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Explicitly Correlated Electrons in Molecules

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1. INTRODUCTION

One of the central challenges of computational molecular investigation is the solution of the time-independent, nonrelativistic Born–Oppenheimer electronic Schrödinger equation. For a system of n electrons and N nuclei with atomic numbers Z_I and interparticle separations r_{ij} and r_{iI}, the eigenvalue equation in atomic units is

$$\left(-\sum_{i=1}^{n}\frac{1}{2}\nabla_i^2-\sum_{i}^{n}\sum_{I}^{N}\frac{Z_I}{r_{iI}}+\sum_{i>j=1}^{n}\frac{1}{r_{ij}}\right)\Psi=E\Psi \quad (1)$$

Accurate approximations to the eigenfunctions and energies provide valuable information for spectroscopy, thermochemistry, and kinetics and form the basis of computational molecular dynamics. They often also are the first step in more accurate treatments that account for nonadiabatic and relativistic effects. The challenge researchers face is to devise numerical methods that are sufficiently accurate to provide reliable predictions while at the same time requiring modest computational resources such that chemically relevant systems can be investigated.

Today, much research is being carried out in the field of quantum chemical methods that make use of explicitly correlated electronic wave functions. Efficient computer codes have recently been developed in the framework of large (commercial) quantum chemical program packages, and the number of applications of these codes is increasing rapidly. By using explicitly correlated electronic wave functions, electronic correlation energies of molecular ground and excited states can be computed close to the limit of a complete basis set at high levels of, for example, coupled-cluster theory. Methods based on a single Slater determinant as a reference wave function have been developed toward practical tools for all kinds of applications, and methods for multireference problems are currently being developed as well as methods for analytical computation of nuclear gradients and (response) properties for ground and excited states.

In this manuscript, we present a comprehensive review of explicitly correlated approaches, beginning with the early ideas and methods and progressing to the state of the art of the field. We give particular prominence to the F12 approach that has received a surge of impetus over the past decade and become a useful tool for routine chemical investigations. Before discussing explicit correlation, however, we first review exact and approximate wave functions from a more general perspective.

2. CORRELATION IN ELECTRONIC WAVE FUNCTIONS

To successfully construct accurate trial electronic wave functions it is important to have a clear understanding of the nature of electronic correlation, where it is, and where it is not represented in common approximate wave function forms. In the following sections, we present a systematic discourse that we hope fulfills this aim and is somewhat pedagogical in nature. Related discourses on this topic can be found in refs 1 and 2.

2.1. Statistical Correlation

The motion of two particles is said to be statistically uncorrelated if the pair probability distribution function factorizes into a product of distribution functions for the individual particles

$$P_{12}(\mathbf{x}_1,\mathbf{x}_2)=P_1(\mathbf{x}_1)P_2(\mathbf{x}_2) \quad (2)$$

Equivalently, this can be expressed in terms of the conditional electron density $P_{12}(\mathbf{x}_1|\mathbf{x}_2)$,[3] the probability distribution function for particle 1 when particle 2 is at $\mathbf{x}_2$. If the particles are statistically uncorrelated, $P_{12}(\mathbf{x}_1|\mathbf{x}_2)$ is independent of the position of particle 2

$$P_{12}(\mathbf{x}_1|\mathbf{x}_2)=\frac{P_{12}(\mathbf{x}_1,\mathbf{x}_2)}{P_2(\mathbf{x}_2)}=P_1(\mathbf{x}_1) \quad (3)$$

Whenever the above identities do not hold, the particles are said to be statistically correlated. If the particles are distinguishable, then $P_1(\mathbf{x})$ and $P_2(\mathbf{x})$ may be different from each other and $P_{12}(\mathbf{x}_1,\mathbf{x}_2)$ can be different for every particle pair. Electrons, however, are indistinguishable, and therefore, for every electron pair

$$P_1(\mathbf{x})=P_2(\mathbf{x})=\frac{1}{n}\rho(\mathbf{x}) \quad (4)$$

$$P_{12}(\mathbf{x}_1,\mathbf{x}_2)=\frac{1}{n(n-1)}\rho_2(\mathbf{x}_1,\mathbf{x}_2) \quad (5)$$

where $\rho(\mathbf{x})$ is the electron density and $\rho_2(\mathbf{x}_1,\mathbf{x}_2)$ is the pair density

$$\rho(\mathbf{x})=n\int d\mathbf{x}_2...\int d\mathbf{x}_n\Psi^*(\mathbf{x},\mathbf{x}_2,...,\mathbf{x}_n)\Psi(\mathbf{x},\mathbf{x}_2,...,\mathbf{x}_n) \quad (6)$$

$$\rho_2(\mathbf{x}_1,\mathbf{x}_2)=n(n-1)\int d\mathbf{x}_3...\int d\mathbf{x}_n\Psi^*(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_n)\Psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_n) \quad (7)$$

$\rho_2(\mathbf{x}_1,\mathbf{x}_2)$ is the probability of finding an electron at position $\mathbf{x}_1$ at the same time as finding another electron at position $\mathbf{x}_2$. Since the electrons are countable, if there is an electron at $\mathbf{x}_1$ then there can only be $n-1$ electrons at $\mathbf{x}_2$ and ρ_2 integrates to $n(n-1)$ (some authors normalize ρ_2 to $(1/2)n(n-1)$ so that $V_{ee}=\int d\mathbf{x}_1\int d\mathbf{x}_2 r_{12}^{-1}\rho_2(\mathbf{x}_1,\mathbf{x}_2)$). Thus, the electrons in an n-electron system are statistically uncorrelated if[4]

$$\rho_2(\mathbf{x}_1,\mathbf{x}_2)=\frac{n-1}{n}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \quad (8)$$

Note that $\mathbf{x}$ is a composite space and spin coordinate $\mathbf{x} = (r_x, r_y, r_z, s)$. The nonrelativistic Hamiltonian is spin free, and in the nonrelativistic limit, the electron repulsion energy only depends on the distribution of the electrons in space. In this respect we are primarily interested in the spatial probability distributions. These are obtained by simply integrating over all the spin coordinates in $\rho(\mathbf{x})$ and $\rho_2(\mathbf{x}_1,\mathbf{x}_2)$ to give $\rho(\mathbf{r})$ and $\rho_2(\mathbf{r}_1,\mathbf{r}_2)$.

Correlation between electrons has two independent sources.

- Fermi correlation: electrons are countable but indistinguishable particles that obey Fermi statistics, which requires that the wave function is antisymmetric with respect to exchange of configurations $\mathbf{x}_1$ and $\mathbf{x}_2$ for any pair of electrons.
- Coulomb correlation: electrons interact through a repulsive Coulomb force $e^2/(4\pi\varepsilon_0 r_{12})$, where r_{12} is the distance between the electrons.

In terms of approximate representations for electronic wave functions, Fermi correlation has two distinct consequences. The first is that any expansion of the wave function has exactly zero contribution from n-electron orbital product wave functions where two or more electrons occupy the same spin orbital. We shall see that this gives rise to correlation between electrons in the statistical sense. The second consequence of Fermi correlation is that the antisymmetry requirement introduces additional correlation, which is referred to as exchange.

In the following sections we illustrate the consequences of the intrinsic entanglement of electrons through Fermi and Coulomb correlation using the simple two-electron systems of helium and molecular hydrogen. However, first, it is instructive to contrast the language used in wave function theory with that used in density functional theory (DFT).

2.1.1. Exchange-Correlation Hole in Density Functional Theory. In density functional theory a pair correlation function $h(\mathbf{x}_1,\mathbf{x}_2)$ is defined through

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)(1 + h(\mathbf{x}_1, \mathbf{x}_2)) \tag{9}$$

The exchange-correlation hole for an electron at $\mathbf{x}_1$ is defined as

$$\rho_{\mathrm{xc}}(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_2)h(\mathbf{x}_1, \mathbf{x}_2) \tag{10}$$

and serves to separate the total electronic interaction energy into a classical interaction calculated from an uncorrelated probability distribution, $\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$, and a "nonclassical" contribution

$$\begin{aligned} V_{ee} &= \frac{1}{2}\int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{1}{r_{12}}\rho_2(\mathbf{x}_1, \mathbf{x}_2) \\ &= \frac{1}{2}\int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{1}{r_{12}}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) + \frac{1}{2}\int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \frac{1}{r_{12}}\rho(\mathbf{x}_1)\rho_{\mathrm{xc}}(\mathbf{x}_1, \mathbf{x}_2) \end{aligned} \tag{11}$$

The pair correlation function, $h(\mathbf{x}_1,\mathbf{x}_2)$, is symmetric and contains both Fermi and Coulomb correlation and also a contribution removing the self-interaction of the electrons. The exchange-correlation hole is related to the conditional electron density through

$$\rho_{\mathrm{xc}}(\mathbf{x}_1, \mathbf{x}_2) = (n-1)P_{12}(\mathbf{x}_2|\mathbf{x}_1) - \rho(\mathbf{x}_2) \tag{12}$$

and therefore

$$\int \mathrm{d}\mathbf{x}_2 \rho_{\mathrm{xc}}(\mathbf{x}_1, \mathbf{x}_2) = -1 \tag{13}$$

This results from the contribution that eliminates self-interaction. The exchange-correlation hole can be partitioned into exchange and (Coulomb) correlation parts, where the exchange part is defined as

$$\rho_{\mathrm{x}}(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_2)h_{\mathrm{HF}}(\mathbf{x}_1, \mathbf{x}_2) \tag{14}$$

and $h_{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2)$ is the pair correlation function for the Hartree−Fock pair density. $\rho_x(\mathbf{x}_1,\mathbf{x}_2)$ contains contributions from both Fermi correlation and the self-interaction correction and thus also satisfies eq 13.

2.1.2. Exchange and Coulomb Holes in Wave Function Theory. In wave function methods the key object of interest is the wave function rather than the density. The Hartree−Fock wave function Ψ_{HF} forms the basis for almost all approximate methods and accounts for Fermi correlation (see below). It is therefore convenient to define a Coulomb hole as

$$h_c = \Psi - \Psi_{\mathrm{HF}} \tag{15}$$

This is the function that must be modeled successfully to obtain accurate solutions to the Schrödinger equation. The (Coulomb) correlation energy is defined similarly[5]

$$E_{\mathrm{corr}} = E_{\mathrm{exact}} - E_{\mathrm{HF}} \tag{16}$$

In fact, such is the importance of Coulomb correlation that this energy is referred to simply as the correlation energy, even though E_{HF} contains the effects of Fermi correlation. Note that we assumed Löwdin's definition, eq 16, of the correlation energy, which is based on a restricted Hartree−Fock (RHF) wave function. Pople and Binkley[6] have given a definition based on an unrestricted Hartree−Fock wave function, but spin contamination makes the separation of Fermi and Coulomb correlation much less well-defined (see also ref 7).

2.1.3. Radial, Angular, and Left−Right Correlation. When visualizing and discussing electron correlation in molecules, it is commonplace to speak of three possibilities.

- Radial correlation: if an electron is close to a nucleus it is more probable for the other electrons to be far out from that nucleus.
- Angular correlation: if an electron is on one side of a nucleus it is more probable for the other electrons to be on the opposite side of that nucleus.
- Left−right correlation: if an electron is close to a nucleus on the left side of a chemical bond it is more probable for the other electrons to be close to the nucleus on the right.

Radial and angular correlation are separable when using a nucleus as the origin and convenient descriptors of correlation in atoms or for correlation close to each nucleus in a molecule. Left−right correlation is convenient for describing correlation in regions between atoms in a molecule. These descriptors are not specific to Fermi or Coulomb correlation and simply refer to the correlation in two-particle probability distribution functions.

2.2. Fermi Correlation: Shell Structure

A Hartree product wave function for an n-electron system has the general form[8−10]

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \prod_{i=1}^{n} \phi_{k_i}(\mathbf{x}_i) \tag{17}$$

where ϕ_{k_1} are orthonormal spin orbitals. The Hartree product wave function may be criticized on several fronts. Although the wave function is an eigenfunction of $\hat{S}_z$, it is not in general an eigenfunction of $\hat{S}^2$. More importantly, however, assigning electron 1 to occupied orbital ϕ_{k_1}, electron 2 to ϕ_{k_2}, and so on, makes

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the implicit assumption that the electrons are distinguishable. Consequently, every pair of electrons *i,j* has a different set of one- and two-particle probability distribution functions

$$P_i(\mathbf{x}_i) = \phi^*_{k_i}(\mathbf{x}_i)\phi_{k_i}(\mathbf{x}_i) \tag{18}$$

$$P_j(\mathbf{x}_j) = \phi^*_{k_j}(\mathbf{x}_j)\phi_{k_j}(\mathbf{x}_j) \tag{19}$$

$$P_{ij}(\mathbf{x}_i, \mathbf{x}_j) = P_i(\mathbf{x}_i)P_j(\mathbf{x}_j) \tag{20}$$

Since for every pair the two-particle probability distribution function factorizes into a product of one-particle distribution functions one may be tempted to say that the electrons are statistically uncorrelated. This is only true if the electronic coordinates are treated as distinguishable. However, because electrons are in fact indistinguishable the correct measure for statistical correlation between electrons is eq 8. For the Hartree product wave function

$$\rho(\mathbf{x}_1) = \sum_{i=1}^{n} P_i(\mathbf{x}_1) \tag{21}$$

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} P_{ij}(\mathbf{x}_1, \mathbf{x}_2) \tag{22}$$

and therefore

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \sum_{i=1}^{n} P_i(\mathbf{x}_1)P_i(\mathbf{x}_2) \tag{23}$$

Thus, the electron pair probability distribution derived from a Hartree product wave function is statistically correlated. To appreciate the nature of this correlation it is perhaps helpful to consider a Hartree product wave function for certain bosonic states where all indistinguishable particles occupy the same orbitals. For such a wave function

$$P_i(\mathbf{x}) = \frac{1}{n}\rho(\mathbf{x}) \qquad \forall\ i = 1, n \tag{24}$$

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \frac{1}{n}\rho(\mathbf{x}_1)\rho(\mathbf{x}_2) \tag{25}$$

and the particles are statistically uncorrelated.

For an electronic Hartree product wave function the probability distribution reflects the shell structure of the electronic distribution where, in accordance with the Pauli exclusion principle, every spin orbital in the Hartree product is different. This is by far the largest correlation between electrons and has the largest impact on the electronic energy.

2.3. Fermi Correlation: Exchange

A Slater determinant wave function for an n-electron system has the general form[11]

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \sqrt{n!}\mathscr{A}\prod_{i=1}^{n}\phi_{k_i}(\mathbf{x}_i) = |\Phi_K\rangle \tag{26}$$

where ϕ_{k_i} are a set of orthonormal spin orbitals and $|\Phi_K\rangle$ denotes a Slater determinant of orbitals k_i. $\mathscr{A}$ projects onto the antisymmetric irreducible representation of the symmetric group

$$\mathscr{A} = \frac{1}{n!}\sum_{u=1}^{n!}\varepsilon_u P_u \tag{27}$$

where ε_u is the parity of a permutation P_u. The fundamental deficiency of the Hartree product representation has been remedied: The Slater determinant is antisymmetric with respect to exchange of any two electrons, as appropriate for fermionic indistinguishable particles. A Slater determinant wave function is an eigenfunction of $\hat{S}_z$, but it is only an eigenfunction of $\hat{S}^2$ for electronic states with closed-shell or high-spin open-shell configurations. For low-spin open-shell configurations, a wave function that is an eigenfunction of both $\hat{S}_z$ and $\hat{S}^2$ can be constructed from a linear combination of Slater determinants

$$\Psi^{S,M_s}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \sum_K c_K|\Phi_K\rangle \tag{28}$$

These are configuration state functions (CSFs). The determinants $|\Phi_K\rangle$ that enter the sum are those with the same spatial occupation, but differing spin occupations with $\hat{S}_z$ eigenvalue M_s and the coefficients c_K are determined by group theoretical considerations.

Antisymmetric wave functions correlate electrons over and above the correlation present in a Hartree product description. For a single Slater determinant the one-electron probability distribution is

$$P_1(\mathbf{x}) = \frac{1}{n}\rho(\mathbf{x}) \tag{29}$$

$$\rho(\mathbf{x}) = \sum_{i=1}^{n}\phi^*_{k_i}(\mathbf{x})\phi_{k_i}(\mathbf{x}) \tag{30}$$

The pair density is given by

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2) = \rho(\mathbf{x}_1)\rho(\mathbf{x}_2) - \sum_{i,j=1}^{n}\phi^*_{k_j}(\mathbf{x}_1)\phi_{k_i}(\mathbf{x}_1)\phi^*_{k_i}(\mathbf{x}_2)\phi_{k_j}(\mathbf{x}_2) \tag{31}$$

The additional correlation that arises from antisymmetry is given by the difference between eqs 31 and 23 and is the exchange component of Fermi correlation

$$-\sum_{\substack{i,j=1 \\ i \neq j}}^{n}\phi^*_{k_j}(\mathbf{x}_1)\phi_{k_i}(\mathbf{x}_1)\phi^*_{k_i}(\mathbf{x}_2)\phi_{k_j}(\mathbf{x}_2) \tag{32}$$

Integrating over the spin coordinates we see that exchange lowers the probability of like-spin electrons being close in space, but has no effect on opposite spin electron pairs. In fact, $\rho_2(\mathbf{x}_1,\mathbf{x}_1) = 0$, that is, there is identically zero probability of finding two electrons with the same spin at the same point in space. This is the exchange hole.

For a single Slater determinant the correlation arising from exchange is always negative. For low-spin open-shell configurations, however, the CSFs are linear combinations of Slater determinants and the antisymmetry requirement can also lead to positive correlation, which is known as a "Fermi heap".

2.3.1. Case Study: He Atom. Let us now illustrate these concepts through a consideration of the three lowest lying energy electronic states of the helium atom. The CSF for the $(1s^2)$ configuration is

$$\Psi^{0,0}_{1^1S} = \varphi_{1s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]2^{-1/2} \tag{33}$$

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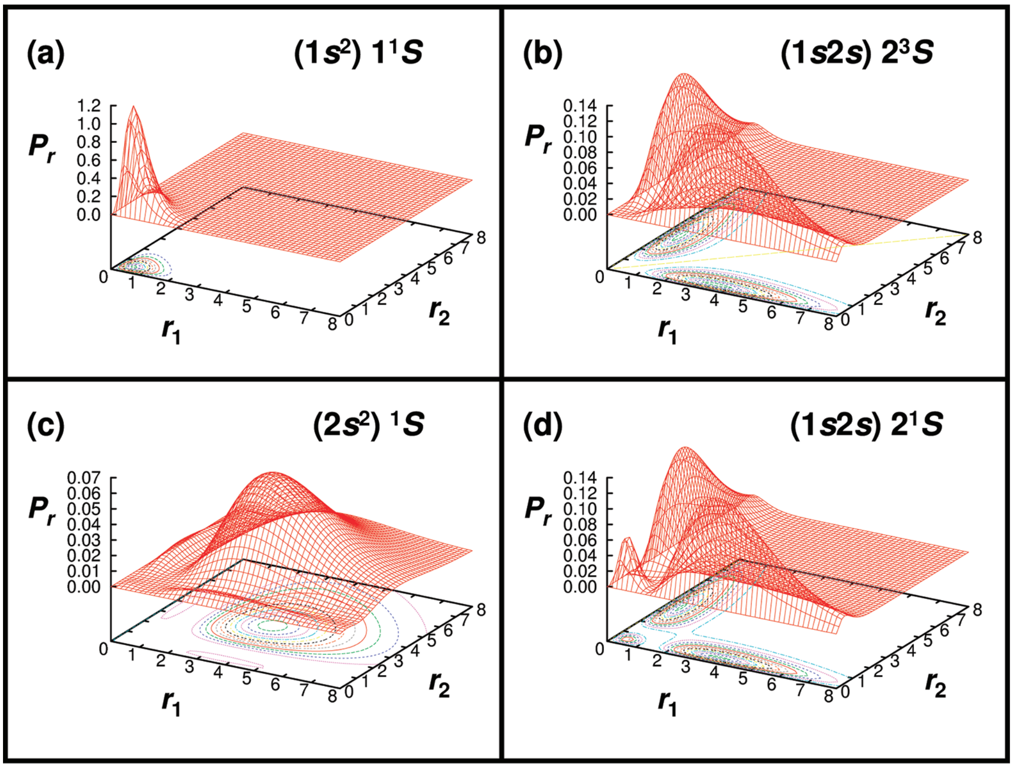

Figure 1. Fermi correlation depicted through the two-electron radial densities in the helium atom for (clockwise from the top left) the 1^1S ground state, the 2^3S and 2^1S singly excited states, and the $(2s^2)^1S$ doubly excited state. The 1s and 2s orbitals used for the excited states were obtained by a variational minimization of the 2^3S state. Reprinted with permission from ref 2. Copyright 2007 John Wiley and Sons.

and for the (1s2s) configuration we get four CSFs: The three components of the triplet-adapted CSF

$$\Psi_{2^3S}^{1,1} = [\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_2) - \varphi_{2s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)]2^{-1/2}\alpha(s_1)\alpha(s_2) \quad (34)$$

$$\Psi_{2^3S}^{1,0} = [\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_2) - \varphi_{2s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)]2^{-1/2}[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)]2^{-1/2} \quad (35)$$

$$\Psi_{2^3S}^{1,-1} = [\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_2) - \varphi_{2s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)]2^{-1/2}\beta(s_1)\beta(s_2) \quad (36)$$

and a singlet-adapted CSF

$$\Psi_{2^1S}^{0,0} = [\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_2) + \varphi_{2s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2)]2^{-1/2}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]2^{-1/2} \quad (37)$$

The 1^1S state and the $M_s = 1,-1$ components of the triplet state are single Slater determinants. The $M_s = 0$ component of the triplet state and the open-shell singlet state 2^1S are plus and minus linear combinations of two Slater determinants

$$\Psi_{2^3S}^{1,0} = (|1s\alpha 2s\beta\rangle + |1s\beta 2s\alpha\rangle)2^{-1/2} \quad (38)$$

$$\Psi_{2^1S}^{0,0} = (|1s\alpha 2s\beta\rangle - |1s\beta 2s\alpha\rangle)2^{-1/2} \quad (39)$$

The extent of electron correlation is very different in the three states 1^1S, 2^3S, and 2^1S. Figure 1 is a plot of the two-particle radial densities $P_r(r_1,r_2) = 16\pi^2 r_1^2 r_2^2 \rho_2(r_1,r_2)$ for the low-lying states of helium (note that since only s orbitals are occupied, ρ_2 does not depend on the angular coordinates of the electrons). Consider first the 1^1S ground state in Figure 1a

$$\rho(\mathbf{r}) = 2\varphi_{1s}^*(\mathbf{r})\varphi_{1s}(\mathbf{r}) \quad (40)$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \quad (41)$$

The spatial probability distribution is therefore statistically uncorrelated. In Figure 1 this is seen by noting that the shape of $P_r(r_1,r_2)$ as a function of r_1 does not depend on r_2; it is only scaled by $P(\mathbf{r}_2)$. The same is true for the $(2s^2)^1S$ doubly excited state in Figure 1c, but it should be realized that these uncorrelated states only exist for two-electron systems, and the electrons are spatially statistically uncorrelated but remain correlated in space-spin configuration space.

Now let us consider the singly excited states 2^3S and 2^1S. The Hartree product wave functions for these two states are degenerate in energy because they have the same spatial probability distributions

$$\rho(\mathbf{r}) = \varphi_{1s}^*(\mathbf{r})\varphi_{1s}(\mathbf{r}) + \varphi_{2s}^*(\mathbf{r})\varphi_{2s}(\mathbf{r}) \quad (42)$$

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{1s}^*(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}^*(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2) + \varphi_{2s}^*(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_1)\varphi_{1s}^*(\mathbf{r}_2)\varphi_{1s}(\mathbf{r}_2) \quad (43)$$

Note the shell structure: when an electron is in the 1s orbital the other electron is in the 2s orbital. In contrast to the Hartree products, the CSFs for the 2^3S and 2^1S states have different two-particle spin-free densities due to the coupling of space and spin

Table 1. Calculated and Experimental IPs and Energy Differences of Helium (in eV)[a]

	Hartree[b]	CSF[b]	Hylleraas[b]	Exp.[c]
IP (1^1S)	23.447	23.447	24.591	24.587
IP (2^3S)	4.359	4.742	4.768	4.767
IP (2^1S)	4.359	3.976	3.972	3.972
$\Delta E(2^3S) - 1^1S$	19.088	18.706	19.823	19.820
$\Delta E\ (2^1S) - 2^3S$	0.000	0.766	0.796	0.796

[a] The orbitals for the excited-state Hartree products and CSFs are those that variationally minimise the 2^3S state. [b] From ref 2. [c] From ref 12.

coordinates through the antisymmetry requirement

$$\begin{aligned}{}^3\rho_2(\mathbf{r}_1, \mathbf{r}_2) = {}& \varphi_{1s}^*(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}^*(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2) \\ &+ \varphi_{2s}^*(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_1)\varphi_{1s}^*(\mathbf{r}_2)\varphi_{1s}(\mathbf{r}_2) \\ &- 2\varphi_{2s}^*(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_1)\varphi_{1s}^*(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2)\end{aligned} \tag{44}$$

$$\begin{aligned}{}^1\rho_2(\mathbf{r}_1, \mathbf{r}_2) = {}& \varphi_{1s}^*(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_1)\varphi_{2s}^*(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2) \\ &+ \varphi_{2s}^*(\mathbf{r}_1)\varphi_{2s}(\mathbf{r}_1)\varphi_{1s}^*(\mathbf{r}_2)\varphi_{1s}(\mathbf{r}_2) \\ &+ 2\varphi_{2s}^*(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_1)\varphi_{1s}^*(\mathbf{r}_2)\varphi_{2s}(\mathbf{r}_2)\end{aligned} \tag{45}$$

In the triplet state there is a Fermi hole, where the exchange term reduces the probability of the two electrons being close together. In Figure 1b this can be seen through the node in $P_r(r_1,r_2)$ along the line $r_1 = r_2$. In the singlet state there is a Fermi heap. In this case the exchange term increases the probability of the two electrons being in the same region of space. This can be seen in Figure 1d, where there is a local maximum in $P_r(r_1,r_2)$ when $r_1 = r_2 = 0.5\ a_0$.

The energetic consequences of the exchange term (the Fermi hole and Fermi heap) is to lower the energy of the triplet and raise the energy of the singlet state, leading to a singlet−triplet splitting in the ionization potentials. Table 1 lists the computed ionization potentials (IPs) using Hartree product and CSF wave function descriptions for the three lowest states of helium. Note that in these illustrative calculations the orbitals for the excited states are taken as those that variationally minimize the 2^3S state. Consequently, the 1^1S and 2^1S states are not orthogonal and the computed IPs for the 2^1S state do not obey the variational principle; the method of Hylleraas will be discussed in section 4.1.1.

2.4. Coulomb Correlation

The IPs computed from CSFs in Table 1 deviate significantly from the experimental values. The primary source of error in these energy differences is that the pair distribution functions do not account for the effects of the Coulombic repulsion between the electrons. The missing correlation is Coulomb correlation. For the ground-state Coulomb correlation is always negative, that is, it always acts to reduce the probability of two electrons being found in the same region of space.

In a Slater determinant or CSF wave function the only variational parameters are the orbital functions. The coefficient of each Hartree product function is determined by antisymmetry, and the wave function does not have sufficient flexibility to account for Coulomb correlation. In Hartree−Fock theory the orbitals are optimized to minimize the energy expectation value and is therefore a mean-field theory, where the Coulomb repulsion between the electrons only influcences the wave function through an effective potential.

One systematically improvable route toward the exact solution to the nonrelativistic Born−Oppenheimer Schrödinger equation, where Coulomb correlation is fully included, is to expand the wave function as a linear combination of Slater determinants with varying electronic configurations. Such a configuration interaction (CI) wave function has the form

$$\Psi = \sum_K c_K |\Phi_K\rangle \tag{46}$$

where in general all possible determinants enter the sum. The way in which the coefficients c_K are determined defines a class of trial wave functions, including Møller−Plesset, coupled-cluster, and full CI wave functions. The convergence properties of eq 46 are discussed in section 3.7.

In Figure 2 we illustrate the way in which a CI wave function accounts for Coulomb correlation between electrons by taking the 1^1S ground state of helium as an example using the set of configurations $1s^2$, 1s2s, $2s^2$, and $2p^2$. The coefficients c_K have been determined variationally using the Rayleigh−Ritz method. The single $1s^2$ configuration has a statistically uncorrelated spin-free pair density. In Figure 2b we see that the 1s2s and $2s^2$ configurations, which contain a radial node through the 2s orbital, introduce radial correlation. The contribution from the 2s configurations acts to decrease the wave function in the region where $r_1 \approx r_2$, lowering the probability of finding the two electrons close together. In Figure 2c we see that the $2p^2$ configurations introduce angular correlation. The combined effect, resulting in the correlation hole of this simple trial wave function, is in Figure 2d. In Figure 2a we see that Coulomb correlation is a very small perturbation to the Hartree−Fock wave function for helium.

2.4.1. Static and Dynamic Correlation.

In the case of helium the fully correlated two-particle density matrix is qualitatively similar to that obtained through a Hartree−Fock description, and Coulomb correlation can thus be considered as a relatively small perturbation of the Hartree−Fock state. The difference purely arises from the fact that the electrons are aware of the instantaneous interactions with the other electrons (in contrast to the mean-field interaction in the Hartree−Fock state), and hence, one usually speaks of dynamic correlation.

At variance to this, there are cases in which more than one Slater determinant (or CSF) leads to a low-lying solution of the Hartree−Fock equation and a qualitatively correct zeroth-order description of the system requires one to include all these configurations. A prominent example is the homolytic cleavage of a bond (cf. the example in section 2.4.2). At least two configurations are necessary to properly describe this process, and the physical interpretation of the wave function suggests a strong right−left correlation of the two electrons involved in the bond. From this picture the notion "static correlation" has emerged. Note, however, that a strict distinction of static and dynamic correlation is not possible in general.

2.4.2. Case Study: Molecular Hydrogen.

Molecular hydrogen serves as an excellent example for the various kinds of Fermi and Coulomb correlation discussed in the previous sections. Consider a minimal basis CI calculation for the low-energy states. The set of CSFs that enter this simple CI calculation are

$$\Psi^{0,0}_{{}^1\Sigma_g^+} = \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]2^{-1/2} \tag{47}$$

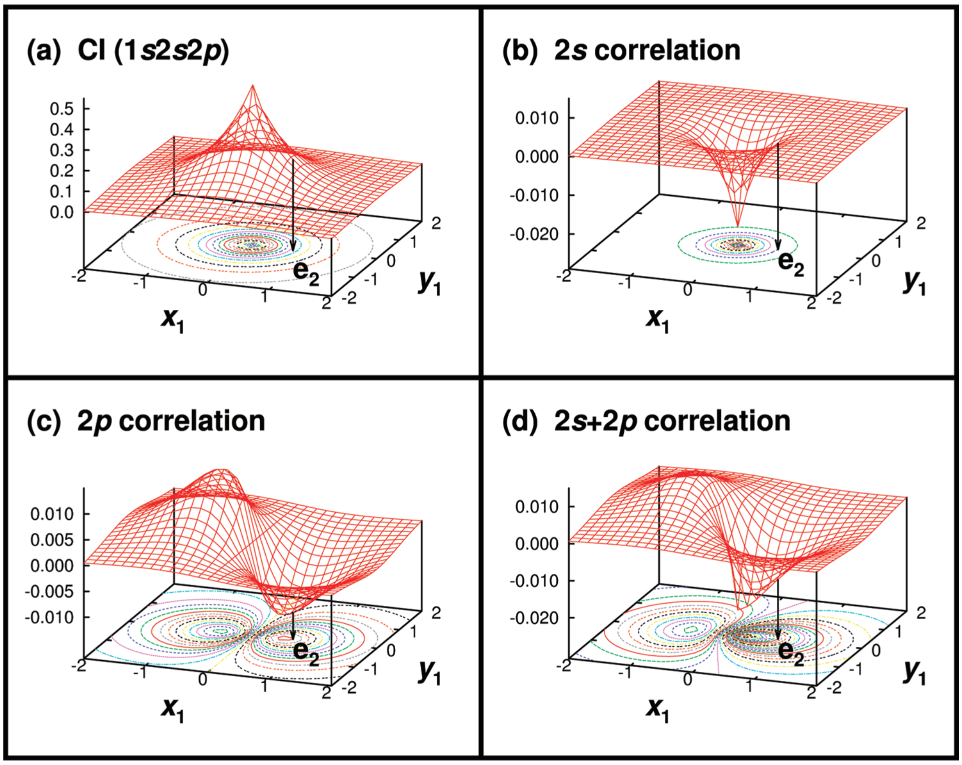

Figure 2. Coulomb correlation in the 1^1S state of the He atom. The He wave function and contributions to it plotted with one electron fixed at 0.65 a_0 from the nucleus, plotted in a plane containing the nucleus and the two electrons (note different scales): (a) the CI wave function calculated from 1s, 2s, and 2p; (b) contribution to the correlation hole from the 2s orbital; (c) contribution to the correlation hole from the 2p orbitals; (d) correlation hole from 2s and 2p. Reprinted with permission from ref 2. Copyright 2007 John Wiley and Sons.

which corresponds to the $(1\sigma_g^2)$ configuration

$$\Psi^{1,1}_{^3\Sigma_u^+} = [\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)]2^{-1/2}\alpha(s_1)\alpha(s_2) \qquad (48)$$

$$\Psi^{1,0}_{^3\Sigma_u^+} = [\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)]2^{-1/2}[\alpha(s_1)\beta(s_2) + \beta(s_1)\alpha(s_2)]2^{-1/2} \qquad (49)$$

$$\Psi^{1,-1}_{^3\Sigma_u^+} = [\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)]2^{-1/2}\beta(s_1)\beta(s_2) \qquad (50)$$

$$\Psi^{0,0}_{^1\Sigma_u^+} = [\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2) + \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)]2^{-1/2}[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]2^{-1/2} \qquad (51)$$

which are the three components of the triplet-adapted CSF and the singlet-adapted CSF corresponding to the configuration $(1\sigma_g 1\sigma_u)$ and

$$\Psi^{0,0}_{^1\Sigma_g^+} = \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)[\alpha(s_1)\beta(s_2) - \beta(s_1)\alpha(s_2)]2^{-1/2} \qquad (52)$$

which is the CSF for the $(1\sigma_u^2)$ configuration. These states are analogous to those of helium, except with the atomic orbitals 1s and 2s replaced by molecular bonding and antibonding orbitals $1\sigma_g$ and $1\sigma_u$, respectively. In Figure 3 we plot the spin-free pair probability distribution functions for the four states obtained by variationally minimizing the energy with respect to the coefficients in the CI expansion eq 46. For each of these states, the projection of the spin-free pair probability distribution function $P_{12}(\mathbf{r}_1,\mathbf{r}_2)$ on the molecular axis (z) is plotted.

In the CI calculation the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ CSFs do not mix with the other states, and these CSFs are plotted in Figure 3b and 3d, respectively. Correlation in these states is purely Fermi type, and the impact of exchange is to completely alter the pair probability distribution. In the triplet state there is a Fermi hole around the Fermi node at $z_1 = z_2$, and if an electron is close to one nucleus, the other electron is much more likely to be found at the other nucleus (strongly negative left−right correlation). For the singlet state (Figure 3d) there is a Fermi heap at $z_1 = z_2$, resulting in strongly positive left−right correlation. It is much more probable to find the two electrons on the same nucleus than on different nuclei.

In the CI calculation the $1\sigma_g^2$ and $1\sigma_u^2$ states mix, which introduces Coulomb correlation. The ground state is statistically uncorrelated at the Hartree−Fock level of theory, but the probability distribution resulting from the CI calculation in Figure 3a is statistically correlated. In this state there is negative left−right correlation, reducing the probability of the two electrons being found close in space. This correlation is entirely due to the instantaneous Coulombic repulsion force between the electrons.

The energetic consequences of Fermi correlation and the strength of mixing of states due to Coulombic interactions both depend heavily on the internuclear separation. In Figure 4 we plot the potential energy curves of the four states. In Figure 4a we see that the open-shell Hartree product functions are degenerate at all bond lengths, the dotted line. Fermi correlation lifts this degeneracy, and the energetic consequences of the antisymmetry

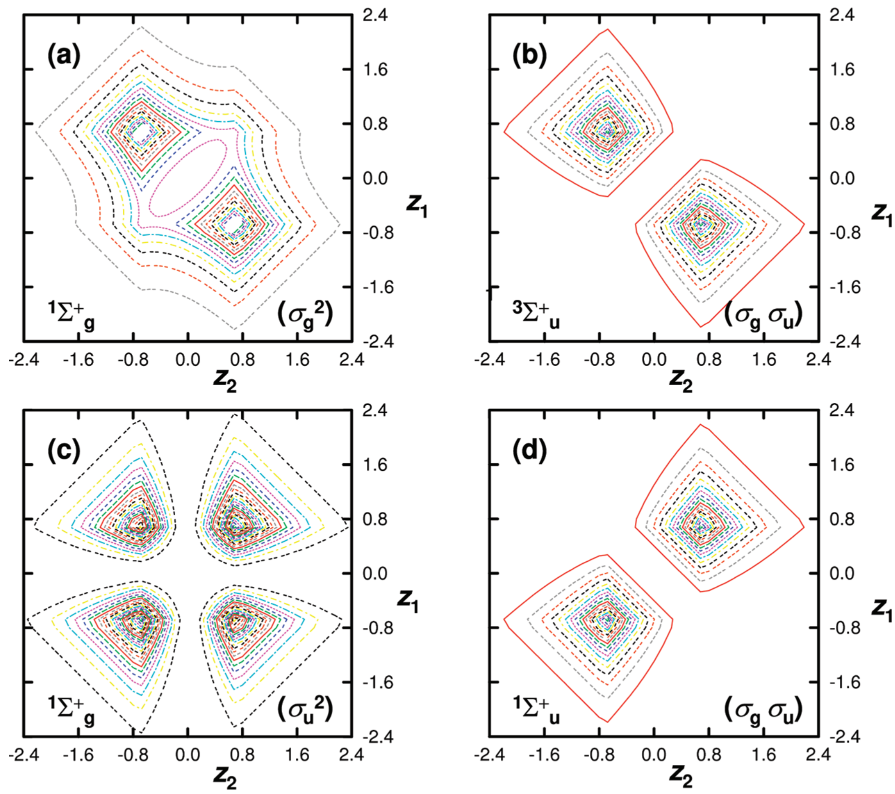

Figure 3. Electron correlation in the hydrogen molecule depicted through axial probability distribution functions for (clockwise from the top left) the $^1\Sigma_g^+$ ground state, the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ singly excited states, and the $(1\sigma_u^2)^1\Sigma_g^+$ doubly excited state. The hydrogen nuclei are located at 0.7 a_0 and −0.7 a_0, and the states have been determined from a CI calculation. Reprinted with permission from ref 2. Copyright 2007 John Wiley and Sons.

requirement (the exchange energy) increases as the bond lengthens due to the increasing energy difference between the two electrons being close together or far apart. Figure 4b illustrates that the closed-shell $1\sigma_g^2$ and $1\sigma_u^2$ CSFs become degenerate at infinite nuclear separation. The pair probability distributions for these states differ only in the probability of the two electrons being found between the nuclei as opposed to close to the nuclei, and neither distribution is left−right correlated (they are both statistically uncorrelated). At short nuclear separations the left−right correlation is weak and the Slater determinants are qualitatively correct. At long bond lengths the energetic consequences of Coulomb correlation are large and the negative left−right correlation fundamentally alters the probability distributions, lifting the degeneracy of the two states. At short separation we speak of dynamic Coulomb correlation, and at large separation we speak of static Coulomb correlation.

3. CUSP CONDITIONS AND ENERGY CONVERGENCE

With the objective of constructing accurate trial wave functions any a priori knowledge of the exact wave function gains importance. As we have seen, the Fermi structure of the electronic wave function is by far the most important aspect to include in wave function approximations. This is elegantly achieved using Slater-determinant-based expansions. In addition to the fermionic nature of electrons, the Coulombic nature of the interactions between the quantum particles additionally dictates the form of the wave function at short interparticle separations. In particular, sharp features appear in the wave function at electron−nucleus and electron−electron coalescence points. These cusps have important ramifications for the choice of basis function used in wave function approximation and have been the driving force behind development of explicitly correlated approaches to electronic structure theory. In the following we review the state of the current knowledge of the exact wave function and the impact on the rate of energy convergence in CI-type wave function approximations.

