}_{pq,ij} - \hat{Q}_{\alpha',i})$ , so the singles are excluded, in line with  $[2]_{R12}$ . The energy expectation value  $\langle\Psi|\hat{H}|\Psi\rangle/\langle\Psi|\Psi\rangle$  is then minimized to determine the amplitudes of the MRCI wave function (the R12 amplitudes are fixed) and the energy. Additional approximations are introduced to simplify MRCI-F12:  $\langle\Psi_{R12}|\hat{H}|\Psi_{R12}\rangle$  is approximated by  $\langle\Psi_{R12}|\hat{H}|\Psi_{R12}\rangle$ ; for most of the terms appearing in the evaluation of the coupling term  $\langle\Psi_{\text{MRCI}}|\hat{H}|\Psi_{R12}\rangle$ ,  $\hat{H}$  is replaced by  $\hat{F}$ . Similarly, MRACPF-F12 is developed, which has much smaller size-extensivity error as compared to MRCI. MRCI-F12 and MRACPF-F12 are applied to the singlet–triplet splitting of methylene, the dissociation energy of ozone, properties of diatomic molecules, and the reaction barrier and exothermicity of the  $F + H_2$  reaction.

Shiozaki and Werner also extended MRCI-F12 to a multistate version, using multiple reference functions to deal with avoided crossings and conical intersections.<sup>190</sup> For a state  $M$ , the MRCI-F12 wave function is parametrized as

$$|\Psi^M\rangle = |\Psi_{\text{MRCI}}\rangle + |\Psi_{R12}\rangle \quad (196) \\ = (t_I^M|I\rangle + t_a^{S,M}|\Phi_S^a\rangle + \sum_N t_{ab}^{ij,MN}|\Phi_{ij,N}^{ab}\rangle) \\ + \sum_N t_{F12}^{MN}\hat{Q}\hat{R}_{12}|N\rangle \quad (197)$$

Therefore, internally contracted doubly external configurations with respect to multiple reference functions, both conventional and explicitly correlated parts, are present in the ansatz to relax the external functions. The projector is essentially the same as in the single state MRCI-F12. For the term  $\langle M|\hat{R}_{12}^+\hat{Q}\hat{H}\hat{Q}\hat{R}_{12}|N\rangle$ , it is approximated by

$$\langle M|\hat{R}_{12}^+\hat{Q}\left(\hat{F} + \frac{1}{2}E_M^{(1)} + \frac{1}{2}E_N^{(1)}\right)\hat{Q}\hat{R}_{12}|N\rangle$$

where  $E_M^{(1)} = \langle M|\hat{H} - \hat{F}|M\rangle$ . To avoid humps on the potential energy surfaces, the reference functions are generated by linear combinations of the CASSCF functions from diagonalizing the Fock operator so that:

$$\langle M|\hat{F}|N\rangle = \delta_{MN}E_M^M \quad (198)$$

The multistate MRCI-F12 and MRACPF-F12 are applied to the avoided crossing of LiF, excited states of ozone, and the  $H_2 + OH(A^2\Sigma^+)$  reaction.

## 6.5. G-CASSCF

The idea of explicit correlation is explored in a different direction by Varganov and Martínez.<sup>191</sup> When studying ab initio nonadiabatic quantum dynamics, it is desirable to describe multiple electronic states accurately and CASPT2 is often used for this purpose, because dynamical correlation is often important to properly treat the states (while CASSCF only considers the static correlation), and it is taken into account by CASPT2 in a relatively efficient manner. However, CASPT2 is rather sensitive to the choice of the active space, partially due to the intricate interplay between static correlation and dynamical correlation. Varganov and Martínez introduced the G-CASSCF method, in which the dynamical correlation is fixed by a geminal  $f_{12}(r_{12})$ . The ansatz for a two electron system reads:

$$|\Psi\rangle = G \sum_I c_I|I\rangle = (1 - f_{12}(r_{12})) \sum_I c_I|I\rangle \quad (199)$$

In the presence of the dynamical correlation, the MCSCF coefficients  $c_I$  and the orbitals are optimized. The method is applied to the ionic and covalent dissociation channels of  $H_2$  and  $HeH^+$ .

## 6.6. MR CABS Singles Correction

In the applications of MR-R12 methods, it is noticed that the R12 correction has significantly reduced the basis error of the dynamical correlation energy so that the basis error in the reference energy needs to be taken care of to achieve a balanced accuracy, a phenomenon also observed in SR-R12 methods. Toward that purpose, Kong and Valeev have developed a singles correction method termed as  $[2]_S$  (“S” stands for “singles”) to deal with the one-particle incompleteness.<sup>192</sup>  $[2]_S$  is a second-order perturbative correction, and the cost of the correction scales as  $o^2X^2$  ( $o$  is the number of occupied orbitals in CASSCF and  $X$  is the dimension of CABS), negligible in comparison to that of the R12 computation.

For the same purpose, Shiozaki and Werner developed a configuration-interaction approach.<sup>177</sup> The missing singly excited configurations due to the incomplete basis are included in the singles wave function ansatz:

$$|\Psi_S^M\rangle = |\tilde{M}\rangle + \sum_N t_{\alpha'}^{i,MN} E_i^{\alpha'} |\tilde{N}\rangle \quad (200)$$

$|\tilde{M}\rangle$  is a unitary transformation of the reference functions  $\{|M\rangle\}$ , which maximizes the overlap with the MRCI-F12 wave functions. Diagonalizing the Hamiltonian in the space  $\{E_i^{\alpha'}|\tilde{N}\rangle\}$  then yields the energy  $E_S^M$ . The CABS singles correction  $\Delta E_S^M$  is defined as  $E_S^M - \langle M|\hat{H}|\tilde{M}\rangle$ .

## 6.7. Comparison of MR-R12 Methods

Because most of the developments in MR-R12 methods are quite recent, the data available in literature are not sufficient to carry out an extensive comparison between the different methods. Here, we present a preliminary comparative study. The data for  $[2]_{R12}$  are from the variant SF- $[2]_{R12}$ , and the reference function  $|0\rangle$  is from CASSCF. When necessary, we will denote the choice of the reference function in parentheses, for example, SF- $[2]_{R12}$ (CAS).

In the following calculations, an exponential correlation factor was adopted,<sup>84</sup>  $f(r_{12}) = \exp(-\gamma r_{12})/\gamma$ . When the aug-cc-pVXZ basis<sup>3</sup> (abbreviated as “aXZ”) was employed as OBS,  $\gamma = 1.5$  was used; with the cc-pVXZ-F12 basis<sup>165</sup> (abbreviated as “XZF”) of Peterson as OBS, the recommended values for  $\gamma$  were adopted. The MRCI (without internal contraction) was based on CASSCF, with core orbitals frozen in MRCI.

In SF-[2]<sub>R12</sub>(CAS), the correlation energy from the explicit correlation is decoupled from the conventional contribution; it is also missing by definition in MRMP2-F12 of Ten-no (third-order MRMP3-F12 would include such effect).<sup>180</sup> As compared to SF-[2]<sub>R12</sub>(CAS), Ten-no's method invoked more dramatic approximations and arrived at a rather simple expression. The two approaches are closely related, but SF-[2]<sub>R12</sub>(CAS) is an alternative, more general treatise of the explicitly correlated terms. To compare the two methods, we computed the excitation energies (<sup>1</sup>D–<sup>3</sup>P) of carbon atom and the atomization energy of CH<sub>2</sub> (<sup>1</sup>A<sub>1</sub> state).<sup>180</sup> For computational details and results, see Table 5. For the C atom excitation energy, the two methods differ by 0.024 eV in aDZ, but the difference decreases to as small as 0.001 eV in aQZ. For the atomization energy of CH<sub>2</sub>, the results are also very similar; in aQZ, the difference is around 0.7 kJ mol<sup>-1</sup> (about 0.007 eV). Considering the rather different approximations introduced in each method, the similarity of the results is remarkable. More testing is needed, however, to make stronger conclusions about the similarities between our SF-[2]<sub>R12</sub>(CAS) method and Ten-no's MRMP-F12 method.