3.1. Regularity Conditions

In 1957 Kato proved that all eigenfunctions of the nonrelativistic Hamiltonian are continuous throughout configuration space, and they have partial derivatives of first order, except at the Coulomb-type singular points on the potential.[13] In other words, Ψ is locally Lipschitz. This important result was the foundation for Kato's famous characterization of the first-order derivative discontinuity at the Coulomb-type singularity: Kato's cusp condition.[13] In 2005, Kato's proof of regularity was sharpened by Fournais et al.,[14] who found that electronic wave functions of atoms and molecules have a representation $\Psi = F\Phi$, where F is an explicit universal factor, locally Lipschitz, and independent of the eigenvalue and the solution Ψ itself and Φ has first-order partial derivatives in all configuration space and second-order partial derivatives, except at the Coulomb-type singular points. The explicit form of F is (in atomic units)

$$F = -\sum_{I=1}^{N}\sum_{i=1}^{n} Z_I r_{iI} + \frac{1}{2}\sum_{i<j=1}^{n} r_{ij} + C_0 \sum_{I=1}^{N}\sum_{i<j=1}^{n} Z_I \mathbf{r}_{iI}\cdot\mathbf{r}_{jI}\ln(r_{iI}^2 + r_{jI}^2) \qquad (53)$$

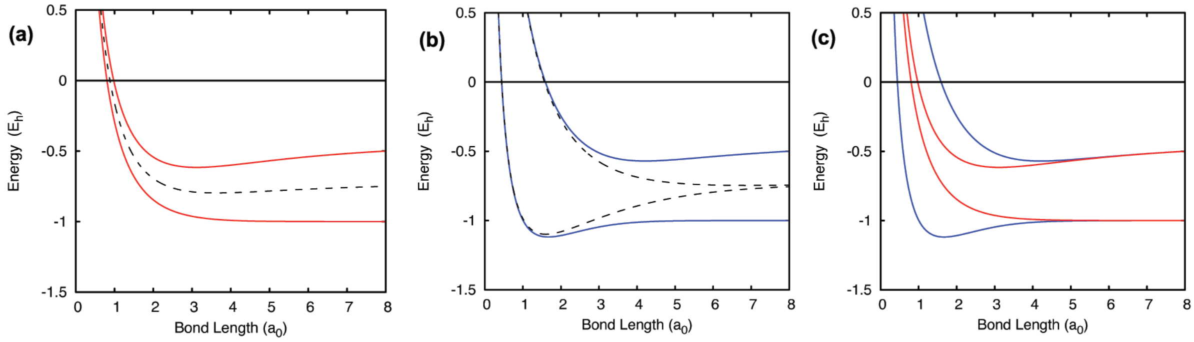

Figure 4. Potential energy curves of the hydrogen molecule. (a) Fermi correlation of open-shell states. The dotted line represents the energy of the Hartree product states; full lines represent the spin-adapted triplet $^3\Sigma_u^+$ (lower curve) and singlet (upper curve) $^1\Sigma_u^+$ states. (b) Coulomb correlation in closed-shell states. The dotted lines represent the CSFs; the full lines represent the variationally optimized linear combinations of these functions. (c) Potential energy curves of the variationally optimized closed-shell states and spin-adapted open-shell states. Reprinted with permssion from ref 2. Copyright 2007 John Wiley and Sons.

where $C_0 = (2 - \pi)/6\pi$ and I runs over the N nuclei, with charge Z_I and i,j run over the n electrons. F embodies three types of coalescence conditions, which we now consider individually in detail using the analysis of Pack and Byers Brown.[15]

3.2. Nuclear Cusp Conditions

In the region of configuration space where an electron is close to a clamped nucleus I and all other particles are well separated, we may expand the spatial component of the exact Born–Oppenheimer, nonrelativistic wave function as a Taylor series in r, the electron–nucleus separation, centered at the nucleus

$$\psi(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_n) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{k=0}^{\nu} r^{l+k} f_{lm}^{k}(\mathbf{r}_2, ..., \mathbf{r}_n) Y_{lm}(\theta, \varphi) + \mathcal{O}(r^{l+\nu}) \quad (54)$$

The coefficients in the series expansion depend parametrically on the positions of the other particles in the system. It is worth noting that an expansion of this kind is possible because of Kato's regularity result. Inserting this wave function expansion into the Schrödinger equation and equating powers of r one finds that the angular coordinates are uncoupled up to $\mathcal{O}(r^{l_0+2})$ in the wave function, where l_0 is the lowest l with nonzero f_{lm}^0 and that for this l

$$f_{lm}^1 = -\frac{Z_I}{(l+1)} f_{lm}^0 \quad (55)$$

This relationship results from the requirement that the singularity in the Coulomb potential $-Z_I/r$ is exactly canceled by a singularity in the kinetic energy. The better known version of this derivative discontinuity condition is the one given by Kato for $l = 0$, which is equivalent to

$$\left. \frac{\partial \widetilde{\psi}^{00}}{\partial r} \right|_{r=0} = -Z_I \psi(r=0) \quad (56)$$

$$\psi = (1 - Z_I r)\psi(r=0) + \mathbf{a}\cdot\mathbf{r} + \mathcal{O}(r^2) \quad (57)$$

where the tilde with superscript 00 denotes projection onto the spherical harmonic Y_{00}. The ramifications of eq 55 for the wave function can be understood from a consideration of the hydrogen atom. Figures 5b and 5d contain plots of the 1s and $2p_z$ wave functions, respectively. For the 1s wave function eq 57 applies and manifests as a cusp in the wave function at the electron–nucleus coalescence point

$$\psi(r) = N\exp(-r) = N(1-r) + \mathcal{O}(r^2) \quad (58)$$

In the limit of $r \to 0$ the wave function depends linearly on r and the second term in eq 57 is absent because only $l = 0$ terms contribute to eq 54 for the 1s orbital. Equation 57 does not apply to the 2p states because the wave function is zero at the nucleus and only $l = 1$ terms enter the expansion in eq 54. Consequently, there is no cusp in the wave function and the derivative discontinuity eq 55 is at second order, which is expressed by the coalescence condition

$$\left. \frac{\partial^2 \widetilde{\psi}^{1m}}{\partial r^2} \right|_{r=0} = -Z_I \left. \frac{\partial \widetilde{\psi}^{1m}}{\partial r} \right|_{r=0} \quad (59)$$

$$\psi = \mathbf{r}\cdot \left. \frac{\partial \psi}{\partial \mathbf{r}} \right|_{r=0} \left(1 - \frac{1}{2} Z_I r\right) + \mathbf{r}\cdot\mathbf{b}\cdot\mathbf{r} + \mathcal{O}(r^3) \quad (60)$$

The tilde with superscript $1m$ denotes projection onto the spherical harmonic Y_{1m}, and $\mathbf{b}$ is a traceless tensor. Electronic states of many-electron systems where the wave function is zero at a nucleus are rare, but for such states with $\prod$ symmetry, eq 60 applies. For states with Δ symmetry, the derivative discontinuity enters at third order and so on. The result eq 55 was first obtained by Pack and Byers Brown,[15] who's analysis went beyond the Born–Oppenheimer approximation using center of mass and relative coordinates, which results in only a minor modification to eq 55. The behavior of the wave function at the nucleus has important consequences for the choice of orbital basis set, which we expand upon in section 3.7.1.

3.3. Electron Coalescence Conditions

The conditions on the wave function at electron–electron coalescence are analogous to those for electron–nucleus coalescence. Pack and Byers Brown's analysis is general to both cases and proceeds in this case by considering the region of configuration space where two electrons are close together and all other particles are well separated. Transforming to the center of mass $\mathbf{s}$ and relative $\mathbf{r}$ coordinates of

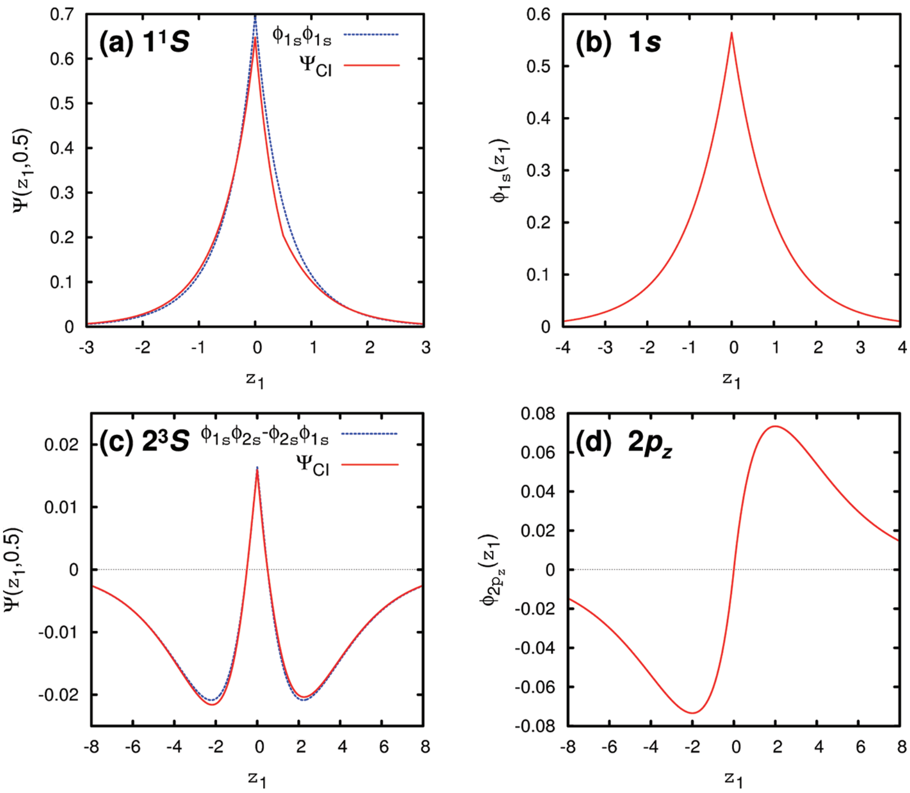

Figure 5. (a) Wave function for the 1^1S helium ground state with an electron fixed at a distance of 0.5 a_0 on the z axis with the nucleus at the origin. (b) 1s wave function of hydrogen. (c) Wave function for the 2^3S helium state with an electron fixed at a distance 0.5 a_0 on the z axis with the nucleus at the origin. (d) $2p_z$ wave function of hydrogen. Reprinted with permissoin from ref 2. Copyright 2007 John Wiley and Sons.

two coalescing electrons

$$\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/2 \tag{61}$$

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{62}$$

the spatial component of the exact wave function is expanded as a Taylor series centered at $r = 0$

$$\psi(\mathbf{r}, \mathbf{s}, \mathbf{r}_3, ..., \mathbf{r}_n) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{k=0}^{\nu} r^{l+k} f_{lm}^{k}(\mathbf{s}, \mathbf{r}_3, ..., \mathbf{r}_n) Y_{lm}(\theta, \varphi) + \mathcal{O}(r^{l+\nu}) \tag{63}$$

Inserting this wave function expansion into the Schrödinger equation and equating powers of r one finds that just as for the electron−nucleus case the angular coordinates are uncoupled up to $\mathcal{O}(r^{l_0+2})$ in the wave function, where l_0 is the lowest l with nonzero f_{lm}^0. The electron−electron derivative discontinuity condition for this l is

$$f_{lm}^1 = \frac{1}{2(l+1)} f_{lm}^0 \tag{64}$$

Note that the $-Z_I$ in eq 55 has been replaced by 1/2. In fact, the general form is with $Z_1Z_2\mu/(l+1)$, where μ is the reduced mass of the coalescing particles with charges Z_1, Z_2. For electron−electron coalescence the lowest l with nonzero f_{lm}^0 depends on the space and spin coupling of the coalescing electrons. The following three situations have been identified in the literature.

3.3.1. Singlet Coalescence. Antisymmetry dictates that $\Psi(\mathbf{x}_1,\mathbf{x}_2,...,\mathbf{x}_n) = -\Psi(\mathbf{x}_2,\mathbf{x}_1,...,\mathbf{x}_n)$. Therefore, for singlet coupled electrons, $\Psi(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n) = \Psi(\mathbf{r}_2,\mathbf{r}_1,...,\mathbf{r}_n)$ and only terms with even l enter in eq 63. For states without special restriction on the spatial symmetry the lowest l with nonzero f_{lm}^0 in eq 63 is $l = 0$. In this case the derivative discontinuity eq 64 is equivalent to Kato's famous cusp condition

$$\left.\frac{\partial\psi}{\partial r}\right|_{r=0} = \frac{1}{2}\psi(r=0) \tag{65}$$

$$\psi = \left(1 + \frac{1}{2}r\right)\psi(r=0) + \mathcal{O}(r^2) \tag{66}$$

This is often referred to as the s-wave coalescence condition, and the electrons are said to have natural spatial parity. Figure 5a is a plot of the exact and Hartree−Fock wave functions for the 1^1S ground state of the helium atom. We plot the radial cut where one electron is located at 0.5 a_0 from the nucleus and the other electron moves along the z axis through the two particles. The nuclear cusp at $z_1 = 0$ is the most obvious feature. The electron−electron cusp is at $z_1 = 0.5$ and characterized by linear dependence on the interelectronic separation. The positive coefficient reflects that Coulomb correlation is always negative and there is a Coulomb hole at electron coalescence. The Hartree−Fock wave function does not possess an electron−electron cusp since it does not contain Coulomb correlation.

3.3.2. Triplet Coalescence. For electrons that are triplet coupled the antisymmetry requirement of the exact wave function dictates that only terms with odd l enter eq 63. In this case, the lowest l with nonzero f^0_{lm} is $l = 1$ and the derivative discontinuity is at second order

$$\left.\frac{\partial^2 \widetilde{\psi}^{1m}}{\partial r^2}\right|_{r=0} = \frac{1}{2}\left.\frac{\partial \widetilde{\psi}^{1m}}{\partial r}\right|_{r=0} \tag{67}$$

$$\psi = \mathbf{r}\cdot\left.\frac{\partial \psi}{\partial \mathbf{r}}\right|_{r=0}\left(1 + \frac{1}{4}r\right) + \mathcal{O}(r^3) \tag{68}$$

This is referred to as the p-wave coalescence condition and is analogous to the nuclear derivative discontinuity in the 2p state of hydrogen. Figure 5d is a plot of a radial cut through the exact and Hartree−Fock wave functions for the 2^3S state of the helium atom. As a result of the antisymmetry requirement both exhibit an exchange hole at $\mathbf{r}_1 = \mathbf{r}_2$, where the wave function is zero. There is no cusp at this point; rather the discontinuity is in the second derivative. As for the singlet case, the Hartree−Fock wave function does not have any derivative discontinuities at the electron coalescence point.

3.3.3. Unnatural Parity Singlet Coalescence. One further possibility was found by Kutzelnigg and Morgan,[16] which results from additional spatial symmetry requirements, in particular the gerade or ungerade parity of the spatial function upon inversion $\Psi(\mathbf{r},\mathbf{s}) = \pm\Psi(-\mathbf{r}, -\mathbf{s})$. The singlet and triplet conditions above apply to their natural parity states, gerade and ungerade, respectively. For ungerade singlet states (unnatural parity), such as the ^1P_u state from a 2p3p configuration, the coupling of space and spin symmetries dictates that the lowest l for which f^0_{lm} is nonzero is $l = 2$. Therefore, the derivative discontinuity is at third order

$$\left.\frac{\partial^3 \widetilde{\psi}^{2m}}{\partial r^3}\right|_{r=0} = \frac{1}{2}\left.\frac{\partial^2 \widetilde{\psi}^{2m}}{\partial r^2}\right|_{r=0} \tag{69}$$

$$\psi = \mathbf{r}\cdot\left.\overline{\frac{\partial^2 \psi}{\partial \mathbf{r}^2}}\right|_{r=0}\cdot\mathbf{r}\left(1 + \frac{1}{6}r\right) + \mathcal{O}(r^4) \tag{70}$$

where the overline is used to denote that the trace has been subtracted. Note that the exchange hole for this case vanishes quadratically with the interelectronic distance, as opposed to linearly for triplet exchange holes. This wide exchange hole makes unnatural parity singlet states energetically favorable over triplet states, and this has been used in a more rigorous generalization of Hund's rules.[17−19]

3.4. Three-Particle Coalescence Conditions

The Jastrow[20] function F in eq 53 accounts for the s-wave electron−nucleus and electron−electron derivative discontinuities, and therefore, Φ is free from all cusps at two-particle coalescence. Equation 53 also contains a contribution for the three-particle cusp where two singlet coupled electrons coalesce at a nucleus. In this region the wave function depends on the logarithm of $r_{1I}^2 + r_{2I}^2$, with a prefactor that depends on the angle between the paths of convergence between the electrons. The necessity for log terms to satisfy the three-particle coalescence in helium and to ensure completeness in an analytic expansion for the ground state of helium had been shown by Fock in 1958.[21,22]

Very little is known about the coalescence conditions for triplet spin-coupled electrons coalescing at a nucleus. The wave function is zero at coalescence, and by analogy one expects that any derivative discontinuities must appear at second order. Just as little is known about three-electron coalescence. The most we can presently say is that the wave function vanishes at coalescence due to the Fermi hole, and therefore, derivative discontinuities can be second order at worst. Hoffmann-Ostenhof et al.[23] give a general analysis of N-particle coalescence for fermions in terms of the hyper-radius $\tilde{r}$ of an N-dimensional sphere. According to their work, the wave function goes asymptotically with $\tilde{r}^2$ for $\tilde{r} \to 0$, which coincides with the behavior of the wave function in the case of the two-electron triplet cusp, in line with the previous argument.

3.5. Second-Order Coalescence Conditions

Recently, a number of authors have probed deeper into the structure of the wave function at two-particle coalescence, extending the analysis of Pack and Byers Brown.[24−26] Upon closer inspection of the Schrödinger equation at short-range interparticle separation r with all other particles well separated one finds that the Y_{lm} are uncoupled up to $\mathcal{O}(r^{l+3})$ and even $\mathcal{O}(r^{l+4})$ for coalescence of identical particles. This leads to the following relations

$$f^2_{lm} = \frac{\mu}{(2l + 3)}\left(\frac{\gamma^2}{\mu(l + 1)} + \hat{S} - E\right)f^0_{lm} \tag{71}$$

$$f^3_{lm} = \frac{\mu\gamma(3l + 4)}{3(l + 1)(2l + 3)(l + 2)}\left(\frac{\gamma^2}{\mu(3l + 4)} + \hat{S} - E\right)f^0_{lm} \tag{72}$$

where $\gamma = Z_1Z_2\mu$ and $\hat{S}$ is the part of the Hamiltonian that is order r^0. Equation 72 holds only for identical particle coalescence. These second-order and third-order coalescence conditions can be formulated as

$$\left.\frac{\partial^{l+k}\widetilde{\psi}^{lm}}{\partial r^{l+k}}\right|_{r=0} = \frac{(l + k)!}{l!}c^k_l(b^k_l + \hat{S} - E)\left.\frac{\partial^l \widetilde{\psi}^{lm}}{\partial r^l}\right|_{r=0} \tag{73}$$

with $k = 2$ and 3 and where l, m, and k relate to eq 63. The coefficients b^k_l and c^k_l are universal, depending only on the nature of the coalescing particles. However, because of the presence of $\hat{S} - E$, the $\mathcal{O}(r^{l+2})$ and $\mathcal{O}(r^{l+3})$ terms in eqs 54 and 63 depend on the molecule and state and vary throughout configuration space.

3.6. Coalescence Conditions and Approximate Wave Functions

Pack and Byers Brown's analysis may be applied to the Hartree−Fock equations for the orbitals in a Slater determinant wave function. One finds that the electron−nucleus coalescence conditions apply to each orbital individually. The same is also true for the Kohn−Sham orbitals in density functional theory.[27] Provided that each orbital in a CI wave function (or in an approximate density in DFT) satisfies the coalescence conditions the trial wave function (and density) also satisfies the coalescence conditions.

Expansions similar to eq 63 may also be inserted into the equations in correlated wave function approximations. For example, in the spin-adapted equations for the first-order pair functions in second-order Møller−Plesset (MP2) theory

$$(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)u^s_{ij} + \hat{Q}_{12}\frac{1}{r_{12}}\Phi^s_{ij} = 0 \tag{74}$$

where $\hat{F}$ and ε_i are the Hartree−Fock operator and orbital eigenvalues, respectively, and $\hat{Q}_{12}$ is the strong-orthogonality operator that projects out the one-particle excitations from $1/r_{12}$ (these are contained in $\hat{F}$). Expanding both the Hartree−Fock pair functions Φ_{ij}^{s} and the first-order pair functions u_{ij}^{s} results in the (natural parity) singlet and triplet MP2 coalescence conditions

$$\left.\frac{\partial u_{ij}^{0}}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\,\Phi_{ij}^{0}(r_{12}=0) \tag{75}$$

$$u_{ij}^{0} = \left(1 + \frac{1}{2}r_{12}\right)\Phi_{ij}^{0}(r_{12}=0) + \mathcal{O}(r_{12}^{2}) \tag{76}$$

$$\left.\frac{\partial^{2}\widetilde{u_{ij}^{1\,1m}}}{\partial r_{12}^{2}}\right|_{r_{12}=0} = \frac{1}{2}\left.\frac{\partial\widetilde{\Phi_{ij}^{0\,1m}}}{\partial r_{12}}\right|_{r_{12}=0} \tag{77}$$

$$u_{ij}^{1} = \mathbf{r}_{12}\cdot\left.\frac{\partial\Phi_{ij}^{1}}{\partial\mathbf{r}_{12}}\right|_{r_{12}=0}\left(1 + \frac{1}{4}r_{12}\right) + \mathcal{O}(r_{12}^{3}) \tag{78}$$

These *s*- and *p*-wave coalescence conditions for the first-order pair functions have gained significant importance in explicitly correlated MP2 and coupled-cluster methods.

Formation of spin-adapted pair functions u_{ij}^{s} and Φ_{ij}^{s} is only possible when the MP2 theory uses a closed-shell reference state. To generalize to the open-shell case it is possible to apply the wave function expansion to spin−orbital pairs.[28] As first understood by Bokhan et al.[29] in this case both the *s*-wave and the *p*-wave coalescence conditions apply.

3.7. Convergence Properties of CI Wave Functions

Now let us turn to the convergence properties of CI-type expansions. We shall see that the rate of convergence is strongly linked to the behavior of the basis functions at the singularities.

The full CI method proceeds by selecting a set of N one-electron basis functions, which define the extent of the set of orbitals from which $\binom{2N}{n}$ n-electron Slater determinant basis functions can be formed. The coefficients c_K in eq 46 are determined by the Rayleigh−Ritz method, where the energy is made stationary with respect to variations in the CI coefficients. This leads to the matrix eigenvalue problem

$$\sum_{L} H_{KL}c_{L} = E\sum_{L} S_{KL}c_{L} \tag{79}$$

where the Hamiltonian and overlap matrix elements are the expectation values

$$H_{KL} = \langle\Phi_K|\hat{H}|\Phi_L\rangle \tag{80}$$

$$S_{KL} = \langle\Phi_K|\Phi_L\rangle \tag{81}$$

In 1977 Klahn and Bingel[30,31] proved that the eigenvalues of the matrix eigenvalue problem converge with increasing N to the eigenvalues of the nonrelativistic, Born−Oppenheimer Schrödinger equation, subject to certain completeness conditions on the set of one-electron basis functions. Specifically, this requires completeness in the first Sobolev space, that is, the space of functions where both the function itself and its derivative are square integrable. Completeness here has the meaning that the error can be made arbitrarily small by increasing the number of functions in the expansion.

The vast majority of molecular electronic structure programs use Gaussian atomic orbital basis functions.[32] Gaussian functions satisfy the required completeness relations, and the energies from a full CI calculation are guaranteed to converge to the exact nonrelativistic Born−Oppenheimer electronic energies. However, this does not guarantee that the convergence will be rapid. The basis-set convergence of both the Hartree−Fock and CI energies have been studied extensively by many authors, both numerically and analytically.[16,33−56] The rates of convergence depend critically on the choice of basis functions and are largely understood.

3.7.1. One-Electron Convergence.

The important aspects of one-electron basis-set convergence may be understood by examining the rate of convergence of the energy expectation value of the hydrogen atom using three choices of Gaussian basis functions[57]

$$\psi_{nlm} = Nr^{n-1}e^{-\eta_l r^2}Y_{lm}(\theta,\varphi);\quad n > l;\, n-l = 1,3,5... \tag{82}$$

$$\psi_{nlm} = Nr^{n-1}e^{-\eta_l r^2}Y_{lm}(\theta,\varphi);\quad n > l;\, n-l = 1,2,3... \tag{83}$$

$$\psi_{klm} = Nr^{l}e^{-\eta_{lk} r^2}Y_{lm}(\theta,\varphi) \tag{84}$$

Applying arguments similar to the theory of Fourier series, Klahn and Morgan[34] were able to demonstrate that the error in the energy expectation value using basis functions eq 82, which is equivalent to a set of Hermite functions, goes as $\sim n^{-3/2}$. By including odd powers of r the convergence becomes exponential. The source of the slow convergence of basis functions eq 82 is the inability to describe the wave function in the vicinity of the singularities of the function being expanded, namely, near the nuclear cusps.[33−35,57] Modern Gaussian-based electronic structure codes use basis functions of type eq 84, which, although they do not contain any derivative discontinuities, can reproduce the cusp to arbitrary precision through ever tighter exponents. In 1986 Klopper and Kutzelnigg[36] studied the hydrogen energy error ε with these basis functions and Huzinaga's set of exponents[58] and found an excellent numerical fit of the form

$$\varepsilon = A\exp(-b\sqrt{n}) \tag{85}$$

Subsequently, Kutzelnigg was able to derive this result analytically for even tempered basis sets.[57] Extrapolation based on eq 85 appears to be useful for many-electron systems.[59] Many researches use a slighly different extrapolation formula, which has a somewhat more empirical justification[60]

$$E_X^{\mathrm{HF}} \approx E_{\mathrm{limit}}^{\mathrm{HF}} + A\exp(-BX) \tag{86}$$

$$E_{\mathrm{limit}}^{\mathrm{HF}} \approx \frac{E_X^{\mathrm{HF}} - bE_{X-1}^{\mathrm{HF}}}{1-b},\; b = e^{-B} = \frac{E_X^{\mathrm{HF}} - E_{X-1}^{\mathrm{HF}}}{E_{X-1}^{\mathrm{HF}} - E_{X-2}^{\mathrm{HF}}} \tag{87}$$

where X is the cardinal number of the basis set (see section 3.7.5). Note that both extrapolation methods require three computed energies to determine the basis-set limit estimate.

Some authors debate the relative merits of choosing Slater-type basis functions over Gaussian basis functions.[61] In particular, Slater-type orbitals have a derivative discontinuity at the nucleus and decay more slowly than Gaussians, although neither Gaussians nor Slater functions have the correct long-range behavior. The incorrect asymptotic behavior of the basis

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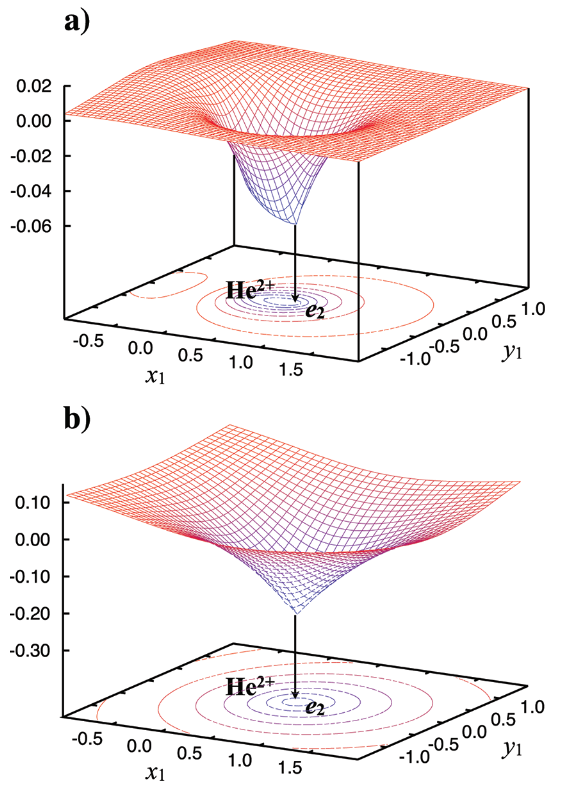

Figure 6. (a) Cut of the Coulomb hole $h_c(x_1,y_1,0.5,0)$ for helium in its ground 1^1S state. The nucleus is at the origin. (b) Jastrow function $J(x_1,y_1)$ where $h_c(x_1,y_1,0.5,0) = J(x_1,y_1)\varphi_{1s}(r_1)\varphi_{1s}(r_2)$.

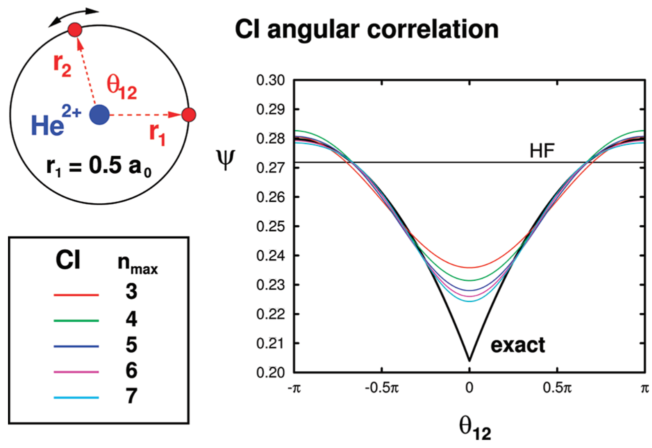

Figure 7. Helium ground-state wave function with both electrons on the same circle of radius 0.5 a_0 computed with the CI approach using increasing basis size with maximum principal quantum number n_{max}. Reprinted with permission from ref 2. Copyright 2007 John Wiley and Sons.

functions at large electron−nucleus distances does not appear to limit the energy convergence rate, at least in the regime of accuracy presently attainable. The situation may, however, be different for properties such as hyperpolarizibilities that depend critically on the fringes of the electron cloud.

3.7.2. Two-Electron Convergence. In Figure 6 we plot the correlation hole (eq 15) for helium in its ground 1^1S state. The correlation cusp is clearly visible at the coalescence point of the two electrons at the bottom of the hole. Contrasting this numerically exact correlation hole with that of the small CI calculation in Figure 2d we see that the only sharp feature in the approximate hole is, erroneously, at the nucleus. This is a result of the very restricted set of configurations adopted in the illustrative CI calculation of section 2.4. Increasing the one-electron basis by increasing the maximum principal quantum number of the atomic orbitals improves the correlation description, and the convergence toward the exact wave function is plotted in Figure 7.

In contrast to the exponential one-electron convergence it is clear that the two-electron convergence is extremely slow. This is true independently of the choice of one-electron basis functions. Away from the nucleus, the only possibility for a function of the smooth atomic orbitals to describe the correlation hole is through a tighter and tighter mesh of radial and angular nodes, which necessitates very large basis sets. It is worth emphasizing that because the cusp itself has zero volume the fact that the smooth basis functions can never reproduce it exactly is not itself a problem. Rather, it is the linear-r_{12} form of the wave function around the cusp that is at the heart of the slow energy convergence. The correlation cusp at electronic coalescence arises as a consequence of their Coulombic interactions. This has two ramifications: the correlation cusp is present in all electronic wave functions, and consequently, all CI-type correlated wave functions suffer from this convergence problem. However, the universal nature and particular functional form of the correlation cusp means that the convergence with basis size is both smooth and predictable, which makes possible extrapolation.

3.7.3. Partial Wave Expansion. Schwartz analyzed the rate of convergence of the second-order helium energy in a $1/Z$ expansion,[33] where the zeroth-order Hamiltonian is the bare-nucleus Hamiltonian. He found that (in atomic units) the partial-wave contributions to the second-order energy have the analytic form

$$E^{(2)} = \sum_{l=0}^{\infty} E_l^{(2)} \tag{88}$$

$$E_l^{(2)} = -\frac{45}{256}\left(l + \frac{1}{2}\right)^{-4} - \frac{225}{1024}\left(l + \frac{1}{2}\right)^{-6} + \dots \tag{89}$$

The $(l + 1/2)^{-4}$ convergence is very slow and results directly from the fact that the CI expansion corresponds to a partial wave expansion of the Coulomb singularity. Following the work of Klahn and Morgan,[34] Hill analyzed the partial wave expansion of the variationally optimized CI energy expectation value.[35] Hill found that

$$E = \sum_{l=0}^{\infty} E_l \tag{90}$$

$$E_l = -3C_1\left(l + \frac{1}{2}\right)^{-4} - 4C_2\left(l + \frac{1}{2}\right)^{-5} + \dots \tag{91}$$

where $C_1 = 2\pi^2 \int_0^\infty |\Psi(r,r,0)|^2 r^5\,dr \approx 0.024742$ and $C_2 = (12\pi/5)\int_0^\infty |\Psi(r,r,0)|^2 r^6\,dr \approx 0.007747$. As for the second-order energy the convergence goes as $(l + 1/2)^{-4}$ with increasing l, but the coefficient is different. This is an example of the interference between correlation model and basis-set effects resulting in differing rates of convergence.[44,48,62−64] The fact that odd powers of $(l + 1/2)$ appear as a result of correlation effects beyond second order was verified by Kutzelnigg and Morgan.[16] Moreover, they were able to show that in many-electron systems different pair contributions converge at different rates. Natural parity singlet pairs converge as $(l + 1/2)^{-4}$, which results from the partial wave expansion of the *s*-wave correlation cusp. Natural parity triplet pairs converge as $(l + 1/2)^{-6}$, which results from a partial wave expansion of the second-order derivative discontinuity at *p*-wave coalescence. Unnatural parity singlet states converge as $(l + 1/2)^{-8}$, which results from the third-order derivative discontinuity at *d*-wave coalescence.

3.7.4. Principal Expansion. Using natural orbitals, which have the same nodal structure as hydrogenic and Laguerre functions, Carroll et al.[38] demonstrated numerically for the 1^1S helium state that, to a good approximation, each orbital provides an energy contribution proportional to

$$\varepsilon_{nlm} \approx -a_l\left(n - \frac{1}{2}\right)^{-6} \tag{92}$$

For $l = 0$, $a_l \approx 0.29$. For $l > 0$, $a_l \approx 0.22$, and the energy contribution from each orbital depends only on its principal quantum number. Consequently, partial wave expansions are rarely used in quantum chemistry, and instead, basis sets are chosen according to a principal expansion where basis sets are increased by including all $\sim n^2$ functions in the next shell. Each shell contributes an amount of energy proportional to n^{-4}. The correlation-consistent basis sets cc-pVXZ of Dunning, Peterson, Woon, and co-workers[65] are constructed on this principle. A basis is expanded by including the set of functions that have approximately equal energy contributions while simultaneously optimizing the exponents and Slater-type-Gaussian contraction coefficients to minimize both the Hartree−Fock and the correlation energies.

3.7.5. Extrapolation. It has been observed numerically that energy convergence both for partial wave expansions and for principal expansions goes as $(L + 1)^{-3}$, where L is the highest angular momentum function present in the one-electron basis.[40,41] For the partial wave expansion of ground-state helium, this may be explained through the following argument. In a CI calculation, the error in the energy due to omitting all terms $l > L$ is $\Delta E_L = E - \sum_{l=0}^{L} E_l$ and can be estimated by summing over the leading term of the contribution from each omitted partial wave

$$\Delta E_L = 3C_1 \sum_{l=L+1}^{\infty}\left(l + \frac{1}{2}\right)^{-4} \approx 3C_1 \int_{L+1/2}^{\infty}\left(l + \frac{1}{2}\right)^{-4} \mathrm{d}l = C_1(L + 1)^{-3} \tag{93}$$

Kutzelnigg recently re-examined the second-order $1/Z$ expansion for two-electron atoms in natural orbitals and confirmed that each shell contributes an amount of energy proportional to n^{-4}, where n is the principal quantum number of the expansion.[55] The cardinal number of the correlation-consistent basis sets X may be identified with both n and $L + 1$, which concurs with the power law error estimate observed by Helgaker et al.[40,41] This provides a simple two-point extrapolation procedure to eliminate the leading basis-set errors

$$E_X^{\mathrm{corr}} \approx E_{\mathrm{limit}}^{\mathrm{corr}} + AX^{-3} + \mathcal{O}(X^{-4}) \tag{94}$$

$$E_{\mathrm{limit}}^{\mathrm{corr}} \approx E_X^{\mathrm{corr}} + (E_Y^{\mathrm{corr}} - E_X^{\mathrm{corr}})\frac{Y^3}{Y^3 - X^3} + \mathcal{O}(X^{-4}) \tag{95}$$

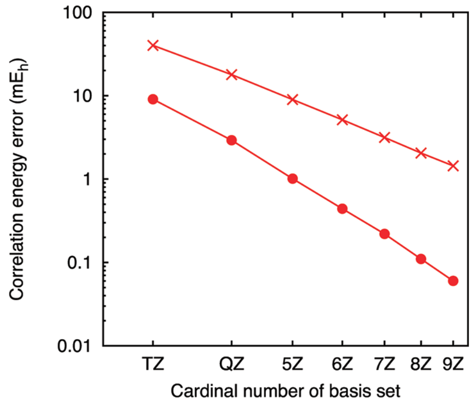

Figure 8. Basis-set errors for the singlet (×) and triplet (●) pair energy contributions to the CCSD correlation energy of neon computed using the cc-pVXZ basis sets.[67]

In pair theories such as MP2 and coupled-cluster singles and doubles (CCSD) the total correlation energy convergence is determined by the natural parity singlet pairs. For triplet pairs, the appropriate power law is X^{-5} and basis-set limit estimation can be improved by extrapolating singlet and triplet pairs separately.[66] The different convergence behavior of singlet and triplet pairs is illustrated in Figure 8, which plots the basis-set errors for the singlet and triplet pair energy contributions to the CCSD energy of neon. The power law extrapolations work well because of the systematic way the correlation-consistent basis sets are constructed, but they are somewhat idealized. Many alternative extrapolation formulas have appeared in the literature, and one of particular note is the Schwenke-type extrapolation[50]

$$E_{\mathrm{limit}}^{\mathrm{corr}} \approx E_X^{\mathrm{corr}} + (E_Y^{\mathrm{corr}} - E_X^{\mathrm{corr}})\frac{Y^p}{Y^p - X^p} \tag{96}$$

3.7.6. Explicit Correlation. Atom-centered basis functions are ill suited to describe the electron-centered features of the correlation hole. In particular, the linear dependence of the wave function on the interelectron separation r_{12} in the region of electron coalescence leads to very slow convergence of the electronic energy with basis size in CI-type expansions of Slater determinants. Although this can be ameliorated by exploiting the smooth and systematic nature of the convergence through extrapolation, large basis sets are still required for high accuracy, which limits the size of systems that can be subject to reliable computational investigation. This review is concerned with an alternative strategy, where basis functions that depend explicitly on r_{12} are incorporated into the wave function expansion. While such expansions converge very rapidly with basis size, *n*-electron Hamiltonian matrix elements no longer factorize into products of one- and two-electron integrals and several alternative strategies have been developed. The focus of this review is on the R12 and F12 methods, which have evolved into practical tools for quantum chemistry. In the next sections we review the alternatives to F12 before giving the established details and latest developments in F12 methodology.

4. *N*-ELECTRON EXPANSIONS

The most widely used numerical approaches of quantum chemistry are based on expansions in terms of (antisymmetrized) products of orthonormalized one-electron functions, the molecular orbitals (MOs). Such MOs are obtained from a mean-field or self-consistent field (SCF) calculation, for example, from a Hartree−Fock calculation, but also Kohn−Sham or other approaches may be employed to generate a set of MOs. In the mean-field approach, the electronic state is represented by a subset of the MOs, the occupied MOs. In terms of spin orbitals $\phi_k(\mathbf{x})$, where $\mathbf{x}$ indicates both spatial and spin coordinates, there are as many occupied spin orbitals as there are electrons, and the antisymmetrized product of the occupied spin orbitals is known as a Slater determinant. Correspondingly, this mean-field description is known as a one-determinantal approximation. The orbital−product approaches are also known as the *algebraic approximation* to quantum chemistry, since the resulting equations can all be formulated in terms of matrix operations.

Having this in mind, let us start our description of the electronic system by performing a Hartree−Fock calculation without any spin restrictions, that is, in an unrestricted Hartree−Fock (UHF) manner, in which the occupied spin orbitals are those orbitals ϕ_k that build the determinant

$$\Phi = \sqrt{n!}\mathscr{A}\phi_1\phi_2\phi_3...\phi_n \tag{97}$$

which minimizes the expectation value

$$E_{\mathrm{HF}} = \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle = \min_{\Phi}\langle\Phi|\hat{H}|\Phi\rangle \tag{98}$$

with respect to orthonormal transformations among all of the orthonormalized MOs (occupied and others). The Hartree−Fock level is often (erroneously) denoted as the "uncorrelated" level, because it does not account for the effects of Coulomb correlation. However, as discussed in sections 2.1−2.3 the Hartree−Fock wave function is highly correlated due to Fermi correlation. The remaining Coulomb correlation (cf. section 2.4) is obtained when the wave function is approximated as a linear combination of determinants, as in the configuration-interaction (CI) method

$$|\mathrm{CI}\rangle = (1 + \hat{T})|\mathrm{HF}\rangle = |\mathrm{HF}\rangle + \sum_{\mu} c_\mu \hat{\tau}_\mu|\mathrm{HF}\rangle \tag{99}$$

In eq 99 the *excitation* operator $\hat{\tau}_\mu$ generates a new Slater determinant by replacing one or more MOs occupied in the reference determinant $|\mathrm{HF}\rangle$ by one or more other orbitals, which are not contained in $|\mathrm{HF}\rangle$. The latter are denoted as *virtual* orbitals. In the following we shall denote occupied MOs with the indices $i, j, k,...$, and the *virtual* orbitals with $a, b, c,...$ Together, the occupied and virtual orbitals form a finite basis set of MOs, which are denoted with the indices $p, q, r,...$ Furthermore, we note that the CI wave function in eq 99 is written in *intermediate normalization*, that is

$$\langle \mathrm{HF}|\mathrm{CI}\rangle = 1 \tag{100}$$

When the excitation operator $\hat{\tau}_\mu$ replaces one orbital it may be written as $\hat{\tau}_i^a = a_a^\dagger a_i$, when two orbitals are replaced as $\hat{\tau}_{ij}^{ab} = a_a^\dagger a_i a_b^\dagger a_j$, when three are replaced as $\hat{\tau}_{ijk}^{abc} = a_a^\dagger a_i a_b^\dagger a_j a_c^\dagger a_k$, and so on. The creation $(a_q^\dagger)$ and annihilation (a_p) operators satisfy the anticommutator relation $[a_p, a_q^\dagger]_+ = \delta_{pq}$, and we note that the excitation operators $\hat{\tau}_\mu$ mutually commute, $[\hat{\tau}_\mu, \hat{\tau}_\nu] = 0$. When only $\hat{\tau}_i^a$ is included the CI approach only contains *single* excitations and the method is denoted as a configuration-interaction singles (CIS) method. With the operators $\hat{\tau}_i^a$ and $\hat{\tau}_{ij}^{ab}$ we obtain the configuration-interaction singles and doubles (CISD) method with $\hat{\tau}_{ijk}^{abc}$ the configuration-interaction singles, doubles, and triples (CISDT) method, and so forth.

Because the CI approach is not size extensive it is not used much any more in modern wave function-based quantum chemistry. Rather, the coupled-cluster (CC) approach has become the method of choice for such calculations. The CC approach is size extensive, which means that the energy scales correctly with the number of electrons in the system. The size extensivity is accomplished by choosing an exponential ansatz for the coupled-cluster wave function

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle; \qquad \hat{T} = \sum_{\mu} t_\mu \hat{\tau}_\mu \tag{101}$$

Hence, the cluster operator $\hat{T}$ is a linear combination of excitation operators $\hat{\tau}_\mu$, each multiplied by a cluster amplitude t_μ. These are determined by multiplying the Schrödinger equation from the left with $\exp(-\hat{T})$ and projecting onto the excited states $\langle\mu| = \langle \mathrm{HF}|\hat{\tau}_\mu^\dagger$

$$\langle\mu|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle = 0 \tag{102}$$

Similarly, the CC energy is obtained from the corresponding projection onto the Hartree−Fock state

$$E_{\mathrm{CC}} = \langle \mathrm{HF}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle \tag{103}$$

There are as many nonlinear amplitude equations, eq 102, as there are amplitudes t_μ.

As in the case of the CI wave function, the cluster operator $\hat{T}$ can be written as a sum of single $(\hat{T}_1)$, double $(\hat{T}_2)$, triple $(\hat{T}_3)$ excitations, and so forth. Hence

$$\begin{aligned}\hat{T} &= \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + ... \\ &= \sum_{ia} t_i^a \hat{\tau}_i^a + \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\hat{\tau}_{ij}^{ab} + \frac{1}{36}\sum_{ijkabc} t_{ijk}^{abc}\hat{\tau}_{ijk}^{abc} + ...\end{aligned} \tag{104}$$

With all excitation operators included up to the level of the n-excitation operator $\hat{T}_n$ for a n-electron system the CC wave function is equivalent with the full configuration interaction (FCI) treatment in the given one-electron basis (MOs). In common applications, however, the wave function is restricted to single excitations (CCS, coupled-cluster singles method), single and double excitations (CCSD, coupled-cluster singles and doubles method), single, double, and triple excitations (CCSDT, coupled-cluster singles, doubles, and triples method), and so on.

It is not the purpose of the present review to discuss the details of standard present-day coupled-cluster theory such as the approximate treatment of triple excitations, CCSD(T), nor to discuss related approaches such as *quadratic* configuration interaction with singles and doubles (QCISD) or Brueckner doubles theory (BD). For details of coupled-cluster theory we refer to textbooks or other review articles, for example, refs 68−71.

There are two points that we want to make here. First, we note that the second order of Møller−Plesset perturbation theory (MP2), which will be discussed in more detail later in this review, is readily obtained by inserting the corresponding perturbation expansions $\hat{T} = \hat{T}^{(1)} + \hat{T}^{(2)} + ...$ and $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$ into the above-mentioned CC equations and collecting all terms up to first order in the amplitudes and second order in the energy

$$0 = \langle\mu|\hat{H}^{(1)} + [\hat{H}^{(0)}, \hat{T}^{(1)}]|\mathrm{HF}\rangle \tag{105}$$

$$E_{\mathrm{MP2}} = E_{\mathrm{Hartree-Fock}} + \langle \mathrm{HF}|[\hat{H}^{(1)}, \hat{T}^{(1)}]|\mathrm{HF}\rangle \tag{106}$$

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where we used that $\langle \mu_k | \hat{H}^{(0)} | \mathrm{HF} \rangle = 0$ for $k \geq 1$ by construction of $H^{(0)}$.

Second, the n-electron expansions (CI, CC, Møller–Plesset theory) discussed in this section are all based on expanding the n-electron wave function in a basis of Slater determinants. Such expansions are not able to satisfy the electronic cusp conditions and consequently it is very difficult (basically impossible, except for very large one-electron basis sets) to accurately describe the Coulomb holes in the wave function (see section 2.4). As a result, the convergence of the CI, CC, and MP2 energies toward their respective basis-set limits (E_∞) is extremely slow. It can be represented as[72]

$$E_N = E_\infty + aN^{-1} \tag{107}$$

or[40]

$$E_X = E_\infty + cX^{-3} \tag{108}$$

where N is the number of basis functions in a principal-expansion (i.e., correlation-consistent) basis set with cardinal number X (see also section 3.7).