To compare SF-[2]<sub>R12</sub> and MRCI-F12, we take as an example the basis set error of the adiabatic excitation energy ( $T_e$ ) from the lowest triplet to the lowest singlet state of methylene,  $E(\tilde{a}^1A_1) - E(\tilde{X}^3B_1)$ . The results are tabulated in Table 6. On

**Table 5. Comparison between [2]<sub>R12</sub> and MRMP2-F12<sup>a</sup>**

	CASSCF	MRMP2	corr	corr+F12	corr+[2] <sub>R12</sub>
C Atom Excitation Energy (eV): <sup>1</sup> D– <sup>3</sup> P					
aDZ	1.595	1.409	-0.186	-0.290	-0.314
aTZ	1.513	1.262	-0.250	-0.307	-0.310
aQZ	1.513	1.228	-0.284	-0.314	-0.315
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> State) Atomization Energy (kJ mol <sup>-1</sup> )					
aDZ	639.5	681.1	41.6	73.6	73.9
aTZ	654.9	715.0	60.0	72.2	71.6
aQZ	656.3	722.7	66.4	72.1	71.4

<sup>a</sup>The “corr” denotes the correlation energy contribution to the properties under investigation. “F12” denotes the pure F12 contribution of MRMP2-F12 (excluding the MRMP2 correlation energy). For all calculations, the 2s and 2p valence orbitals define the active space. The core orbitals are optimized in state-specific CASSCF computations and then frozen in the MRMP2. The geometry of CH<sub>2</sub> ( $D_{2h}$  symmetry) and the MRMP2 and MRMP2-F12 energies are taken from ref 180:  $R_{CH} = 1.1068 \text{ \AA}$ , and  $\angle HCH = 102.03^\circ$ . “aXZ” refers to the aug-cc-pVXZ basis set.

one hand, even in DZF, SF-[2]<sub>R12</sub> reduces the basis error from 0.048 eV to a very small value of 0.003 eV, even better than the quality in QZF; moreover, the correlation energy contribution to  $T_e$  quickly converges, once SF-[2]<sub>R12</sub> is included. For example, with SF-[2]<sub>R12</sub>, the difference between TZF and QZF is as small as 0.001 eV, in contrast to 0.01 eV without the correction. Therefore, the convergence (to the SF-[2]<sub>R12</sub> basis limit) is greatly accelerated. On the other hand, as compared to the CBS limit value, we notice that SF-[2]<sub>R12</sub> overestimates the CBS limit of the correlation energy; for example, in QZF, the SF-[2]<sub>R12</sub> corrected  $T_e$  is -0.075 eV, 0.008 eV lower than the estimated CBS value. It is clear from the table that even with SF-[2]<sub>R12</sub>, the rapid initial convergence to the CBS limit becomes slow in the asymptotic limit. In comparison, MRCI-F12<sup>186</sup> converges to the exact limit more quickly. The major difference of SF-[2]<sub>R12</sub>(CAS) from MRCI-F12, in which the conventional correlation is optimized in the presence of the explicit correlation, is the lack of first-order coupling between the conventional and R12 correlation wave function contributions. The R12 correction is based purely on CASSCF and is independent of the correlation models, either MRCI and MRPT, etc. Essentially, the “interference effect” between the correlation methods and basis-set hierarchies<sup>193,194</sup> is not taken into account in SF-[2]<sub>R12</sub>(CAS). Such an approach is expected to converge to the basis set limit as slowly as the correlation energy itself, just like its slowly convergent single-reference counterpart, the difference between the basis set error of MP2 and CCSD. To estimate the magnitude of the interference effect, we computed the MP2 and CCSD basis set errors with MP2-R12 and d-CCSD(2)<sub>R12</sub><sup>144</sup> for the two states, and the results are contained in Table 6 (only R12 contributions to  $T_e$  are shown). Comparison of the two sets of data spotlights the interference effect: the difference converges quite slowly, and even at QZF, the difference is still as large as 0.019 eV. This effect should and does extend to MR methods, and it accounts for the major difference between SF-[2]<sub>R12</sub> and MRCI-F12. We emphasize that the issue under discussion is not inherent in the general theory SF-[2]<sub>R12</sub>; it emerges only because we are investigating the particular variant SF-[2]<sub>R12</sub>(CAS) and employ the uncorrelated CASSCF reference functions (in the sense that the dynamical correlation is missing). Work to account for the interference effect within our scheme is currently underway, and preliminary results look promising. In the end, we stress that even the estimated MRCI CBS limit still differs from the experimental value by about 0.04 eV, much larger than the interference effect at TZF or QZF. Thence judging from the particular case study, even with CASSCF references, practically SF-[2]<sub>R12</sub> is a