To improve the slow convergence significantly we must go beyond expanding the wave function using determinants, that is, antisymmetrized products of one-electron functions, eq 97. Obviously, the next step beyond products of one-electron functions (orbitals) is to include two-particle functions (geminals), for example, in terms of the n-electron basis functions

$$\Psi = \sqrt{n!}\mathscr{A} f(\mathbf{x}_1, \mathbf{x}_2)\phi_k(\mathbf{x}_3)...\phi_m(\mathbf{x}_n) \tag{109}$$

In the following subsections, several examples of expansions beyond (antisymmetrized) products of one-electron functions will be discussed. The corresponding expansions are referred to as "explicitly correlated wave functions". See also refs 73–75.

4.1. Hylleraas-Type Wave Functions

4.1.1. He Atom. The first successful electronic-structure computation using an explicitly correlated wave function was the calculation on the He ground state by Hylleraas in 1929.[76] In his classical paper[76] Hylleraas carried out a calculation on the 1^1S ground state of the He atom using the coordinates

$$s = r_1 + r_2; \qquad t = r_1 - r_2; \qquad u = r_{12} \tag{110}$$

where r_1 is the distance of electron 1 from the nucleus, r_2 is the distance of electron 2 from the nucleus, and r_{12} the distance between the two electrons. In the Hylleraas expansion the spatial part of the He ground-state wave function is written as

$$\Psi_N = \exp(-\zeta s) \sum_{k=1}^{N} c_k s^{l_k} t^{2m_k} u^{n_k} \tag{111}$$

Only even powers of t contribute to singlet states, which have a symmetric spatial part and an antisymmetric spin function. With only 3 terms, that is, with the spatial wave function

$$\Psi_3 = \exp(-\zeta s)(c_1 + c_2 u + c_3 t^2) \tag{112}$$

Hylleraas obtained the energy $E = -2.90243\ E_\mathrm{h}$, after variationally optimizing both the linear parameters c_k and the nonlinear parameter ζ (which was determined to $\zeta = 1.82\ a_0^{-1}$).

It is interesting to note[77] that prior to using an explicitly correlated wave function Hylleraas had tried to solve the He ground-state problem using a conventional CI expansion. This expansion was found to converge unacceptably slowly, however. Hylleraas was thus one of the first researchers to suffer from the slow convergence of the conventional CI expansion. This convergence problem was solved using an explicitly correlated wave function. Hylleraas' choice was, however, not motivated by a consideration of the singularities of the Hamiltonian and the related electron–electron cusp. This was done by Slater in 1928.[78] This author analyzed the properties of the He wave function and found that the Coulomb singularity in the Hamiltonian imposes a certain behavior on the wave function at the electron–electron coalescence point. Slater therefore suggested that the wave function should be multiplied by a factor of $\exp(r_{12}/2)$ in order to model the behavior at the coalescence point. In Slater's work[78] it is noted that "*It can be easily shown, however, that the correct wave function for the S states should approach $e^{-2(r_1+r_2)+r_{12}/2}$ at small r's; when [the Hamiltonian] H operates on this, the result is in terms of zero order in the r's.*"

Indeed, Slater's function $\Psi = e^{-2(r_1+r_2)+r_{12}/2}$ satisfies Kato's cusp condition

$$\left.\frac{\partial\widetilde{\Psi}}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi(r_{12} = 0) \tag{113}$$

where the wide tilde indicates spherical averaging. Furthermore, a Taylor expansion of Slater's r_{12}-dependent wave function factor yields $\exp(r_{12}/2) = 1 + (1/2)r_{12} + \mathscr{O}(r_{12}^2)$, and thus, the correct linear dependence on the interelectronic coordinate for small r_{12}, as is the case in present-day R12 methods that use wave functions with linear r_{12} terms.

Hence, both Slater and Hylleraas may be seen as the persons who introduced explicitly correlated wave functions to electronic structure theory. Slater's function $e^{-\zeta(r_1+r_2)+\gamma r_{12}}$ was proposed in 1928, but the first computations with explicitly correlated wave functions were carried out by Hylleraas in 1929 (in fact, Hylleraas also studied a function of the type $e^{-\zeta(r_1+r_2)+\gamma r_{12}}$). Concerning Slater's function $e^{-2(r_1+r_2)+r_{12}/2}$ we note that the correlation function $\chi(r_{12}) = \exp(r_{12}/2)$ seemed physically unreasonable to Hartree and Ingman.[79] These authors argued that the function $\chi(r_{12})$ should approach a constant value for $r_{12} \to \infty$ and that it should decrease to a smaller value for $r_{12} \to 0$. They therefore suggested to use the trial wave function

$$\exp(-\zeta[r_1 + r_2])[1 - c\exp(-\gamma r_{12})] \tag{114}$$

with $\zeta > 0$ and $\gamma > 0$. As will become clear later in the present review, this 1933 wave function of Hartree and Ingman contains the correlation factor that is used in modern F12 methods. Today, these factors are referred to as Slater-type geminals (STG). It seems appropriate to relate this factor to the work by Slater.

Keeping ζ fixed, Hylleraas found that the 6-term function

$$\Psi_6 = \exp(-1.82s)(c_1 + c_2 u + c_3 t^2 + c_4 s + c_5 s^2 + c_6 u^2) \tag{115}$$

yields the energy $E = -2.90324\ E_\mathrm{h}$.[76] For this 6-term function, however, it was found later that the variationally optimal nonlinear parameter is $\zeta = 1.76\ a_0^{-1}$, and with this value, the energy becomes $E = -2.90333\ E_\mathrm{h}$.[80–82] Furthermore, with another 6-term Hylleraas expansion

$$\tilde{\Psi}_6 = \exp(-\zeta s)(c_1 + c_2 u + c_3 t^2 + c_4 s^2 u + c_5 s^3 u + c_6 u^2) \tag{116}$$

a still lower energy of $E = -2.90345\ E_\mathrm{h}$ can be obtained ($\zeta = 1.86\ a_0^{-1}$).[83] In a systematic approach the He ground-state energy can be computed from an N-term Hylleraas expansion with all terms that satisfy $l_k + 2m_k + n_k \leq L_\mathrm{max}$. With $L_\mathrm{max} = 6$,

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a 50-term Hylleraas expansion and *micro*hartree accuracy in the ground-state energy is obtained; with $L_{\max} = 13$, a 308-term Hylleraas expansion yielding *nano*hartree accuracy is obtained.[84]

Much progress was achieved in the decade from 1955 to 1965.[85] Pekeris[86−88] succeeded to perform large-scale Hylleraas calculations using Laguerre polynomials multiplied by an exponential using perimetric coordinates of the form $x = (1/2)(u + t)$, $y = (1/2)(u - t)$, and $z = s - u$ as variables, and several authors have suggested to extend and/or modify the original Hylleraas expansion. For example, Kinoshita suggested to allow for negative powers[89,90]

$$\Psi_N = \exp(-\zeta s) \sum_{k=1}^{N} c_k s^{l_k} (t/u)^{2m_k} (u/s)^{n_k} \tag{117}$$

H. M. Schwartz proposed using half-integer powers[91,92]

$$\Psi_N = \exp(-\zeta s) \sum_{k=1}^{N} c_k s^{l_k/2} t^{2m_k} u^{n_k/2} \tag{118}$$

C. Schwartz[93] suggested using half-integer powers of s only

$$\Psi_N = \exp(-\zeta s) \sum_{k=1}^{N} c_k s^{l_k/2} t^{2m_k} u^{n_k} \tag{119}$$

He performed calculations with all terms up to $l_k/2 + 2m_k + n_k \leq 8(1/2)$.

Motivated by the Fock expansion,[21,22,94,95] several researchers included logarithmic terms into the Hylleraas wave functions. Such logarithmic terms are needed to describe the wave function at the point of coalescence of three particles (i.e., in He, both electrons at the nucleus).[96] In 1966, for example, the calculations by Frankowski and Pekeris[97] were carried out using terms such as ln s, $(\ln s)^2$, and $(s^2 + t^2)^{1/2}$ in expansions of the type

$$\Psi_N = \exp(-\zeta s) \sum_{k=1}^{N} c_k s^{l_k} t^{2m_k} u^{n_k} (s^2 + t^2)^{i_k/2} (\ln s)^{j_k} \tag{120}$$

yielding the He ground-state energy $E = -2.9037243770326\ E_\mathrm{h}$ from a 1078-term wave function. Logarithmic terms were again investigated some 20−25 years later (ca. 1986−1990),[98−101] but it was also found at the same time that similarly accurate results can be obtained from a Hylleraas expansion, not with logarithmic terms but with a "double basis set" instead.[102−105] The "double basis set" consists of the basis functions

$$\{\Phi_0, \Phi_{ijk}(\alpha_A, \beta_A), \Phi_{ijk}(\alpha_B, \beta_B)\} \tag{121}$$

$$\Phi_{ijk}(\alpha, \beta) = (1 + \hat{P}_{12}) r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2) \tag{122}$$

where $\hat{P}_{12}$ permutes r_1 and r_2. Of course, this concept of "double basis set" can be extended to that of a "triple basis set", and so forth, and with a "triple basis set", Drake and co-workers have been able to compute the He ground-state energy with about 20-significant-digits accuracy.[106] Note that this result was obtained without logarithmic terms. Even more accurate calculations are possible for He, however, with up to 40-significant-digits accuracy. For example, C. Schwartz[107] obtained an accuracy of about 35 decimal places using the original scheme of Hylleraas plus a combination of negative powers and a logarithm of the Hylleraas coordinate s. A 25-significant-digits accuracy was obtained by Korobov[108] using an expansion in terms of Slater-type geminals (Φ_k)

$$\Psi_N = \sum_{k=1}^{N/2} \{c_k \Re(\Phi_k) + d_k \Im(\Phi_k)\};$$
$$\Phi_k = \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}) \tag{123}$$

where α_k, β_k, and γ_k are complex parameters. Forty significant digits were finally obtained by Nakashima and Nakatsuji[109] using the free iterative complement interaction (ICI) method. For the He atom, this method is similar to a Hylleraas-type expansion. Consider, for example, the functions

$$\Phi_1^{(0)} = \exp(-\zeta^{(0)} s);$$
$$\Phi_2^{(0)} = \exp(-\zeta^{(0)} s) \ln(s + u);$$
$$g = (s^2 - t^2)/(4sZ) + u \tag{124}$$

where Z is the atomic number. In free ICI calculations, at each order n, new basis functions are generated by applying both g and $g\hat{H}$ to all k basis functions $\Phi_k^{(n-1)}$ of order $n-1$, and the energy is obtained from an expansion in this new basis

$$\Psi^{(n)} = \sum_{k=1}^{M_n} c_k^{(n)} \Phi_k^{(n)} \tag{125}$$

by variationally optimizing the $c_k^{(n)}$'s as well as the exponent $\zeta^{(n)}$. This procedure leads to an ultimate wave function expansion of the form

$$\Psi^{(n)} = \exp(-\zeta^{(n)} s) \sum_{k=1}^{M_n} c_k^{(n)} s^{l_k} t^{2m_k} u^{n_k} [\ln(s + u)]^{j_k} \tag{126}$$

at free-ICI order n, where $l_k \in \mathbb{Z}$, $m_k \in \mathbb{N}$, $n_k \in \mathbb{N}$, and $j_k \in \{0,1\}$. Table 2 provides an overview of some of the most recent and most accurate calculations of the ground state of the He atom. The purpose of this table is not to provide a complete overview of explicitly correlated calculations on He but rather to give a few examples from the recent literature.

Of course, all of the approaches just mentioned can not only be applied to the 1^1S ground state of He but also and equally well to electronically excited states as well as to all He-like ions such as

Table 2. Nonrelativistic Born−Oppenheimer (i.e., infinite nuclear mass) Ground-State Energy of Helium

system	K^a	E/E_h	function	ref
He	600	−2.903724377022	ECG	110
	600	−2.903724377033	LECG[b]	110
	616	−2.903724377034073	Hylleraas[c]	102
	308	−2.9037243770341144	Hylleraas[d]	111, 112
	2114	−2.903724377034119582	Hylleraas[e]	105
	4648	−2.90372437703411959822999	Hy-CI	113
	2358	−2.903724377034119598305	Hylleraas[e]	106
	5200	−2.903724377034119592311587	STG[f]	108, 114
	10 257	−2.903724377034119598311592 2451944044400495	Hylleraas[g]	107
	22 709	−2.903724377034119598311592 2451944044466969	free ICI[h]	109, 115

[a] Number of terms in the expansion. [b] ECG expansion plus terms linear in r_1, r_2, or r_{12}. [c] Hylleraas wave function (double basis set). [d] Hylleraas wave function (fractional and negative powers of s and u). [e] Hylleraas wave function (triple basis set). [f] Slater-type geminals. [g] Hylleraas wave function with negative powers and ln(s). [h] Free iterative-complement-interaction method; Hylleraas type with ln($s + u$).

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H^-, Li^+, and so on. However, since such computations do not add much (there may be some symmetry issues) to the topic of the present review, we here focus on the He ground state. Besides electronically excited states, He-like ions, their properties, and so forth, the more interesting question is how Hylleraas-type trial wave functions may be designed for *many*-electron systems such as Li, Be, B, C, and so on. A further important question is how a *compact* trial wave function may be designed that is suitable for generalizations toward electronic-structure computations on polyatomic molecules.

Concerning the latter question we note that there is a very rich early literature on various *compact* wave functions for two-electron systems in which, for example, functions such as[116−124]

$$\Psi = \exp(-2[r_1 + r_2])\chi(r_{12}) \tag{127}$$

$$\Psi = \exp(-\zeta[r_1 + r_2])\exp(-\gamma r_{12}) \tag{128}$$

$$\Psi = \exp(-\zeta[r_1 + r_2])(1 + cr_{12}) \tag{129}$$

$$\Psi = \exp(-\zeta[r_1 + r_2])(1 - c\exp[-\gamma r_{12}]) \tag{130}$$

$$\Psi = \varphi(r_1)\varphi(r_2)(1 + cr_{12}) \tag{131}$$

$$\Psi = \varphi(r_1)\varphi(r_2)\chi(r_{12}) \tag{132}$$

$$\Psi = [\varphi(r_1)\phi(r_2) + \phi(r_1)\varphi(r_2)]\chi(r_{12}) \tag{133}$$

$$\Psi = (1 + cr_{12})\sum_{p \le q} c_{pq}[\varphi_p(1)\varphi_q(2) + \varphi_q(1)\varphi_p(2)] \tag{134}$$

$$\Psi = (1 - c\exp[-\gamma r_{12}])\sum_{p \le q} c_{pq}[\varphi_p(1)\varphi_q(2) + \varphi_q(1)\varphi_p(2)] \tag{135}$$

have been studied. Equations 134 and 135 contain CI expansions that are multiplied by a correlation factor. With respect to the other functions, the orbitals $\varphi(r)$, $\phi(r)$, and/or the correlation factor $\chi(r_{12})$ are obtained numerically by solving the appropriate differential equations or expanded in one-electron and/or two-electron basis sets, respectively. Later in this review we shall see that today functions of these types are indeed used for calculations on polyatomic molecules (e.g., with terms such as $(1 + cr_{12})$ or $(1 - c\exp[-\gamma r_{12}])$).

Let us first consider many-electron atoms. Obviously, Hylleraas' ansatz could be extended in a straightforward manner toward many-electron atoms by including not only the coordinate r_{12} but also the other interelectronic coordinates r_{13}, r_{23}, r_{14}, r_{24}, r_{34}, and so forth, into the many-electron wave function. In the most general Hylleraas wave function products such as $r_{12}r_{13}$, $r_{12}r_{13}r_{14}$, and so on, occur. In the following we will refer to the corresponding computations as Hyleraas-type calculations. One can, however, make the restriction that no products of interelectronic coordinates shall occur, only individual linear terms. This was, presumably for the first time, done in the landmark paper by James and Coolidge on the Li atom from 1936,[125] and this is the essence of the Hylleraas-configuration-interaction (Hy-CI) method. Let us consider the Li atom, for which a general Hylleraas-type expansion can be written as[126−132]

$$\Psi = \sum_{\mu=1}^{K} c_\mu \mathcal{A}(\Phi_\mu \chi_1) \tag{136}$$

where $\mathcal{A}$ is the (three-electron) antisymmetrizer and Φ_μ is a spatial basis function of the type

$$r_1^{k_1} r_2^{k_2} r_3^{k_3} r_{12}^{k_4} r_{13}^{k_5} r_{23}^{k_6} \exp(-\zeta_1 r_1 - \zeta_2 r_2 - \zeta_3 r_3)\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \tag{137}$$

where

$$\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha \tag{138}$$

is a spin function with spin angular momentum 1/2 (doublet). It was shown that inclusion of the second linearly independent spin function

$$\chi_2 = 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha \tag{139}$$

is not necessary to obtain the correct basis-set limit for the energy.[133] $\mathcal{Y}^{LM}_{(\ell_1\ell_2)\ell_{12},\ell_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is a vector-coupled product of spherical harmonics for the three electrons forming a state of total angular momentum L.[129] Not only the $1s^22s\ ^2S$ ground state but also excited states such as $1s^22p\ ^2P$ and $1s^23d\ ^2D$ can be treated in this manner. Multiple basis sets are constructed by replication of the basis functions, eq 137, with different exponents ζ_1,ζ_2,ζ_3.[130]

The Hylleraas-configuration-interaction (Hy-CI) method[125,134] (for an n-electron atom) is defined as follows

$$\Psi = \sum_{m=1}^{K} c_m \hat{O}(L^2)\mathcal{A}(\chi_j r_{12}^{\nu_m} \prod_{i=1}^{n} \varphi_{i_m}) \tag{140}$$

where $\hat{O}(L^2)$ is an idempotent orbital angular momentum projection operator, $\mathcal{A}$ the usual n-electron antisymmetrizer, χ_j an n-electron spin function (e.g., such as χ_1 of eq 138 or χ_2 of eq 139), and φ_{im} a one-electron spatial orbital (Slater-type orbital, STO). Configurations without ($\nu_m = 0$) and with ($\nu_m = 1$) the Hylleraas coordinate r_{12} are included.

The advantage of the Hy-CI method in comparison with methods that use general Hylleraas-type wave functions of the form eq 137 is that in the Hy-CI method the types of integrals are restricted to one-, two-, three-, and four-electron integrals. Thus, the Hy-CI method may have some potential to be applied to atoms with more than three or four electrons. The complexity of the integrals will not increase when the number of electrons becomes larger. In contrast, using a general Hylleraas-type wave function would require one to compute four-electron integrals for a four-electron atom, five-electron integrals for a five-electron atom, and so on. Furthermore, high accuracy can be obtained with only one r_{12} term per configuration in addition to terms without r_{12} dependence. Products such as $r_{12}r_{13}r_{23}$... seem not absolutely necessary, at least not for the Li atom. In recent work, Sims and Hagstrom note that when accurate wave functions are considered products of odd powers of r_{ij} contribute only at the subnanohartree level.[135] A similar conclusion was drawn by Thakkar and co-workers,[136] who in their study on the lithium isoelectronic series noted that compact and accurate results may possibly be obtained from wave functions in which the restriction is imposed that no term has more than one of the powers of the interelectronic distances.

We note in passing that it is also possible to design approaches in between the general Hylleraas scheme and the Hy-CI method.

Table 3. Nonrelativistic Born−Oppenheimer Ground-State Energies of Three-, Four-, Five-, and Six-Electron Atoms

system	K^a	E/E_h	function	ref
Li	10 000	−7.4780603238	ECG	163
	16 764	−7.4780603234519	Hy-CI	135
	9576	−7.4780603238897	Hylleraas[b]	131
	9577	−7.4780603238924	Hylleraas[b]	130
	13 944	−7.478060323909560	Hylleraas[b]	132
Be	5306	−14.6673547	Hylleraas[c]	139
	41 871	−14.667356411	Hy-CI	164
	10 000	−14.667356486	ECG	165, 166
B	5100	−24.65386608(250)	ECG	167
C	500	−37.84012879	ECG	168

[a] Number of terms in the expansion. [b] Generalized Hylleraas wave function. [c] Double-linked Hylleraas wave function.

For example, Kleindienst and Lüchow[137] proposed a Hylleraas-type method with linear terms r_{ij} and "double-linked" terms $r_{ij}r_{kl}$. The many-electron integrals[138] were implemented for this "double-linked" Hylleraas-configuration-interaction expansion, and calculations were performed on the Be atom.[139]

In any case, already for the Hy-CI methods many-electron integrals up to the level of four-electron integrals are needed. Two- and three-electron integrals occur over the following operators (where k is 1 or 2)

$$1/r_{12}; \quad r_{12}^k; \quad r_{12}r_{13}; \quad r_{12}^k/r_{13}; \quad r_{12}r_{13}/r_{23} \tag{141}$$

together with four-electron integrals over the operators

$$r_{12}r_{13}/r_{14}; \quad r_{12}r_{13}/r_{34}; \quad r_{12}r_{34}/r_{23} \tag{142}$$

Further integrals are required for the kinetic energy and nuclear attraction parts of the Hamiltonian. Progress on evaluating all of these integrals has been reported over a long period of time.[140−162] In particular, the "fully linked" three-electon integral $r_{12}r_{13}/r_{23}$ requires special attention, and important progress toward its analytical and efficient evaluation has been reported in the last few decades.[146−148,154,158] Despite the progress in (atomic) many-electron integral evaluation, benchmark calculations using Hylleraas-type wave functions or the Hy-CI method have thus far been restricted to atoms not larger than Be (Clary and Handy[169] performed Hy-CI calculations on the Ne atom in 1976, but they obtained only ca. 73.5% of the correlation energy due to computational constraints). Results for the atoms Li and Be are shown in Table 3. Boron and larger atoms seem to remain a computational challenge. Very accurate results from the ECG method (exponentionally correlated Gaussians, section 4.2.1) have been reported, however, for boron.[167] In ref 168 the value for the C atom was obtained from a rather short expansion with only 500 terms, and the total energy has not yet converged to within one millihartree of the basis-set limit.

Despite the limited range of applications we note that relativistic and finite-mass effects, including corrections due to quantum electrodynamics (QED), have been computed for the small atoms with unprecedented accuracy for ground and excited states. In the present review, however, we focus on the general aspects of *nonrelativistic* wave function expansions that depend on the interelectronic coordinates r_{ij} and are less interested in the numerous and more specialized applications of Hylleraas-type wave functions.

Table 4. Nonrelativistic Born−Oppenheimer Ground-State Energies (in E_h) of the Atoms H−Ne, Including Their Cations and Anions, As Obtained in Ref 172

X	E_{X^+}	refs 170, 171	E_X	refs 170,171.	E_{X^-}
			Hartree−Fock (ROHF) energy		
H			−0.499995		−0.487901
He	−1.999943		−2.861627		
Li	−7.236411		−7.432723	−7.432727	−7.428219
Be	−14.277372	−14.277395	−14.573013	−14.573023	
B	−24.237547	−24.237575	−24.529037	−24.529061	−24.519187
C	−37.292175	−37.292224	−37.688574	−37.688619	−37.708800
N	−53.887924	−53.888005	−54.400857	−54.400934	
O	−74.372458	−74.372606	−74.809265	−74.809398	−74.789624
F	−98.831501	−98.831720	−99.409140	−99.409349	−99.459263
Ne	−127.817494	−127.817814	−128.546789	−128.547098	
			correlation energy		
H					−0.039822
He			−0.042041		
Li	−0.043500		−0.045336	−0.04533	−0.072542
Be	−0.047364	−0.04737	−0.094321	−0.09434	
B	−0.111260	−0.11134	−0.124779	−0.12485	−0.144985
C	−0.138590	−0.13880	−0.156231	−0.15640	−0.182637
N	−0.166193	−0.16661	−0.188061	−0.18831	
O	−0.193991	−0.19423	−0.257627	−0.25794	−0.331258
F	−0.260984	−0.26109	−0.324284	−0.32453	−0.400123
Ne	−0.325389	−0.32529	−0.390485	−0.39047	
			total energy		
H			−0.499995		−0.527723
He	−1.999943		−2.903668		
Li	−7.279911		−7.478058		−7.500761
Be	−14.324736		−14.667334		
B	−24.348807		−24.653816		−24.664172
C	−37.430765		−37.844805		−37.891437
N	−54.054116		−54.588917		
O	−74.566449		−75.066892		−75.120882
F	−99.092485		−99.733424		−99.859386
Ne	−128.142884		−128.937274		

The Hylleraas, Hy-CI, and ECG methods aim at reaching ultimate accuracy for few-electron atoms and small molecules. In contrast, as we shall see further below in this review, the much more economical R12 and F12 methods aim at reaching reasonably high accuracy at low costs for larger systems. In Table 4, therefore, we list the total correlation energies of the atoms, cations, and anions of H through Ne. These total correlation energies are compared with the estimated basis-set limits of Davidson and co-workers.[170,171] We observe that the correlation energies obtained at the F12 level[172] agree to within a few tenths of a millihartree with those of Davidson and co-workers.[170,171] While Hylleraas, Hy-CI, and ECG calculations are able to provide much more accurate correlation energies for atomic systems with up to 4 (Be) or 5 (B) electrons than the F12 approach, the F12 total energies are probably the most accurate "directly computed" ground-state energies for the atoms C−Ne. Neither extrapolation techniques nor empirical corrections have been used in the F12 calculations, but explicitly correlated calculations were combined with conventional CI-type calculations. The F12 total energy for B from Table 4 ($-24.653816\ E_h$) is almost as accurate as the ECG value from Table 3 ($-24.653866\ E_h$), which is remarkable in view of the fact that already the error in the Hartree−Fock energy, which is part of the F12 total energy, amounts to 24 μE_h. From the energies reported in Table 4, ionization energies and electron affinities are obtained that compare well (within a few tenths of a meV) with the corresponding experimental values and earlier benchmark calculations.[172,173]

In the next section we shall have a look at Hylleraas- and Hy-CI-type expansions for linear (e.g., H_2) and nonlinear (e.g., H_3^+ as simplest example) molecules. Hy-CI calculations have also been reported for LiH, He_2^+, and He_2, but these calculations were done in 1977 and were not as accurate as would be possible today.[174,175] Also, more recently, Hylleraas-type wave functions have been applied to molecules such as the LiH molecule, but the required integrals were not computed analytically but rather by means of Monte Carlo numerical integration techniques. See, for example, ref 176.

4.1.2. H_2 and H_3^+ Molecules. The first explicitly correlated wave function for a molecule, that is, the hydrogen molecule, was proposed by James and Coolidge in 1933.[177,178] Millihartree accuracy ($E = -1.173559\ E_h$) at $R = 1.4\ a_0$ was obtained using a compact 13-term expansion.[179,180] The James−Coolidge ansatz was employed by Kołos and Wolniewicz in their landmark papers of 1964/65.[181,182] In the James−Coolidge calculations, elliptic coordinates and wave functions of the type

$$\xi_i = (r_{iA} + r_{iB})/R; \quad \eta_i = (r_{iA} - r_{iB})/R,$$
$$\exp(-\alpha\xi_1 - \beta\xi_2)\xi_1^k\eta_1^l\xi_2^m\eta_2^n r_{12}^\mu \tag{143}$$

were used, where R is the internuclear distance and where r_{iA} and r_{iB} denote the distances of electron i from the two nuclei (A and B). Kołos and Wolniewicz[183] extended the ansatz of James and Coolidge to enable a proper dissociation of the molecule. Recent results for the ground state of the hydrogen molecule are presented in Table 5, including not only the James−Coolidge and Kołos−Wolniewicz ansätze but also energies obtained from the free ICI[184,185] and ECG[186,187] methods. It is seen that the difference in accuracy is small between wave functions using Hylleraas-/James−Coolidge-type basis functions and exponentially correlated Gaussians (concerning H_2 (see also ref 188)). Both methods can probably be pushed further to even more accurate variational ground-state energies. Finally, as for the atomic systems, we note that not only the ground-state energy has been of interest, of course. Non-Born−Oppenheimer and relativistic effects, excited states, H_2-like ions such as HeH^+ and so on, have also been studied.

Concerning H_3^+, pioneering work on the Hy-CI method was done by Preiskorn, Clementi, and co-workers[189−193] in the decade 1982−1992, computing all of the integrals analytically that are needed in calculations with basis sets of Gaussian atomic orbitals.[194] Their Hy-CI energy for H_3^+ is given in Table 5. More recently, potential energy hypersurfaces have also been computed using the CISD-R12 method as well as using exponentially correlated Gaussians, and an overview of the corresponding results, including rovibrational levels, is presented in ref 195.

In terms of a set of spin orbitals $\{\phi_{i_k}\}$, the antisymmetrized Hy-CI wave function for a general n-electron polyatomic molecule can be written as

$$\Psi_{\text{Hy-CI}} = \sum_{k=1}^{K} c_k \mathcal{A} r_{12}^{\mu_k} \prod_{i=1}^{n} \phi_{i_k}(\mathbf{x}_i) \tag{144}$$

with μ_k being either 0 or 1. Only two-electron integrals are required for computations on the H_3^+ molecule, of course, and in general the complexity of the Hy-CI method is restricted to (eight-center) four-electron integrals.

Kutzelnigg's CISD-R12 ansatz[208] for two-electron systems may be regarded as a special case of the Hy-CI ansatz with only one two-electron basis function that depends on r_{12}

$$\Psi_{\text{CISD}}(1,2) = c_0 r_{12}\Phi_0(1,2) + \sum_{k=1}^{K-1} c_k\Phi_k(1,2) \tag{145}$$

where $\Phi_0(1,2)$ is a two-electron reference determinant built from a doubly occupied molecular orbital (obtained from either the bare-nuclear-Hamiltonian problem or a Hartree−Fock calculation) and where $\Phi_k(1,2)$ are all of the two-electron determinants that can be built from a given one-electron basis.

Table 5 shows Hy-CI and CISD-R12 energies for H_3^+, but note that the one-electron basis used in the CISD-R12 calculation is much larger than in the Hy-CI calculation. Furthermore, the CISD-R12 energy is not strictly variational, because the following approximation was made when evaluating the matrix elements of the Hamiltonian

$$\langle\Phi_k|\hat{H}_0 r_{12}|\Phi_0\rangle \approx \langle\Phi_k|[\hat{H}_0, r_{12}]|\Phi_0\rangle + E_0\langle\Phi_k|r_{12}|\Phi_0\rangle \tag{146}$$

where $\hat{H}_0 = \hat{h}(1) + \hat{h}(2)$ and E_0 is the energy of the reference determinant. In the H_3^+ molecule the reference determinant is not an exact eigenfunction of $\hat{H}_0$.

It is noteworthy that the early 1993 work on the CISD-R12 approach already contained an approximation to the Hamiltonian matrix elements (between the explicitly correlated function and the conventional determinants) that is reminiscent of the "approximation C" that is used in modern explicitly correlated F12 theory. We shall come back to this point in section 4.5.

Table 5. Nonrelativistic Born−Oppenheimer Ground-State Energies of H_2 ($R = 1.4011\ a_0$) and H_3^+ ($R = 1.65\ a_0$)

system	K^a	E/E_h	function	ref
H_2	883	−1.174475930742	KW[b]	196
	1200	−1.174475931211	ECG	186
	7034	−1.174475931399840	JC[c]	197
	6776	−1.174475931400027	free ICI[d]	184, 185
	4800	−1.174475931400135	ECG	187
	22 363	−1.17447593140021599	JC[c]	198
H_3^+	700	−1.3438220	ECG	199
	e	−1.3438279	Hy-CI	192
	f	−1.3438341	CISD-R12	200, 201
	g	−1.34383509	CISD-R12	200, 202
	600	−1.343835624	ECG	203−205
	1000	−1.3438356250187	ECG	206, 207

[a] Number of terms in the expansion. [b] Kołos−Wolniewicz wave function. [c] James−Coolidge wave function. [d] Free iterative-complement-interaction method. [e] 13s5p3d atomic orbital basis. [f] CISD-R12 calculation in a 10s8p6d4f atomic orbital basis. [g] CISD-R12 calculation in a 30s20p12d9f atomic orbital basis.

4.2. Gaussians

Since 1960, when Boys[209] and Singer[210−213] introduced Gaussian basis functions including electron−nucleus distances as well as interelectronic distances ("functions with direct correlation") to quantum chemistry for calculations on polyatomic molecules, numerous applications of these many-electron Gaussian functions have been published. For example, Lester and Krauss[214,215] applied two-electron Gaussians (Gaussian geminals) in calculations on two-electron systems such as He, H_2, and H_3^+. They also presented the general formulas for the necessary integrals.[214] Important theorems concerning the completeness of the correlated Gaussian basis set were given by King.[216] The calculations on two-electron systems were encouraging, and it became clear that Gaussian geminals are well suited to describe the overall shape of the Coulomb hole well, despite the fact that they have no cusps at the points of electron−electron coalescence.[217] Also, Salmon and Poshusta employed Gaussian geminals in their calculations on the H_3^+ ion,[218] and Karunakaran and Christoffersen performed variational calculations on the LiH molecule with Gaussian geminals.[219]

It is perhaps interesting to note that Boys not only introduced the well-known Gaussian-type orbitals (GTO) to quantum chemistry, which are one-electron functions, but also Gaussian-type geminals (GTG), which are two-electron functions. Boys also pointed out how to compute the integrals.[209] Usually, in the literature, Boys' work is cited with respect to use of GTOs.[32]

A GTG has the following general form

$$G_\mu^0(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\alpha_\mu r_{1P_\mu}^2 - \beta_\mu r_{2Q_\mu}^2 - \gamma_\mu r_{12}^2) \tag{147}$$

with

$$r_{1P_\mu} = |\mathbf{r}_1 - \mathbf{P}_\mu|, \quad r_{2Q_\mu} = |\mathbf{r}_2 - \mathbf{Q}_\mu|, \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2| \tag{148}$$

r_{1P_μ} and r_{2Q_μ} are the distances of the electrons 1 and 2 from the centers $\mathbf{P}_\mu$ and $\mathbf{Q}_\mu$, respectively, which may be chosen individually and freely for each basis function G_μ^0 (floating lobe functions). Furthermore, r_{12} is the interelectronic distance and α_μ, β_μ, and γ_μ are Gaussian exponents, which are allowed to be negative as long as the GTG is square integrable. Hence, each two-electron GTG basis function contains 9 nonlinear parameters (3 Gaussian exponents and 6 coordinates).

The GTGs can also be used with Cartesian prefactors, that is, in the form

$$G_\mu(\mathbf{r}_1, \mathbf{r}_2) = x_{1P_\mu}^{k_{\mu_x}} y_{1P_\mu}^{k_{\mu_y}} z_{1P_\mu}^{k_{\mu_z}} x_{2Q_\mu}^{l_{\mu_x}} y_{2Q_\mu}^{l_{\mu_y}} z_{2Q_\mu}^{l_{\mu_z}} \exp(-\alpha_\mu r_{1P_\mu}^2 - \beta_\mu r_{2Q_\mu}^2 - \gamma_\mu r_{12}^2) \tag{149}$$

and obviously, wave functions for two-electron systems can directly be expanded in terms of such Cartesian GTGs

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{A}\{\Theta^{S,M_S}(\sigma_1, \sigma_2)\mathcal{P}_R[\sum_{\mu=1}^{K} c_\mu G_\mu(\mathbf{r}_1, \mathbf{r}_2)]\} \tag{150}$$

where $\mathbf{x} = \{\mathbf{r},\sigma\}$ contains spatial and spin coordinates, $\mathcal{A}$ is the usual antisymmetrizer, $\Theta(\sigma_1,\sigma_2)$ a proper spin function corresponding to the quantum numbers S and M_S, and $\mathcal{P}_R$ the symmetry projector accounting for symmetry adaptation (projector onto the relevant irreducible representation R of the symmetry group of the molecule). The c_μ are linear parameters. Of course, it is also possible to expand the two-electron wave function in terms of the Gaussian-lobe geminals G_μ^0.

When many-electron methods such as Møller−Plesset perturbation theory through second (MP2) and third (MP3) order—and so forth—or coupled-cluster theory with double (CCD) or coupled-cluster theory with single and double excitations (CCSD) are formulated (in first quantized form) in terms of *pair functions* that describe the correlation between electrons in two occupied Hartree−Fock orbitals, then eq 150 can be used to expand these pair functions. Such methods have been developed for calculations on many-electron atoms and molecules for about 30 years,[220−225] including calculations in the framework of symmetry-adapted perturbation theory for treating intermolecular correlation energies.[226−229] In 1982, Szalewicz and co-workers[230] proposed using a special functional for such calculations. We shall discuss the corresponding GTG pair theories further below, but first, we shall be concerned with *variational* calculations using GTGs or products of those. The corresponding methods are today known as methods using exponentially correlated Gaussians (ECG).

4.2.1. ECGs: Exponentially Correlated Gaussians.

For a two-electron system, ECG calculations are variational methods[231] with eq 150 as a two-electron wave function. Hence, the linear variational parameters are optimized by minimizing the expectation value

$$E_{\mathrm{ECG}} = \langle\Psi(\mathbf{x}_1, \mathbf{x}_2)|\hat{H}|\Psi(\mathbf{x}_1, \mathbf{x}_2)\rangle/\langle\Psi(\mathbf{x}_1, \mathbf{x}_2)|\Psi(\mathbf{x}_1, \mathbf{x}_2)\rangle = \min \tag{151}$$

where $\hat{H}$ is the Hamiltonian of the atom or molecule.

ECG calculations have, for example, been performed on the singlet ground states of He, H_2, and H_3^+. In these cases, the spin function takes the form

$$\Theta^{0,0}(\sigma_1, \sigma_2) = \frac{1}{\sqrt{2}}\{\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\} \tag{152}$$

Tables 2 and 5 show a few selected ECG results for two-electron systems in comparison with those obtained from (extended) Hylleraas- and James−Coolidge-type wave functions. The ground state of the He atom can virtually be computed with arbitrary accuracy, which becomes clear from the work of Nakashima and co-workers,[109,115] who report the ground-state energy of He with ca. 40 digits. With a 600-term ECG expansion, the error in the He ground-state energy is only about 0.01 nanohartree. Interestingly, already for the H_2 molecule, the 4800-term ECG wave function of Cencek and Szalewicz[187] is competitive with the Hylleraas- and James−Coolidge-type wave functions, and for the H_3^+ molecule-ion the ECG method is certainly the method of choice to compute an accurate potential energy hypersurface.[205] The above also applies to other two-electron systems such as HeH^+.[232]

Calculations on atomic systems with up to 3 electrons can accurately be carried out using Hylleraas-type wave functions, but beyond 3 electrons the most accurate ground- and excited-state energies to date are obtained by the ECG ansatz, which is applicable to molecules with 3 electrons (such as H_3)[233,234] and in general to systems with 4−6 electrons. These systems include molecules such as LiH,[235,236] LiH^-,[237] BH,[238] the H_2[239] and He dimers,[187,240,241] and the atoms beryllium,[242,243] boron,[167] and carbon.[168]

In the ECG approach, the spatial part of the electronic wave function of an n-electron system is represented by the linear combination

$$\Psi(\mathbf{r}) = \sum_{k=1}^{K} c_k \Phi_k(\mathbf{r}) \tag{153}$$

$$\Phi_k(\mathbf{r}) = \exp[-(\mathbf{r}-\mathbf{s}_k)\cdot(\mathbf{A}_k \otimes \mathbf{I}_3)(\mathbf{r}-\mathbf{s}_k)] \tag{154}$$

where $\mathbf{r}$ is a $3n$-dimensional vector formed by the vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, ..., $\mathbf{r}_n$ stacked on top of each other, $\mathbf{A}_k$ a symmetric $n \times n$ matrix, $\mathbf{I}_3$ the 3×3 identity matrix, and $\otimes$ is the Kronecker product symbol. The $3n$-dimensional vector $\mathbf{s}_k$ is a "shift vector" that generates floating centers of the Gaussians. The matrix $\mathbf{A}_k$ is a positive definite matrix and is therefore best represented in the Cholesky-decomposed form $\mathbf{A}_k = \mathbf{L}_k\mathbf{L}_k^T$, where $\mathbf{L}_k$ is a lower triangular matrix and $\mathbf{L}_k^T$ its transpose. The basis functions in eq 154 may be multiplied by Cartesian factors such as x_1, and so on, to facilitate the description of atomic P states, diatomic π states, and the like. Also, prefactors such as r_1, r_{12}, and r_{12}^2 have been investigated.[110,166] The elements of $\mathbf{A}_k$ and $\mathbf{s}_k$ constitute a large number of nonlinear variational parameters that must be optimized very carefully in order to obtain highly accurate results.

To conclude this subsection, we note that the form in eq 154 is equivalent with the notation chosen by Cencek and Rychlewski[244] in their pioneering work on the ECG method. In that work, the ECG wave function was written as

$$\Psi = \sum_{k=1}^{K} c_k \Phi_k \tag{155}$$

$$\Phi_k = \mathscr{A}\left\{\chi\mathscr{P}_R\left[\exp\Big(-\sum_{i<j}\beta_{ij;k}r_{ij}^2\Big)\prod_{i=1}^{n} g_{i_k}(\mathbf{r}_i)\right]\right\} \tag{156}$$

where $g_{ik}(\mathbf{r}_i)$ is a usual Cartesian Gaussian basis function (i.e., one-electron basis function), $\mathscr{A}$ the n-electron antisymmetrizer, $\mathscr{P}_R$ the symmetry projector onto the irreducible representation R of the molecular point group, and χ an appropriate n-electron spin function. In the same manner that the Hy-CI method is a simplification of the full Hylleraas approach, Cencek and Rychlewski[245] investigated the "single" exponentionally correlated Gaussian (SECG) model in which only *one* Gaussian geminal is considered at a time

$$\Phi_k = \mathscr{A}\left\{\chi\mathscr{P}_R\left[\exp(-\beta_k r_{12}^2)\prod_{i=1}^{n} g_{i_k}(\mathbf{r}_i)\right]\right\} \tag{157}$$

The advantage of the SECG method is that the complexity of the many-electron integrals in a Rayleigh–Ritz variational calculation is limited to the level of four-electron integrals.

Finally, we note that since 1991/1992 Kozlowski and Adamowicz[246−250] utilized ECG-type basis functions for generating *nonadiabatic* many-body wave functions.

4.2.2. GTGs: Gaussian-Type Geminals. In 1970−72 Pan and King[220,221] proposed using Gaussian geminals for electron-pair correlation, that is, for the expansion of the pair functions of the first-order wave function of Møller−Plesset perturbation theory. Already in these early works ca. 87−88% of the all-electron MP2 correlation energy of the Ne atom was obtained in this manner.

In 1982 Szalewicz, Jeziorski, and Monkhorst proposed a new functional for variational calculations of atomic and molecular second-order (MP2) correlation energies using Gaussian geminals: the weak-orthogonality (WO) functional.[230] In a series of papers[251−255] this new approach was applied to the systems He, Be, H_2, and LiH, not only at the level of second-order perturbation theory but also at the third-order perturbation theory[252] and coupled-cluster levels.[253]

For a discussion of this WO functional consider the following pair equation for the first- and higher-order (coupled-cluster) pair functions $\tilde{\tau}_{ij}$

$$(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)\tilde{\tau}_{ij} = R_{ij}(\tilde{\tau}) \tag{158}$$

where $\hat{F}_1$ and $\hat{F}_2$ are the Fock operators of electrons 1 and 2 and where ε_i and ε_j are the orbital energies of the occupied orbitals i and j. This pair equation must be satisfied together with the strong-orthogonality requirements

$$(1-\hat{O}_1)(1-\hat{O}_2)\tilde{\tau}_{ij} = \tilde{\tau}_{ij} \tag{159}$$

$$(1-\hat{O}_1)(1-\hat{O}_2)R_{ij}(\tilde{\tau}) = R_{ij}(\tilde{\tau}) \tag{160}$$

$\hat{O}$ is the projection operator onto the space of occupied spin orbitals, $\hat{O} = \sum_i |i\rangle\langle i|$. When these strong-orthogonality requirements are satisfied, the pair functions $\tilde{\tau}_{ij}$ may be obtained by minimizing the functional

$${}^{SO}L(\tilde{\tau}_{ij}) = \langle\tilde{\tau}_{ij}|\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j|\tilde{\tau}_{ij}\rangle - 2\langle\tilde{\tau}_{ij}|R_{ij}(\tilde{\tau})\rangle \tag{161}$$

This functional, introduced by Sinanoğlu,[256,257] shall be referred to as the strong-orthogonality (SO) functional in the following. (In passing, we note that it was recognized by Sinanoğlu already in the original work that this functional facilitates introduction of r_{12}-dependent functions into many-electron systems.)

At the MP2 level, the right-hand-side $R_{ij}(\tilde{\tau})$ is simply $-(1-\hat{O}_1)$-$(1-\hat{O}_2)r_{12}^{-1}|ij\rangle$, where $|ij\rangle \equiv |\phi_i\phi_j|$ is the two-electron Slater determinant built from the two spin orbitals i and j. At higher levels, $R_{ij}(\tilde{\tau})$ is a function of the (strongly orthogonal) pair functions $\tilde{\tau}_{kl}$.

Let us now consider the pair function τ_{ij}, which is expanded in a basis of Gaussian geminals G_μ as in eq 150, that is, $\tau_{ij} = \sum_{\mu=1}^{K} c_\mu^{ij} G_\mu$. This pair function τ_{ij} is *not* strongly orthogonal to the Hartree−Fock reference determinant, that is, it does *not* satisfy the strong-orthogonality requirement in eq 160. Of course, acting with the projection operator $(1-\hat{O}_1)(1-\hat{O}_2)$ onto the geminals expansion τ_{ij} would yield a strongly orthogonal pair function $\tilde{\tau}_{ij} = (1-\hat{O}_1)(1-\hat{O}_2)\tau_{ij}$, but inserting this pair function into eq 161 would give rise to up to four-electron integrals already at the MP2 level (due to the Fock matrix elements $\langle\tilde{\tau}_{ij}|\hat{F}_1 + \hat{F}_2|\tilde{\tau}_{ij}\rangle$). Therefore, Szalewicz et al. suggested minimizing the WO functional

$${}^{WO}L(\tau_{ij}) = \langle\tau_{ij}|\hat{\hat{F}}_1 + \hat{\hat{F}}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle - 2\langle\tilde{\tau}_{ij}|R_{ij}(\tilde{\tau})\rangle \tag{162}$$

with

$$\hat{\hat{F}} = \hat{F} + \Delta_{ij}\hat{O}; \quad \Delta_{ij} = \frac{1}{2}(\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta \tag{163}$$

ε_1 is the smallest orbital energy, and η is a positive parameter. At the MP2 level, eq 162 becomes

$${}^{WO}L(\tau_{ij}) = \langle\tau_{ij}|\hat{\hat{F}}_1 + \hat{\hat{F}}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle - 2\langle\tilde{\tau}_{ij}|r_{12}^{-1}|ij\rangle \tag{164}$$

No SO projection operator is applied in the first term on the right-hand side, that is, only the raw geminals expansion τ_{ij} is inserted here. By this means, four-electron integrals are avoided. The SO projection operator is still present in the second term on the right-hand side of eq 164, but this only gives rise to three-electron integrals. At higher orders of perturbation theory or at the level of coupled-cluster theory, however, the SO projection operators in the term $\langle\tilde{\tau}_{ij}|R_{ij}(\tilde{\tau})\rangle$ would give rise to four-electron (at the third order) and five-electron integrals (at the fourth order) if it were evaluated without further approximations.[254] Obviously, significant simplifications are obtained by computing R_{ij} not from the strongly orthogonal pair functions $\tilde{\tau}_{ij} = (1-\hat{O}_1)(1-\hat{O}_2)\tau_{ij}$ but rather from some functions χ_{ij} that are obtained by expanding $\tilde{\tau}_{ij}$ in the basis set of Gaussian geminals, that is

$$\chi_{ij} = \sum_{\mu=1}^{K} d_\mu^{ij} G_\mu;$$

$$\sum_{\nu=1}^{K} \langle G_\mu|G_\nu\rangle d_\nu^{ij} = \langle G_\mu|(1-\hat{O}_1)(1-\hat{O}_2)\tau_{ij}\rangle, \ \forall\ \mu \tag{165}$$

This approach is referred to as the *weak orthogonality with projection* (WOP) approach.[254] The corresponding functional may be sketched as

$$^{WOP}L(\tau_{ij}) = \langle\tau_{ij}|\hat{\hat{F}}_1 + \hat{\hat{F}}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle - 2\langle\tilde{\tau}_{ij}|R_{ij}(\chi)\rangle \tag{166}$$

The WOP functional produces accurate third- and higher-order energies, but evaluation of the term $\langle\tilde{\tau}_{ij}|R_{ij}(\chi)\rangle$ is very time consuming due to the larger number of three-electron integrals that occur in such a calculation. When we rewrite the SO projection operator that is contained in $\tilde{\tau}_{ij}$ in eq 166 in the form

$$(1-\hat{O}_1)(1-\hat{O}_2) = 1 - \hat{O}_1\hat{O}_2 - \hat{O}_1(1-\hat{O}_2) - (1-\hat{O}_1)\hat{O}_2 \tag{167}$$

we find that the last two terms give rise to the three-electron integrals. Hence, these can easily be avoided when the *super weak orthogonality* (SWO) approach is applied, that is, when the terms with $\hat{O}_1(1-\hat{O}_2)$ and $(1-\hat{O}_1)\hat{O}_2$ are neglected. In combination with the projection of the WOP approach, this yields the SWOP method (*super weak orthogonality with projection*)

$$^{SWOP}L(\tau_{ij}) = \langle\tau_{ij}|\hat{\hat{F}}_1 + \hat{\hat{F}}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle - 2\langle\tau_{ij}|(1-\hat{O}_1\hat{O}_2)R_{ij}(\chi)\rangle \tag{168}$$

The above discussion of the approaches WO, SWO, WOP, and SWOP is only meant to provide a rough sketch of the ideas that have been developed for using Gaussian geminals in pair theories. For details, we refer the reader to the original literature[254] as well as to recent reviews[75,258] because the theory is, in fact, a little more complex than indicated here. For example, the SWO functional used at the coupled-cluster level is not fully comparable with the one shown above, which applies to the MP2 level. The bottom line is that four- and five-electron integrals can entirely be avoided at the coupled-cluster level when the model is limited to the *factorizable* coupled-cluster-doubles level (FCCD). If the nonfactorizable contributions to R_{ij} shall be computed, then four-electron integrals must be evaluated. Their number is $N_{bas}{}^2K^3$, where N_{bas} is the number of one-electron (Hartree−Fock) basis functions and K the number of geminals. Inclusion of single excitations was worked out by Bukowski et al.,[259] and it was found that neither the difference between CCD and FCCD nor the difference between CCSD and CCD is sensitive to the electron−electron cusp, and thus, these differences are not difficult to converge in a conventional orbital−product expansion. Hence, a cost-efficient and accurate approach consists of computing FCCD energies using GTGs and full CCSD energies using orbital−product expansions.[260,261]

Gaussian-type geminal basis sets for correlation-energy calculations are usually obtained by optimization of the second-order energy functional. For a discussion of the optimization of the nonlinear parameters see ref 262. More recently, an IEPA-like functional (*independent electron-pair approximation* functional) has been investigated for the purpose of optimizing the nonlinear parameters for subsequent coupled-cluster applications.[263]

Thus far, GTG calculations have been restricted to systems not larger than 10 electrons. At the MP2 level, for example, the H_2O molecule was computed,[264] and at the coupled-cluster level, the Ne atom was treated.[255] The GTG approach was also used to compute a very accurate He···He pair potential in 1996/97.[265,266] At the internuclear distance of R = 5.6 a_0, the currently most accurate and reliable values for the electronic dissociation energy are D_e/k_B = −10.9996(105),[267] −11.0037(31),[261] and −11.0006(2) K.[187]

We conclude this subsection by noting that the analytical calculation of first-order properties has been developed for GTG basis sets (see also section 8.2). The analytical approach was applied to calculation of the second- and third-order correlation corrections to the lowest multipole moments of the molecules H_2 and LiH.[268]

4.2.3. GG*n* Methods: GTGs Combined with Orbital Expansions. Motivated by the success of the R12 methods (cf. section 4.5), Persson and Taylor[269] suggested combining GTG and orbital expansions in 1991. The idea was to replace the linear r_{12} term of the R12 theories by a short linear combination of Gaussian geminals. It appeared to be possible to fit the electron−electron distance r_{12} with only a few (6−9) Gaussian functions with good accuracy, although the electron cusp, of course, is not satisfied. Nevertheless, it was known that it should be possible to achieve high accuracy and rapid basis-set convergence with Gaussian geminals. The overall shape of the Coulomb hole for a wide range of electron−electron distances (which can be represented well with Gaussian geminals) seemed to be much more important than the electron cusp itself.[217] One can rationalize the rapid basis-set convergence with Gaussian geminals by noting that the cusp at r_{12} = 0 should to be of minor importance for calculation of the electronic energy because the volume element $4\pi r_{12}^2$ suppresses contributions for very short r_{12}, but Kutzelnigg[195] argues that "*the smallness of the domain in which the singularity really matters does not affect the rate of convergence of a Fourier-type expansion*".

At the level of Møller−Plesset second-order (MP2) theory, the Persson−Taylor ansatz for the pair function τ_{ij} with a *contracted* GTG is

$$\tau_{ij} = (1-\hat{V}_1\hat{V}_2)g(r_{12})\sum_{xy} c_{ij}^{xy}|xy\rangle + \sum_{ab} c_{ij}^{ab}|ab\rangle \tag{169}$$

with

$$g(r_{12}) = \sum_{m=1}^{m_{GTG}} b_m[1-\exp(-\gamma_m r_{12}^2)] \tag{170}$$

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The coefficients c_{ij}^{xy} and c_{ij}^{ab} are obtained by minimizing the weak-orthogonality (WO) functional

$$
\begin{aligned}
{}^{WO}L(\tau_{ij}) &= \langle\tau_{ij}|\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle \\
&\quad + 2\langle\tau_{ij}|(1-\hat{O}_1)(1-\hat{O}_2)r_{12}^{-1}|ij\rangle \\
&\quad + \Delta_{ij}\langle\tau_{ij}|\hat{O}_1 + \hat{O}_2|\tau_{ij}\rangle \geq E_{ij}^{\text{exact}} \qquad (171)
\end{aligned}
$$

where the factor Δ_{ij} of the last term, which may be interpreted as a "penalty" term, is a level shift defined by $\Delta_{ij} = (1/2)(\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta$ with $\varepsilon_1 \leq \varepsilon_k\ \forall k$ and $\eta \geq 0$. The projection operators in eqs 169 and 171 are

$$\hat{O} = \sum_i |i\rangle\langle i|; \qquad \hat{V} = \sum_a |a\rangle\langle a| \qquad (172)$$

Typically, the sets of exponents γ_m in the correlation factor are chosen to be even-tempered series of the type $\gamma_m = \alpha\beta^{m-1}$ with $\beta = 3$. For example, for $m_{\text{GTG}} = 3, 6, 9$, or 12 one may choose $\alpha = 1/3$, $1/9$, $1/27$, or $1/243$, respectively. In the approach with contracted GTGs, the (contraction) coefficients b_m were obtained by the least-squares minimization

$$\chi^2 = \int_0^{x_{\max}} e^{-2x}[x - \sum_{m=1}^{m_{\text{GTG}}} b_m(1 - e^{-\gamma_m r_{12}^2})]^2 \mathrm{d}x \qquad (173)$$

where the fitting range was chosen as $x_{\max} = 2$, 5, or 10 a_0. It was soon realized,[269] however, that an obvious way to improve the results is to optimize the coefficients of the Gaussians, for example, by means of the variational principle, rather than constraining them by the fit. This leads to the Persson−Taylor ansatz for the pair function τ_{ij} with *un*contracted GTGs

$$
\begin{aligned}
\tau_{ij} &= (1 - \hat{V}_1\hat{V}_2)\sum_{m=1}^{m_{\text{GTG}}} \exp(-\gamma_m r_{12}^2)\sum_{xy} c_{ij}^{xy;m}|xy\rangle \\
&\quad + \sum_{ab} c_{ij}^{ab}|ab\rangle \qquad (174)
\end{aligned}
$$

Note that the projection operator $(1 - \hat{V}_1\hat{V}_2)$ is introduced here to minimize the couplings between the conventional and the explicitly correlated parts of the pair function without having any effect on the final pair function or energy.

One major advantage of this approach is that all variational parameters are linear. No tedious and time-consuming optimization of nonlinear parameters, which, for example, may be determined using methods based upon the random-tempering approaches developed by Poshusta[270,271] and Alexander and co-workers[199,272−274] or using methods based on Fletcher−Powell or Newton−Raphson procedures,[244,275] are needed in the Persson−Taylor ansatz. However, as we shall outline below, the ansatz may not be sufficiently flexible to reduce the strong-orthogonality penalty, depending on the choice of *xy*.

As in the work of Szalewicz and co-workers (cf. section 4.2.2), the WO functional was used to avoid evaluation of four-electron integrals. The intention of the Persson-Taylor ansatz was to develop a method that would provide results similar to the MP2-R12 method but without the need to insert resolution of the identity approximations that violate the upper-bound property of the Hylleraas functional. Even though evaluation of the necessary three-electron integrals is tedious and time consuming,[276−278] it was argued that in an integral-direct manner this evaluation would perform favorably on massive parallel computer architectures and that due to the short range of the Gaussians $\exp(-\gamma_m r_{12}^2)$ efficient integral screening, in particular, in the framework of local-correlation methods,[279−284] would eventually lead to a method that scales linearly with the size of the system (the scaling with the size of the one-electron basis would still remain N^6, of course, with N the number of basis functions per atom).

Table 6. GG0 All-Electron Second-Order Correlation Energy[b] (in mE_h) of the Ne Atom in the aug-cc-pCVTZ(spd) Basis of Ref 286[a]

	GTG basis with 9 primitives	
functional	contracted	uncontracted
SO[c]	−384.3	−385.5[d]
IO[e]	−369.6	
WO[f]	−345.3	−353.9[g]

[a] Data taken from ref 288. [b] The most accurate estimate of the basis-set limit is −388.131 mE_h, obtained from FEM-MP2 calculations.[289] [c] Strong-orthogonality functional; computed using RI approximations. [d] Cf. refs 287 and 288. [e] Intermediate-orthogonality functional of Tew et al.[288] (η = 0.1 E_h). [f] Weak-orthogonality functional (η = 0.1 E_h). [g] Cf. ref 286.

In the original ansatz of Persson and Taylor, the sum over x,y was restricted to $xy = ij$. The ansatz can be extended to run over all occupied orbitals ($xy \in kl$) in the sense of the orbital-invariant formulation of the MP2-R12 method in ref 285. This ansatz is known as *kl* ansatz or the GG0 approach. In the more flexible GG1 approach, also those GTGs are included, where either x or y refers to a virtual orbital: $xy \in \{kl,kb,al\}$. Finally, all MOs are included in the GG2 approach, with $xy \in \{kl,kb,al,ab\}$. Obviously, the GGn performance improves with increasing geminal level n, but at the same time, determination of the coefficients $c_{ij}^{xy;m}$ becomes more difficult. On one hand, the dimension of the set of linear equations becomes very large, and on the other hand, these equations become more prone to (near) linear dependencies and numerical instabilities.

Unexpectedly, recent results by Dahle et al.[286] revealed that the performance of the GG0 method is startlingly poor. In the aug-cc-pCVDZ basis and using a *primitive* set of 9 GTGs, the value of −333.1 mE_h was computed for the all-electron second-order correlation energy of the Ne atom. The corresponding MP2-F12 value (see section 6.4) using a *single contraction* of the same 9 GTGs is −380.6 mE_h. This difference between the two calculations was highly unexpected because one expects that the MP2 value will be lowered when a contracted GTG basis is decontracted to a primitive basis. Such energy lowering due to decontraction of the GTG basis is indeed observed in the work by Valeev.[287] Hence, according to common sense, Dahle's value (−333.1 mE_h) should have been *lower* than the corresponding MP2-F12 value (−380.6 mE_h), but it is not. On the contrary, the difference is very large (almost 50 mE_h) with the wrong sign. The apparent contradiction is resolved by recognizing that the GG0 expansion is unable to form strongly orthogonal pairs.[288] Hence, the GG0 expansion is not well suited for use with the WO functional. The poor performance of the GG0 calculation is not due to the GG0 ansatz itself but rather to its use in conjunction with the WO functional.

The poor performance of the combination GG0/WO is also illustrated in Table 6, which shows results for the Ne atom in the aug-cc-pCVTZ(spd) basis of ref 286. MP2-F12 calculations using the same 9 GTGs as in the GG0 calculations yield energies of −384.3 and −385.5 mE_h with a contracted and uncontracted GTG basis, respectively. Even though it is not much, the energy is *lowered* by decontracting the GTG basis, as expected.

As an improvement to the WO functional, Tew and co-workers suggested use of an *intermediate-orthogonality* (IO) functional.[288] The result obtained from this functional is also shown in Table 6. The IO functional is defined as follows

$$\begin{aligned} {}^{IO}L(\tau_{ij}) &= \langle \tau_{ij}|\hat{P}_{12}(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)\hat{P}_{12}|\tau_{ij}\rangle \\ &+ 2\langle \tau_{ij}|(1-\hat{O}_1)(1-\hat{O}_2)r_{12}^{-1}|ij\rangle \\ &+ \Delta_{ij}\langle \tau_{ij}|\hat{O}_1(1-\hat{P}_2) \\ &+ (1-\hat{P}_1)\hat{O}_2|\tau_{ij}\rangle \geq E_{ij}^{\text{exact}} \end{aligned} \tag{175}$$

with

$$\hat{P}_{12} = 1 - \hat{O}_1\hat{O}_2 - \hat{O}_1\hat{V}_2 - \hat{V}_1\hat{O}_2;$$
$$\Delta_{ij} = \frac{1}{2}(\varepsilon_i + \varepsilon_j) - \varepsilon_1 + \eta \tag{176}$$

Since the one-electron projection operators in $\hat{P}_{12}$ occur in pairs, no four-electron integrals aris, and for any positive η the IO functional provides a strict upper bound to the MP2 correlation energy (when using exact Hartree−Fock orbitals and evaluating the three-electron integrals analytically).

When using the WO functional, the quality of the computed energy depends on the ability of the chosen geminal basis to form strongly orthogonal pairs. In the limit of a complete geminal basis,[264,290] the pair function satisfies the strong-orthogonality condition and the exact MP2 energy is obtained, but the GG0 geminal basis is by far not flexible enough to yield high-quality results. In the IO functional, however, the strong-orthogonality violating single excitations within the finite MO basis are projected out. The only strong-orthogonality violating components of the explicitly correlated geminals that enter the functional are those that correspond to single excitations outside the finite MO space. When using the IO functional, the geminal basis needs only to be flexible enough to zero these terms.

To date, the IO functional has not been used much, but for future work in the field of GG*n* methods (or other MP2 methods in which all integrals are computed exactly and which provide strict upper bounds) it certainly deserves attention.

As mentioned above, the GG*n* methods may have some potential especially in combination with local-correlation methods.[279−284] Indeed, Polly and co-workers developed a corresponding local MP2 (LMP2) method with GTGs and the WO functional.[291] In this LMP2-GTG method, the *local* pair functions for the localized orbitals i and j are

$$\begin{aligned} \tau_{ij} &= (1-\hat{V}_1\hat{V}_2)\sum_{m=1}^{m_{\text{GTG}}}\exp(-\gamma_m r_{12}^2)\sum_{k\in P_s(ij)}\sum_{\mu\in[ij]} c_{ij}^{k\mu;m}|k\mu\rangle \\ &+ \sum_{ab\in[ij]} c_{ij}^{ab}|\tilde{a}\tilde{b}\rangle \end{aligned} \tag{177}$$

where k is an localized occupied orbital from the list $P_s(ij)$, μ is an atomic orbital (basis function), and $\tilde{a}$ and $\tilde{b}$ are projected atomic orbitals[279,282] (PAOs). The summation over μ is restricted to the pair domain $[ij]$, and the summation of k is limited to the list $P_s(ij)$, which includes all localized occupied MOs k for which either (ik) or (kj) is a "strong pair". Roughly, this LMP2-GTG

Table 7. Valence-Shell Second-Order Pair Energies of C_2H_4 with Respect to Localized Occupied Orbitals; η = 0.5 E_h in the Calculations with the WO Functional[a]

pair	LMP2			best estimate[b]
	cc-pVDZ[c]	+9GTG[d]	cc-pV5Z[e]	ref 293
$\sigma_{CC}{}^2$	−15.45	−25.50	−25.24	−26.77
$\sigma_{CH}{}^2$	−22.77	−30.79	−30.75	−31.59
$\pi_{CC}{}^2$	−23.05	−27.33	−27.13	−27.88
$\sigma_{CC}-\sigma_{CH}$	−8.29	−11.02	−11.32	−11.72
$\sigma_{CC}-\pi_{CC}$	−29.11	−37.66	−38.09	−39.40
$\sigma_{CH}-\pi_{CC}$	−13.91	−17.32	−17.98	−18.26
$\sigma_{CH}-\sigma'_{CH}$ (geminal)	−10.43	−13.39	−13.77	−13.86
$\sigma_{CH}-\sigma'_{CH}$ (cis)	−1.10	−1.31	−1.41	−1.42
$\sigma_{CH}-\sigma'_{CH}$ (trans)	−1.17	−1.39	−1.44	−1.38

[a] Data taken from ref 291. [b] Obtained at the MP2-R12 level in the C:19s14p8d6f4g3h2i/H:9s6p4d3f2g basis by adding 60% of the MP2-R12/A energy to 40% of the MP2-R12/B energy.[293] [c] LMP2 pair energies obtained in the cc-pVDZ basis. [d] LMP2 pair energies obtained in the cc-pVDZ basis after adding 9 GTGs. [e] LMP2 pair energies obtained in the cc-pV5Z basis.

method corresponds to the GG1 approach. Two further remarks are appropriate: first, the factor Δ_{ij} of the weak-orthogonality functional is computed from the diagonal Fock matrix elements, that is, $\Delta_{ij} = (1/2)(f_{ii} + f_{jj}) - f_{11} + \eta$, such that the upper-bound property of the WO functional is not strictly valid any more; second, the projection $(1 - \hat{V}_1\hat{V}_2)$ has thus far been carried out only using *canonical* virtual orbitals (not PAOs).

In Table 7 LMP2-GTG results for ethene (C_2H_4) are collected, and pair energies with respect to Pipek-Mezey localized orbitals[292] are presented. A comparison with the work of Samson and Klopper[293] is made, although these authors used the Boys localization scheme[294] (only the valence orbitals within the molecular plane, that is, the σ-type orbitals were localized, leaving the π-type orbital unchanged). Clearly, adding 9 GTGs to the correlation-consistent double-ζ (cc-pVDZ) basis yields approximately quintuple-zeta (cc-pV5Z) quality pair energies, but we note that the LMP2-GTG calculations are very time consuming (according to ref 291, they were tractable only in the cc-pVDZ basis). Furthermore, the cc-pVDZ+9GTG and cc-pV5Z results are still several millihartrees away from the basis-set limit pair energies.[293] Note that the latter add up[293] to a total valence-shell MP2 correlation energy of −373.6 mE_h, which compares well with the value obtained in ref 295: −373.0 ± 0.2 mE_h (at a slightly different geometry).

4.3. Transcorrelated Methods

A different approach, based on a similarity transformation of the Hamiltonian, was proposed by Hirschfelder in 1963.[296] In his approach the wave function takes the form $\psi = J\Phi$, where J depends on the interelectronic distances. He showed that Φ may be determined using a similarity transformed Hamiltonian $H' = J^{-1}\hat{H}J$ where, if J is properly chosen, H' is free from Coulomb singularities, thereby simplifying construction of Φ. This method was pursued by Jankowski,[297,298] and in 1969 Boys and Handy established a practical method for determination of parameters in both J and Φ, which required evaluation of at most three-electron integrals.[299−302] Boys and Handy chose to use a single Slater determinant of spin orbitals for Φ and a Jastrow factor formed of

Table 8. Hamiltonian Commutator Expansion in the Transcorrelated Method

	kinetic energy	potential energy
$\hat{H}$	$-(1/2)\Sigma_i\nabla_i^2$	$-\Sigma_{iA}Z_Ar_{iA}^{-1}+\Sigma_{i<j}r_{ij}^{-1}$
$[\hat{H},C]$	$-\Sigma_{j\neq i}((1/2)\nabla_i^2C_{ij}+\nabla_iC_{ij}\cdot\nabla_i)$	0
$(1/2)[[\hat{H},C],C]$	$-(1/2)\Sigma_{j,k\neq i}\nabla_iC_{ij}\cdot\nabla_iC_{ik}$	0
$(1/6)[[[\hat{H},C],C],C]$	0	0

a product of two-electron correlation functions and 1-electron orbital relaxation functions

$$J = \prod_{i<j} \exp\left(\sum_\mu D_\mu G_\mu(\mathbf{r}_i, \mathbf{r}_j) + \sum_\lambda d_\lambda[g_\lambda(\mathbf{r}_i) + g_\lambda(\mathbf{r}_j)]\right) \tag{178}$$

$$= \exp(C) = \exp\left(\sum_{i<j} C_{ij}\right) \tag{179}$$

The original equations for determining the orbitals and the wave function parameters D_μ and d_λ were

$$\langle\delta\Phi|\hat{H} + [\hat{H}, C] + \frac{1}{2}[[\hat{H}, C], C] - E|\Phi\rangle = 0 \tag{180}$$

$$\langle G_\mu\Phi|\hat{H} + [\hat{H}, C] + \frac{1}{2}[[\hat{H}, C], C] - E|\Phi\rangle = 0 \tag{181}$$

$$\langle g_\lambda\Phi|[\hat{H}, C]|\Phi\rangle = 0 \tag{182}$$

The significance of the last equation is both to remove the redundancy between g_λ and the orbitals and to make the transcorrelated Hamiltonian as hermitian as possible for orbital optimization. The energy is evaluated by projection

$$E = \langle\Phi|H'|\Phi\rangle \tag{183}$$

Boys and Handy chose the following one- and two-electron functions for the Jastrow factor

$$G_1(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}\frac{ar_{12}}{a + r_{12}} \tag{184}$$

$$G_\mu(\mathbf{r}_1, \mathbf{r}_2) = (\tilde{r}_{1A}^i\tilde{r}_{2B}^j + \tilde{r}_{2A}^i\tilde{r}_{1B}^j)\tilde{r}_{12}^k \tag{185}$$

$$g_\lambda(\mathbf{r}_1) = \frac{\mathbf{r}_{1A}}{a + r_{1A}} \tag{186}$$

$$\tilde{\mathbf{r}} = \frac{\mathbf{r}}{a + r} \tag{187}$$

The correlation factor is linear at short-range interparticle separations and satisfies the electron and nucleus cusps. At long-range interelectronic separations the correlation factor is constant and the wave function tends to an antisymmetrised orbital product function. Table 8 lists the commutator expansion for the transcorrelated Hamiltonian. Since C only contains one- and two-electron functions, the expansion truncates at three-electron operators.

The transcorrelated method of Boys and Handy was further refined by Handy, who reduced the problems associated with the lack of a variational upper bound to the energy for the similarity-transformed Hamiltonian. He proposed replacing eq 181 with a minimization of the transcorrelated variance

$$U^{\mathrm{TC}} = \langle\{(H' - E)\Phi\}^2\rangle \tag{188}$$

Handy also replaced the Jastrow factor functions with Gaussian orbital and geminal functions where the one-, two-, and three-electron integrals have simple analytic forms. Handy applied his approach to the ground-state energies of He, H_2, LiH, and H_2O.[303,304]

The transcorrelated method has received a moderate level of renewed interest over the past decade. In 1998 Nooijen and Bartlett suggested using a frozen similarity transformation instead of optimizing the factor J.[305] Ten-no adopted this approach in his examination of the transcorrelated method in 2000, giving efficient formulas for the three-electron integration.[306,307] Ten-no chose a coupled-cluster wave function for Φ and expanded H' as $\hat{F} + \hat{V}$, where $\hat{F}$ is the usual Fock operator and evaluated the amplitudes in the coupled-cluster wave function using second-order perturbation theory. His results were intermediate between basis-set limit MP2 and MP3 quality, indicating that some 3-body correlation effects have been captured, but he found that a more flexible one-electron basis is required in comparison with other explicitly correlated methods. In similar work in 2003 Zweistra et al.[308] used a Gaussian damped Jastrow factor in combination with a CI expansion for Φ. Luo and co-workers analyzed the transcorrelated method from a quantum Monte Carlo perspective,[309] and very recently, Luo introduced a variational formulation of the transcorrelated method,[310,311] which amounts to replacing the nonhermitian equation for the orbital optimization eq 180 with the hermitian equation

$$\langle\delta\Phi|\hat{H} + \frac{1}{2}[[\hat{H}, C], C] - E|\Phi\rangle = 0 \tag{189}$$

Luo found that the numerical stability is greatly improved, while the quality of the wave function is not adversely effected.

4.4. Quantum Monte Carlo Methods

A very different way to deal with high-dimensional or analytically intractable integrals is Monte Carlo integration. In fact, quantum Monte Carlo (QMC) methods have a close relation to explicitly correlated methods; a detailed discussion, however, is not the scope of the present review, and we refer the reader to refs 312−314. The aforementioned relation is most obvious for variational Monte Carlo methods,[315,316] which try to evaluate the N-dimensional integral of a trial wave function's energy expectation value by stochastic integration. The wave function ansatz can be, in principle, arbitrarily complex. In particular, it can take care of the cusp conditions by employing Jastrow factors in the ansatz, like those of Boys-Handy type, eq 178, as used in the work of Schmidt and Moskowitz,[317] or improved versions thereof (see, e.g., ref 318). Likewise, the free complement local Schrödinger equation (FC LSE) method of Nakatsuji and coworkers[109,115,176,184,185] may be viewed as a special version of variational Monte Carlo. Jastrow factors are also used for the guide functions in diffusion Monte Carlo.[319−321]

First molecular applications of QMC, on H_3^+, have been reported by Anderson.[320] The method features a favorable N^3 scaling with system size, and also linear scaling approaches have been reported.[322] However, the better scaling comes along with a rather huge prefactor as the statistical error decays only with the inverse square root of the computer time. On the other hand, very efficient parallel algorithms exist, making possible applications to large systems, like interactions of DNA base pairs,[323] excited states of free-base porphyrin,[324] the chromophore of green fluorescent protein,[325] or retinal.[326]

4.5. R12 Methods

In 1985 Kutzelnigg proposed a new explicitly correlated approach, the R12 method.[208] The key idea of this work was, as stated in ref 208, that "*traditional CI is not really bad, it only has difficulties to represent the wave function at those regions of configuration space where one interelectronic distance r_{ij} approaches zero*." Hence, the basic idea was to begin the wave function expansion with just a few (two-electron) basis functions that depend explicitly on the interelectronic distances r_{ij} and to continue with adding a conventional CI expansion in terms of antisymmetrized orbital products. In his 1985 paper[208] Kutzelnigg focused on the He atom, for which numerical results were obtained using the ansatz

$$\Psi_{\text{CISD-R12}} = \left(1 + \frac{1}{2}r_{12}\right)\Phi_0(1,2) + \sum_{p,q} c_{pq}|\phi_p(1)\phi_q(2)| \tag{190}$$

where $\Phi_0(1,2) = N_\alpha \exp\{-\alpha(r_1 + r_2)\}\chi$ with a spin function χ and a normalization constant N_α. For the two-electron system He, only one single explicitly correlated basis function was added, and the general idea for many-electron systems was to add *one* explicitly correlated basis function for each pair of electrons. Noting that

$$\begin{aligned}\hat{H} &= \hat{T}_1 + \hat{T}_2 - \frac{\alpha}{r_1} - \frac{\alpha}{r_2} + \frac{\alpha - Z}{r_1} + \frac{\alpha - Z}{r_2} + \frac{1}{r_{12}} \\ &= \hat{H}_0 + \frac{\alpha - Z}{r_1} + \frac{\alpha - Z}{r_2} + \frac{1}{r_{12}}\end{aligned} \tag{191}$$

eq 190 is somewhat special in the sense that $\Phi_0(1,2)$ is an exact eigenfunction of $\hat{H}_0$, the bare-nuclear Hamiltonian, $\hat{H}_0\Phi_0(1,2) = E_0\Phi_0(1,2)$. This allows for exact reformulations of the type

$$\hat{H}_0 r_{12}\Phi_0(1,2) = [\hat{H}_0, r_{12}]\Phi_0(1,2) + r_{12}E_0\Phi_0(1,2) \tag{192}$$

The reference function $\Phi_0(1,2)$ was optimized by minimization of the matrix element H_{00}

$$H_{00} = \langle\Phi_0(1,2)\left(1 + \frac{1}{2}r_{12}\right)|\hat{H}|\left(1 + \frac{1}{2}r_{12}\right)\Phi_0(1,2)\rangle/S_{00} \tag{193}$$

$$S_{00} = \langle\Phi_0(1,2)\left(1 + \frac{1}{2}r_{12}\right)|\left(1 + \frac{1}{2}r_{12}\right)\Phi_0(1,2)\rangle \tag{194}$$

which was denoted as "overhead". For He, α was optimized to $\alpha = 1.885\ a_0^{-1}$ and the corresponding overhead was $H_{00} = -2.888718\ E_h$. Hence, about 64% of the correlation energy was obtained already from the explicitly correlated basis function $(1 + (1/2)r_{12})\Phi_0$, and the conventional CI expansion was only needed for the remaining 36%. It was found that the convergence of this conventional CI expansion for the remainder was rather fast (microhartree accuracy was already obtained with only up to *h*-type functions in the one-electron basis set used for the CI expansion).

In ref 208 Kutzelnigg not only presents results for He and He-like ions but also, more importantly, discusses possible generalizations toward (molecular) many-electron systems. Such generalizations are discussed in terms of partial-wave expansions.

Let us regard the conventional CI approach as an approximation to the CISD-R12 method in which the term $r_{12}\Phi_0$ is expanded in a basis of Slater determinants

$$r_{12}\Phi_0 = \sum_{p,q} \tilde{c}_{pq}|pq\rangle; \qquad |pq\rangle \equiv |\phi_p(1)\phi_q(2)| \tag{195}$$

Hence,

$$1 = \langle\Phi_0|r_{12}^{-1}|r_{12}\Phi_0\rangle = \sum_{p,q} \tilde{c}_{pq}\langle\Phi_0|r_{12}^{-1}|pq\rangle \tag{196}$$

The slow convergence of the conventional CI comes mainly from the expansion, eq 196, whose l increments in terms of a partial-wave expansion go as $(l + 1/2)^{-4}$, that is, as the l increments in the conventional CI approach. Similarly, the l increments of

$$\langle\Phi_0 r_{12}|r_{12}^{-1}|r_{12}\Phi_0\rangle = \sum_{p,q}\sum_{r,s} \tilde{c}_{pq}\tilde{c}_{rs}\langle pq|r_{12}^{-1}|rs\rangle \tag{197}$$

go as $(l + 1/2)^{-5}$. Concerning many-electron atoms, Kutzelnigg argued that integrals such as

$$\langle\Phi|r_{12}r_{23}^{-1}|\Phi\rangle; \qquad \langle\Phi|r_{12}r_{23}^{-1}r_{34}|\Phi\rangle \tag{198}$$

have finite l expansions and that integrals such as

$$\langle\Phi|r_{12}r_{23}^{-1}r_{13}|\Phi\rangle \tag{199}$$

have an infinite but comparably fast rate of convergence, namely, $(l + 1/2)^{-6}$. Hence, the key idea of Kutzelnigg's R12 method is to evaluate slowly convergent but trivial expansions such as eq 196 exactly, that is, as closed sums of partial wave amplitudes, but to use basis-set expansions for difficult many-electron integrals that are characterized by quickly convergent expansions.

In ref 200 Kutzelnigg's CISD-R12 ansatz was applied to the H_2 and H_3^+ molecules, not only with Φ_0 being the (approximate) eigenfunction of the bare nuclear Hamiltonian but also with Φ_0 being the Hartree−Fock reference determinant. Moreover, two different approaches were applied to compute the matrix elements that occur due to the coupling between the reference determinant Φ_0 and the conventional determinants $|\phi_p\phi_q|$. Let us consider the two approaches in the case of the Hartree−Fock reference determinant. The Hamiltonian can be written as $\hat{H} = \hat{F} + r_{12}^{-1} - \hat{J} + \hat{K}$, where $\hat{F}$, $\hat{J}$, and $\hat{K}$ are *two*-electron operators (sum of two *one*-electron operators). In the first approach, the above-mentioned matrix elements are evaluated as

$$\begin{aligned}\langle pq|(\hat{F} + r_{12}^{-1} - \hat{J} + \hat{K})r_{12}|\Phi_0\rangle &\approx \langle pq|\Phi_0\rangle + 2\varepsilon_1\langle pq|r_{12}|\Phi_0\rangle \\ &+ \langle pq|[\hat{T}, r_{12}]|\Phi_0\rangle - \langle pq|r_{12}(\hat{J} - \hat{K})|\Phi_0\rangle\end{aligned} \tag{200}$$

where ε_1 is the orbital energy of the doubly occupied orbital φ_1. In this first approach it is assumed that Φ_0 is an exact eigenfunction of the Fock operator $\hat{F}$. The integrals with $r_{12}(\hat{J} - \hat{K})$ were computed by inserting a resolution of the identity. In the second approach the same matrix elements are evaluated as

$$\begin{aligned}\langle pq|(\hat{F} + r_{12}^{-1} - \hat{J} + \hat{K})r_{12}|\Phi_0\rangle &\approx \langle pq|\Phi_0\rangle \\ &+ (\varepsilon_p + \varepsilon_q)\langle pq|r_{12}|\Phi_0\rangle - \langle pq|(\hat{J} - \hat{K})r_{12}|\Phi_0\rangle\end{aligned} \tag{201}$$

In this second approach it is assumed that all orbitals ϕ_p are eigenfunctions of the Fock operator. In both approaches, the matrix element H_{00} was computed in exactly the same manner after some reformulations involving the double commutator

Table 9. CISD-R12 Energy of H_2 ($R = 1.4\ a_0$) in Hartree, Obtained from Calculations *with* Commutator $[\hat{T},r_{12}]$, That Is, Using eq 200, and from Calculations *without* Commutator $[\hat{T},r_{12}]$, That Is, Using eq 201[a]

basis	eq 200	eq 201	difference
10s	−1.173138	−1.172117	0.001021
10s8p	−1.174357	−1.174414	−0.000057
10s8p6d	−1.174454	−1.174456	−0.000002
10s8p6d4f	−1.174467	−1.174468	−0.000001

[a] Data taken from ref 200.

$[r_{12},[\hat{T},r_{12}]] = 2$, with the kinetic energy operator for the two electrons, $\hat{T} = \hat{T}_1 + \hat{T}_2 = -(1/2)(\nabla_1^2 + \nabla_2^2)$. Table 9 shows results for the H_2 molecule obtained from the two approaches using various basis sets. The difference between the two approaches is small in reasonably large basis sets (10s8p6d and 10s8p6d4f). In ref 200 it was argued that the "simplifications" due to using eq 201 are not really important, because calculation of the commutator integrals $[\hat{T},r_{12}]$ is neither difficult nor time consuming. Nevertheless, the two-electron integrals over the operator $[\hat{T},r_{12}]$ are often avoided in present-day F12 theories, as proposed by Kedžuch et al. in 2005.[327] In the recent F12 literature, the approach of ref 327 is sometimes referred to as "approximation C".

The generalization of Kutzelnigg's R12 ansatz toward molecular many-electron systems was accomplished at the MP2 level in 1987.[328] At this level the second-order correlation energy $E^{(2)}$ is given as a sum of pair energies E_{ij}, which are obtained by minimizing the Hylleraas functional

$$L(\tau_{ij}) = \langle \tau_{ij}|\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j|\tau_{ij}\rangle + 2\langle \tau_{ij}|r_{12}^{-1}|ij\rangle \geq E_{ij}^{\text{exact}} \tag{202}$$

where $\hat{F}_1$ and $\hat{F}_2$ are the Fock operators for electrons 1 and 2, respectively, and where $|ij\rangle$ is a two-electron Slater determinant built from the spin orbitals ϕ_i and ϕ_j with orbital energies ε_i and ε_j, respectively. The MP2-R12 ansatz, as proposed in 1987, is

$$\tau_{ij} = \frac{1}{2}c_{ij}(1-\hat{O}_1)(1-\hat{O}_2)r_{12}|ij\rangle + \chi_{ij}; \quad \chi_{ij} = \sum_{a,b} c_{ij}^{ab}|ab\rangle \tag{203}$$

where

$$\hat{O}_\mu = \sum_i |\phi_i(\mu)\rangle\langle\phi_i(\mu)| \equiv \sum_i |i\rangle\langle i| \tag{204}$$

is the projection operator (for electron μ) onto the space of occupied orbitals.

Interestingly, in Kutzelnigg's original work it was suggested to keep the coefficient c_{ij} fixed to $c_{ij} = 1$. The numerical results from this "fixed coefficient" ansatz were disappointing, however, and the c_{ij}'s were therefore treated as linear variational parameters in the 1987 work.[328] The results were much improved by optimizing the c_{ij}'s by minimizing the Hylleraas functional, but the drawback of this approach was that the corresponding MP2-R12 method was not invariant with respect to orthogonal transformations among the occupied orbitals. This drawback was remedied in 1991 by extending the ansatz to[285]

$$\tau_{ij} = \frac{1}{2}(1-\hat{O}_1)(1-\hat{O}_2)r_{12}\sum_{kl} c_{ij}^{kl}|kl\rangle + \chi_{ij} \tag{205}$$

This is interesting from a historical perspective because in modern R12 theories the linear term r_{12} is replaced by the function[329] (see also section 6.6.1)

$$f_{12} = f(r_{12}) = \frac{1}{\gamma}\{1 - \exp(-\gamma r_{12})\} \tag{206}$$

where γ is a "length-scale" parameter. When using this function of r_{12} it turned out to be advantageous to return to the form

$$\tau_{ij} = \frac{1}{2}c_{ij}(1-\hat{O}_1)(1-\hat{O}_2)f_{12}|ij\rangle + \chi_{ij} \tag{207}$$

and to fix the coefficients c_{ij} to the values required to satisfy the *s*- and *p*-wave cusp conditions (rational generator approach, also known as SP ansatz).[330] Today, eq 207 is often referred to as the MP2-F12 method (keeping the name MP2-R12 for the corresponding method with the linear r_{12} term), and it is recommended to use this method with fixed c_{ij}. In other words, research has gone in a circle. If the functions f_{12}, which are known as Slater-type geminals, had been considered already in the original work in 1987, then there would have been no need to treat the coefficients c_{ij} as variational parameters nor to extend the ansatz in the sense of eq 205.