**Table 6. Comparison between [2]<sub>R12</sub> and MRCI-F12 for the Singlet–Triplet Separation of CH<sub>2</sub> in eV: <sup>1</sup>A<sub>1</sub>–<sup>3</sup>B<sub>1</sub><sup>a</sup>**

	CASSCF	MRCI	corr	corr+F12	corr+[2] <sub>R12</sub>	MP2-R12	CCSD(2) <sub>R12</sub>
DZF	0.457	0.438	-0.019	-0.054	-0.070	-0.093	-0.034
TZF	0.437	0.391	-0.047	-0.065	-0.074	-0.046	-0.012
QZF	0.436	0.379	-0.057	-0.067	-0.075	-0.027	-0.006
CBS	0.435	0.368	-0.067				
exp (ref 195)	0.406						
DMC (ref 196)	0.406(4)						

<sup>a</sup>The “corr” denotes the correlation energy contribution to the properties under investigation. “F12” denotes the pure F12 contribution of MRCI-F12 (excluding the MRCI correlation energy). For all calculations, the 2s and 2p valence orbitals define the active space. The core orbitals are optimized in state-specific CASSCF computations and then frozen in the MRCI. The geometries, MRCI/MRCI-F12 (the SFIX version) energies, and CBS limits are taken from ref 186 (Table 4). “XZF” refers to the cc-pVXZ-F12 basis set. “DMC” stands for diffusion Quantum Monte Carlo. MP2-R12 and CCSD(2)<sub>R12</sub> refer to purely the R12 contributions (excluding the conventional contributions).

very reasonable approximation to the more rigorous MRCI-F12, if other high order effects are not considered.

### 6.8. Summary

The development of MR-R12 methods within the modern R12 framework has started only recently. Among the methods developed so far, MRMP2-F12 of Ten-no and SO/SF-[2]<sub>R12</sub> methods of Valeev et al. are the simplest. Both are applicable within the second-order multi reference perturbation theory framework. The latter have also been applied to arbitrary correlated wave function, requiring only up to 2-RDM. When using a CASSCF function instead of the correlated total wave function as the reference, the cost of [2]<sub>R12</sub> is similar to a single-reference MP2-R12. Both MRMP2-F12 and [2]<sub>R12</sub> are posteriori corrections and can be viewed as relatively simple extensions to MP2-R12. CASPT2-F12 and MRCI-F12 are more rigorous R12 methods; the coupling between conventional and explicitly correlated terms is included, and the amplitudes of the conventional part are optimized in the presence of explicit correlation.

## 7. CONCLUSION

This concludes our Review of recent developments in explicitly correlated R12/F12 methods of electronic structure. R12 methods are broadly applicable, efficient realizations of the same ideas that go back to the work by Hylleraas and Slater in the late 1920s. By employing interelectronic distances explicitly in the wave function expansion, the R12 methods dramatically decrease the basis set error of accurate wave function methods and yield much smaller errors at the same cost. The keys to R12 methods practicality are (1) their use of explicitly correlated terms alongside the standard determinantal terms, and (2) the ingenious use of the resolution of the identity (RI) to approximate three- and four-electron integrals in terms of only one- and two-electron integrals. The essential features of this idea were described by Werner Kutzelnigg in 1985; many technical advances had to happen since then to turn R12 methods practical and usable by chemists today. Among the key advances are the introduction of a short-range (exponential) geminal as correlation factor, robust numerical approximations for many-electron integrals, and simplified coupled-cluster R12 methods. This list will surely be extended in the years to come.

The current technology of R12 methods has been especially optimized for computation of valence correlation energies for molecules including the first three rows of the Periodic Table. The use of specialized cc-pVXZ-F12 basis sets of Peterson et al.<sup>165,204</sup> in combination with simplified CCSD(T)-R12 methods permits essentially black-box applications: the user only needs to specify the cardinal number of the cc-pVXZ-F12 basis sets, and all other “parameters” of the R12 theory (RI basis set, geminal exponent, etc.) can be determined automatically. On the other hand, there are still problematic cases that demand user intervention. For example, the recent application of CC-R12 methods to the potential energy of argon dimer<sup>197</sup> noted poor performance of the R12 methodology, whereas it should be likely attributed to the use of basis sets that are poorly suited for computations on such dispersion-bound species.

We must comment on whether the current R12 technology can compete with the basis set extrapolation methods. In modern quantum chemistry, there are a number of basis set extrapolation methods, the main two groups being extrapolations with correlation consistent basis set families of Dunning<sup>198</sup> and the CBS model chemistries of Petersson and co-workers.<sup>199</sup> Among the

most often used extrapolation formula for correlation energies is the inverse cubic extrapolation of Helgaker et al.<sup>200</sup>

$$E(X) = E_{\text{CBS}} + \frac{a}{X^3} \quad (201)$$

where  $E(X)$  is the correlation energy computed with a correlation consistent basis set with cardinal number  $X$ ,  $E_{\text{CBS}}$  is the complete basis set limit, and  $a$  is a parameter determined by fitting, typically to  $E(X)$  and  $E(X + 1)$ . Equation 201 can be motivated from the analysis of natural orbital expansion for a two-electron atom (eq 28), but all extrapolation formulas should be considered empirical. Equation 201 and similar formulas are currently the dominant method to account for the basis set incompleteness of molecular energy when high accuracy is sought. The success of the extrapolation approaches is due to their simplicity and effectiveness. Their obvious limitation, however, is that they do not improve the wave function directly; hence only some (not all) properties can be improved. The advantage of R12 methods is that all properties can, in principle, be improved. Do R12 methods offer comparable or superior performance to extrapolation methods for energies and other properties?

In the regime of ultrahigh accuracy necessary for computational spectroscopic studies, the R12 methods have been established as superior to extrapolation due to their improved asymptotic convergence rate.<sup>201,202</sup> In the chemical accuracy regime, the answer seems to be also “yes”. For reaction energies, Köhn and Tew find that already with the cc-pVDZ-F12 basis the explicitly correlated CCSD energies have smaller basis set error than the energies extrapolated from conventional aug-cc-pVTZ and QZ CCSD energies, the latter clearly more expensive than the former. Similarly, a recent comparison of R12 methods and extrapolation for harmonic and anharmonic vibrational frequencies by Huang, Valeev, and Lee<sup>149</sup> suggested that the R12 methods are always at least as reliable as extrapolated results. While more extensive benchmarking is needed, the R12 methods should now be preferred for all practical computations that require high accuracy.

In conclusion, we will turn our attention to the future of R12 methods. Explicitly correlated wave functions are as old as quantum mechanics itself, and they played a role in establishing it as a quantitatively correct theory of atoms and molecules. Yet they did not emerge as broadly applicable computational tools until the mid 2000s. Looking back, the development of R12 theory looks like a series of tackling the most pressing issues of the time: basic framework (Kutzelnigg 1985), CC-R12 (Noga 1992), efficient resolution of the identity (Klopper 2002, Valeev 2004, Ten-no 2004), short-ranged correlation factor and cusp conditions (Ten-no 2004), practical CC-R12 (Klopper 2005, Adler 2007, Valeev 2008), and R12-optimized basis sets (Peterson 2008). Our safe guess is that the attention of the community will be focused on solving the current problems of modern R12 theory. Now we are at a point where R12 methods are ready to be used by chemists. Therefore, we foresee a major effort to make R12 methods widely applicable and black-box. In fact, we anticipate that, thanks to R12 methods, the basis set some day will no longer be a required part of computation's input. There is much room for developing analytic algorithms for computing properties with R12 wave functions, to be usable in a routine manner. We are likely to see the development of R12 variants of new methods, for example, such as those used for strong correlation, as well as cross-fertilization of ideas with other methods, such as Quantum Monte Carlo.