Already in the years 1987−1990[328,331] the MP2-R12 method could be applied to molecules such as H_2O and the carbocations $C_2H_5^+$ and $C_3H_7^+$. This had become possible because of a number of assumptions, or rather approximations, that made this explicitly correlated theory applicable to polyatomic, many-electron systems. These approximations became later known as "standard approximations" in a series of articles on the general R12 theories published in 1991.[332−334] They are as follows: (a) It is assumed that the occupied MOs ϕ_i are eigenfunctions of the exact Fock operator $\hat{F}$ rather than of its approximation in the finite basis $\{\phi_p\}$ used for the calculation. This assumption is today known as *generalized Brillouin condition*, GBC. It allows for the reformulation

$$\begin{aligned}\frac{1}{2}\{\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j\}r_{12}|ij\rangle &\approx \frac{1}{2}[\hat{F}_1 + \hat{F}_2, r_{12}]|ij\rangle \\ &= \frac{1}{2}[\hat{T}_1 + \hat{T}_2, r_{12}]|ij\rangle \\ &\quad - \frac{1}{2}[\hat{K}_1 + \hat{K}_2, r_{12}]|ij\rangle \\ &= -\frac{1}{2}\frac{\mathbf{r}_{12}}{r_{12}}\cdot(\nabla_1 - \nabla_2)|ij\rangle - \frac{1}{r_{12}}|ij\rangle \\ &\quad -\frac{1}{2}[\hat{K}_1 + \hat{K}_2, r_{12}]|ij\rangle\end{aligned} \tag{208}$$

where $\hat{T}$ is the kinetic energy operator and $\hat{K}$ the exchange operator. The Coulomb operator $\hat{J}$ is local and commutes with r_{12}. Furthermore, in ref 331 it is recommended to orthogonalize the explicitly correlated part of the pair function $\tau_{ij} - \chi_{ij}$ to all pairs constructable in the given basis $\{\phi_p\}$, that is, to define

$$\omega_{ij} = (1 - \hat{P}_1\hat{P}_2)(\tau_{ij} - \chi_{ij}); \quad \hat{P} = \sum_p |p\rangle\langle p| \tag{209}$$

One then obtains

$$\tau_{ij} = \frac{1}{2}c_{ij}(1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{P}_2 + \hat{P}_1\hat{O}_2 - \hat{P}_1\hat{P}_2)r_{12}|ij\rangle + \chi_{ij} \tag{210}$$

(b) If it is now assumed that an *extended Brillouin condition* (EBC) is satisfied, according to which the matrix elements of the Fock operator $\hat{F}$ vanish between functions contained in the basis and functions not contained in the basis, it is found that the Hylleraas functional decomposes as

$$L(\tau_{ij}) \approx L(\omega_{ij}) + L(\chi_{ij}) \tag{211}$$

where $L(\chi_{ij})$ is just the conventional, finite-basis MP2 functional and $L(\omega_{ij})$ the basis-set incompleteness correction to it. The decomposition implies that both functionals may be computed independently.

(c) A resolution of the identity approximation $1 \approx \hat{P}_\mu$ (RI approximation or completeness relation) is inserted into the terms of $L(\omega_{ij})$ that arise from the isolated operators $\hat{O}_1$ and $\hat{O}_2$, which have no partner projection operator for the other electron. This yields

$$1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{P}_2 + \hat{P}_1\hat{O}_2 - \hat{P}_1\hat{P}_2 \approx 1 - \hat{P}_1\hat{P}_2 \tag{212}$$

for the corresponding terms.

Concerning approximation (a) above, we note in passing that orthogonalizing the explicitly correlated part of the pair function to all pairs constructable in the given basis $\{\phi_p\}$, as done in ref 331 in 1990, is equivalent to orthogonalizing it to all virtual pairs $\{|ab\rangle\}$

$$\omega_{ij} = (1 - \hat{V}_1\hat{V}_2)(\tau_{ij} - \chi_{ij}); \quad \hat{V} = \sum_a |a\rangle\langle a| \tag{213}$$

because

$$\begin{aligned}(1 - \hat{V}_1\hat{V}_2)&(1 - \hat{O}_1)(1 - \hat{O}_2) \\ &= 1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{P}_2 + \hat{P}_1\hat{O}_2 - \hat{P}_1\hat{P}_2\end{aligned} \tag{214}$$

Hence, the particular forms of the explicitly correlated pair functions chosen by Wind et al.,[335,336] by Valeev,[337] and in the original work[328,331] are equivalent.

In the early work on the MP2-R12 method,[285,328,331−334,338,339] it was noted that, in the ansatz for the pair function τ_{ij}, the strong orthogonality projector $(1 - \hat{O}_1)(1 - \hat{O}_2)$ could be replaced by the operator $(1 - \hat{P}_1)(1 - \hat{P}_2)$ without changing the final working equations. Consider, for example, the integral $\langle\tau_{ij}|r_{12}^{-1}|ij\rangle$. According to eq 210, this integral is evaluated as

$$\begin{aligned}\langle\tau_{ij}|r_{12}^{-1}|ij\rangle = \frac{1}{2}\, c_{ij}\langle ij|r_{12}(1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{P}_2 \\ + \hat{P}_1\hat{O}_2 - \hat{P}_1\hat{P}_2)r_{12}^{-1}|ij\rangle + \langle\chi_{ij}|r_{12}^{-1}|ij\rangle\end{aligned} \tag{215}$$

Then, invoking the RI approximation eq 212 yields

$$\langle\tau_{ij}|r_{12}^{-1}|ij\rangle \approx \frac{1}{2}\, c_{ij}\langle ij|r_{12}(1 - \hat{P}_1\hat{P}_2)r_{12}^{-1}|ij\rangle + \langle\chi_{ij}|r_{12}^{-1}|ij\rangle \tag{216}$$

Taking

$$\begin{aligned}\tilde{\tau}_{ij} &= \frac{1}{2}\, c_{ij}(1 - \hat{P}_1)(1 - \hat{P}_2)r_{12}|ij\rangle + \chi_{ij} \\ &= \frac{1}{2}\, c_{ij}(1 - \hat{P}_1 - \hat{P}_2 + \hat{P}_1\hat{P}_2)r_{12}|ij\rangle + \chi_{ij}\end{aligned} \tag{217}$$

as ansatz for the pair function yields the same final working equation as when the terms with the isolated operators $\hat{P}_1$ and $\hat{P}_2$ are evaluated using the RI approximation, that is, by means of replacing $-\hat{P}_1$ and $-\hat{P}_2$ both by $-\hat{P}_1\hat{P}_2$

$$\langle\tilde{\tau}_{ij}|r_{12}^{-1}|ij\rangle \approx \frac{1}{2}\, c_{ij}\langle ij|r_{12}(1 - \hat{P}_1\hat{P}_2)r_{12}^{-1}|ij\rangle + \langle\chi_{ij}|r_{12}^{-1}|ij\rangle \tag{218}$$

The important point to make here is that in the early days of R12 method development, due to the approximations made (GBC, EBC, and RI approximation), there was no difference whatsoever between using $(1 - \hat{P}_1)(1 - \hat{P}_2)$, $(1 - \hat{O}_1)(1 - \hat{O}_2)$, or $(1 - \hat{V}_1\hat{V}_2)(1 - \hat{O}_1)(1 - \hat{O}_2)$ as a projection operator. The final working equations and final results were the same. In modern R12/F12 theory, however, in which, for example, some three-electron integrals are evaluated exactly[335,336] or in which an auxiliary basis set[340] is used for the RI approximation, the different projection operators are no longer equivalent. They may be referred to as "ansatz 1" (with $\hat{P}$) and "ansatz 2" (with $\hat{O}$), respectively[340] (see section 6.1 for details).

Before turning to CI and CC calculations using R12 terms, let us have a look at the MP2-R12 working equations of the early work,[328,331,338] in which the total pair energy E_{ij} is a sum of two terms: the conventional MP2 pair energy e_{ij}^{MP2} plus the basis-set incompleteness correction e_{ij}^{R12}

$$e_{ij}^{\mathrm{R12}} = \sum_{k=1}^{3} \langle ij|r_{12}(1 - \hat{P}_1\hat{P}_2)A_k|ij\rangle \tag{219}$$

with

$$A_1 = \left(c_{ij} - \frac{1}{2}\, c_{ij}^2\right) r_{12}^{-1} \tag{220}$$

$$A_2 = -\frac{1}{4}\, c_{ij}^2 \frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2) \tag{221}$$

$$A_3 = -\frac{1}{4}\, c_{ij}^2[\hat{K}_1 + \hat{K}_2, r_{12}] \tag{222}$$

If the term A_3 is ignored (known as "approximation A") it follows that

$$e_{ij}^{\mathrm{R12}} = (2c_{ij} - c_{ij}^2)V_{ij} + c_{ij}^2 U_{ij} \tag{223}$$

$$V_{ij} = \frac{1}{2} - \frac{1}{2} \sum_{p<q} \langle ij|r_{12}|pq\rangle\langle pq|r_{12}^{-1}|ij\rangle \tag{224}$$

$$U_{ij} = \frac{3}{4} - \frac{1}{4} \sum_{p<q} \langle ij|r_{12}|pq\rangle\langle pq|\frac{\mathbf{r}_{12}}{r_{12}} \cdot (\nabla_1 - \nabla_2)|ij\rangle \tag{225}$$

Optimizing e_{ij}^{R12} with respect with c_{ij} gives $c_{ij} = V_{ij}/(V_{ij} - U_{ij})$. In conventional MP2 theory the partial-wave expansion (in the atomic case) has energy increments proportional to $(l + 1/2)^{-4}$, to $(l + 1/2)^{-6}$, and so on, for each saturated shell of one-electron basis functions with angular momentum quantum number l. The slowly convergent $(l + 1/2)^{-4}$ energy increments are canceled by the term A_1; the somewhat faster but still slowly convergent $(l + 1/2)^{-6}$ energy increments are canceled by the terms A_2 and A_3. Thus, increments on the order of $(l + 1/2)^{-8}$ may be expected if all terms A_1, A_2, and A_3 are computed (known as "approximation B"), which would result in a truncation error on the order of L^{-7} when the basis set is truncated after the saturated shell of basis functions with $l = L$. For approximation A, the expected truncation error is on the order of L^{-5}.

In approximation B only the term A_3^m in

$$A_3 = A_3^p - A_3^m = -\frac{1}{4}\, c_{ij}^2(\hat{K}_1 + \hat{K}_2)r_{12} + \frac{1}{4}\, c_{ij}^2 r_{12}(\hat{K}_1 + \hat{K}_2) \tag{226}$$

needs to be computed,[332] because the term A_3^p vanishes due to the RI approximation. This is reasonable because in the atomic case the partial wave expansion of A_3^m goes as $(l + 1/2)^{-6}$ whereas that of A_3^p goes as $(l + 1/2)^{-8}$. The latter can thus be ignored.

Finally, we note that the MP2-R12 method has also been implemented by Valeev and co-workers within the framework of the open-source MPQC package.[49,341−349] Furthermore, as first noted by Bearpark and Handy,[339] the integrals needed for the MP2-R12 method may be used to define basis-set quality diagnostics with respect to basis-set completeness.[339,350] Such diagnostics are related to the ability of the given one-electron basis set to describe the Coulomb hole in coupled-cluster calculations.[351]

All matrix elements required for a closed-shell CISD, CEPA, MP2, or MP3 calculation with linear r_{12} terms were published in a paper by Kutzelnigg and Klopper in 1991.[332] First results at the CID-R12 and CEPA-R12 levels were also published in that year (single excitations were included later at the coupled-cluster level).[352] In this work, the CID-R12 wave function was written as

$$\Psi_{\text{CID-R12}} = \Phi + \frac{1}{2}\sum_{ij} c_{ij}\Phi_{ij} + \frac{1}{4}\sum_{ijab} t_{ij}^{ab}\Phi_{ij}^{ab} \tag{227}$$

where $\Phi_{ij}^{ab} = \hat{\tau}_{ij}^{ab}\Phi$ is a standard doubly substituted determinant (double excitation) and where

$$\Phi_{ij} = \frac{1}{4}\sum_{\alpha\beta}\langle ij|r_{12}|\alpha\beta\rangle\hat{\tau}_{ij}^{\alpha\beta}\Phi - \frac{1}{4}\sum_{ab}\langle ij|r_{12}|ab\rangle\hat{\tau}_{ij}^{ab}\Phi \tag{228}$$

is the explicitly correlated linear r_{12} term. As will be detailed later, the indices α,β denote a *complete set* of virtual orbitals while the indices a,b denote the finite set of virtual orbitals obtained from the underlying Hartree−Fock calculation, which was carried out in a finite set of atomic orbitals (see section 6.1). Concerning eq 228 we note two things: first, the linear r_{12} terms are not (yet) generalized to the orbital-invariant form of ref 285, that is, as Φ_{ij}^{kl} with coefficients c_{ij}^{kl}, and second, the effect of the second term of the right-hand side of eq 228 is to project out all double excitations constructable in the given finite basis, that is, equivalent with adding the projection operator $(1 - \hat{V}_1\hat{V}_2)$. The explicitly correlated linear r_{12} term Φ_{ij} of eq 228 is obtained from the Hartree−Fock determinant by replacing the spin−orbital pair

$$|ij\rangle = \frac{1}{\sqrt{2}}[\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)] \tag{229}$$

by

$$\frac{1}{2}(1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2)r_{12}|ij\rangle \tag{230}$$

In other words, the ansatz chosen in the early 1991 papers is the same as in modern F12 theories, in which the projection operator eq 246 is used. CID-R12 and CEPA-R12 calculations were performed on systems such as Ne, Ar, H_2O, and N_2.[352]

Coupled-cluster R12 theories were developed in 1992, shortly after extension of the MP2-R12 methods toward an orbital-invariant theory.[285] On one hand, the orbital-invariant formulation was an important step forward because it enabled accurate calculations on extended systems such as Be and Mg clusters, the benzene−argon potential and other van der Waals complexes, HF and H_2O clusters, [10]annulene, and ferrocene.[72,353−363] (These calculations had also been made possible by virtue of a newly developed integral package[364] and an efficient, Turbomole-based implementation.[353,365]) On the other hand, the orbital-invariant formulation turned out to facilitate a clear and consistent diagrammatic formulation of coupled-cluster R12 theory.[74,366−370] The explicitly correlated coupled-cluster-singles-and-doubles ansatz (CCSD-R12) is as follows[366]

$$\Psi_{\text{CCSD-R12}} = \exp(\hat{S})\Phi \tag{231}$$

$$\hat{S} = \hat{T}_1 + \hat{T}_2 + \hat{\mathscr{R}}; \quad \hat{\mathscr{R}} = \frac{1}{4}\sum_{ij}\sum_{kl} c_{ij}^{kl}\hat{R}_{ij}^{kl} \tag{232}$$

$$\hat{R}_{ij}^{kl} = \frac{1}{4}\sum_{\alpha\beta}\langle kl|r_{12}|\alpha\beta\rangle\hat{\tau}_{ij}^{\alpha\beta} - \frac{1}{4}\sum_{ab}\langle kl|r_{12}|ab\rangle\hat{\tau}_{ij}^{ab} \tag{233}$$

Hence, the standard double excitations are projected out, as in the CID-R12 and CEPA-R12 cases. In contrast to the early MP3-R12, CID-R12, and CEPA-R12 studies, however, the orbital-invariant formulation is used and single excitations are included. Moreover, Noga and Kutzelnigg also derived the necessary matrix elements and integrals for explicitly correlated coupled-cluster singles, doubles, and triples (CCSDT-R12) calculations.[367] Further developments such as an integral-direct implementation,[368] a CCSD-R12 theory for open-shell atoms and molecules,[371,372] code parallelization, and improved triple excitations[373] followed quickly thereafter, all within the program package Dirccr12.[374]

The early CCSD-R12 and CCSD(T)-R12 methods were successfully applied for benchmark calculations on small to medium-sized molecules using large basis sets.[346,375−394] These benchmark studies include calculations of equilibrium geometries, harmonic vibrational frequencies, and potential energy hypersurfaces at (or very close to) the basis-set limit of CCSD(T) theory.

5. STRATEGIES FOR AVOIDING *N*-ELECTRON INTEGRALS

In the Hylleraas-type and ECG methods the wave function expansions are inserted into a Rayleigh−Ritz variational optimization. Each resulting Hamiltonian matrix element requires $n!$ evaluations of n-electron integrals where all n electronic coordinates are coupled through the explicit dependence on all r_{ij}. Even for the ECG method where each integral has a known analytic form and is cheap to evaluate, the exponential scaling of the method has so far prevented calculations beyond 6-electron systems. For an explicitly correlated theory to be of practical use in applications to systems with more than a few electrons it is essential that the Hamiltonian matrix elements in the working equations can be evaluated with a low computational cost and in a way that does not scale exponentially with system size.

Researchers have utilized a variety of ingenious strategies for overcoming the n-electron integral problem, many of which have been discussed in the above historical narrative. The n-electron issue is key to all explicitly correlated approaches, and it is appropriate here to provide a concise summary linking and contrasting the approaches thus far proposed in the literature.

5.1. Restricting the Wave Function Parameter Space

Restricting the n-electron basis functions such that only a few, m, electronic coordinates are explicitly coupled at a time reduces the dimension of the nonfactorizable component of the n-electron electron repulsion integrals to at most $\min[n,2m]$. Variational flexibility and therefore accuracy is traded for computational simplification. When combined with the Rayleigh−Ritz variational approach, this kind of restriction of the wave function parameter space breaks size extensivity in the same way that truncated CI wave functions are not size extensive. The Hy-CI, SECG, and CISD-R12 methods are all examples of this approach with $m = 2$. Note, however, that in the Hy-CI and SECG methods the wave function can account for n-body electron correlation through the nonexplicitly correlated part of the wave function, whereas only 2-body correlation effects are parametrized in the CISD-R12 method.

5.2. Nonvariational Approaches

Wave function parameter space may be reduced while retaining size extensivity provided that the wave function has the structure

$$\psi = \mathcal{A} \exp\left(\sum_i g_1(\mathbf{x}_i) + \sum_{i<j} g_{12}(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i<j<k} g_{123}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + ... \right) \tag{234}$$

Clearly, even wave functions truncated after g_{12} contain terms with all n electronic coordinates explicitly coupled. However, by abandoning the Rayleigh−Ritz variational approach in favor of projection methods, the dimension of the nonfactorizable integrals that enter the working equations can be drastically reduced. One example is the transcorrelated approach, where no terms beyond g_{12} appear. Here, at most three-electron explicitly coupled integrals are required, independent of the number of electrons in the system. If g_{123} terms were to be included in a transcorrelated method, then five-electron integrals would be required. In general, wave function terms explicitly coupling m electronic coordinates require $(2m - 1)$-electron integrals.

Explicitly correlated Møller−Plesset and coupled-cluster wave functions are further important examples of this technique, and indeed, the CCSD approach differs from the transcorrelated method primarily in that, in the language of second quantization, only excitation rather than both excitation and de-excitation operators enter the wave function parametrization. In the explicitly correlated MP2 and CCSD approaches, where no terms beyond g_{12} appear, up to three-electron integrals are required for MP2 and up to four-electron integrals for CCSD. This, however, assumes that g_1 and g_{12} are strongly orthogonal, which is not in general the case. Enforcing strong orthogonality through the use of projection operators introduces additional four-electron integrals in MP2 and five-electron integrals in CCSD. It should be noted that the accuracy of explicitly correlated CCSD theory is limited because only 2-body correlation effects are parametrized. Higher-order correlation effects can be included through triple and higher excitations either with or without explicitly correlated $g_{123...}$ terms.

5.3. Weak Orthogonality

The weak orthogonality functional, discussed in section 4.2.2, helps to further reduce the dimensionality of the required integrals in explicitly correlated theories. The many-electron integrals arising from enforcing strong orthogonality (see the previous section) can be avoided by dropping the strong orthogonality projectors from the equations and introducing a penalty function that vanishes when the functions g_1 and g_{12} satisfy the strong orthogonality conditions. This is successful provided that the parametrization of g_1 and g_{12} has sufficient flexibility for the functions to become strongly orthogonal through optimization.

5.4. Stochastic Numerical Integration

Stochastic numerical integration is another way to deal with high-dimensional integrals. It is used in variational Monte Carlo and related methods (see section 4.4). The efficient sampling of the energy integral $\langle\Psi_T|\hat{H}|\Psi_T\rangle/\langle\Psi_T|\Psi_T\rangle$ over a trial wave function $\Psi_T(\mathbf{x})$ requires a low variance of the local energy

$$E_L(\mathbf{x}) = \frac{\hat{H}\Psi_T(\mathbf{x})}{\Psi_T(\mathbf{x})} \tag{235}$$

which for the exact wave function is a constant. Use of trial wave functions that fulfill the cusp conditions avoids singularities and greatly improves the convergence of the Monte Carlo integration. Otherwise, the method puts no limit on the complexity of Ψ_L as it only requires evaluation of eq 235 at random values of $\mathbf{x}$.

5.5. Resolution of the Identity

Integrals where m electronic coordinates are explicitly coupled through pairwise coupling terms can be approximated by successive insertions of an approximate resolution of the identity (RI)

$$1 \approx \hat{P}'' = \sum_{p''} |p''\rangle\langle p''| \tag{236}$$

For example

$$\langle pqr|r_{12}r_{23}^{-1}|stu\rangle \approx \sum_{p''} \langle pq|r_{12}|sp''\rangle\langle p''r|r_{12}^{-1}|tu\rangle \tag{237}$$

If the set of orthonormal orbitals p'' was complete then the resolution of the identity would be exact. In practice, use of a finite set of orbitals results in a residual error in the approximate integral. The magnitude of the error for each RI insertion depends on the rate of convergence of the expansion, which depends on the particular operators in the integrand. For the atomic case the RI insertion is equivalent to a partial wave expansion and the convergence properties are well known. A typical RI error for the above integral using a standard RI basis set is 0.01%.[336] While use of the RI approximation makes mE_h accuracy difficult to obtain even for small systems, all three-, four-, and five-electron integrals in explicitly correlated CCSD theory can be constructed from two-electron integrals, which ensures that the computational scaling is reduced to $\mathcal{N}^6$ (see also sections 6.2 and 6.3).

5.6. Numerical Quadrature

Numerical quadrature can be used as an alternative to RI as a method for decomposing many-electron integrals into sums of products of lower-index objects. For example, electron repulsion integrals can be represented as sums of two- and three-center objects over grid points[395,396]

$$(pr|r_{12}^{-1}|qs) \approx \sum_g w(\mathbf{r}_g)\phi_p(\mathbf{r}_g)\phi_r(\mathbf{r}_g)\langle q|r_{1g}^{-1}|s\rangle \tag{238}$$

where $w(\mathbf{r}_g)$ is the weight of the quadrature grid point $\mathbf{r}_g$. Applied to three-electron integrals, numerical quadrature yields

$$\langle pqr|r_{12}^{-1}f_{23}|stu\rangle \approx \sum_g w(\mathbf{r}_g)\phi_q(\mathbf{r}_g)\phi_t(\mathbf{r}_g)\langle p|r_{1g}^{-1}|s\rangle\langle r|f_{1g}|u\rangle \tag{239}$$

(Note that this three-electron integral is over orbital products, not Slater determinants, and can also be written as $(ps|r_{12}^{-1}|qt|f_{23}|ru)$.) This approach was applied by Ten-no in his early work on the transcorrelated method[306,307] and more recently in MP2-F12 theory[330] and CCSD(F12) theory.[397]

5.7. Two-Electron Integrals

In retrospect, insertion of completeness relations into the many-electron integrals of the early R12 methods was the main clue to success of these methods. By virtue of the completeness relations, or resolution of the identity approximations, three- and more-electron integrals could be avoided completely and made the methods applicable to many-electron polyatomic molecules. With respect to the R12 methods, in which linear correlation factors of the type r_{12} are employed, we furthermore note that the integrals over the electron−nucleus Coulomb attraction $-Z_C r_{12}/r_{1C}$, where r_{1C} is the distance of electron 1 from the nucleus C with atomic number Z_C and which would have required a numerical integration, are also avoided. This was achieved by introducing the commutator of the bare nuclear Hamiltonian, or the Fock operator, with the linear r_{12} term, because the Coulomb operator commutes with r_{12}. After this introduction of commutators the remaining integrals are

$$r_{12}^{-1};\quad f_{12};\quad f_{12}^2;\quad r_{12}^{-1}f_{12};\quad [\hat{T}_1 + \hat{T}_2, f_{12}];$$
$$[f_{12}, [\hat{T}_1 + \hat{T}_2, f_{12}]] = |\nabla_1 f_{12}|^2 + |\nabla_2 f_{12}|^2 \tag{240}$$

which here are given for the general case that the correlation factor f_{12} is a function of the interelectronic distance, $f_{12} \equiv f(r_{12})$.

Integral formulas for the two-electron integrals that arise with linear r_{12} terms can be found in refs 194 and 364 (see also refs 338 and 341). The only integral that needs some further consideration is the commutator integral $[\hat{T}_1 + \hat{T}_1, f_{12}]$. In various F12 implementations, this integral is avoided by means of the "approximation C" of Kedžuch et al.,[327] but it can in fact easily be computed from

$$(ab|[\hat{T}_1, f_{12}]|cd) = \frac{1}{2}(\Delta_A - \Delta_B)(ab|f_{12}|cd) \tag{241}$$

where a, b, c, and d denote atomic basis functions at the centers **A**, **B**, **C**, and **D**. For correlation factors of the type $f_{12} = r_{12}\exp(-\gamma r_{12}^2)$ or for correlation factors f_{12} expanded in a basis of Gaussian geminals integral formulas are reported in refs 398−400. Finally, we note that also the necessary integrals that occur with Slater-type geminals $f_{12} = \exp(-\gamma r_{12})$ can be computed analytically.[329,401,402]

6. GENERAL F12 THEORY

Today's F12 methods have emerged during the past decade from the original R12 methods through several conceptual and technical developments, which aimed at making these explicitly correlated approaches applicable to larger polyatomic systems and further enhance the basis-set convergence. As outlined in section 4.5, R12 methods augment the conventional excitations into products of unoccupied one-electron orbitals by excitations of electron pairs into explicitly correlated pair functions, which are constructed as $\hat{Q}_{12}r_{12}\phi_i\phi_j$, where r_{12} is the interelectronic distance and $\hat{Q}_{12}$ is a strong-orthogonality projector (vide infra). F12 methods employ more flexible pair functions of the form $\hat{Q}_{12}f_{12}\phi_i\phi_j$, where f_{12} can be any function of r_{12} of the form $f(r_{12}) = r_{12} + \mathcal{O}(r_{12}^2)$. The increased flexibility allows one to describe a much larger region of the Coulomb correlation hole. Today, the predominant choice for the correlation factor f_{12} is a Slater-type function (cf. discussions in sections 4.1.1 and 6.6.1)

$$f_{12} = \frac{1}{\gamma}(1 - \exp(-\gamma r_{12})) \tag{242}$$

The exponent γ is a length-scale parameter and accounts for how strongly the interelectronic interaction is on average screened by the circumjacent electron density. Slater-type geminal functions (STGs) describe very efficiently the correlation hole and alone recover a large fraction of the dynamic pair correlation energy, that is, without conventional excitations into orbital products.[403]

A key development has also been introduction of a complementary auxiliary basis set (CABS) which is used in addition to the orbital basis for the resolution of the identity (RI) in the factorization of many-electron integrals.[337,340] This made it possible to use medium-sized standard basis sets for R12 and F12 methods, which reduced the costs of such calculations significantly.

Together with other methodological advances, including robust density fitting for the additional integrals,[413,414] efficient integral evaluation techniques,[329,330,400−402,406,407] systematic approximations,[327,340,408−410] combination with local methods,[407,411−413] and specially optimized orbital and complementary auxiliary basis sets,[414−417] these developments have converted the original R12 methods into efficient tools for electronic structure calculations on polyatomic molecules. They are capable to recover already with optimized double-ζ basis sets about 98% of the basis-set limit correlation energy—an accuracy which in conventional calculations is first reached with large quintuple-zeta basis sets.

Originally developed at the MP2-F12 level, these techniques have during the last 5−10 years carried over to other correlated wave function methods such as, for example, several coupled-cluster models,[29,397,418−429] CASPT2-F12,[430,431] and MRCI-F12.[432,433] In the following subsections we will describe the general ansatz of F12 theories and the approximations made to evaluate or avoid three- and four-electron integrals and briefly show how the F12 theory can be combined with some standard correlated wave function methods.

6.1. General Ansatz

Correlated wave function methods are most conveniently presented using the formalism of second quantization outlined in section 4. For the following we use again the convention introduced in the latter section that indices i,j,k,l,m,n refer to orbitals occupied in the Hartree−Fock (or reference state), a,b,c,d to virtual orbitals and p,q,r,s to any orbital within the finite orbital basis. To represent excitations into the explicitly correlated pair functions in second quantization, we introduce formally an additional basis for the complementary space which together with the orbital basis forms a complete basis for the one-electron Hilbert space. For functions of the complementary space we use indeces $\alpha_\perp,\beta_\perp$, while indeces α,β denote any virtual orbitals within or outside the finite orbital space (see Figure 9). The orbitals in the complementary auxiliary basis set (CABS) used to improve the RI span a subspace of the full complementary space and will be denoted with indeces a',b'.

The general form of the geminals used today in F12 methods is

$$|w_{xy}\rangle = \hat{Q}_{12}f_{12}\hat{S}_{xy}|\phi_x\phi_y\rangle \tag{243}$$

where $|\phi_x\phi_y\rangle$ is a two-electron determinant and the rational generator $\hat{S}_{xy}$ ensures that the s- and p-wave coalescence conditions are satisfied

$$\hat{S}_{xy}\varphi_x(1)\varphi_y(2)\sigma_x(1)\sigma_y(2) = \left(\frac{3}{8}\varphi_x(1)\varphi_y(2) + \frac{1}{8}\varphi_y(1)\varphi_x(2)\right)\sigma_x(1)\sigma_y(2) \tag{244}$$

In the last equation φ_x and σ_x are, respectively, the spatial and spin components of a spin orbital ϕ_x. The set of orbitals x,y, from

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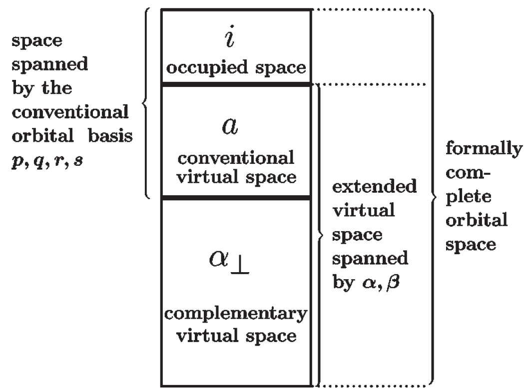

Figure 9. Orbital subspaces used in F12 calculations and their notation.

which the geminals are constructed, is usually chosen as the set of active occupied orbitals. Within the complete basis for the virtual space α,β, introduced above, double excitations into the geminals can be expressed as

$$|w_{xy}\rangle = \sum_{\alpha<\beta} w_{\alpha\beta}^{xy} a_\alpha^\dagger a_\beta^\dagger |\mathrm{vac}\rangle \tag{245}$$

with overlap matrix elements $w_{\alpha\beta}^{xy} = \langle\alpha\beta|w_{xy}\rangle$ and the vacuum state $|\mathrm{vac}\rangle$. In the following we will for double excitations also use the shorthand notation $a_{ij}^{\alpha\beta} = a_\alpha^\dagger a_i a_\beta^\dagger a_j$.

For the strong-orthogonality projector $\hat{Q}_{12}$ there are two ansätze in use. The choice that leads to the most accurate description of the correlation hole is referred to as ansatz 2 and defined as

$$\hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2)(1-\hat{V}_1\hat{V}_2) \tag{246}$$

where $\hat{O}_i$ projects onto the space of (active and frozen) occupied and $\hat{V}_i$ onto the space of active virtual orbitals

$$\hat{O}_1 = \sum_i |\phi_i(1)\rangle\langle\phi_i(1)| \tag{247}$$

$$\hat{V}_1 = \sum_a |\phi_a(1)\rangle\langle\phi_a(1)| \tag{248}$$

Thus, $\hat{Q}_{12}$ projects out of the functions $f_{12}|xy\rangle$ any contributions of occupied pairs $|ij\rangle$ or singly excited pairs $|i\alpha\rangle$, which ensures that the excitations into geminals are pure double excitations and have no Pauli-forbidden components. Furthermore, the factor $(1-\hat{V}_1\hat{V}_2)$ keeps the geminals orthogonal to all conventional doubly excited pairs $|ab\rangle$. This minimizes the coupling between amplitudes for conventional and explicitly correlated double excitations and guarantees that approximations made in evaluating the geminal contributions will not change the basis-set limit of a wave function method. Some authors denote the choice for the projector in eq 246 as "ansatz 3" and reserve the notation "ansatz 2" for projection with $(1-\hat{O}_1)(1-\hat{O}_2)$. These two expressions for the strong orthogonality projector lead indeed to wave function ansätze which would be equivalent if double excitations into orbital products and into geminals are treated on the same footing and no approximations are made in the evaluation of matrix elements. The projector $(1-\hat{O}_1)(1-\hat{O}_2)$ leads, however, to a strong coupling between the two sets of double excitations and expressions for the geminal contributions to the wave function that do not vanish in the limit of a complete one-electron basis set. This is inconvenient as approximations for the matrix elements then also affect the basis-set limit. To avoid these problems modern implementations employ for ansatz 2 the projector in the form given in eq 246 with the additional orthogonalization onto the space spanned by the double excitations into orbital products, $(1-\hat{V}_1\hat{V}_2)$.

An alternative choice for the strong orthogonality projector, denoted as ansatz 1, is

$$\hat{Q}_{12}^{(1)} = (1-\hat{P}_1)(1-\hat{P}_2) \tag{249}$$

with $\hat{P}_i = \hat{O}_i + \hat{V}_i$. It restricts the F12 geminals to the space of $|\alpha_\perp\beta_\perp\rangle$, that is, in contrast to ansatz 2, also contributions from pair functions $|a\beta_\perp\rangle$ are projected out. This reduces the number of coupling terms between geminal and conventional excitations in the equations for the wave function amplitudes and thus to much simpler working equations but also to a significantly less accurate description of the Coulomb hole. Therefore, most modern F12 methods use ansatz 2 for the dominant geminal contributions, while ansatz 1 is usually only employed for small higher-order terms.

6.2. Auxiliary Basis Sets

In practical calculations, the strong orthogonality projectors are partially approximated by a resolution of the identity in a finite basis set

$$1 \approx \hat{P}'' = \sum_{p''} |p''\rangle\langle p''| \tag{250}$$

This allows one to avoid calculation of three- and four-electron AO (atomic orbital) integrals, which for polyatomic molecules becomes soon prohibitively expensive, by expanding them in products of two-electron integrals (vide infra). The first implementations of R12 methods[208,285,328,331−334,336,337,434] used the orbital basis set (OBS) for the RI approximations, that is, $\hat{P}'' = \hat{P}$. With $\hat{P}_1 \approx \hat{P}_1\hat{P}_2$, the strong orthogonality projector for ansatz 1 then takes the simple form

$$\hat{Q}_{12}^{(1)} = 1 - \hat{P}_1 - \hat{P}_2 + \hat{P}_1\hat{P}_2 \approx 1 - \hat{P}_1\hat{P}_2 \tag{251}$$

This approach was (in combination with a few more approximations) termed "standard approximation" (vide infra). With a careful choice how the RI approximation is introduced, this approximation does not infringe the fast convergence with the angular momentum of the basis functions. It imposes, however, the requirement that the atomic orbital basis sets are saturated for the angular momenta included in the basis set. This hindered the applicability of these methods, since they required specially designed large one-electron basis sets. Klopper and Samson[340] showed that this restriction on the orbital basis sets can be lifted by introducing an auxiliary basis set for the RI approximation, for example, for ansatz 1

$$\hat{Q}_{12}^{(1)} = 1 - \hat{P}_1\hat{P}_2'' - \hat{P}_1''\hat{P}_2 + \hat{P}_1\hat{P}_2 \tag{252}$$

This auxiliary basis-set approximation (ABS) allowed us to use standard orbital basis sets for R12 calculations. Only the auxiliary basis $\{p''\}$ had to be specially designed: for an accurate RI it has to cover the space of the orbital basis and should be saturated for angular momenta up to $L_{max} + 2L_{occ}$, where L_{max} is the highest angular momentum of the OBS and L_{occ} the highest angular momentum of the occupied Hartree−Fock orbitals. Valeev[337] recognized that the numerical accuracy of the RI can be improved and the computational costs for it reduced if only the projection onto the orthogonal complement $\hat{P}^\perp = \Sigma_{\alpha_\perp}|\phi_{\alpha_\perp}\rangle\langle\phi_{\alpha_\perp}|$ is

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approximated with an auxiliary basis set as $\hat{P}^{\perp} \approx \hat{P}' = \sum_{a'}|\phi_{a'}\rangle\langle\phi_{a'}|$. This is equivalent to constructing the basis for the RI as the union of the orbital basis and a complementary auxiliary basis set (CABS)

$$1 \approx \hat{P} + \hat{P}' \tag{253}$$

The projector for ansatz 1 becomes with this approximation

$$\hat{Q}_{12}^{(1)} = 1 - \hat{P}_1\hat{P}_2 - \hat{P}_1\hat{P}_2' - \hat{P}_1'\hat{P}_2 \tag{254}$$

and the projector for ansatz 2 in eq 246 can—within the CABS approximation—be rewritten as

$$\hat{Q}_{12} \approx 1 - \hat{P}_1\hat{P}_2 - \hat{O}_1\hat{P}_2' - \hat{P}_1'\hat{O}_2 \tag{255}$$

For some matrix elements, also the contribution of the unit operator would result in three- or four-electron integrals. In these cases, the even more approximate form

$$\hat{Q}_{12} \approx \hat{P}_1'\hat{P}_2' + \hat{V}_1\hat{P}_2' + \hat{P}_1'\hat{V}_2 \tag{256}$$

of the projector for ansatz 2 is applied to obtain feasible working equations. The corresponding approximation for ansatz 1 is

$$\hat{Q}_{12}^{(1)} \approx \hat{P}_1'\hat{P}_2' \tag{257}$$

With an empty CA basis, that is, if $\hat{P}_1'$ and $\hat{P}_2'$ vanish, the projectors for both ansätze in eqs 255 and 254 reduce to $\hat{Q}_{12} = 1 - \hat{P}_1\hat{P}_2$, which is the approximation for the strong orthogonality projector used in the standard approximation of the original R12 methods (cf. section 4.5).

All of the above approximate forms of the projector $\hat{Q}_{12}$ given in eqs 251−257 do not eliminate all strong-orthogonality violating components from the pair functions: even with the CABS approach the contributions $\hat{O}_1\hat{R}_2$ and $\hat{R}_1\hat{O}_2$ where $\hat{R} = 1 - \hat{P} - \hat{P}'$ remain. Therefore, MP2-R12 and MP2-F12 energies are not bounded from below, although in practical calculations an overestimation of the MP2 correlation energy due to approximations for the projector has mainly been observed for the original MP2-R12 method without auxiliary basis set, while with the ABS and CABS approaches this problem can be avoided using a sufficiently accuracte auxiliary basis.[340]

6.3. Many-Electron Integrals and Standard Approximations

Augmentation of a conventional correlated wave function ansatz with excitations into geminals leads to additional matrix elements over the one- and two-electron parts of the Hamiltonian and the unit operator (i.e., overlap matrix elements). The "standard approximation" (SA) denotes the set of approximations and assumptions used in the original R12 methods to evaluate these matrix elements. The most important assumption has been that the resolution of the identity can be well represented in the orbital basis set, that is, $\hat{Q}_{12} \approx 1 - \hat{P}_1\hat{P}_2$. For the evaluation of matrix elements involving the Fock operator it was further assumed that the orbital space is closed under the Fock operator, that is, that the generalized Brillouin condition (GBC)

$$f_{i\alpha_\perp} = 0 \tag{258}$$

and the extended Brillouin condition (EBC)

$$f_{p\alpha_\perp} = 0 \tag{259}$$

are fulfilled. In some variants—indicated by letter codes A, A', B, C, etc. (vide infra)—certain terms were neglected. Today, one avoids (at least for the most important terms) such severe approximations to keep the demands for the orbital and CA basis sets as low as possible.