Table 7. Definition of Orthonormal Spin-Orbital Spaces Utilized in This Review

space	symbols	description	support <sup>a</sup>	comments
$\{i\}$	$i,j,k,l,m,n,o,w,x,y$	occupied Hartree–Fock	OBS	
$\{a\}$	$a,b,c,d$	unoccupied (virtual) Hartree–Fock	OBS	$\{i\} \cap \{a\} = \emptyset$
$\{p\}$	$p,q,r,s$	any Hartree–Fock	OBS	$\{p\} = \{i\} \cup \{a\}$
$\{\alpha\}$	$\alpha,\beta,\gamma,\delta$	any unoccupied	CBS	$\{i\} \cap \{\alpha\} = \emptyset, \{a\} \cap \{\alpha\} = \{a\}$
$\{\alpha'\}$	$\alpha',\beta',\gamma',\delta'$	any unoccupied not in $\{a\}$	CBS	$\{a\} \cap \{\alpha'\} = \emptyset, \{\alpha'\} \cap \{\alpha\} = \{\alpha'\}$
$\{\kappa\}$	$\kappa,\lambda,\mu,\nu$	any	CBS	$\{\kappa\} = \{i\} \cup \{\alpha\}, \{\kappa\} = \{p\} \cup \{\alpha'\}$
$\{a'\}$	$a',b',c',d'$	CABS = any in $\text{ABS} \perp \{p\}$	ABS	$\langle p a'\rangle = 0$
$\{p'\}$	$p',q',r',s'$	any in ABS	ABS	

<sup>a</sup> OBS = orbital basis set, ABS = auxiliary basis set, CBS = formal complete basis set.

We also posit that the ideas of R12 methods are likely to be useful in other contexts, such as in quantum chemical computations with nonstandard numerical representations. Quantum chemistry is attempting to solve a highly singular, highly dimensional, partial differential equation, which is complicated enough, and we should deliberately use all of the a priori knowledge we have. The R12 methods have taught us that very few terms, with some or no adjustable parameters, can describe the nonanalytic behavior of the wave function near the electron–electron singularities. In finite-element representations, the appearance of non-analytic, or high-frequency, components in the wave function mandates the use of finely spaced grids. In one-electron methods, such as plane-wave DFT, the high-frequency components that include the electron–nuclear cusp are problematic and require the use of pseudopotentials; in correlation methods, analogous issues will appear due to the interelectronic cusp. Just like the use of pseudopotentials in DFT lead to much more efficient numerical representations of electronic orbitals, addition of explicitly correlated terms in the R12 spirit will reduce the complexity of numerical representation of the two-electron wave functions.

Despite the lack of certainty about the new ideas and directions that may be spurred by the R12 methodology, we are certain that some sections of this Review will need to be updated soon to keep up with the rapid pace of progress in the field. The R12 methods have deservedly garnered much attention in the theoretical chemistry community, and the number of studies and applications of R12 methods will continue to increase rapidly.

## APPENDIX: NOTATION

The present notation is similar to that used in other R12 studies.<sup>82,85,120,203</sup>

Orthonormal spin–orbital spaces are defined in Table 7. Tensor notation for second-quantized expressions has been described in detail elsewhere, for example, refs 204 and 82. There is a direct correspondence between tensor and Dirac notations:

$$O_p^q = \langle p|O(1)|q\rangle \quad (202)$$

$$G_{pq}^{rs} = \langle pq|G(1,2)|rs\rangle \quad (203)$$

Antisymmetrized matrix elements are denoted with a horizontal line above the operator symbol:

$$\overline{G}_{pq}^{rs} = G_{pq}^{rs} - G_{pq}^{sr} \quad (204)$$

Summation is implied over all pairs of indices that appear in the same term of an expression both in bra and in ket (the Einstein

summation convention). When diagonal matrix elements ( $O_p^p$ ) appear in an expression, then the summation is shown explicitly.