For the following discussion of post-Hartree−Fock methods it is convenient to partition the Hamiltonian as

$$\hat{H} = \hat{F}^{(0)} + \hat{F}^{(1)} + \hat{\Phi} \tag{260}$$

where $\hat{F}^{(0)}$ and $\hat{F}^{(1)}$ are the zeroth- and first-order contributions to the Fock operator

$$\hat{F}^{(0)} = \hat{F} - \hat{F}^{(1)} = \sum_{ij} f_{ij}a_i^\dagger a_j + \sum_{\alpha\beta} f_{\alpha\beta}a_\alpha^\dagger a_\beta \tag{261}$$

$$\hat{F}^{(1)} = \sum_{i\alpha} f_{i\alpha}a_i^\dagger a_\alpha + \sum_{\alpha i} f_{\alpha i}a_\alpha^\dagger a_i \tag{262}$$

and $\hat{\Phi}$ is the electron fluctuation potential, $\hat{\Phi} = \hat{H} - \hat{F}$. For F12 variants of single-reference pair theories, such as MP2, CCSD, CISD, or CEPA, the most important additional matrix elements needed are

$$V_{rs}^{xy} = \langle rs|r_{12}^{-1}|w_{xy}\rangle = \hat{S}_{xy}\langle rs|r_{12}^{-1}\hat{Q}_{12}f_{12}|xy\rangle \tag{263}$$

$$P_{vw}^{xy} = \langle w_{vw}|r_{12}^{-1}|w_{xy}\rangle = \hat{S}_{vw}\hat{S}_{xy}\langle vw|f_{12}\hat{Q}_{12}r_{12}^{-1}\hat{Q}_{12}f_{12}|xy\rangle \tag{264}$$

$$\begin{aligned} Z_{vw,p}^{xy,q} &= \langle w_{vw}, p|(1-\hat{p}_{13})r_{13}^{-1} + (1-\hat{p}_{23})r_{23}^{-1}|w_{xy}, q\rangle \\ &= \hat{S}_{vw}\hat{S}_{xy}\langle vw, p|f_{12}\hat{Q}_{12}((1-\hat{p}_{13})r_{13}^{-1} + (1-\hat{p}_{23})r_{23}^{-1})\hat{Q}_{12}f_{12}|xy, q\rangle \end{aligned} \tag{265}$$

$$C_{ab}^{xy} = \langle ab|\hat{F}^{(0)}|w_{xy}\rangle = \hat{S}_{xy}\langle ab|(\hat{F}_1^{(0)} + \hat{F}_2^{(0)})\hat{Q}_{12}f_{12}|xy\rangle \tag{266}$$

$$B_{vw}^{xy} = \langle w_{vw}|\hat{F}^{(0)}|w_{xy}\rangle = \hat{S}_{vw}\hat{S}_{xy}\langle vw|f_{12}\hat{Q}_{12}(\hat{F}_1^{(0)} + \hat{F}_2^{(0)})\hat{Q}_{12}f_{12}|xy\rangle \tag{267}$$

$$X_{vw}^{xy} = \langle w_{vw}|w_{xy}\rangle = \hat{S}_{vw}\hat{S}_{xy}\langle vw|f_{12}\hat{Q}_{12}f_{12}|xy\rangle \tag{268}$$

In eq 265 the operator $\hat{p}_{ij}$ exchanges two electrons and the comma indicates that the third index is not antisymmetrized. All other terms or intermediates involving the geminals can be evaluated by directly approximating the complementary space by the CABS using eq 256 or 257, since the corresponding partial wave expansions are either rapidly convergent or finite.[367,422,435]

Taking the intermediate V as an example, one sees that if $\hat{Q}_{12}$ were used as defined in eq 246 this would, due to the terms linear in the one-electron projectors $\hat{O}_1$ and $\hat{O}_2$, give rise to three-electron integrals

$$\begin{aligned} &\int\int \phi_r(1)\phi_s(2)r_{12}^{-1}\hat{O}_1 f_{12}\phi_x(1)\phi_y(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &= \sum_m \int \phi_s(2)\left\{\int \phi_r(1)r_{12}^{-1}\phi_m(1)\mathrm{d}\tau_1 \cdot \int \phi_m(3)f_{23}\phi_x(3)d\tau_3\right\}\phi_y(2)\mathrm{d}\tau_2 \end{aligned} \tag{269}$$

$$= \sum_m \langle rsm|r_{12}^{-1}f_{23}|myx\rangle \tag{270}$$

where in the last equation $\langle rsm|r_{12}^{-1}f_{23}|myx\rangle$ is an integral over orbital products, not Slater determinants. Even four-electron integrals would be required for evaluation of the intermediates B, P, and Z. This is avoided by inserting an approximate resolution of the identity (RI). In the CABS approach the basis set for the RI is chosen as the union of the orbital basis and a complementary auxiliary basis, which leads to the expressions in eqs 255 and 256. The more accurate form in eq 255, where the CABS orbitals are only used to approximate the contribution from the space spanned by the functions $|i\alpha_\perp\rangle$, is applied whenever the integrals for the unity in $\hat{Q}_{12}$ do not result in three-electron integrals. Inserting eq 255 into the expression for the intermediate V leads to

$$V_{rs}^{xy} = \hat{S}_{xy}\left(\langle rs|r_{12}^{-1}f_{12}|xy\rangle - \sum_{p>q}\langle rs|r_{12}^{-1}|pq\rangle\langle pq|f_{12}|xy\rangle - \sum_{ma'}\langle rs|r_{12}^{-1}|ma'\rangle\langle ma'|f_{12}|xy\rangle\right) \quad (271)$$

A similar expression is obtained for the X intermediate. With the shorthand notation

$$g_{rs}^{pq} = \langle rs|r_{12}^{-1}|pq\rangle \quad (272)$$

$$r_{rs}^{xy} = \hat{S}_{xy}\langle rs|f_{12}|xy\rangle \quad (273)$$

$$v_{rs}^{xy} = \hat{S}_{xy}\langle rs|r_{12}^{-1}f_{12}|xy\rangle \quad (274)$$

$$x_{vw}^{xy} = \hat{S}_{vw}\hat{S}_{xy}\langle vw|f_{12}^2|xy\rangle \quad (275)$$

for the required two-electron integrals, the expressions for the intermediates V and X become

$$V_{rs}^{xy} = v_{rs}^{xy} - \sum_{p>q} r_{pq}^{xy}g_{rs}^{pq} - \sum_{ma'} r_{ma'}^{xy}g_{rs}^{ma'} \quad (276)$$

$$X_{rs}^{xy} = x_{rs}^{xy} - \sum_{p>q} r_{pq}^{xy}r_{rs}^{pq} - \sum_{ma'} r_{ma'}^{xy}r_{rs}^{ma'} \quad (277)$$

The most involved intermediate is B. Together with V it determines the leading explicitly correlated contributions to the wave function and the energy and must therefore be evaluated with high accuracy. The most important terms arise from the kinetic energy operator since these should balance, in the Schrödinger equation, the contribution from the Coulomb interaction r_{12}^{-1} at the interelectronic cusp. However, due to the Coulomb and exchange parts of the Fock operator, already the contributions from the unity in $\hat{Q}_{12}$ give rise to three-electron integrals. This dilemma is partially solved by splitting the Fock operator into its contributions

$$\hat{F} = \hat{T} + \hat{V} + \hat{J} - \hat{K} \quad (278)$$

where $\hat{T}$ is the kinetic energy operator, $\hat{V}$ is the nuclear potential, and $\hat{J}$ and $\hat{K}$ are, respectively, the Coulomb and exchange operators and applying different approximations for the different contributions. For the unity in $\hat{Q}_{12}$ as many contributions as possible should be evaluated without inserting a resolution of the identity. This can be achieved by rewriting this part as

$$\langle vw|f_{12}(\hat{F}_1 + \hat{F}_2)f_{12}|xy\rangle = \frac{1}{2}\langle vw|[f_{12},[\hat{F}_1 + \hat{F}_2,f_{12}]]|xy\rangle + \frac{1}{2}\langle vw|(\hat{F}_1 + \hat{F}_2)f_{12}^2|xy\rangle + \frac{1}{2}\langle vw|f_{12}^2(\hat{F}_1 + \hat{F}_2)|xy\rangle \quad (279)$$

The nested commutator in the first term on the right-hand side vanishes for the multiplicative operators in $\hat{F}$ (i.e., $\hat{V}$ and $\hat{J}$), while for $\hat{T}$ the following identity holds

$$\frac{1}{2}[f_{12},[\hat{T}_1 + \hat{T}_2,f_{12}]] = |\nabla_1 f_{12}|^2 \quad (280)$$

The matrix element in eq 279 can thus be rewritten as

$$\langle vw|f_{12}(\hat{F}_1 + \hat{F}_2)f_{12}|xy\rangle = \langle vw||\nabla_1 f_{12}|^2|xy\rangle + \frac{1}{2}\langle vw|[f_{12},[\hat{K}_1 + \hat{K}_2,f_{12}]]|xy\rangle + \frac{1}{2}\langle vw|(\hat{F}_1 + \hat{F}_2)f_{12}^2|xy\rangle + \frac{1}{2}\langle vw|f_{12}^2(\hat{F}_1 + \hat{F}_2)|xy\rangle \quad (281)$$

The integrals of $|\nabla_1 f_{12}|^2$ can, with the common correlation factors, be calculated analytically with costs not much higher than for the integrals of f_{12} itself. For the R12 methods, $|\nabla_1 r_{12}|^2 = 1$, and for the exponential correlation factor $(1/\gamma)(1 - e^{-\gamma r_{12}})$ one obtains $|\nabla_1 f_{12}|^2 = e^{-2\gamma r_{12}}$. This allows one to evaluate the first (and most important) contribution in eq 281 with high accuracy and to insert approximate resolutions of the identity in finite basis sets only for those parts that necessarily lead to three-electron integrals. The particular way in which the remaining contributions to B are evaluated, which approximations are used and whether or not certain terms are neglected, has led to a bewildering array of acronyms for MP2-R12 and MP2-F12 theories, such as the so-called approximations A, A', B, and C, sometimes combined with additional approximations indicated with asterisks, etc. For the details, we refer the interested reader to the literature.[327,334,340,408,410,436,437]

In the approximations A and A' the contributions from $\hat{V}$, $\hat{J}$, and $\hat{K}$ are partially neglected to reduce the computational complexity. This reduces somewhat the accuracy achieved but leads to some computational savings at the MP2 level. The variants B and C neglect no terms but differ slightly in how the approximate resolutions of the identity are inserted. Almost all programs employ the variants B or C beyond MP2-F12 theory, since for more costly methods no real saving is gained from further approximations for the B intermediate.

The intermediate C is evaluated with the approximate $\hat{Q}_{12}$ given in eq 256, which leads to the expression

$$C_{ab}^{xy} = \sum_{c'}(r_{ac'}^{xy}f_b^{c'} + r_{c'b}^{xy}f_a^{c'}) \quad (282)$$

The intermediate C_{ab}^{xy} appears in equations for the wave function amplitudes only in connection with the contributions of double excitations into the functions $|a\beta_\perp\rangle$ which are not at all present with ansatz 1 or with the standard approximations applied in the original R12 methods. Since these contributions are rather small and decline quickly with increasing orbital basis sets, direct insertion of the RI for this intermediate does not affect the overall basis convergence of F12 methods.

The intermediate P only appears in contributions that are of fourth and higher order in Møller−Plesset perturbation theory and (at least) quadratic in the amplitudes for excitations into geminals. The intermediate Z occurs in third- and higher-order terms which are at least second order in the geminal contribution to the wave function. The individual contributions from the intermediates P and Z can be sizable but cancel each other systematically (see section 7.1). Therefore, most modern F12 methods neglect such contributions altogether. For a discussion of P, Z, and other intermediates for such higher-order terms we refer to the literature (see, for example, ref 367 or 438).

6.4. MP2-F12 Theory

Møller–Plesset perturbation theory through second order, MP2, is the correlated wave function method with the least computational complexity. It is thus a good example to illustrate how the geminals introduced in F12 theory are combined with a wave function expansion in conventional Slater determinants. At the same time, MP2 is also an important test ground for the different ansätze and approximations.

To derive the working equations for Møller–Plesset perturbation theory we first partition the Hamiltonian as

$$\hat{H} = E^{(0)} + \hat{F}_N^{(0)} + \hat{F}_N^{(1)} + \hat{\Phi}_N \tag{283}$$

where $E^{(0)} = E_{\mathrm{HF}}$ is the zeroth-order or Hartree–Fock energy and $\hat{F}_N^{(0)}$ the normal ordered part of the diagonal occupied/occupied and virtual/virtual blocks of the Fock operator $\hat{F}^{(0)}$ (cf. eq 261)

$$\hat{F}_N^{(0)} = \hat{F}^{(0)} - \langle \mathrm{HF}|\hat{F}^{(0)}|\mathrm{HF}\rangle \tag{284}$$

$\hat{F}_N^{(0)}$ is used as the zeroth-order Hamiltonian, and the perturbation is defined as the sum of the off-diagonal occupied/virtual blocks $\hat{F}_N^{(1)} = \hat{F}^{(1)}$ of the Fock operator and the normal ordered fluctuation potential given by $\hat{\Phi}_N$

$$\hat{\Phi}_N = \hat{\Phi} - \langle \mathrm{HF}|\hat{\Phi}|\mathrm{HF}\rangle = \hat{H} - E_{\mathrm{HF}} - \hat{F}_N \tag{285}$$

If the Hartree–Fock reference wave function fulfills the Brillouin condition, that is, the matrix elements f_{ia} and f_{ai} of $\hat{F}^{(0)}$ are zero, the MP2 energy correction is given by

$$\Delta E_{\mathrm{MP2}} = \langle \mathrm{HF}|\hat{\Phi}_N|\mathrm{MP1}\rangle \tag{286}$$

The first-order wave function MP1 can be written as

$$|\mathrm{MP1}\rangle = \hat{T}_2^{(1)}|\mathrm{HF}\rangle \tag{287}$$

with

$$\hat{T}_2^{(1)} = \sum_{\substack{i>j\\a>b}} t_{ab}^{ij(1)} a_a^\dagger a_i a_b^\dagger a_j = \sum_{\substack{i>j\\a>b}} t_{ab}^{ij(1)} a_{ij}^{ab} \tag{288}$$

The double-excitation amplitudes $t_{ab}^{ij(1)}$ are determined by requiring that the projection of the first-order Schrödinger equation

$$(E^{(0)} + \hat{F}_N^{(0)})|\mathrm{MP1}\rangle + \hat{\Phi}_N|\mathrm{HF}\rangle = E^{(0)}|\mathrm{MP1}\rangle + E^{(1)}|\mathrm{HF}\rangle \tag{289}$$

on the doubly excited determinants $\langle{}_{ab}^{ij}| = \langle \mathrm{HF}|a_j^\dagger a_b a_i^\dagger a_a = (\mathrm{HF}|a_{ij}^{ab})^\dagger$ vanishes

$$\langle{}_{ab}^{ij}|(\hat{F}_N^{(0)}|\mathrm{MP1}\rangle + \hat{\Phi}_N|\mathrm{HF}\rangle) = \langle{}_{ab}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle = 0 \tag{290}$$

Alternatively, the expression for E_{MP2} in eq 286 and the condition for the first-order wave function amplitudes, eq 290, can be combined into the variational Hylleraas functional

$$H_{\mathrm{MP2}} = \langle \mathrm{HF}|\hat{\Phi}_N\hat{T}_2^{(1)}|\mathrm{HF}\rangle + \sum_{\substack{i>j\\a>b}} t_{ab}^{ij(1)}\langle{}_{ab}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle \tag{291}$$

which is a special case of a Lagrange functional. We have then $E_{\mathrm{MP2}} = H_{\mathrm{MP2}}$, and the amplitudes are determined by the variational condition

$$\frac{dH_{\mathrm{MP2}}}{dt_{ab}^{ij(1)}} = 0 \tag{292}$$

Note that in eqs 290 and 291 the index N (indicating normal ordering of the operators) can be dropped as subtracting the expectation values for $|\mathrm{HF}\rangle$ from $\hat{F}^{(0)}$ and $\hat{\Phi}$ has in these equations no effect.

In MP2-F12 theory the set of conventional double excitations a_{ij}^{ab} is augmented by the excitations into the explicitly correlated geminals $|w_{xy}\rangle$ defined in eq 243 or 245 in section 6.1

$$|\mathrm{MP1\text{-}F12}\rangle = (\hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)})|\mathrm{HF}\rangle \tag{293}$$

with

$$\hat{T}_{2'}^{(1)} = \sum_{\substack{i>j\\x>y}} c_{xy}^{ij(1)} \sum_{\alpha>\beta} w_{\alpha\beta}^{xy} a_{ij}^{\alpha\beta} \tag{294}$$

Two alternative (but equivalent) expressions for the F12 double excitation operator $\hat{T}_{2'}^{(1)}$ are

$$\hat{T}_{2'}^{(1)} = \sum_{\substack{i>j\\x>y}} c_{xy}^{ij(1)}\tau_{ij}^{xy} = \sum_{\substack{i>j\\x>y}} t_{\alpha\beta}^{ij(1)} a_{ij}^{\alpha\beta} \tag{295}$$

with excitation operators τ_{ij}^{xy} and the amplitudes $t_{\alpha\beta}^{ij}$ defined as

$$\tau_{ij}^{xy} = \sum_{\alpha>\beta} w_{\alpha\beta}^{xy} a_{ij}^{\alpha\beta} \quad \text{and} \quad t_{\alpha\beta}^{ij} = \sum_{x>y} c_{xy}^{ij} w_{\alpha\beta}^{xy} \tag{296}$$

The form of $\hat{T}_{2'}^{(1)}$ on the right-hand side of eq 295 is sometimes useful for comparing contributions from double excitations into geminals with their conventional counterparts, but it should be kept in mind that the additional variable parameters in F12 theory are the coefficients c_{xy}^{ij}. To determine the coefficients $c_{xy}^{ij(1)}$ that enter in $\hat{T}_{2'}^{(1)}$, also the projection manifold for the first-order Schrödinger equation is extended by the double excitations into geminals. This leads to a coupled set of equations for the conventional double-excitation amplitudes $t_{ab}^{ij(1)}$ and the coefficients $c_{xy}^{ij(1)}$

$$\langle{}_{ab}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle = 0 \tag{297}$$

$$\langle{}_{xy}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle = 0 \tag{298}$$

with the bra states $\langle{}_{xy}^{ij}| = \mathrm{HF}|(\tau_{ij}^{xy})^\dagger$. The MP2-F12 energy is given by

$$\begin{aligned}\Delta E_{\mathrm{MP2\text{-}F12}} &= \langle \mathrm{HF}|\hat{\Phi}_N|\mathrm{MP1\text{-}F12}\rangle\\ &= \langle \mathrm{HF}|\hat{\Phi}_N(\hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)})|\mathrm{HF}\rangle\end{aligned} \tag{299}$$

The last three equations can again be cast into a variational Hylleraas functional

$$\begin{aligned}H_{\mathrm{MP2\text{-}F12}} &= \langle \mathrm{HF}|\hat{\Phi}_N(\hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)})|\mathrm{HF}\rangle\\ &\quad + \sum_{\substack{i>j\\a>b}} t_{ab}^{ij(1)}\langle{}_{ab}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle\\ &\quad + \sum_{\substack{i>j\\a>b}} c_{xy}^{ij(1)}\langle{}_{xy}^{ij}|[\hat{F}_N^{(0)}, \hat{T}_2^{(1)} + \hat{T}_{2'}^{(1)}] + \hat{\Phi}_N|\mathrm{HF}\rangle\end{aligned} \tag{300}$$

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which is now required to be stationary with respect to variations of $t_{ab}^{ij(1)}$ and $c_{xy}^{ij(1)}$.

With the matrix elements introduced in eqs 263–268 the equations for the MP2-F12 energy and the first-order amplitudes become

$$\Delta E_{\text{MP2-F12}} = \sum_{\substack{i>j\\a>b}} t_{ab}^{ij(1)} g_{ij}^{ab} + \sum_{\substack{i>j\\a>b}} c_{xy}^{ij(1)} V_{ij}^{xy} \tag{301}$$

$$0 = \sum_{c} \left(t_{ac}^{ij(1)} f_{cb} + t_{cb}^{ij(1)} f_{ca}\right) - \sum_{k} \left(t_{ab}^{ik(1)} f_{kj} + t_{ab}^{kj(1)} f_{ki}\right) + \sum_{x>y} C_{ab}^{xy} c_{xy}^{ij(1)} + g_{ab}^{ij} \tag{302}$$

$$0 = \sum_{v>w} B_{xy}^{vw} c_{vw}^{ij(1)} - \sum_{v>w} X_{xy}^{vw} \sum_{k} \left(c_{vw}^{ik(1)} f_{kj} + c_{vw}^{kj(1)} f_{ki}\right) + \sum_{a>b} C_{ab}^{xy} t_{ab}^{ij(1)} + V_{ij}^{xy} \tag{303}$$

The coupled equations for $t_{ac}^{ij(1)}$ and $c_{vw}^{ik(1)}$ can be solved directly in this form with computational costs scaling as $\mathcal{O}(\mathcal{N}^6)$ with the system size, in contrast to a conventional MP2 calculation with costs scaling as $\mathcal{O}(\mathcal{N}^5)$. The computationally most demanding steps of a MP2-F12 calculation are the calculations of the matrix elements of B, V, X, and C. This motivated the development of several more cost-efficient approximations.[327,340,408,410]

In eqs 302–303 the matrix elements C_{ab}^{xy} cause a coupling between the equations for the amplitudes $t_{ab}^{ij(1)}$ of the conventional double excitations and the equations for the geminal coefficients $c_{xy}^{ij(1)}$. These matrix elements vanish with ansatz 1 for the strong orthogonality projector or with the original standard approximations and the MP2-F12 energy becomes

$$\Delta E_{\text{MP2-F12}}^{\text{ansatz1}} = \Delta E_{\text{MP2}} + \Delta E_{\text{F12}}^{\text{ansatz1}} \tag{304}$$

where ΔE_{MP2} is the conventional MP2 energy

$$\Delta E_{\text{MP2}} = -\sum_{\substack{i>j\\a>b}} \frac{\langle ab|r_{12}^{-1}|ij\rangle^2}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{305}$$

and $\Delta E_{\text{F12}}^{\text{ansatz1}}$ a basis-set incompleteness correction from the geminal contribution

$$\Delta E_{\text{F12}}^{\text{ansatz1}} = \sum_{\substack{i>j\\x>y}} c_{xy}^{ij(1)} V_{ij}^{xy} \tag{306}$$

Such a partitioning of the MP2-F12 energy can also be obtained for ansatz 2 if the equations are slightly reformulated. In a (semi)canonical molecular orbital basis, which diagonalizes the occupied and virtual blocks $F^{(0)}$ such that $f_{ij} = \delta_{ij}\varepsilon_i$ and $f_{ab} = \delta_{ab}\varepsilon_a$, the general expression for the MP2-F12 energy can be written as

$$\Delta E_{\text{MP2-F12}} = \Delta E_{\text{MP2}} + \Delta E_{\text{F12}}; \qquad \Delta E_{\text{F12}} = \sum_{\substack{i>j\\x>y}} c_{xy}^{ij(1)} \tilde{V}_{ij}^{xy} \tag{307}$$

where the modified V_{ij}^{xy} intermediate is defined as

$$\tilde{V}_{ij}^{xy} = V_{ij}^{xy} - \sum_{a>b} C_{ab}^{xy} \frac{\langle ab|r_{12}^{-1}|ij\rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \tag{308}$$

Also, the equations for the geminal coefficients $c_{vw}^{ij(1)}$ can be rewritten such that an explicit reference to the amplitudes of the conventional double excitations is avoided

$$0 = \sum_{v>w} \left\{ B_{xy}^{vw} - (\varepsilon_i + \varepsilon_j) X_{xy}^{vw} - \sum_{a>b} \frac{C_{ab}^{xy} C_{ab}^{vw}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \right\} c_{vw}^{ij(1)} + \tilde{V}_{ij}^{xy} \tag{309}$$

The last equation is particularly useful in connection with the so-called SP approach, where the coefficients c_{xy}^{ij} are fixed by the s- and p-wave coalescence conditions at the interelectronic cusp at $c_{xy}^{ij} = \delta_{ix}\delta_{jy} - \delta_{iy}\delta_{jx}$ instead of optimizing them. The correlation energy is then not calculated through eq 301, since this would be too inaccurate, but through the variationally stable Hylleraas functional for the MP2-F12 energy, which can be written using eq 309

$$H_{\text{MP2-F12}} = \Delta E_{\text{MP2}} + \sum_{\substack{i>j\\x>y}} c_{xy}^{ij} \sum_{v>w} \left\{ B_{xy}^{vw} - (\varepsilon_i + \varepsilon_j) X_{xy}^{vw} - \sum_{a>b} \frac{C_{ab}^{xy} C_{ab}^{vw}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \right\} c_{vw}^{ij(1)} + 2 \sum_{\substack{i>j\\x>y}} c_{xy}^{ij} \tilde{V}_{ij}^{xy} \tag{310}$$

For the SP approach, where $c_{xy}^{ij} = \delta_{ix}\delta_{jy} - \delta_{iy}\delta_{jx}$, the last equation reduces to

$$H_{\text{MP2-F12}}^{\text{SP}} = \Delta E_{\text{MP2}} + \sum_{i>j} \left\{ B_{ij}^{ij} - (\varepsilon_i + \varepsilon_j) X_{ij}^{ij} - \sum_{a>b} \frac{C_{ab}^{ij} C_{ab}^{ij}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \right\} + 2 \sum_{i>j} \tilde{V}_{ij}^{ij} \tag{311}$$

Due to the diagonal structure of the coefficients c_{xy}^{ij} the SP approach requires calculation of only a small subset of the matrix elements of B, V, and X and the MP2-F12 energy can be computed with $\mathcal{O}(\mathcal{N}^5)$ scaling costs, that is, with the same scaling as a conventional MP2 calculation. Because of the larger number of integrals and intermediates required for an MP2-F12 calculation, the prefactor of the computational costs is larger than for a conventional calculation in the same orbital basis set, but this is—depending on the required accuracy with respect the basis-set errors—partially or completely outweighed by the much faster basis-set convergence, which allows use of smaller basis sets. The MP2-F12 method was reviewed in 2006, providing details of the approximations made, the techniques used for the integral evaluation, and the like.[439] More details of the MP2-F12 method, including the most recent developments and some large-scale calculations that illustrate its range of application, can be found in a recent article[440] on the implementation[441−443] of the MP2-F12 method in the TURBOMOLE program package. Figure 10 provides an illustration of the performance of the MP2-F12 method. For the model cluster $CH_3OH\cdots HAl(OH)(OSiH_3)_3$, taken from the work of Svelle et al.,[444] the electron-correlation contribution to the interaction energy (ΔE in mE_h; the basis-set limit is 13.42 mE_h) with respect to dissociation into the fragments CH_3OH and $HAl(OH)(OSiH_3)_3$ is shown. The geometries of the fragments were kept fixed. The much improved basis-set convergence of the

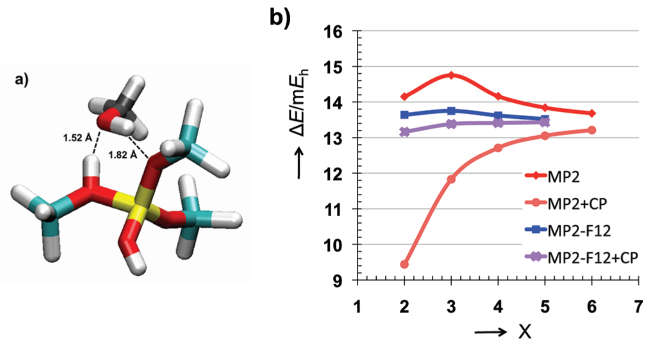

Figure 10. (a) Frozen-core MP2/aug-cc-pV(T+d)Z equilibrium geometry of the model complex $CH_3OH\cdots HAl(OH)(OSiH_3)_3$. Color code: H, white; C, gray; Al, yellow; Si, cyan; O, red. (b) Basis-set convergence of the magnitude of the electron-correlation contribution to the interaction energy as a function of the cardinal number X of the aug-cc-pV(X+d)Z basis sets obtained at the frozen-core MP2 and MP2-F12 levels with and without counterpoise (CP) correction. Data taken from ref 440.

MP2-F12 model is obvious. Moreover, the counterpoise corrections[445] to the electron-correlation contribution to the interaction energy are much smaller at the MP2-F12 level than at the conventional MP2 level. Accurate results can also be obtained using basis-set extrapolation techniques, but as noted in ref 446, basis-set extrapolation schemes should be applied to the *counterpoise-corrected* conventional MP2 values, which show a monotonic behavior.

6.5. CCSD-F12 Theory

As mentioned in section 4, coupled-cluster theory employs for the correlated wave function an exponential parametrization

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle \tag{312}$$

where $\hat{T}$ is called cluster operator and consists of a linear combination of excitation operators, $\hat{T} = \sum_\mu t_\mu \hat{\tau}_\mu$. Instead of the Hartree–Fock wave function HF, also other wave functions, for instance, from a Kohn–Sham density functional theory or from a multiconfigurational self-consistent field calculation, can be used as a reference for the coupled-cluster expansion, which leads then to the wave function ansatz $|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{Ref}\rangle$. In the standard coupled-cluster methods the amplitudes t_μ are determined by solving a projected Schrödinger equation which can be obtained in two different ways. Projecting the Schrödinger equation for $|\mathrm{CC}\rangle$ directly onto the reference wave function and the bra states $\langle\mu| = \langle\mathrm{Ref}|\hat{\tau}_\mu^\dagger$ gives the so-called unlinked form of the cluster equations

$$\langle\mu|(\hat{H} - E_{\mathrm{CC}})|\mathrm{CC}\rangle = 0 \tag{313}$$

Alternatively, the Schrödinger equation can be transformed before the projection with the inverse of $\exp(\hat{T})$, which results in the linked cluster equations introduced in section 4

$$\langle\mu|\exp(-\hat{T})(\hat{H} - E_{\mathrm{CC}})|\mathrm{CC}\rangle = 0 \tag{314}$$

The two forms of the cluster equations, eqs 313 and 314, are equivalent if no other approximations are made than a truncation of the manifold of excitation operators $\hat{\tau}_\mu$ that are included in the cluster operator $\hat{T}$, and this truncation is made such that the projection manifold $\{\langle\mathrm{Ref}|,\langle\mu|\}$ is closed under de-excitation. The latter criterion is fulfilled if for all excitation operators $\hat{\tau}_\mu$, $\hat{\tau}_\nu$ included in $\hat{T}$ also $\hat{\tau}_\mu^\dagger\hat{\tau}_\nu$ is included unless $\hat{\tau}_\mu^\dagger\hat{\tau}_\nu\,|\mathrm{Ref}\rangle = 0$. For example, if the excitation operators $a_a^\dagger a_j$ and $a_a^\dagger a_i a_b^\dagger a_j$ are included, also the single-excitation $a_b^\dagger a_i$ is needed for a projection manifold that is closed under de-excitation.

With the unlinked form of the cluster equations the working equations are similar to those of configuration interaction (CI) theory and coupled electron pair approximations (CEPA)

$$\langle\mu|(\hat{H} - E_{\mathrm{CC}})\left(\hat{T} + \frac{1}{2}\hat{T}^2 + \dots\right)|\mathrm{Ref}\rangle = 0 \tag{315}$$

On the other hand, one can exploit with the linked form of the cluster equations that the nested commutator expansion of the similarity-transformed Hamiltonian $\exp(-\hat{T})\hat{H}\exp(\hat{T})$ truncates at four nested commutators

$$\exp(-\hat{T})\hat{H}\exp(\hat{T}) = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{4!}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}] \tag{316}$$

The latter expansion is also termwise size extensive, that is, in the linked form of the cluster equations

$$\langle\mu|\hat{H} - E_{\mathrm{CC}} + [\hat{H},\hat{T}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{6}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{4!}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]|\mathrm{Ref}\rangle = 0 \tag{317}$$

any commutator can be neglected without violating the size-extensive structure of coupled-cluster theory.

For single-reference coupled-cluster calculations the reference wave function $|\mathrm{Ref}\rangle$ is usually chosen as a single Slater determinant with orbitals optimized in a preceding Hartree–Fock calculation, $|\mathrm{HF}\rangle$. We restrict the following discussion to this case. The cluster operator $\hat{T}$ can then be expanded in terms of excitation levels as

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \dots \tag{318}$$

where $\hat{T}_i$ includes excitation operators which promote i electrons from orbitals occupied in $|\mathrm{HF}\rangle$ to unoccupied molecular orbitals. Truncating $\hat{T}$ after a maximum excitation level and including up to this level all possible excitations out of the set of active occupied orbitals into a set of active unoccupied orbitals gives the standard hierarchy of coupled-cluster models CCSD (coupled-cluster with singles and doubles), CCSDT (coupled-cluster with singles, doubles, and triples), etc. Note that for these methods the projection manifold is closed under de-excitation, and thus, the linked and unlinked forms of the cluster equations are equivalent. At the CCSD level the equations are greatly simplified by using $\hat{T}_1$-transformed operators, defined as

$$\tilde{\hat{H}} = \exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1) \tag{319}$$

The linked cluster equations for CCSD are then given by

$$E_{\mathrm{CCSD}} = \langle\mathrm{HF}|\tilde{\hat{H}} + [\hat{H},\hat{T}_2]|\mathrm{HF}\rangle \tag{320}$$

$$0 = \langle\mu_1|\tilde{\hat{H}} + [\tilde{\hat{H}},\hat{T}_2]|\mathrm{HF}\rangle \tag{321}$$

$$0 = \langle\mu_2|\tilde{\hat{\Phi}} + [\tilde{\hat{H}},\hat{T}_2] + \frac{1}{2}[[\hat{H},\hat{T}_2],\hat{T}_2]|\mathrm{HF}\rangle \tag{322}$$

where $\langle \mu_1|$ and $\langle \mu_2|$ are, respectively, the singly and doubly excited determinants of the projection manifold. For later reference we will abbreviate the right-hand side of eq 321 as $\Omega_{\mu_1,\mathrm{CCSD}}$ and that of eq 322 as $\Omega_{\mu_2,\mathrm{CCSD}}$.

Explicitly correlated coupled-cluster theory with single and double excitations has recently been reviewed by Tew et al.[425] and Werner et al.[426] In CCSD-F12 theory, the cluster operator and the projection manifold are extended similarly as in the MP2-F12 approach by accounting for additional double excitations into the F12 geminals

$$\hat{T}_{2'} = \sum_{\substack{i>j \\ x>y}} c_{xy}^{ij} \tau_{ij}^{xy} \tag{323}$$

The expression for the energy and the linked cluster equations for CCSD-F12 become

$$E_{\mathrm{CCSD\text{-}F12}} = E_{\mathrm{CCSD}} + \langle \mathrm{HF}|[\hat{H}, \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{324}$$

$$0 = \Omega_{\mu_1,\mathrm{CCSD}} + \langle \mu_1|[\tilde{\hat{H}}, \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{325}$$

$$0 = \Omega_{\mu_2,\mathrm{CCSD}} + \langle \mu_2|[\tilde{\hat{H}}, \hat{T}_{2'}] + [[\hat{H}, \hat{T}_{2'}], \hat{T}_2] + \frac{1}{2}[[\hat{H}, \hat{T}_{2'}], \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{326}$$

$$0 = \langle \mu_{2'}|\tilde{\hat{\Phi}} + [\tilde{\hat{H}}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2}[[\hat{H}, \hat{T}_2 + \hat{T}_{2'}], \hat{T}_2 + \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{327}$$

In the last equation, $\langle \mu_{2'}|$ are the additional bra states obtained from the double excitations into the F12 geminals, $\langle {}^{ij}_{xy}| = \langle \mathrm{HF}|(\tau_{ij}^{xy})^\dagger$. The above equations are formally identical to conventional CCSD except that there are now in addition to double excitations into orbital pairs also those into F12 geminals. The size extensivity, the orbital invariance, and also the basis-set limit of CCSD are retained. For both ansatz 1 and 2 $\langle \mu_{2'}|[[\hat{H}, \hat{T}_2], \hat{T}_2]|\mathrm{HF}\rangle = 0$, and eq 327 can also be written as

$$0 = \langle \mu_{2'}|\tilde{\hat{\Phi}} + [\tilde{\hat{H}}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2}[[\hat{H}, 2\hat{T}_2 + \hat{T}_{2'}], \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{328}$$

For ansatz 1 or within the original standard approximations also $\langle \mu_2|[[\hat{H}, \hat{T}_{2'}], \hat{T}_{2'}]|\mathrm{HF}\rangle = 0$.

Similar as for MP2-F12, an attractive alternative to optimizing the geminal coefficients c_{xy}^{ij} is to predetermine them by the coalescence conditions at the interelectronic cusp as $c_{xy}^{ij} = \delta_{ix}\delta_{jy} - \delta_{iy}\delta_{jx}$. In this so-called CCSD-F12-SP approach the amplitudes for conventional excitations are optimized by solving eqs 325 and 326 in the presence of the fixed geminal contributions. This approach is numerically less sensitive to the accuracy of the RI approximations and several contributions of $\hat{T}_{2'}$ can be precontracted, which reduces significantly the computational costs. The energy for the SP approach is calculated from the Lagrange functional

$$E_{\mathrm{CCSD\text{-}F12\text{-}SP}} = E_{\mathrm{CCSD}} + \langle \mathrm{HF}|[\hat{H}, \hat{T}_{2'}]|\mathrm{HF}\rangle + \sum_{i>j} \langle {}^{ij}_{ij}|\tilde{\hat{\Phi}} + [\tilde{\hat{H}}, \hat{T}_2 + \hat{T}_{2'}] + \frac{1}{2}[[\hat{H}, 2\hat{T}_2 + \hat{T}_{2'}], \hat{T}_{2'}]|\mathrm{HF}\rangle \tag{329}$$

In the last equation we used explicitly correlated bra states defined as

$$\langle {}^{ij}_{ij}| = \sum_{x>y} c_{xy}^{ij} \langle \mathrm{HF}|(\tau_{ij}^{xy})^\dagger \tag{330}$$

With the strong orthogonality projector for ansatz 1, eq 249, and also for the original standard approximation, $\hat{Q}_{12} = 1 - \hat{P}_1\hat{P}_2$, the projection manifold for CCSD-F12 is closed under de-excitation. However, for ansatz 2, eq 246, which is the most accurate choice, this is not the case. The combination of a conventional single de-excitation $a_i^\dagger a_a$ with a double excitation into a geminal τ_{ij}^{xy} gives with ansatz 2 single excitations into the orthogonal complement of the orbital basis with $a_i^\dagger a_a \tau_{ij}^{xy}|\mathrm{HF}\rangle \neq 0$, which cannot be expanded in the singly excited states $|{}^a_i\rangle$. For ansatz 2, linked and unlinked cluster equations are therefore not completely equivalent. They differ in the equations for the geminal coefficients by $\langle \mu_{2'}|\hat{T}_1\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle$, which is only present in the linked form of the equations. However, this term is of high order in the fluctuation potential and for most circumstances negligibly small.

6.6. Geminal Basis Functions

F12 methods, to a large part, owe their success to the fact that a high percentage of the dynamic correlation energy can be recovered with just a single geminal basis function in the correlation treatment of each pair of occupied orbitals. This fact becomes even more remarkable when considering that the explicit r_{12} dependence of the geminal functions enters only as a spherical correlation factor. It is appropriate therefore to discuss the physics behind the choice of geminal basis function and the situations where the geminal basis should be extended.

6.6.1. Correlation Factor. The original choice of $r_{12}|\phi_i\phi_j\rangle$ to correlate a Hartree–Fock orbital pair $|\phi_i\phi_j\rangle$ was motivated by the coalescence conditions of the first-order pair functions (see section 3.6). The function $r_{12}|\phi_i\phi_j\rangle$ is a very close fit to the correlation hole at short-range r_{12}. However, because the correlation hole integrates to zero, it was recognized that the linear r_{12} correlation factor is unphysical at long-range r_{12}. A variety of correlation factors have been tested, including r_{12} with Gaussian,[398] exponential and complementary error function damping,[447,448] and the exponential and complementary error functions themselves.[329,406,409,447,448] The results of a comparison due to Tew and Klopper[447,448] demonstrated that the Slater-type geminal is the best choice in the F12 approach. Tew and Klopper[447] computed the optimum correlation factor for a series of two-electron ions, defined as the function $f(r_{12})$, such that $f(r_{12})\Psi_{\mathrm{HF}}$ has the maximum overlap with a tightly converged Hylleraas wave function. The results are plotted in Figure 11 for both the 1^1S and the 2^3S states.

Although the function $r_{12}e^{-\gamma r_{12}}$ is also a good candidate, the faster rate of decay to a constant of $(1 - e^{-\gamma r_{12}})$ appears to be advantageous, giving a better separation of short- and long-range correlation effects.[448] While the Jastrow factor for the short-range correlation is close to spherical in nature (see Figure 6), this is certainly not the case for long-range correlation. In F12 methods, the long-range correlation is parametrized through expansion in excited-state configurations.

The necessary two-electron integrals for the overlap, Coulomb and kinetic energy terms in the CCSD-F12 working equations, can be solved analytically for the Slater-type correlation factor but are significantly more complicated than standard electron repulsion integrals.[329,401,402] In many programs, the Slater

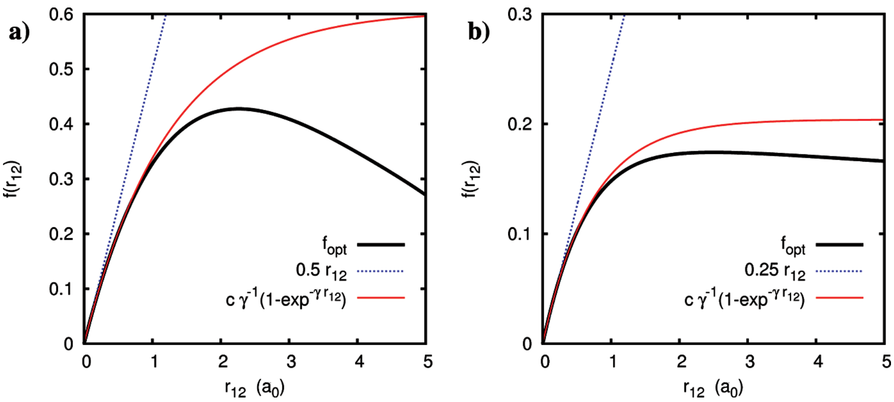

Figure 11. (a) R12 and F12 correlation factors ($c = 0.49$, $\gamma = 0.81\ a_0^{-1}$) compared to the optimum factor for 1^1S helium. (b) R12 and F12 correlation factors ($c = 0.29$, $\gamma = 1.40\ a_0^{-1}$) compared to the optimum factor for 2^3S helium. Reprinted with permission from ref 425. Copyright 2010 Springer.

function is expanded as a linear combination of Gaussians (STG-nG contraction)

$$\sum_i^n c_i e^{-\alpha_i r_{12}^2} \approx e^{-\gamma r_{12}} \tag{331}$$

The integrals for the Gaussian geminals resulting from the STG-nG contraction are well known and date back to Boys and Singer.[209,210] The necessary recursion formulas for integral evaluation have been reported in refs 398 and 400 for the McMurchy−Davidson and Obara−Saika recursive schemes, respectively, and the coefficients c_i for the STG-nG fit with $n = 3, 4, 5$, and 6 can be found in ref 447 or, alternatively, computed using the prescription in ref 410.

In Table 10 we list the coefficients c and exponents γ in a STG fit to the optimum correlation factors for the helium isoelectronic series of cations in their ^1S ground states, refit from the data in ref 447. Note that c is not expected to be exactly 1/2 but is very close to 1/2 because $\Psi \approx \Psi_{\mathrm{HF}}$ (see section 3.3.1). γ closely follows $a(Z - b)$ with $a = 0.7177$ and $b = 0.8481$, which may be interpreted as the length scale of the correlation hole shrinking in proportion to the contraction of the electron density. As remarked by Tew and Klopper[447] and Valeev,[287] shortly after the introduction of STG-type correlation factors, different exponents γ are expected to be appropriate for correlating core and valence orbitals and significant differences are expected between anions, cations, and neutral species.

The length-scale parameter γ has been of considerable interest, and the stability of the energy with respect to the choice of γ is very often tested. Fortunately, there is significant redundancy between the F12 geminal function and the orbital configuration expansion, and in practice, the dependence on γ is weak. Figure 12 is a plot of statistical measures of the basis-set errors in the CCSD-F12 correlation energy as a function of the exponent γ in the STG correlation factor (actually, the CCSD(F12) method was used (see section 7.2)). The test set consists of 58 compounds of H, C, N, O, and F. For the valence orbitals of these molecules, $\gamma = 1\ a_0^{-1}$ works extremely well.

A number of authors have investigated the dependence of the MP2-F12 energy on γ for heavier elements, including Zn and Zn^{2+}[449] and hydrides of N, P, As, and Sb.[437] Much larger values of γ, toward $2\ a_0^{-1}$, were found to be appropriate for molecules with heavy elements. Additionally, Bischoff et al.[437] found that the optimum γ depended on which orbital pair was being correlated. Low γ values are appropriate for valence electron pairs,

Table 10. Parameters for the Fit $c\gamma^{-1}(1 - e^{-\gamma r_{12}})$ to the Optimum Correlation Factor for He and Its Isoelectronic Series of Cations[a]

Z	2	3	4	5	6	7	8
c	0.49	0.49	0.49	0.49	0.49	0.49	0.49
γ (a_0^{-1})	0.81	1.55	2.27	2.99	3.70	4.42	5.12
$a(Z-b)$	0.83	1.54	2.26	2.98	3.70	4.42	5.13

[a] Taken from ref 425.

whereas the tighter electron densities in the core and d and f shells warranted higher exponents. In 2008 Tew[25] derived an analytic formula for the optimum γ for a given occupied pair in MP2-F12 calculations based on the second-order coalescence conditions (see section 3.5), but this has not yet been tested numerically.

6.6.2. Multiple Geminals. In 2006 Valeev[287,450] performed MP2 calculations using a set of geminals with a range of Gaussian correlation factor exponents, which may be viewed as a decontracted set in eq 331. For the small molecules tested, the improvement upon decontraction was small, underlining the near optimum form of the Slater function. The principal improvement came from the better description of core and core−valence correlation since the geminal basis could adapt to the different length scales. It is interesting to note that the geminal basis for these calculations is the same as in the GG0 method of Dahle et al.,[286] but Valeev used the strong-orthogonality functional and RI rather than the weak-orthogonality functional to determine the pair function parameters. Unfortunately, Valeev's approach is not compatible with the SP ansatz, which is important for both computational efficiency and reducing basis-set superposition errors.[448] Additionally, to make the B matrix positive definite, it was necessary to perform a singular value decomposition to eliminate the near dependencies in the geminal basis.

A pragmatic alternative has been developed simultaneously by Werner et al.[451] and Tew and Götz.[452] Here, Hartree−Fock orbital pairs are classified as either core, core−valence, or valence and a different correlation factor is used for each type. For core and core−valence pairs a correlation factor exponent of $2\ a_0^{-1}$ is appropriate, and for valence pairs an exponent of $1\ a_0^{-1}$ or even smaller is appropriate. While such an approach breaks orbital invariance, it may be used in combination with the SP ansatz. Furthermore, since only the integrals are affected, this approach is easily incorporated in CCSD-F12 calculations.