Matrix elements of one- and two-body operators featured in the R12 theory are denoted as follows:

$$\begin{aligned} F_p^q &= \langle p|\hat{F}_1|q\rangle & K_p^q &= \sum_m g_{mp}^{qm} \\ g_{pq}^{rs} &= \langle pq|r_{12}^{-1}|rs\rangle & r_{pq}^{rs} &= \langle pq|f(r_{12})|rs\rangle \\ r, [T, r]_{pq}^{rs} &= \langle pq|[f(r_{12}), [\hat{T}_1 + \hat{T}_2, f(r_{12})]]|rs\rangle & (r^2)_{pq}^{rs} &= \langle pq|f(r_{12})^2|rs\rangle \\ (gr)_{pq}^{rs} &= \langle pq|r_{12}^{-1}f(r_{12})|rs\rangle & (gr^2)_{pq}^{rs} &= \langle pq|r_{12}^{-1}f(r_{12})^2|rs\rangle \end{aligned}$$

where  $\hat{T}_i$  and  $\hat{F}_i$  are the kinetic energy and Fock operator for the  $i$ th electron, respectively. The present notation for the matrix elements uses capital letters for all one-electron operators and lower case character for all two-electron operators. The matrix elements of the Fock operator are denoted  $F_p^q$  and should not be confused with matrix elements of the correlation factor,  $f(r_{12})$ , denoted as  $r_{pq}^{rs}$ .

It is important to distinguish pairs of orbital indices that correspond to the correlation operator ( $R_{\alpha\beta}^{ij}$ ) from the usual pairs of occupied MO indices  $ij$ . We will therefore use a separate group of occupied orbital symbols to indicate such pairs of indices ( $xyow$ ), for example:

$$V_{ij}^{xy} = \frac{1}{2} \overline{R}_{\alpha\beta}^{xy} \overline{g}_{ij}^{\alpha\beta} \quad (205)$$

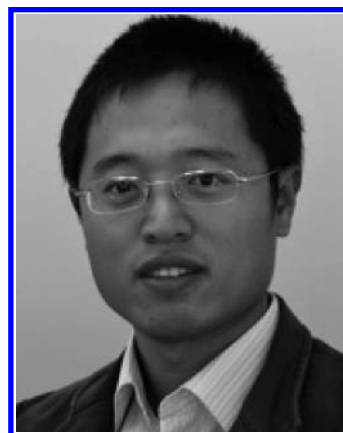
The non-Hermitian character of  $V$  is thus apparent.

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Dr. Florian A. Bischoff received both his Diplom and his Ph.D. from the University of Karlsruhe in 2006 and 2009, respectively. His work under the supervision of Prof. Dr. Wim Klopper included the development of explicitly correlated methods suited for heavy elements, and the treatment of highly singular operators in the R12 framework. Currently, he is a postdoctoral associate at Virginia Tech on a German Academic Exchange Service (DAAD) Fellowship; his current work focuses on developing multiresolution representations for many-body electronic structure in molecules.



Prof. Edward F. Valeev received his M.Sc. in Chemistry in 1996 from the Higher Chemistry College of the Russian Academy of Sciences, located in Moscow, Russia. His thesis work focused on structural studies of buckminsterfullerene derivatives under the supervision of Dr. Yuri L. Slovokhotov. His Ph.D. work with Prof. Henry F. Schaefer III at the University of Georgia involved the development of explicitly correlated electronic structure methodology. After completing his Ph.D. in December 2000, he held a research scientist post at the School of Chemistry and Biochemistry at Georgia Tech, with a joint research

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