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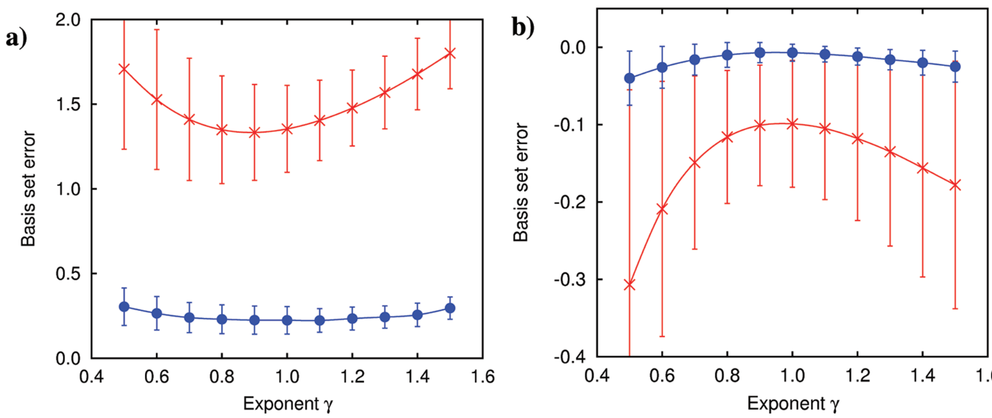

Figure 12. (a) Mean basis-set errors (kJ mol^{-1} per valence electron) in the valence CCSD(F12)/cc-pVXZ-F12 correlation energies over 58 molecules for X = D (×) and T (●) as a function of γ (a_0^{-1}). The standard deviation is given as an error bar. (b) Mean basis-set errors (kJ mol^{-1} per valence electron) in the valence CCSD(F12)-SP/cc-pVXZ-F12 correlation contribution to 53 (pseudo) heats of formation for X = D (×) and T (●) as a function of γ (a_0^{-1}). The standard deviation is given as an error bar. Reprinted with permission from ref 425. Copyright 2010 Springer.

6.6.3. Open-Shell Aspects. For open-shell calculations it is impossible to satisfy the MP2 coalescence conditions using the functions $f(r_{12})|\varphi_i\varphi_j\rangle$ only.[29] The reason for this is that both the *s*-wave and the *p*-wave coalescence conditions apply to pairs of opposite-spin electrons in a spin−orbital formulation. To satisfy the *s*-wave coalescence conditions requires that the spatial component of the first-order pair function u_{ij} for opposite spin pairs obeys

$$(1 + \hat{p}_{12})u_{ij} = \frac{1}{2}\hat{Q}_{12}r_{12}(\varphi_i(1)\varphi_j(2) + \varphi_j(1)\varphi_i(2)) + \mathcal{O}(r_{12}^2) \tag{332}$$

where $\phi_i = \varphi_i\alpha$ and $\phi_j = \varphi_j\beta$ and $\hat{p}_{12}$ permutes electrons 1 and 2. To satisfy the *p*-wave coalescence conditions requires that

$$(1 - \hat{p}_{12})u_{ij} = \frac{1}{4}\hat{Q}_{12}r_{12}(\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)) + \mathcal{O}(r_{12}^3) \tag{333}$$

Therefore, to satisfy both the *s*- and the *p*-wave coalescence conditions we have

$$|u_{ij}\rangle = \frac{3}{8}\hat{Q}_{12}r_{12}|\varphi_i\alpha\varphi_j\beta\rangle + \frac{1}{8}\hat{Q}_{12}r_{12}|\varphi_j\alpha\varphi_i\beta\rangle + \mathcal{O}(r_{12}^3) \tag{334}$$

The second determinant is referred to as a spin-flipped geminal function where φ_i, the spatial component of ϕ_i, now acquires β spin φ_j, the spatial component of ϕ_j now acquires α spin. Inclusion of spin-flipped geminals to satisfy both the *s*- and the *p*- wave coalescence conditions is vital to ensure that the energy converges as $(L + 1)^{-7}$ and is therefore necessary for a balanced treatment of open- and closed-shell species.[28,453] For UHF-based calculations, this doubles the computation time of an MP2-F12 calculation, but since only the integrals and MP2-F12 intermediates are affected, there is no additional expense in the CCSD iterations. For ROHF-based calculations, inclusion of spin-flipped geminals carries almost no additional cost. The spin-flipped geminals are included in the formulation in section 6.1 through the rational generator in eq 243.

For completeness, we note that Wilke and Schaefer[454,455] presented an explicitly correlated second-order perturbation theory and coupled-cluster singes and doubles theory for high-spin open-shell states in the framework of Z-averaged perturbation theory. Their ZAPT-F12 approach allows for a spin-restricted formalism with equivalent α and β subspaces, similar in cost to closed-shell calculations.

6.6.4. Extension of the Generating Orbital Space. The standard choice for the orbitals *x*, *y* that generate the geminal, namely, their restriction to occupied orbitals of the Hartree−Fock reference function, is fully sufficient for calculating the ground-state energy including derivative properties such as equilibrium structures and harmonic frequencies. This also holds true for static electric properties calculated as orbital *relaxed* derivatives of the ground-state energy, as the geminal basis needs only be suited to describing the correlation hole of the ground state. For example, using finite difference techniques, Franke et al.[456] demonstrated that the basis-set convergence of the static electrical properties of F^-, Ne, and HF are greatly accelerated using the standard CCSD(T)-R12 method. However, the orbital unrelaxed approach is favored in coupled-cluster response theory, particularly for calculation of frequency-dependent properties, because singularities from the Hartree−Fock reference would spoil the pole structure of the resulting response function at the correlated level. In the orbital unrelaxed approach the geminal basis functions $f(r_{12})|ij\rangle$ alone are not appropriate for parametrizing the response function.[457] For example, in calculations of single excitation energies it is necessary to include basis functions of the type $f(r_{12})|ia\rangle$ to give a balanced treatment of the ground and excited states.[458] In general, the F12 cluster operator becomes

$$\hat{T}_{2'} = \sum_{\substack{i>j,\alpha>\beta\\k>l}} c_{kl}^{ij} w_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta} + \sum_{\substack{i>j,\alpha>\beta\\kb}} c_{kb}^{ij} w_{\alpha\beta}^{kb} a_{ij}^{\alpha\beta} + \sum_{\substack{i>j,\alpha>\beta\\a>b}} c_{ab}^{ij} w_{\alpha\beta}^{ab} a_{ij}^{\alpha\beta} \tag{335}$$

A similar extension was discussed for the GG*n* methods (see section 4.2.3). The computational cost of including all such geminals is prohibitively large, however, so Neiss et al.[458] proposed transforming the virtual orbitals *a*,*b* by diagonalizing the virtual−virtual block of the MP2 density matrix. Then only a few virtuals from each symmetry are required in response calculations in addition to the geminals constructed from the occupied pairs. This approach was dubbed "R12+" and has been applied successfully to compute excitation energies,[458] electric polarizibilites and hyperpolarizibilities,[459,460] and excited-state structures and harmonic frequencies.[461,462] The R12+ method is not compatible with the SP ansatz and requires optimization of the geminal amplitudes.

An alternative approach that extends the SP ansatz has been pursued by Köhn and co-workers.[463−465] The extended SP ansatz (XSP ansatz) uses a general geminal operator

$$\hat{R} = \hat{R}^{(hh)} + \hat{R}^{(hp)} + \hat{R}^{(pp)} \tag{336}$$

$$= \sum_{\substack{i>j \\ \alpha>\beta}} w_{\alpha\beta}^{ij} a_{ij}^{\alpha\beta} + \sum_{\substack{i,a \\ \alpha>\beta}} w_{\alpha\beta}^{ia} a_{ia}^{\alpha\beta} + \sum_{\substack{a>b \\ \alpha>\beta}} w_{\alpha\beta}^{ab} a_{ab}^{\alpha\beta} \tag{337}$$

We recall that the matrix elements over the geminal factor involve appropriate symmetrization of the orbitals such that the cusp conditions are fulfilled (see eq 244)

$$w_{\alpha\beta}^{pq} = \hat{S}_{pq} \langle \alpha\beta | \hat{Q}_{12} f_{12} | pq \rangle \tag{338}$$

The superscripts in eq 336 refer to the type of orbitals to which f_{12} is applied: Pairs of occupied orbitals ("hole" orbitals, hence abbreviated hh), pairs of occupied and virtual orbitals ("hole" and "particle" orbitals, hp), and pairs of virtual orbitals (pp). This geminal operator is then used for a cluster ansatz of the form $\{e^{\hat{R}}\}e^{\hat{T}}|\mathrm{HF}\rangle$, where the curly brackets denote a normal-ordered exponential, in order to avoid a nonterminating series of self-contractions of $\hat{R}$. When acting on a Hartree−Fock reference function, the following rearrangements are equivalent to the above cluster ansatz

$$e^{\hat{T}} e^{-\hat{T}} \{e^{\hat{R}}\} e^{\hat{T}} |\mathrm{HF}\rangle$$

$$= e^{\hat{T}} \left\{ \exp\left(\hat{R} + [\hat{R}, \hat{T}] + \frac{1}{2}[[\hat{R}, \hat{T}], \hat{T}] \right) \right\} |\mathrm{HF}\rangle \tag{339}$$

$$= \exp\left(\hat{T} + \hat{R}^{(hh)} + [\hat{R}^{(hp)}, \hat{T}] + ([\hat{R}^{(pp)}, \hat{T}])_{\mathrm{c.b.}} + \frac{1}{2}[[\hat{R}^{(pp)}, \hat{T}], \hat{T}] \right) |\mathrm{HF}\rangle \tag{340}$$

The index c.b. denotes "closed from below" which means (alluding to the respective diagrams) that all particle annihilation indices of $\hat{R}^{(pp)}$ are fully connected to $\hat{T}$. In this case, all summands in the exponential commute and give a nonvanishing linear term when acting on the reference function.

With the first two terms in the argument of the exponential, eq 340, we recover the usual SP ansatz, $\hat{T}_{2'} = \hat{R}^{(hh)}$, which is restricted to geminals generated from occupied orbitals. The next terms suggest a way to extend the cluster operator with further geminal contributions, in the following we will restrict the discussion to $[\hat{R}^{(hp)}, \hat{T}]$. This introduces contributions like $[\hat{R}^{(hp)}, \hat{T}_1]$ and $[\hat{R}^{(hp)}, \hat{T}_2]$ which are effective two and three-body operators, as illustrated by their diagrammatic representations, Figure 13. $[\hat{R}^{(hp)}, \hat{T}_1]$ introduces geminal functions like $f(r_{12})|ia\rangle$ and helps to obtain a balanced description of ground and excited states in response calculations (see sections 8.3 and 8.4). The commutator with $\hat{T}_2$, on the other hand, introduces the necessary geminal functions to enhance the basis-set convergence of connected triple excitations in, for example, CCSD(T) calculations (see section 6.8).

6.7. CABS Singles

F12-type geminal functions accelerate the basis-set convergence in the double-excitation space, but by construction they have no contribution to the single excitations. Furthermore, when small orbital basis sets are used to compute the Hartree−Fock reference determinant, there is a substantial basis-set error in the Hartree−Fock energy resulting from the incomplete parametrization of the Hartree−Fock orbitals. All of these issues can be addressed by extending the parameter set for single excitations beyond that of the Hartree−Fock orbital space.

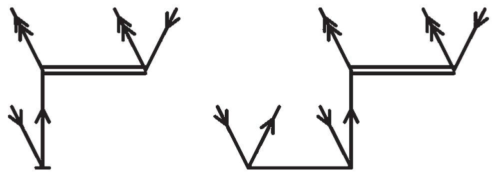

Figure 13. Representation of $[\hat{R}^{(hp)}, \hat{T}_1]$ and $[\hat{R}^{(hp)}, \hat{T}_2]$ in terms of the corresponding Brandow-type diagrams. The single bar denotes the $\hat{T}_1$ or $\hat{T}_2$ operator, respectively, and the double bar is the $\hat{R}$ operator; double arrows denote excitations into the formally complete virtual space (we implicitly assume the presence of the projector $\hat{Q}_{12}$ for $\hat{R}$). For each diagram, the number of pairs of in- and out-going arrows determines the rank of the operator.

In 2007 Noga et al.[466] defined new single excitations using the one-electron component of the geminal functions, and in an approach analogous to the dual basis-set work of Wolinski and Pulay[467] (see also refs 468 and 469), they computed a second-order energy correction in this basis. It was quickly realized that the second-order energy is a perturbative basis-set incompleteness correction to the Hartree−Fock energy and has no contribution to singles correlation. As suggested by Adler et al.,[428] the more natural parametrization of the new singles is therefore done in terms of the orbitals of the CA basis[427,436,470]

$$\hat{T}_{1'} = \sum_{ia'} t_{a'}^{i} a_{i}^{a'} \tag{341}$$

Köhn and Tew[471] performed a systematic investigation of the effect of including single excitations into CA orbitals in the CCSD-F12 method, which extends the basis for both HF and correlation contributions. A series of truncated models was defined based on perturbation arguments similar to those used to construct the CC2 and CC3 methods. Note that Møller−Plesset partitioning of the Hamiltonian, eq 283, implies that $\hat{T}_{1'}$ is first order in the perturbation. The conclusions were clear: The dominant energy contribution for both total and relative energies is the Hartree−Fock basis-set error correction. For closed-shell molecules considered as single-reference cases, the improvement in the singles correlation energy is unimportant. Moreover, a second-order perturbative Hartree−Fock energy correction is almost as accurate as a second-order iterative CCS correction and is much cheaper to evaluate. Contributions beyond second order are smaller than the error in the incompleteness of the unified orbital plus CA basis sets for standard choices of RI basis sets.

The CABS singles second-order energy correction is obtained by solving[427]

$$E^{(S2)} = E_{\mathrm{HF}} + \langle \mathrm{HF} | [\hat{F}^{(1)}, \hat{T}_1 + \hat{T}_{1'}] | \mathrm{HF} \rangle = E_{\mathrm{HF}} + f_i^a t_a^i + f_i^{a'} t_{a'}^i \tag{342}$$

$$0 = \langle \mu_1 | \hat{F}^{(1)} + [\hat{F}^{(0)}, \hat{T}_1 + \hat{T}_{1'}] | \mathrm{HF} \rangle = f_a^i + f_a^b t_b^i - f_j^i t_a^j + f_a^{b'} t_{b'}^i \tag{343}$$

$$0 = \langle \mu_{1'} | \hat{F}^{(1)} + [\hat{F}^{(0)}, \hat{T}_1 + \hat{T}_{1'}] | \mathrm{HF} \rangle = f_{a'}^i + f_{a'}^{b'} t_{b'}^i - f_j^i t_{a'}^j + f_{a'}^b t_b^i \tag{344}$$

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where summation over repeated indices is assumed. At second order this energy correction is entirely decoupled from the MP2-F12 doubles energy correction and the singles and doubles amplitudes are determined independently. All of the Fock matrix elements are required for constructing the B intermediate, and the cost of computing $\Delta E^{(S2)}$ is negligible compared to both the underlying HF calculation and the MP2-F12 energy correction. For ROHF open-shell calculations both $\hat{T}_1$ and $\hat{T}_{1'}$ introduce spin contamination, and Knizia et al. derived spin-free expressions where the CABS singles correct for the ROHF energy without introducing spin contamination.[436]

Table 11 is taken from ref 427 and lists the rms basis-set errors for Hartree−Fock calculations on reaction energies, atomization energies, ionization potentials, and electron affinities with and without the CABS singles correction. For a HF/aug-cc-pVXZ calculation the cc-pVXZ JKFIT basis set was used for CABS. The basis-set limit was taken as the aug-cc-pV6Z value, and the ROHF method was used for all open-shell calculations.

The CABS singles correction reduces the Hartree−Fock basis-set errors by an order of magnitude and, despite its perturbative rather than variational nature, is sufficient to ensure that the basis-set errors in the Hartree−Fock energies are not larger than those of the CCSD-F12 correlation energies. In the context of response theory, however, the basis-set incompleteness in the singles correlation contribution becomes important. Here, an iterative CABS singles approach is appropriate that includes coupling terms between the singles and doubles amplitudes.[463,465,471]

Very recently, Kong and Valeev[472] devised a CABS singles correction for CASSCF wave functions. They investigated two choices for the zeroth-order Hamiltonian, $\hat{H}_F^{(0)}$ and $\hat{H}_D^{(0)}$

$$\hat{H}_F^{(0)} = \hat{P}\hat{F}\hat{P} + f_{a'}^{b'} a_{b'}^{a'} + (f_{a'}^{b} a_{b}^{a'} + f_{a}^{b'} a_{b'}^{a}) \tag{345}$$

$$\hat{H}_D^{(0)} = \hat{P}\hat{H}\hat{P} + f_{a'}^{b'} a_{b'}^{a'} + (f_{a'}^{b} a_{b}^{a'} + f_{a}^{b'} a_{b'}^{a}) \tag{346}$$

f_q^p are the matrix elements of the CASSCF Fock operator, and $\hat{P}$ projects onto the OBS. Although $\hat{H}_F^{(0)}$ is the correct zeroth-order Hamiltonian for a CASSCF calculation, the more complete $\hat{H}_D^{(0)}$ Hamiltonian was found to give superior basis-set corrections. The energy correction is computed using second-order Rayleigh−Schrödinger perturbation theory and requires only 1- and 2-particle reduced density matrices (evaluated from the CASSCF wave function)

$$\Delta E^{(2)} = f_i^{a'} t_{a'}^{j} \gamma_j^i \tag{347}$$

$$0 = f_a^b t_b^j \gamma_j^i - \left(f_j^k \gamma_k^i + \frac{1}{2} g_{jk}^{lm} \lambda_{lm}^{ik} \right) t_a^j + f_a^{b'} t_{b'}^j \gamma_j^i \tag{348}$$

$$0 = f_{a'}^j \gamma_j^i + f_{a'}^{b'} t_{b'}^j \gamma_j^i - \left(f_j^k \gamma_k^i + \frac{1}{2} g_{jk}^{lm} \lambda_{lm}^{ik} \right) t_{a'}^j + f_{a'}^b t_b^j \gamma_j^i \tag{349}$$

Here, $\lambda_{rs}^{pq} = \gamma_{rs}^{pq} - \gamma_r^p \gamma_s^q + \gamma_s^p \gamma_r^q$ is the two-particle cumulant and γ_p^q and γ_{rs}^{pq} are the 1- and 2-particle reduced density matrices, respectively. The equations for the $\hat{H}_F^{(0)}$ zeroth-order Hamiltonian are obtained by replacing the intermediate $(f_j^k \gamma_k^i + (1/2) g_{jk}^{lm} \lambda_{lm}^{ik})$ with $f_l^k(\lambda_{jk}^{il} - \gamma_k^i \gamma_j^k)$. The two methods have essentially the same computational cost, $\mathcal{O}(O^2X^2)$, where O and X are the number of occupied and CABS orbitals, respectively. This is one order lower scaling than the underlying CASSCF calculation, which scales as $\mathcal{O}(O^4V)$, where V is the number of virtual orbitals.

Table 11. Hartree−Fock RMS Basis Set Errors for Open- and Closed-Shell Reaction Energies (kJ mol^{-1}), Atomization Energies (kJ mol^{-1}), Ionization Potentials (meV), and Electron Affinities (meV) with and without the CABS Singles Correction[a]

method	basis	RE(cs)	RE(os)	AE	IP	EA
RHF	aug-cc-pVDZ	13.45	28.88	24.39	65.14	76.22
	aug-cc-pVTZ	2.07	3.61	3.47	11.07	11.80
	aug-cc-pVQZ	0.49	1.17	0.82	2.27	3.58
	aug-cc-pV5Z	0.17	0.35	0.25	0.59	0.98
$E^{(S2)}$	aug-cc-pVDZ	1.79	2.22	1.64	8.16	8.04
	aug-cc-pVTZ	0.48	0.54	0.29	2.76	1.80
	aug-cc-pVQZ	0.18	0.17	0.13	1.04	1.01

[a] Data taken from ref 427.

For a single Slater determinant λ_{rs}^{pq} vanishes and γ_q^p reduces to a delta function. Hence, in the single-reference limit eqs 342−344 are recovered. The performance of the CASSCF CABS singles correction is similar to the Hartree−Fock case and consistent over potential energy surfaces.

6.8. Explicitly Correlated Triples

Inclusion of the cluster operator which describes connected triple excitations

$$\hat{T}_3 = \sum_{\substack{i>j>k \\ a>b>c}} t_{abc}^{ijk} a_{ijk}^{abc} \tag{350}$$

is vital for obtaining quantitative results in coupled-cluster theory. A very accurate estimate of the $\hat{T}_3$ contribution is obtained by the noniterative CCSD(T) correction.[473,474] The amplitudes are obtained from the second-order equations in Møller−Plesset perturbation theory by substituting the converged $\hat{T}_2$ amplitudes from CCSD for the first-order amplitudes. The corresponding fourth-order energy expression can be written as a Hylleraas functional

$$H_4 = \langle \mathrm{HF}|\hat{T}_3^\dagger[\hat{F}_N^{(0)}, \hat{T}_3] + \hat{T}_3^\dagger[\hat{\Phi}_N, \hat{T}_2] + \hat{T}_2^\dagger[\hat{\Phi}_N, \hat{T}_3]|\mathrm{HF}\rangle \tag{351}$$

The stationarity condition leads to the amplitude equations for $\hat{T}_3$

$$\langle_{abc}^{ijk}|[\hat{F}_N^{(0)}, \hat{T}_3] + [\hat{\Phi}_N, \hat{T}_2]|\mathrm{HF}\rangle = 0 \tag{352}$$

The pure fourth-order correction is known in the literature as the CCSD+T(CCSD) or CCSD[T] method.[475] It was later recognized that much improved results could be obtained by adding the couplings to the $\hat{T}_1$ equations, which formally are fifth order in perturbation theory;[473,474] for a rationalization see, e.g., ref 476. The CCSD(T) energy then reads

$$E_{(T)} = E_4 + E_5 \tag{353}$$

$$= \langle \mathrm{HF}|\hat{T}_2^\dagger[\hat{\Phi}_N, \hat{T}_3]|\mathrm{HF}\rangle + \langle \mathrm{HF}|\hat{T}_1^\dagger[\hat{\Phi}_N, \hat{T}_3]|\mathrm{HF}\rangle \tag{354}$$

$$= -\langle \mathrm{HF}|\hat{T}_3^\dagger \hat{F}_N^{(0)} \hat{T}_3|\mathrm{HF}\rangle + \langle \mathrm{HF}|\hat{T}_1^\dagger[\hat{\Phi}_N, \hat{T}_3]|\mathrm{HF}\rangle \tag{355}$$

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Table 12. RMS Basis Set Errors in the Isolated $E_{(T)}$ Contribution to Reaction Energies of Closed-Shell Molecules (REc) and Open-Shell Molecules (REo), as Well as Atomization Energies (AE), Ionization Potentials (IP), and Electron Affinities (EA)[a]

method/basis	REc/kJ mol^{-1}	REo/kJ mol^{-1}	AE/kJ mol^{-1}	IP/meV	EA/meV
Conv/CBS[DT]	0.713	0.611	0.604	2.15	2.14
Conv/CBS[TQ]	0.144	0.136	0.130	0.64	1.52
Conv/CBS[Q5]	0.032	0.062	0.092	0.24	0.44
(T)/aVDZ	2.683	5.930	8.767	33.40	42.09
(T*)/aVDZ	1.375	3.779	3.671	24.34	26.19
(T)/aVTZ	1.292	1.670	2.470	10.51	13.07
(T*)/aVTZ	0.564	0.822	0.368	4.97	4.63
(T)/aVQZ	0.604	0.731	1.066	4.58	5.78
(T*)/aVQZ	0.227	0.380	0.150	1.67	1.87

[a] Listed are the root mean square deviations from the basis-set limit estimate from conventional CCSD(T)/CBS[56] extrapolations. The first three lines are conventional extrapolated values; the remaining lines are the nonextrapolated results obtained by evaluation of the conventional expression, eq 353, with $\hat{T}_1$ and $\hat{T}_2$ from CCSD-F12a (cf. section 7.3) calculations with $\gamma = 1.0\ a_0^{-1}$. (T*) denotes the scaled energies, eq 357. Data taken from ref 427.

where in the last equality the stationarity condition was used to rewrite the forth-order term, such that it can directly be evaluated from the amplitudes. For canonical orbitals, the $\hat{T}_3$ amplitudes take the explicit form

$$t_{abc}^{ijk} = -\hat{\hat{P}}_{abc}^{ijk} \frac{\sum_d g_{ab}^{id} t_{dc}^{jk} - \sum_l g_{al}^{ij} t_{bc}^{lk}}{\varepsilon_a + \varepsilon_b + \varepsilon_c - \varepsilon_i - \varepsilon_j - \varepsilon_k} \qquad (356)$$

where the operator $\hat{\hat{P}}_{abc}^{ijk}$ ensures the appropriate antisymmetry of the amplitudes.

The correlation factor introduced in R12 and F12 theory by design only takes care of pair correlation. Hence, starting with early work on CC-R12 theory,[366,367] explicit correlation for connected triples is not considered. Instead, after a CCSD-R12 or CCSD-F12 calculation, the conventional expression, eq 352, is used; see, for example, refs 419−421 and 428. There also exist a number of works which include conventional higher-order cluster operators up to $\hat{T}_4$, both for energy[477,478] and response calculations.[465] The numerical results from all these publications show that the basis-set convergence of $E_{(T)}$, or any other correlation contribution beyond the pair level, is not improved. For total correlation energies this may seem justified as usually the contribution of connected triples is by 1 order of magnitude smaller than the CCSD correlation energy. This observation, however, does not necessarily carry over to relative energies.

In fact, it was found that particularly in F12 theory the error in the $E_{(T)}$ contribution can become dominant, as demonstrated by Knizia et al. in refs 427 and 479. The same authors also suggested a scaled $\hat{T}_3$ correction, denoted (T*), which is defined as

$$E_{(T^*)} = E_{(T)} \times \frac{E_{\text{MP2-F12}}}{E_{\text{MP2}}} \qquad (357)$$

In Table 12 the $E_{(T)}$ error statistics for a number of test sets are listed. It is found that the uncorrected $E_{(T)}$ can have very large basis-set errors for the smaller basis sets. For the aug-cc-pVQZ basis the deviations are below 1 kJ mol^{-1}, but they are usually larger than the error in the CCSD correlation energy (see ref 427). The correction, eq 357, leads to clearly more satisfactory results; nevertheless, a more rigorous treatment of $E_{(T)}$ seems desirable within F12 theory. This issue was addressed recently by Köhn.[464,480]

First, some considerations are in place about the type of short-range correlation that governs the convergence behavior of $E_{(T)}$. We can distinguish two cases: (a) two-electron coalescence with correlated motion of a third electron at some distance away and (b) a genuine three-electron coalescence. Thus far, the latter issue has not received much attention in the literature and not much is known about the functional behavior in such a case. There is clear evidence, however, that b is much less important than a.

In case b, as discussed in section 3.4, the wave function must vanish by virtue of the exclusion principle, as at least two electrons must be triplet coupled. Hence, the convergence of the partial wave expansion cannot be worse than in the triplet case of two-electron coalescence which shows an $(L + 1)^{-5}$ behavior. In case a, also singlet coalescence is possible, leading to a $(L + 1)^{-3}$ convergence in line with empirical observations.[481] The task is hence to find an appropriate ansatz for a $\hat{T}_{3'}$ operator that incorporates geminal contributions into a connected triples cluster. One way to achieve this is the extended SP ansatz (XSP ansatz)[438,464] (see section 6.6.4). The expansion, eq 340, suggests considering

$$\hat{T}_{3'} = [\hat{R}^{(hp)}, \hat{T}_2] \qquad (358)$$

as the leading order geminal correction to connected triple-excitation clusters. The diagrammatic representation of this expression, Figure 13, immediately reveals the three-body character of the operator. It also suggests a direct physical interpretation in the spirit of case a (see above): $\hat{R}^{(hp)}$describes a short-range scattering of two electrons, the correlation of this close pair with a third electron (at some distance) is included by $\hat{T}_2$.

The working equations are obtained from the fourth-order Hylleraas functional, eq 351, by substituting $\hat{T}_3 + \hat{T}_{3'}$ for $\hat{T}_3$. Stationarity with respect to the conventional triples amplitudes leads to a modified set of equations

$$\langle_{abc}^{ijk}|[\hat{F}_N^{(0)}, \hat{T}_3] + [\hat{F}_N^{(0)}, \hat{T}_{3'}] + [\hat{\Phi}_N, \hat{T}_2 + \hat{T}_{2'}]|\text{HF}\rangle = 0 \qquad (359)$$

The explicitly correlated part, eq 358, has no additional unknown amplitudes. In analogy to the SP approach for CCSD-F12 (section 6.5), the energy contributions are instead evaluated from a modified energy functional. Hence, for the fourth-order energy contribution, we obtain

$$E_{4,\text{F12}} = -\langle\text{HF}|\hat{T}_3^\dagger \hat{F}_N^{(0)} \hat{T}_3|\text{HF}\rangle + 2\langle\text{HF}|(\hat{T}_2^\dagger + \hat{T}_{2'}^\dagger)[\hat{\Phi}_N, \hat{T}_{3'}]|\text{HF}\rangle + \langle\text{HF}|\hat{T}_{3'}^\dagger \hat{F}_N^{(0)} \hat{T}_3|\text{HF}\rangle \qquad (360)$$

while the fifth-order energy is simply

$$E_{5,\text{F12}} = \langle \text{HF}|\hat{T}_1^\dagger[\hat{\Phi}_N, \hat{T}_3 + \hat{T}_{3'}]|\text{HF}\rangle \qquad (361)$$

In addition, there is a fourth-order contribution with the Fock matrix

$$E_{4\text{F},\text{F12}} = \langle \text{HF}|\hat{T}_2^\dagger[\hat{F}_N^{(1)}, \hat{T}_3 + \hat{T}_{3'}]|\text{HF}\rangle \qquad (362)$$

The purely conventional contribution in eq 362 vanishes if the Brillouin condition is fulfilled; neglect of the corresponding F12 part implies the assumption of the GBC.

Full expansion of these equations leads to a rather large number of terms. These can effectively be reduced by applying the standard approximation scheme, and the resultant method will be denoted as (T)-XSP' in the following. A detailed discussion of the resulting working equations can be found in ref 480. The main observations can be summarized as follows.

- The overall scaling of the method remains at $\mathcal{N}^7$, where $\mathcal{N}$ is a measure of the size of the system. With the exception of one term (discussed below), all additional F12 terms arising from eqs 360−362 scale with $\mathcal{N}^6$ only. Likewise, the calculation time for all necessary additional F12 intermediates scales with $\mathcal{N}^6$ at most.
- The coupling between $\hat{T}_{2'}$ and $\hat{T}_{3'}$ (a part of the second term of eq 360) leads to a term involving the intermediate $Z_{ij}^{ab} = \sum_k (Z_{ik,j}^{ak,b} + Z_{jk,i}^{bk,a} + Z_{ij,k}^{ak,b})$, where $Z_{vw,p}^{xy,q}$ is defined in eq 265. Building this intermediate requires $\mathcal{N}^7$ scaling steps, which without additional approximations even includes a cubic scaling with the number of CABS functions. The effort can be reduced to terms with at most linear dependence on the CABS; nevertheless, the amount of additional computation time (in comparison to the conventional expression) is large. Precise statements are difficult to draw from the present pilot implementation, but it is clear that future applications of this method will critically depend on a more efficient treatment of this contribution. We note that this problem is alleviated for iterative approaches, like CCSDT, and that Z_{ij}^{ab} does not contribute to response properties and may hence be neglected in such calculations.

The numerical effect of the geminal correction for $\hat{T}_3$ clusters can be illustrated by the following examples. For the Ne atom, the rate of convergence of the partial wave expansion is investigated.[480] Figure 14 shows a double logarithmic plot of the CCSD correlation energy and $E_{(T)}$ as a function of the maximum angular momentum quantum number L included in the expansion. A large uncontracted 20s14p11d9f7g5h3i basis set was used for these calculations in order to provide a sufficiently saturated basis for each angular momentum.

For conventional CCSD and CCSD(T) correlation energies the expected $(L + b)^{-3}$ convergence is found (due to the presence of triplet pairs, $b \neq 1$, as a pure $(L + 1)^{-3}$ behavior holds for singlet pairs only). Using the CCSD(F12*) method (which is an accurate approximation to full CCSD-F12, cf. section 7.5), a nearly ideal $(L + 1)^{-7}$ behavior arises. Inserting the $\hat{T}_1 + \hat{T}_2$ amplitudes from this calculation into the conventional energy expression, eq 353, seems to give a close to converged E_5 contribution but the dominating E_4 contribution is not improved. The overall convergence is $(L + b)^{-3}$ (not shown in Figure 14); just like in the conventional case, but the total $E_{(T)}$ typically deviates further from the basis-set limit. The latter effect is possibly due to the $\hat{T}_2$ amplitudes' avoiding the cusp region in the presence of $\hat{T}_{2'}$. Adding the first part of the correction terms (not including the Z intermediate) improves the energy but leads to a $(L + 1)^{-5}$ behavior only. Only when Z is included, the $(L + 1)^{-7}$ convergence of F12 methods is recovered, leading to a run of the $E_{(T)}$ energy that is perfectly parallel to the CCSD(F12*) correlation energy. This also indicates that virtually all significant short-range contributions are recovered with ansatz, eq 358. Genuine three-electron coalescence seems hence to be of minor importance.

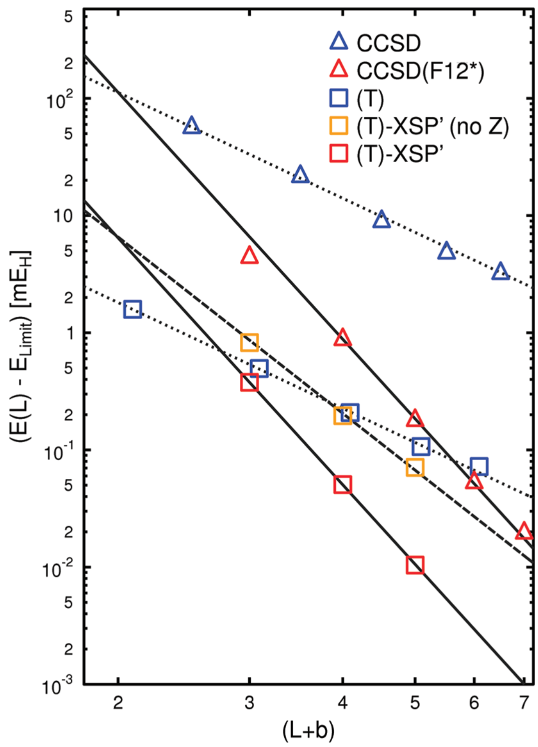

Figure 14. Basis-set convergence of the CCSD(T) correlation energy of the Ne atom. Double logarithmic plot of the deviations from the estimated basis-set limit as a function of $(L + b)$ for CCSD and CCSD(F12*) correlation energies (the latter is an accurate approximation to full CCSD-F12, cf. section 7.5) and for the (T) and (T)-XSP′ corrections (without and with contribution from the Z intermediate, see text). The conventional CCSD calculations fit best to $(L + 0.51)^{-3}$, while for the conventional (T) correction, $(L + 0.09)^{-3}$ is found. The F12 results, (T)-XSP′, show an $(L + 1)^{-7}$ behavior. Omitting the Z contribution from (T)-XSP′, however, reduces the rate of convergence to $(L + 1)^{-5}$. Reprinted with permission in part from ref 480. Copyright 2010 American Institute of Physics.

Effects of including $\hat{T}_{3'}$ are also present for reaction energies. Figure 15 provides a graphical representation based on the data from ref 480. While CCSD(F12*) in conjunction with the reoptimized cc-pVTZ-F12 basis set greatly outperforms conventional CCSD/aug-cc-pV6Z calculations (Figure 15, left), much of the gain is lost in the standard approach with a conventional (T) correction due to the rather inaccurate $E_{(T)}$ contributions (Figure 15, right, dotted curve). This shortcoming is significantly removed using the corrected expression, eq 360.

6.9. Multireference Methods

Most work on R12 or F12 theory has so far focused on single-reference theories, that is, a single determinant is assumed to be a proper zeroth-order description of the electronic state (see section 2),. This assumption breaks down for many open-shell cases, for instance, biradicals or transition metal compounds.

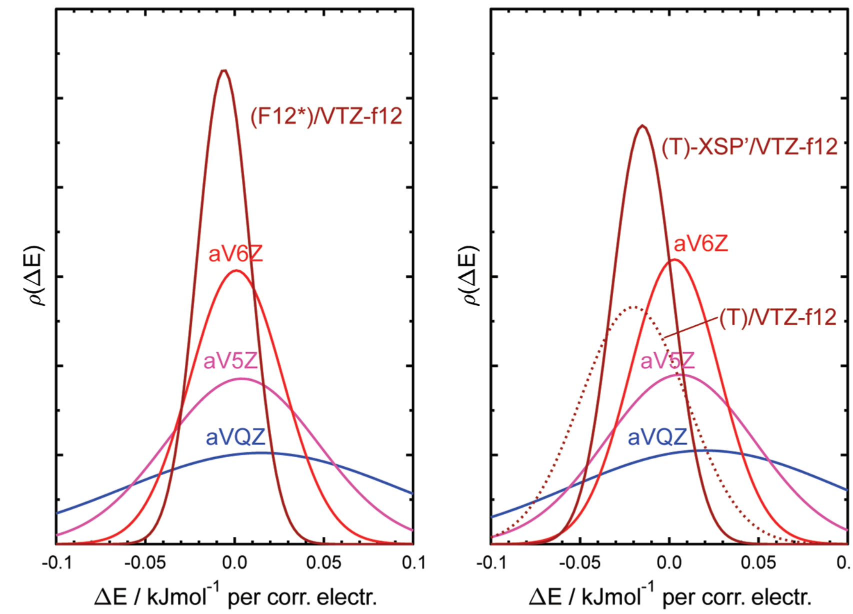

Figure 15. Basis-set error of the CCSD (left) and CCSD(T) (right) correlation contribution to reaction energies (adapted from ref 480, assuming Gaussian distributions). The error is normalized to the number of valence electrons. The curves labeled "aV*X*Z" refer to conventional calculations using the aug-cc-pV*X*Z basis sets; the F12 calculations were done with the CCSD(F12*) method (cf. section 7.5) and the cc-pVTZ-F12 basis set. "(T)" uses the conventional expression, eq 355, "(T)-XSP′" uses eq 360.

Hence, multireference methods are a necessary extension of the quantum chemist's toolbox, and as the problem of short-range correlations persists, the transfer of explicitly correlated techniques to such methods is desired. The field of explicitly correlated multireference methods is rather undeveloped, and work for modern F12 theory has only started recently. Below, we will start with a short historical overview of the developments followed by a more detailed description of the approaches.

6.9.1. Overview. Pioneering work in this area dates back to the 1990s when Gdanitz combined linear R12 theory and multireference configuration interaction (MRCI)[482−484] or the approximately size-extensive multireference averaged coupled-pair functional (MRACPF).[485] The standard approximation scheme was used to arrive at feasible working equations. A number of applications were reported, for example, calculation of atomic ground states and ionization potentials,[486] electron affinities,[487] as well as potential energy surfaces of N_2,[484] Be_2,[488] He_2,[46,489] Ne_2,[490] HF,[491] and the F+ H_2 $\rightarrow$ HF + H reaction.[492] Also, the valence excited states of CH_2 were investigated.[493]

One drawback of the approach was the use of an uncontracted basis which leads to difficulties in maintaining an orbital-invariant theory without running into serious numerical difficulties.[484,488] This problem can be solved in the framework of F12 theory using Slater-type geminals, as initially demonstrated by Ten-no[430] for the case of multireference MP2 (MRMP2).[494] Using the SP ansatz, the geminal contribution can be formulated in an internally contracted manner (see next section for details) which both is orbital invariant and numerically stable.

In the same spirit as Ten-no's ansatz, Torheyden and Valeev proposed a generalized perturbative correction to arbitrary wave functions, including MRCI wave functions as a particular example.[495] Their ansatz is applied to the complete wave function which on the one hand leads to a very general theory; on the other hand, the working equations scale with the sixth power of the *entire* orbital basis set, which renders the method rather expensive in practice.

Most recently, Shiozaki et al. extended the work of Ten-no within the context of internally contracted multireference expansions. These authors reported the implementation of CASPT2-F12[431] and MRCI-F12, also including the approximately size-consistent modifications MRACPF and MRAQCC.[432,433] Furthermore, Kedžuch et al.[496] recently developed an explicitly correlated multireference Brillouin−Wigner coupled-cluster singles and doubles method (MR BW-CCSD-F12) based upon the standard approximation.[496,497] First pilot applications were reported for a model system consisting of four hydrogen atoms and for the F_2 molecule.

For completeness, we note that Varganov and Martínez combined a CASSCF wave function with a Slater-type correlation factor.[498] No strong orthogonality projector was applied, and the structure of the theory is more related to Hylleraas-CI than to genuine F12 theory. Results were reported for two-electron systems only.

6.9.2. Details of the Theories. The starting point in multireference theories is the definition of a set of determinants which span the reference function $|\Psi_0\rangle$. All orbitals, which are occupied in at least one of these determinants, are called internal orbitals, and we will in the following use the indices i, j, k, ..., for these. A distinction of closed-shell orbitals (that is, doubly occupied for all reference determinants) and active orbitals (occupied for a subset of reference determinants) will not be necessary in the following. Usually the properly spin-coupled linear combinations, called configuration state functions (CSFs), are considered as the basic building blocks of the wave functions.

The uncontracted MRCI singles and doubles wave function can be represented as

$$|\Psi\rangle = |\Psi_0\rangle + |\Psi_i\rangle + |\Psi_s\rangle + |\Psi_d\rangle = \sum_{I_0} c^{I_0}|\Phi_{I_0}\rangle + \sum_I c^I|\Phi_I\rangle + \sum_{S,a} c_a^S|\Phi_S^a\rangle + \sum_{D,ab} c_{ab}^D|\Phi_D^{ab}\rangle \tag{363}$$

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Here, $|\Psi_0\rangle$ is the reference wave function (with c^{I_0} obtained from an MCSCF calculation), while $|\Psi_i\rangle$ collects all internal contributions to the correlated CI wave function. These consist of the CSFs $|\Phi_I\rangle$ which span the reference state and those which are generated by considering all single and double excitations from the former which remain within the internal orbital space. In the case of a complete active space, the set of CSFs spanning $|\Psi_i\rangle$ is identical to the one that spans the reference state $|\Psi_0\rangle$. $|\Psi_s\rangle$ consists of all singly external CSFs $|\Phi_S^a\rangle$, where S runs over all possibilities to create a hole in the reference functions and a denotes the virtual (external) orbital that is occupied instead. Similarly, $|\Psi_d\rangle$ consists of all doubly external CSFs $|\Phi_D^{ab}\rangle$. The respective coefficients can be evaluated variationally. Approximately size-extensive energies can be obtained either using the Davidson correction[499] or self-consistently using MRACPF[485] or variants thereof. Using intermediate normalization, $\langle\Psi_0|\Psi\rangle = 1$, the MRACPF energy functional is

$$\mathscr{F} = \frac{\langle\Psi|\hat{H} - E_0|\Psi\rangle}{1 + g_i\langle\Psi_i|\Psi_i\rangle + g_e(\langle\Psi_s|\Psi_s\rangle + \langle\Psi_d|\Psi_d\rangle)} \tag{364}$$

where the parameters are chosen as $g_i = 1$ and $g_e = 2/n$, n being the number of correlated electrons.

Explicitly correlated contributions are included, in line with the philosophy of R12 and F12 theory for single-reference methods, by augmenting the expansion eq 363 with a term containing the geminal contribution. The original ansatz of Gdanitz is[482,483]

$$|\psi_{d'}\rangle = \sum_K \sum_{(ij)_K} \sum_{k>l} c_{kl}^{(ij)_K,K} \sum_{\alpha>\beta} \bar{w}_{\alpha\beta}^{kl} a_{(ij)_K}^{\alpha\beta} |\Phi_K\rangle \tag{365}$$

The index K enumerates all reference determinants (indeed determinants rather than CSFs are considered here), k, l run over all internal orbitals, while the pair of internal orbitals $(ij)_K$ is restricted to those occupied in determinant $|\Phi_K\rangle$. The matrix element over the correlation factor is defined as

$$\bar{w}_{\alpha\beta}^{ij} = \langle\alpha\beta|(1 - \hat{V}_1\hat{V}_2)r_{12}|ij\rangle \tag{366}$$

which ensures that all configurations created by eq 365 are orthogonal to those of the conventional expansion, eq 363.

A fully orbital invariant implementation of the method is difficult as it requires optimization of $c_{kl}^{(ij)_K,K}$. This, however, is hampered by near linear dependencies.[484] In actual calculations only unitary invariance between subsets of orbitals is considered, where for a given i, j only those k, l are taken into account which form corresponding antibonding or bonding orbitals. The idea is to maintain unitary invariance for orbital pairs that describe bond breaking.[484] Alternative schemes were considered as well, for instance, "contracted geminals", where the coefficients $c_{kl}^{(ij)_I,I}$ were obtained by first-order perturbation theory.[488]

With Slater-type correlation factors, the complications arising for an unitary invariant formulation can be circumvented by making use of the SP ansatz. For the MRMP2 method,[494] Ten-no considered the following contracted ansatz for the additional explicitly correlated terms[430]

$$|\psi_{d'}\rangle = \sum_{\substack{i>j \\ \alpha>\beta}} w_{\alpha\beta}^{ij} a_{ij}^{\alpha\beta} \sum_K c^K|\Phi_K\rangle \tag{367}$$

In this equation, the expansion of the reference function in terms of determinants $|\Psi_0\rangle = c^K|\Phi_K\rangle$ was used in order to emphasize the internally contracted nature of the ansatz. Note that otherwise the MRMP2 method is based on an uncontracted expansion, which has the same principle structure as given in eq 363.

The further derivation of the energy expressions in Ten-no's work includes the assumptions of the standard approximation, in particular, the EBC, eq 259. In addition, the B matrix was restricted to approximation A. This leads to a very simple energy expression for the F12 correction

$$\Delta E = \sum_{\substack{i>j \\ k>l}} \gamma_{kl}^{ij}(B_{ij}^{kl} + 2V_{ij}^{kl}) \tag{368}$$

where $\gamma_{ij}^{kl} = \langle\Psi_0|a_{ij}^{kl}|\Psi_0\rangle$ is the internal part of the reduced two-particle density matrix of the reference state. The intermediates B and V are just the obvious generalizations of the single-reference case with the index range extended to all internal orbitals.

In close analogy to the above ansatz, Torheyden and Valeev proposed a perturbative correction denoted $[2]_{\text{F12}}$ that is applicable to arbitrary wave functions.[495] The ansatz is constructed from the entire conventional wave function $|\Psi\rangle$, for example, a MRCI wave function, as defined above. It reads

$$|\psi_{d'}\rangle = \sum_{\substack{p>q \\ r>s}} c_{rs}^{pq} \sum_{\kappa>\lambda} \hat{S}\tilde{w}_{\kappa\lambda}^{rs} \tilde{a}_{pq}^{\kappa\lambda}|\Psi\rangle \tag{369}$$

where κ, λ, ... run over the entire formally complete orbital space and $\tilde{a}_{pq}^{\kappa\lambda} = a_{pq}^{\kappa\lambda} - a_p^r\gamma_q^\lambda\delta_r^\kappa + a_q^r\gamma_p^\lambda\delta_r^\kappa + a_p^r\gamma_q^\kappa\delta_r^\lambda - a_q^r\gamma_p^\kappa\delta_r^\lambda + \gamma_{pq}^{rs}(\delta_r^\kappa\delta_s^\lambda - \delta_s^\kappa\delta_r^\lambda)$ is the generalized normal ordered excitation operator, as defined by Kutzelnigg and Mukherjee.[500] γ_p^r and γ_{pq}^{rs} are the reduced one- and two-particle density matrices of $|\Psi\rangle$.

The matrix elements over the correlation factor $\tilde{w}_{\kappa\lambda}^{rs}$ are defined as in single-reference theory but with a projector $\hat{Q}_P = 1 - \hat{P}_1\hat{P}_2$ (which effectively removes those parts which are already covered by the wave function $|\Psi\rangle$). The additional projector

$$\hat{S} = 1 - \sum_{st\alpha_\perp} a_s^{\alpha_\perp}|\Psi\rangle(\gamma^{-1})_{st}\langle\Psi|a_{\alpha_\perp}^t \tag{370}$$

projects out those configurations which are only single excitations with respect to $|\Psi\rangle$; the necessary inverse of the metric can be expressed by γ^{-1}, the inverse of the one-particle density matrix.

In the further derivation of explicit expressions a number of approximations are made, mainly inspired by the standard approximation (denoted "screening approximations" by Valeev). In addition, the contributions from three- and four-particle reduced density matrices are approximated by lower-order cumulants.[501] A Hylleraas functional can be formulated that allows one to solve for the expansion coefficients in eq 369, c_{rs}^{pq}, or to evaluate the energy taking advantage of the SP ansatz. With this an energy expression for the correction term is obtained that bears some resemblance with Ten-no's formula, eq 368. However, the approximations employed by Torheyden and Valeev go beyond approximation A. The $[2]_{\text{F12}}$ correction then becomes

$$\Delta E = \sum_{\substack{p>q \\ r>s}} \left(\gamma_{rs}^{pq}\tilde{B}_{pq}^{rs} - \phi_{rs}^{pq}\tilde{X}_{pq}^{rs} + 2\gamma_{rs}^{pq}\tilde{V}_{pq}^{rs}\right) \tag{371}$$

For details of the definitions of the modified intermediates $\tilde{B}$, $\tilde{X}$, and $\tilde{V}$ we refer to the original article.[495] We only note that the definition of $\tilde{B}$ builds upon approximation C but includes some further terms from the cumulant expansion. The matrix elements ϕ_{rs}^{pq} contain products of the Fock matrix and cumulants.

The main difference from eq 368, however, lies in the summation over the complete computational basis (instead of internal orbitals). Hence, the expressions scale with the sixth power of the entire orbital basis set, which is rather expensive. Consequently, only results for small basis sets have been reported.[495]

A more compact representation of the CI wave function is obtained by use of internally contracted schemes. The approach of Werner and Knowles uses the following CI wave function[502]

$$|\Psi_{\mathrm{CI}}\rangle = \sum_{I_0} c^{I_0}|\Phi_{I_0}\rangle + \sum_{I} c^{I}|\Phi_{I}\rangle + \sum_{S,a} c_a^S|\Phi_S^a\rangle + \sum_{\substack{p,i>j\\a>b}} c_{ab}^{ij,p}|\Phi_{ij,p}^{ab}\rangle \tag{372}$$

In contrast to the uncontracted wave function, eq 363, contracted doubly external configurations $|\Phi_{ij,p}^{ab}\rangle = E_{ij,p}^{ab}|\Psi_0\rangle$ are employed. The E_i^a are spin-free excitation operators (summed over spin, $E_i^a = a_{i\alpha}^{a\alpha} + a_{i\beta}^{a\beta}$), and orthogonally spin-adapted double excitations are obtained as $E_{ij,+1}^{ab} = (1 + \delta_{ij})^{-1}(E_i^aE_j^b + E_j^aE_i^b)$ and $E_{ij,-1}^{ab} = E_i^aE_j^b - E_j^aE_i^b$.

Shiozaki et al. recently presented an implementation of CASPT2-F12[431] and MRCI-F12[432,433] based on the above ansatz which is augmented by

$$t|\psi_{d'}\rangle = t(\hat{Q}_P + \hat{Q}_S)[\sum_{\substack{p,i>j\\\alpha>\beta}} \tilde{w}_{\alpha\beta}^{ij,p}E_{ij,p}^{\alpha\beta} + \sum_{i,\alpha,j,m} \tilde{w}_{\alpha m}^{ij}E_{ij}^{\alpha m}]|\Psi_0\rangle \tag{373}$$

t is a global scaling factor, see below, and

$$\tilde{w}_{\alpha\beta}^{ij,p} = r_{\alpha,\beta}^{i,j} + pr_{\alpha,\beta}^{j,i} \tag{374}$$

$$\tilde{w}_{\alpha m}^{ij} = r_{\alpha,m}^{i,j} \tag{375}$$

where $r_{\alpha,\beta}^{i,j}$ is the integral over the correlation factor including the rational generator but *without* antisymmetrization. The projector $\hat{Q}_P$ removes $\tilde{w}_{ab}^{ij}$ contributions, and $\hat{Q}_S$ removes the single-excitation contributions but allows for semi-internal doubles

$$\hat{Q}_S = |\Phi_S^{\alpha_\perp}\rangle\langle\Phi_S^{\alpha_\perp}|\left[1 - E_i^{\alpha_\perp}|\Psi_0\rangle(\gamma^{-1})_{ij}\langle\Psi_0|E_{\alpha_\perp}^j\right] \tag{376}$$

The intermediates that result from the doubly external geminal, eq 374, resemble those of the single-reference theory, with occupied indices replaced by all internal indices. The additional semi-internal geminal contribution gives rise to additional terms, which can be evaluated by direct expansion in the CABS.

The working equations for MRCI-F12 can be derived from the Lagrange functional

$$L = \frac{\langle\Psi CI|\hat{H}|\Psi_{CI}\rangle + 2\langle\Psi CI|\hat{H}|\psi_{d'}\rangle t + \langle\Psi_{d'}|\hat{H}|\psi_{d'}\rangle t^2}{(\langle\Psi_{CI}|\Psi_{CI}\rangle + \langle\psi_{d'}|\psi_{d'}\rangle t^2)} + 2\lambda(\langle\Psi_0|\Psi_{CI} + \psi_{d'}\rangle - 1) \tag{377}$$

In order to enforce the cusp conditions, one must set $t = 1$. In this case the Lagrange multiplier λ takes care of the intermediate normalization with respect to $|\Psi_0\rangle$. If t is used as a variation parameter, λ can be set to zero and one obtains the usual CI eigenvalue problem. In general, the variation of t is problematic as this scaling is global and hence violates size consistency. For CI theories, however, pragmatic considerations render this option acceptable, as it significantly facilitates the theory, particularly if more than one state is considered at a time (see refs 432 and 433).

The coupling terms $\langle\Psi_{\mathrm{CI}}|\hat{H}|\Psi_{d'}\rangle$ can be evaluated along the same lines as in single-reference theory. The analogous intermediates occur in conjunction with the appropriate coupling coefficients from CI theory. For the geminal–geminal part, $\langle\Psi_{d'}|\hat{H}|\Psi_{d'}\rangle$, the same efficiency considerations emerge as for coupled-cluster theory (see section 7). In this respect, the work of Shiozaki et al. sticks to the F12b scheme (section 7.3), which features nearly vanishing computational overhead as compared to the conventional implementation.

In Table 13 some sample results from ref 432 are collected which demonstrate the use of the approach. Comparison with the CASSCF convergence shows that the remaining error is dominated by the basis-set incompleteness in the underlying reference function. A scheme analogous to the CABS singles correction (section 6.7) was not considered in that work; a possible second-order correction was recently proposed by Kong and Valeev[472] (see section 6.7).

7. COMPUTATIONALLY EFFICIENT FORMULATIONS

As detailed above, explicitly correlated methods with linear and Slater-type correlation factors by now have a rather long history, but they have only recently started to become standard tools in quantum chemistry. This is mainly owing to their higher complexity in comparison to conventional orbital expansions, which required a series of developments in order to arrive at computationally efficient implementations.

Certainly, the main development target is coupled-cluster theory, since for these methods, CCSD(T) in particular, basis-set errors determine the accuracy and the need for extremely large basis sets significantly reduces the range of applicability.[67,70,503] One of the main obstacles in formulating and implementing a CCSD-F12 method, as compared to MP2-F12, is the large number of extra terms that occur in a straightforward expansion.[367,438] Initial implementations of CCSD-R12[366,371] were therefore based on the standard approximation which leads to significant reductions in the number of terms.[337] Extensions of this approach to Slater-type correlation factors were reported in more recent works.[29,435,504] A full implementation in the CABS formalism that takes care of all terms has only recently been achieved using automated implementation techniques.[422,505,506]

A perturbational analysis, however, shows that only a limited number of terms contribute significantly (section 7.1). This analysis may serve as a posthoc justification of the various approximations to full CCSD-F12 that have been suggested in the past years and which we will discuss subsequently, including a comparison of the working equations in section 7.6.

Alongside this, there have been a number of further important developments such as density fitting techniques (section 7.7) and local correlation methods (section 7.8) which originally have been worked out for conventional methods. For F12 methods these ideas seem to both work better and have an even larger impact on computational efficiency than for traditional methods. F12 methods are particuarly well suited to localization techniques.

A final issue is basis sets, as detailed in section 7.9. The success of the auxiliary basis-set approaches was mainly that one could avoid the use of the specialized (and in fact large) basis sets that are required for the standard approximation. Being able to use the basis sets established for conventional calculations made possible direct comparisons of conventional and F12 methods and has certainly contributed to the acceptance of F12 methods. It was then recognized, however, that F12 methods can give more accurate results for a basis set of a given size if reoptimized exponents are used (see section 7.9.1). Similarly, the issue of developing optimal auxiliary basis sets for the RI and density fitting helped to improve the efficiency of calculations (sections 7.9.2 and 7.9.3).

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Table 13. Spectroscopic Constants of OH, C_2, and O_2 As Calculated with MRCI and MRCI-F12 Wave Functions (including the Davidson correction) and the aug-cc-pVXZ Basis Sets (abbreviated as aVXZ)[a]

molecule, state	CASSCF	MRCI	MRCI-F12	CASSCF	MRCI	MRCI-F12	CASSCF	MRCI	MRCI-F12
OH, $X^2\Pi$		r_e (expt. 0.970)			ω_e (expt. 3737.8)			D_e (expt. 106.6)	
aVDZ	0.980	0.980	0.972	3700.3	3685.4	3725.8	95.8	99.4	104.6
aVTZ	0.975	0.974	0.972	3714.0	3711.3	3725.5	96.7	104.5	106.4
aVQZ	0.974	0.971	0.971	3723.1	3729.8	3733.2	96.9	106.2	107.0
aV5Z	0.973	0.971	0.971	3724.8	3733.4	3734.2	96.9	106.7	107.1
CBS[56]		0.971			3734.9			107.1	
C_2, $X^1\Sigma_g^+$		r_e (expt. 1.243)			ω_e (expt. 1854.7)			D_e (expt. 146 ± 3)	
aVDZ	1.267	1.274	1.262	1843.2	1800.7	1844.2	139.0	128.3	137.9
aVTZ	1.255	1.253	1.248	1839.1	1828.9	1844.5	142.5	139.4	143.0
aVQZ	1.254	1.248	1.246	1841.7	1843.6	1850.2	143.2	142.8	144.3
aV5Z	1.253	1.247	1.246	1842.2	1847.9	1851.2	143.3	143.7	144.5
CBS[56]		1.246			1851.1			144.6	
O_2, $X^3\Sigma_g^-$		r_e (expt. 1.208)			ω_e (expt. 1580.2)			D_e (expt. 120.6)	
aVDZ	1.221	1.225	1.215	1542.8	1536.3	1575.2	91.2	107.5	114.9
aVTZ	1.218	1.217	1.213	1536.5	1550.0	1567.4	94.4	115.1	118.3
aVQZ	1.215	1.212	1.210	1547.8	1571.9	1579.8	95.1	118.1	119.6
aV5Z	1.215	1.211	1.210	1548.1	1575.9	1580.3	95.1	118.9	119.7
CBS[56]		1.210			1581.2			119.7	

[a] Bond lengths r_e are given in Angstroms, harmonic frequencies in cm^{-1}, and dissociation energies in kcal/mol. CBS[56] denotes the X^{-3} basis-set extrapolation of the conventional result. All values taken from ref 432.

7.1. Perturbational Analysis

The analysis[438] is based on the following partitioning of the (normal-ordered) Hamiltonian

$$\hat{H} = E_{\mathrm{HF}} + \hat{F}_N^{(0)} + \hat{F}_N^{(1)} + \hat{\Phi}_N^{(1)} \tag{378}$$

where the superscripts denote the formal order, $E_{\mathrm{HF}} = \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle$ the Hartree–Fock energy, $\hat{F}_N$ the Fock operator, and $\hat{\Phi}_N$ the fluctuation potential. The zeroth- and first-order Fock operators $\hat{F}_N^{(0)}$ and $\hat{F}_N^{(1)}$, respectively, correspond to those in eq 283. A number of alternative partitionings have been considered by Noga et al.[466] The first-order part is further subdivided into a part that lies within the orbital basis set and a part that couples the occupied orbitals and the complementary space

$$F^{(1)} = \sigma F^{(\sigma)} + \tau F^{(\tau)} \tag{379}$$

$$= \sigma \sum_{ai} (f_a^i a_i^a + f_i^a a_a^i) + \tau \sum_{\alpha_\perp i} (f_{\alpha_\perp}^i a_i^{\alpha_\perp} + f_i^{\alpha_\perp} a_{\alpha_\perp}^i) \tag{380}$$

More importantly, the fluctuation potential is split into three parts with strength parameters λ, μ, and ν

$$\hat{\Phi}_N^{(1)} = \lambda \hat{\Phi}_N^{(\lambda)} + \nu \hat{\Phi}_N^{(\nu)} + \mu \hat{\Phi}_N^{(\mu)} \tag{381}$$

with

$$\hat{\Phi}_N^{(\mu)} = \sum_{\substack{p>r\\ q>s}} g_{pr}^{qs} a_{qs}^{pr} \tag{382}$$

$$\hat{\Phi}_N^{(\nu)} = \sum_{\substack{p,\gamma_\perp\\ q>s}} (g_{p\gamma_\perp}^{qs} a_{qs}^{p\gamma_\perp} + g_{qs}^{p\gamma_\perp} a_{p\gamma_\perp}^{qs}) \tag{383}$$

$$\hat{\Phi}_N^{(\mu)} = \text{the remainder} \tag{384}$$

The idea behind this additional partitioning is that the different parts of the first-order Hamiltonian give rise to perturbations of different "strength". The perturbation associated with λ remains within the finite orbital basis set and gives rise to the major part of correlation effects. The parts associated with μ and ν lead to the correction terms for the incompleteness of the finite orbital basis set. While $\hat{\Phi}^{(\mu)}$ leads to integrals with nontruncating partial wave expansions, the integrals due to $\hat{\Phi}_{(\nu)}^N$ will, in the atomic case, truncate at some finite angular momentum $L = 3L_{\max}$, where $L_{\max}$ is the maximum angular momentum contained in the finite orbital basis set.

Perturbation theory immediately gives that $\hat{T}_2$ is first order in λ. The part of $\hat{T}_{2'}$ that completely excites into the complementary space is first order in μ

$$\hat{T}_{2'}^{(\mu)} = \sum_{\substack{i>j\\ \alpha_\perp>\beta_\perp}} w_{\alpha_\perp\beta_\perp}^{ij} a_{ij}^{\alpha_\perp\beta_\perp} \tag{385}$$

while the remainder is first order in ν

$$\hat{T}_{2'}^{(\nu)} = \sum_{\substack{i>j\\ a\beta_\perp}} w_{a\beta_\perp}^{ij} a_{ij}^{a\beta_\perp} \tag{386}$$

Likewise, T_1 and $T_{1'}$ are first order in σ and τ, respectively.

Furthermore, the CCSD-F12 Lagrange functional

$$L = E_{\text{CCSD-F12}} + \sum_{\mu_1} \lambda_{\mu_1} \Omega_{\mu_1,\text{CCSD-F12}} + \sum_{\mu_2} \lambda_{\mu_2} \Omega_{\mu_2,\text{CCSD-F12}} + \sum_{\mu_{2'}} \lambda_{\mu_{2'}} \Omega_{\mu_{2'},\text{CCSD-F12}} \tag{387}$$

can be defined, where $E_{\text{CCSD-F12}}$ is the energy expression, eq 324, augmented with the residuals $\Omega_{\mu_i,\text{CCSD-F12}}$, eqs 325−327, as constraints and corresponding Lagrange multipliers λ_{μ_i}. The Lagrange multipliers have the same leading order in perturbation theory as the corresponding cluster operators. Thus, each term of eq 387 can be assigned an order of the general form $\sigma^s\tau^t\lambda^l\mu^m\nu^n$. We now can classify the terms according to the following three criteria.

1 The total order in perturbation theory, $s + t + l + m + n$.
2 The order of the geminal correction, $m + n$.
3 The order in strong coupling to the complementary space, m, leading to the terms present with ansatz 1 (or in the standard approximation).

Formally, the relative importance of the terms should decrease with increasing order, and they should decrease faster for weak perturbations like $\hat{\Phi}_N^{(\nu)}$. The validity of this assumption has also been demonstrated numerically.[438] Here, we will discuss an explicit example, as given in Table 14. The numbers are based on ref 438, where the entire CCSD-F12 Lagrange functional was evaluated perturbatively using the t_a^i and t_{ab}^{ij} amplitudes of a preceding conventional CCSD calculation.

The analysis shows that the most significant F12 contributions come from second- and third-order terms and from the terms that survive under the assumptions of the standard approximation. This observation basically explains the success of the truncated methods described in the subsequent sections.

In addition, Table 14 is divided into "(F12) terms" and terms "beyond (F12)" which will become more clear in the next section. Here, we only note that the terms "beyond (F12)" can be large individually but cancel very systematically (in particular, the third-order "ladder" and "ring" terms, which correspond to the P and Z intermediate (see section 6.3)). In particular, for larger basis sets their contributions to total correlation energies and reaction energies becomes negligibly small.

Table 14. Analysis of F12 Contributions for the Total CCSD Correlation Energy E_c of F_2O (limit − 865.13 mE_h) and the CCSD Correlation Energy Contribution ΔE_c to the Reaction $F_2O + CF_2 \rightarrow 2\ F_2 + CO$ (limit − 10.9 kJ mol^{-1})^a

order	E_c/mE_h cc-pVDZ-F12	E_c/mE_h cc-pVTZ-F12	ΔE_c/kJ mol^{-1} cc-pVDZ-F12	ΔE_c/kJ mol^{-1} cc-pVTZ-F12
conv.	−701.02	−803.22	−29.81	−18.96
(F12) terms				
μ^2	−154.74	−69.27	11.60	5.43
$\lambda\nu$	−9.27	−3.58	3.47	1.65
$\lambda\mu^2$	34.75	22.20	1.58	0.28
$\lambda\nu^2$	−10.87	−3.85	−0.41	0.59
$\sigma\mu^2$	1.50	0.59	−2.12	−0.80
third order (rem.)	−0.13	0.01	0.00	−0.02
$\lambda^2\mu^2$	6.21	2.66	1.24	0.53
fourth order (rem.)	0.51	0.14	−0.28	−0.17
fifth order (rem.)	0.00	0.00	0.00	0.00
sum conv + (F12)	−833.08	−854.32	−14.73	−11.46
beyond (F12)				
μ^3 (ladder)	39.97	12.34	−3.36	−0.99
μ^3 (ring)	−46.95	−13.21	4.91	1.47
$\lambda^2\mu^2$	1.78	0.52	−0.26	−0.06
Rem.	0.48	0.05	−0.18	−0.03
sum beyond (F12)	−4.72	−0.30	1.12	0.38

^{a} Adapted from the data sets underlying ref 438.

7.2. CCSD(F12)

The CCSD(F12) approximation was first considered for linear R12 theory and described in the work of Fliegl et al.;[418,419] the generalization to F12 theory was later reported by Tew et al.;[420] a variant of CCSD(F12) using numerical quadrature was published by Bokhan et al.[397]

The reasoning for the approximation is as follows: the fluctuation potential $\hat{\Phi}_N$ and the $T_{2'}$ amplitudes are considered first order. On the basis of this classification all terms are removed from the full CCSD-F12 equations which are higher than second order. The working equations are hence (cf. the full CCSD-F12 equations, eq 324−327)

$$E_{\text{CCSD(F12)}} = E_{\text{CCSD}} + \langle \text{HF}|[\tilde{\tilde{H}}, \hat{T}_{2'}]|\text{HF}\rangle \tag{388}$$

$$0 = \Omega_{\mu_1,\text{CCSD}} + \langle \mu_1|[\tilde{\tilde{H}}, \hat{T}_{2'}]|\text{HF}\rangle \tag{389}$$

$$0 = \Omega_{\mu_2,\text{CCSD}} + \langle \mu_2|[\tilde{\tilde{H}}, \hat{T}_{2'}] + [[\hat{\Phi}_N, \hat{T}_2], \hat{T}_{2'}]|\text{HF}\rangle \tag{390}$$

$$0 = \langle \mu_{2'}|\tilde{\tilde{\Phi}}_N + [\hat{F}_N, \hat{T}_{2'}] + [\tilde{\tilde{H}}, \hat{T}_2]|\text{HF}\rangle \tag{391}$$

with E_{CCSD} denoting the conventional energy expression and $\Omega_{\mu_1,\text{CCSD}}$ and $\Omega_{\mu_2,\text{CCSD}}$ as a short cut for the conventional residuals.

The (F12) approximation effectively removes all terms nonlinear in $\hat{T}_{2'}$ and the terms arising from $\langle\mu_2|[\Phi_N, T_{2'}]|\text{HF}\rangle$. In comparison to MP2-F12 theory, no new types of special F12 intermediates occur, except for the V intermediate which is generalized to V_{pq}^{ij} to include contributions of $T_{2'}$ to the μ_2 residual and vice versa.

The overall computational scaling of CCSD(F12) is $\mathcal{N}^6$, i.e., the same as for conventional CCSD. This has to be contrasted with the situation for MP2-F12 (which has a less favorable scaling than conventional MP2) and full CCSD-F12: The latter requires, if the geminal coefficients are optimized, noniterative $\mathcal{N}^7$ and $\mathcal{N}^8$ steps.[371,438] Nevertheless, CCSD(F12) still requires in each iteration evaluation of computationally demanding terms which scale with O^3V^2X, where O, V, and X are the number of occupied, virtual, and auxiliary basis orbitals, respectively. Hence, a single iteration usually takes 3−5 times longer than in a conventional calculation.

The iterative cost can be reduced by the SP ansatz.[423] The energy is then obtained from the modified energy functional (see also eqs 329 and 330)

$$E_{\text{CCSD(F12)-SP}} = E_{\text{CCSD}} + \langle \text{HF}|[H, \hat{T}_{2'}]|\text{HF}\rangle + \sum_{i>j} \langle {}^{ij}_{ij}|\tilde{\tilde{\Phi}}_N + [\hat{F}_N^{(0)}, \hat{T}_{2'}] + [\tilde{\tilde{H}}, \hat{T}_2]|\text{HF}\rangle \tag{392}$$

while the set of equations reduces to those originating from the projections onto the conventional excitation manifold, eqs 389 and 390. However, there still remains one O^3V^2X scaling term which in comparison to conventional CCSD causes a factor of 2−3 in each iteration.

The SP ansatz induces only negligible loss in accuracy, particularly for relative energies, as shown in Table 15. At the

Table 15. Basis Set Error Statistics for the CCSD Correlation Contribution to Reaction Energies over a Set of 53 Reactions (kJ mol^{-1} per valence electron)[a]

	conv.			(F12)		(F12)-SP	
basis	mean	σ	basis	mean	σ	mean	σ
cc-pVDZ	−0.95	0.86					
cc-pVTZ	−0.26	0.29	cc-pVDZ-F12	−0.07	0.09	−0.10	0.08
cc-pVQZ	−0.07	0.10	cc-pVTZ-F12	−0.01	0.02	−0.01	0.01
cc-pV5Z	−0.03	0.05	cc-pVQZ-F12	0.00	0.00	0.00	0.00

[a] Adapted from ref 425.

same time, it is numerically significantly more stable and avoids the geminal basis-set superposition error.[448]

7.3. CCSD-F12a and CCSD-F12b

Keeping only the leading order F12 corrections and a strict avoidance of all cost-intensive terms is the basic idea behind the CCSD-F12x (x = a, b) methods of Werner and co-workers.[427,428] In fact, these authors were the first to demonstrate the potential of F12 to enhance the accuracy of the underlying methodology without a significant increase in computation time.

One of the ingredients of their method is the fixed amplitude approximation (SP ansatz), as described above. As an alternative, they also considered fixed coefficients c_{kl}^{ij} determined by a preceding MP2-F12 step. The energy functional is either

$$E_{\mathrm{F12}a} = E_{\mathrm{CCSD}} + \langle \mathrm{HF}|[\hat{\Phi}_N, T_{2'}]|\mathrm{HF}\rangle + \sum_{i>j} \langle_{ij}^{ij}|\hat{\Phi}_N + [\hat{F}_N, \hat{T}_{2'} + \hat{T}_2]|\mathrm{HF}\rangle \tag{393}$$

which constitutes the CCSD-F12a variant or

$$E_{\mathrm{F12b}} = E_{\mathrm{CCSD-F12a}} + \sum_{i>j} \langle_{ij}^{ij}|\hat{Q}_{12}^{(0)}\{(\tilde{\Phi}_N - \hat{\Phi}_N) + [\tilde{\hat{\Phi}}_N, \hat{T}_2]\}|\mathrm{HF}\rangle \tag{394}$$

which is the CCSD-F12b variant. Here, we used the projector $\hat{Q}_{12}^{(0)} = 1 - \hat{P}_1\hat{P}_2$ to indicate two important approximations in the F12x approach: First, this projector selects only the standard approximation terms, and second, the V intermediate will be calculated according to the approximate form, cf. eq 276

$$V_{pq}^{ij} = v_{pq}^{ij} - \sum_{r>s} r_{rs}^{ij} g_{pq}^{rs} \tag{395}$$

which effectively avoids the need to calculate two-electron repulsion integrals with two virtual and one CABS index. Note that for the V_{kl}^{ij} contributions occurring in eq 393 the above approximation is not used.

The residual functions for both variants, CCSD-F12a and CCSD-F12b, are the same. They can be written in short-hand as

$$0 = \Omega_{\mu_1,\mathrm{CCSD}} + \langle \mu_1|[\hat{\Phi}_N, \hat{Q}_{12}^{(0)}\hat{T}_{2'}]|\mathrm{HF}\rangle \tag{396}$$

$$0 = \Omega_{\mu_2,\mathrm{CCSD}} + \langle \mu_2|[\hat{\Phi}_N, \hat{Q}_{12}^{(0)}\hat{T}_{2'}] + [[\hat{\Phi}_N, \hat{T}_1], \hat{Q}_{12}^{(0)}\hat{T}_{2'}]|\mathrm{HF}\rangle \tag{397}$$

Comparing with the equations for CCSD(F12), eqs 388−391, it becomes apparent that CCSD-F12x is a subset of the latter, but numerical experience shows that these terms indeed have the biggest effect on improving CCSD toward the basis-set limit.

This is clearly reflected in Table 16: In comparison to the conventional results, both CCSD-F12a and F12b significantly reduce the error in, for example, reaction energies. For double- and triple-ζ basis sets, both methods perform equally well, whereas for larger basis sets the CCSD-F12a results deteriorate due to the method's tendency to overshoot the basis-set limit.

7.4. CCSD(2)$_{\overline{\mathrm{F12}}}$

In a series of papers, Valeev and co-workers worked out a slightly different approach to adding explicitly correlated terms to coupled-cluster calculations.[421,507,508] Instead of extending the CCSD equations with geminal dependent terms, an a posteriori correction is formulated, based on a Löwdin partitioning of the CCSD similarity transformed Hamiltonian. The resulting model was called CCSD(2)$_{\mathrm{F12}}$ or CCSD(2)$_{\overline{\mathrm{F12}}}$ if the SP ansatz is used. If, in addition, a noniterative correction for the effect of connected triples clusters is applied, the naming changes to CCSD(T)$_{\mathrm{F12}}$. We note that Valeev uses the names CCSD(2)$_{\mathrm{R12}}$, CCSD(T)$_{\mathrm{R12}}$, etc., irrespective of the actual correlation factor in use, but for consistency we prefer to write "F12" whenever Slater-type correlation factors are employed.

In the derivation of the theory, the similarity transformed Hamiltonian matrix

$$\overline{H}_{\mu\nu} = \langle \mu|e^{-\hat{T}_1 - \hat{T}_2}\hat{H}e^{\hat{T}_1 + \hat{T}_2}|\nu\rangle \tag{398}$$

is partitioned by defining an internal and an external space. The former consists of the reference state and the singles and doubles excitation manifold, $\{|\mathrm{HF}\rangle, |\mu_1\rangle, |\mu_2\rangle\}$, while the external space includes only either the geminal doubles $\{|\mu_{2'}\rangle\}$ or the geminal doubles and some higher excitations if, for example, the derivation of the (T) correction is considered at the same time.[421] The two spaces impose a block structure on $\overline{H}$ which now is written as a zeroth- and first-order part

$$\overline{H} = \begin{pmatrix} \overline{H}_{PP} & 0 \\ 0 & \overline{H}_{QQ}^{(0)} \end{pmatrix} + \begin{pmatrix} 0 & \overline{H}_{PQ} \\ \overline{H}_{QP} & \overline{H}_{QQ}^{(1)} \end{pmatrix} \tag{399}$$

The zeroth-order part of the external block is $\overline{H}_{QQ}^{(0)} = \langle \mu_{2'}|\hat{F}_N + E^{(0)}|\mu_{2'}\rangle$, where $E^{(0)}$ the zeroth-order energy which equals the CCSD energy. Perturbation theory gives the first nonvanishing energy correction at second order according to

$$E^{(2)} = -\Lambda_P^{(0)}\overline{H}_{PQ}(\hat{H}_{QQ}^{(0)} - E^{(0)}S_{QQ})^{-1}\overline{H}_{QP}R_P^{(0)} \tag{400}$$

The $E^{(0)}S_{QQ}$ term in the denominator cancels the respective energy shift in the definition of $\overline{H}_{QQ}^{(0)}$, and we are hence left with determining the inverse of $B_{mn}^{kl} - (\varepsilon_i + \varepsilon_j)X_{mn}^{kl}$ just like in MP2-F12 theory. On expanding the zeroth-order left and right eigenvectors $\Lambda^{(0)}$ and $R^{(0)}$ one obtains $\Lambda_P^{(0)}\overline{H}_{PQ} = \langle \mathrm{HF}|\overline{H}|\mu_{2'}\rangle + \langle \Lambda|H|\mu_{2'}\rangle$ and $\overline{H}_{QP}R_P^{(0)} = \langle \mu_{2'}|\overline{H}|\mathrm{HF}\rangle$. In addition, a number of further approximations are made: In particular, only the standard approximation terms are retained, including the extended Brillouin condition, eq 259. The necessary F12 intermediates, however, are evaluated fully for ansatz 2, including all CABS contributions (at variance to the approach taken for CCSD-F12x). All singles contributions are neglected, and the Lagrange multipliers Λ are approximated by the T amplitudes. In a recent modification of the approach[349] the use of the EBC was abandoned,

Table 16. RMS Basis Set Errors of CCSD and CCSD-F12x Reaction Energies of Closed-Shell Molecules (REc) and Open-Shell Molecules (REo) as well as Atomization Energies (AE), Ionization Potentials (IP), and Electron Affinities (EA)[a]

method	basis	REc/kJ mol^{-1}	REo/kJ mol^{-1}	AE/kJ mol^{-1}	IP/meV	EA/meV
CCSD	aVDZ	18.74	51.97	80.49	245.72	177.76
	aVTZ	6.80	18.65	24.94	98.10	72.18
	aVQZ	2.46	6.71	8.84	40.10	28.00
	aV5Z	1.23	3.09	4.17	20.54	14.64
CCSD-F12a	aVDZ	2.68	4.68	7.03	51.96	34.93
	aVTZ	1.28	1.29	1.86	9.23	11.76
	aVQZ	0.51	1.24	2.17	9.10	11.38
CCSD-F12b	aVDZ	2.34	5.00	10.23	70.84	50.22
	aVTZ	1.18	1.81	2.14	21.80	14.83
	aVQZ	0.59	0.68	0.70	5.20	3.76

[a] Adapted from ref 427.

resulting in significantly improved results (see also refs 427 and 509). The final energy expression is

$$E_{(2)_{\rm F12}} = -\sum_{\mu_{2'}\nu_{2'}} \langle {\rm HF}|(1+\hat{T}_2^\dagger)\hat{\Phi}|\mu_{2'}\rangle\langle\mu_{2'}|\hat{F}_N|\nu_{2'}\rangle^{-1} \times\langle\nu_{2'}|\Phi(1+\hat{T}_2)|{\rm HF}\rangle \qquad (401)$$

Equivalently, the energy can be obtained from minimizing the modified Hylleraas functional

$$H_{(2)_{\rm F12}} = \sum_{\substack{i>j\\x>y}} \bar{c}_{ij}^{xy}\langle{}^{xy}_{ij}|[\hat{F},\hat{T}_{2'}]|{\rm HF}\rangle + 2\sum_{\substack{i>j\\x>y}} \bar{c}_{ij}^{xy}\langle{}^{ij}_{xy}|\hat{\Phi} + [\hat{\Phi},\hat{T}_2]|{\rm HF}\rangle \qquad (402)$$

This also encompasses the possibility to use the SP ansatz, which defines the CCSD$(2)_{\overline{\rm F12}}$ method. This form also reveals a close relation to the CCSD-F12b method (see section 7.6).

7.5. CCSD[F12] and CCSD(F12*)

Inspired by the success of the CCSD-F12x methods, Hättig and co-workers[509] recently reinvestigated the CCSD(F12) method. A term-by-term analysis, as discussed in section 7.1, revealed that basically all computationally demanding terms can either be precomputed (within the SP ansatz) or give negligible contributions. Two approximations were considered: In a first approximation, called CCSD[F12], a strict truncation at third order is applied. In comparison to CCSD(F12)-SP, this changes the energy expression to

$$E_{\rm CCSD[F12]} = E_{\rm CCSD} + \langle{\rm HF}|[\Phi_N,\hat{T}_{2'}]|{\rm HF}\rangle + \sum_{i>j}\langle{}^{ij}_{ij}|\hat{\Phi} + [\hat{F}_N^{(0)},\hat{T}_{2'}] + [\hat{H},\hat{T}_1+\hat{T}_2]|{\rm HF}\rangle \qquad (403)$$

and the residual equations become

$$0 = \Omega_{\mu_1,{\rm CCSD}} + \langle\mu_1|[\hat{H},\hat{T}_{2'}]|{\rm HF}\rangle \qquad (404)$$

$$0 = \Omega_{\mu_2,{\rm CCSD}} + \langle\mu_2|[\hat{H},\hat{T}_{2'}]|{\rm HF}\rangle \qquad (405)$$

Numerical experience shows that this method is nearly as accurate as CCSD(F12) while causing only negligible computational overhead in the residual equations. For systems with strong correlation effects, however, some noticeable deviations from CCSD(F12) occur which can be traced down to terms nonlinear in the cluster operator (see section 7.6). It thus seemed necessary to include selected higher-order terms. As implied by the above numerical analysis, the most important higher-order terms are those which remain under the standard approximation. The resulting method was termed CCSD(F12*).

Using again the modified projector $\hat{Q}_{12}^{(0)}$ to indicate the selection of the standard approximation terms, the energy expression can be written as

$$E_{\rm CCSD(F12^*)} = E_{\rm CCSD[F12]} + \sum_{i>j}\langle{}^{ij}_{ij}|\hat{Q}_{12}^{(0)}\frac{1}{2}[[\hat{H},\hat{T}_1],\hat{T}_1]|{\rm HF}\rangle \qquad (406)$$

and the residuals read

$$0 = \Omega_{\mu_1,{\rm CCSD[F12]}} + \langle\mu_1|[[\hat{H},\hat{T}_1],\hat{Q}_{12}^{(0)}\hat{T}_{2'}]|{\rm HF}\rangle \qquad (407)$$

$$0 = \Omega_{\mu_2,{\rm CCSD[F12]}} + \langle\mu_2|[[\hat{H},\hat{T}_1+\hat{T}_2],\hat{Q}_{12}^{(0)}\hat{T}_{2'}]|{\rm HF}\rangle + \langle\mu_2|\frac{1}{2}[[[\hat{H},\hat{T}_1],\hat{T}_1],\hat{Q}_{12}^{(0)}\hat{T}_{2'}]|{\rm HF}\rangle \qquad (408)$$

The only matrix element containing the correlation factor that arises from the extra terms in eqs 406−408 is a V-type intermediate. In the evaluation of this intermediate, in contrast to the CCSD-F12x methods, the projector $\hat{Q}_{12}^{(0)}$ is replaced by the original ansatz 2 projector, as defined in eq 246.

Numerically, CCSD(F12*) leads to essentially the same results as CCSD(F12). The additional terms, in comparison to CCSD[F12], do not cause any further iterative overhead, as will be apparent from the explicit expressions in the next section.

7.6. Synopsis of Approximate CCSD-F12 Methods

All methods from the last three sections are closely related to each other, as a comparison of the working equations reveals. A closer look at the explicit expressions also shows why, compared to a conventional implementation, only little computational overhead is caused by the additional terms, once the extra work for evaluating the integrals is done.

All methods that we consider in this section employ the SP ansatz $c_{xy}^{ij} = \delta_x^i\delta_y^j - \delta_x^j\delta_y^i$. We will use the matrix elements V_{pq}^{ij} and C_{ab}^{ij} as defined in eqs 263 and 266 and in addition the effective one-body intermediates

$$V_p^i = \sum_k V_{pk}^{ik} \qquad (409)$$

$$C_a^i = \sum_{kc'} f_k^{c'} r_{ac'}^{ik} \qquad (410)$$

Table 17. Synopsis of the Working Equations for the Methods Described in Sections 7.3−7.5[a]

	E-1	E-2	E-3	E-4	E-5	E-6	E-7	method
$\Delta E =$	$\Delta E^{\text{geminal}}_{\text{MP2-F12}}$	$+(1/4)[C^{\dagger}]^{ab}_{ij}t^{ij}_{ab}$	$+V^{a}_{i}t^{i}_{a}$	$+(1/4)V^{ab}_{ij}t^{ij}_{ab}$	$+U^{a}_{i}t^{i}_{a}$	$+(1/4)U^{ab}_{ij}t^{ij}_{ab}$	$+(1/2)V^{ab}_{ij}t^{i}_{a}t^{j}_{b}$	(F12*)
	×	×	×	×	×	×		[F12]
	×	×						F12a
	×	×	×	×			×	F12b
	×	$(\times)^{b}$	$(\times)^{c}$	×				$(2)_{\overline{\text{F12}}}$

	R1-1	R1-2	R1-3	R1-4	method
$\Delta\Omega^{i}_{a} =$	V^{i}_{a}	$+U^{i}_{a}$	$+C^{i}_{a}$	$-V^{i}_{k}t^{k}_{a}$	(F12*)
	×	×	×		[F12]
	×				F12a
	×				F12b
	$(\times)^{c}$				$(2)_{\overline{\text{F12}}}$

	R2-1	R2-2	R2-3	R2-4	R2-5	R2-6	R2-7	method
$\Delta\Omega^{ij}_{ab} =$	C^{ij}_{ab}	$+V^{ij}_{ab}$	$+U^{ij}_{ab}$	$-\hat{P}_{ab}V^{ij}_{ak}t^{k}_{b}$	$+(1/2)V^{ij}_{kl}t^{kl}_{ab}$	$-\hat{P}_{ij}V^{j}_{k}t^{ik}_{ab}$	$+V^{ij}_{kl}t^{k}_{a}t^{l}_{b}$	(F12*)
	×	×	×					[F12]
	×	×		×				F12a
	×	×		×				F12b
	$(\times)^{b}$	×						$(2)_{\overline{\text{F12}}}$

[a] Note that $(2)_{\overline{\text{F12}}}$ is not iterated to self-consistency, rather $\Delta E + \Sigma_{\mu_2} T^{\dagger}_{\mu_2}\Omega_{\mu_2}$ is evaluated using the unaltered conventional CCSD amplitudes. For brevity the Einstein summation convention is used. Due to restricted summations, additional prefactors arise, for example, $(1/4)[C^{\dagger}]^{ab}_{ij}t^{ij}_{ab} = \Sigma_{a>b, i>j}[C^{\dagger}]^{ab}_{ij}t^{ij}_{ab}$. The effect of $\hat{P}_{ab}$ is $\hat{P}_{ab}A^{ij}_{ab} = A^{ij}_{ab} - A^{ij}_{ba}$ and analogous for $\hat{P}_{ij}$. [b] Neglected in the original formulation; see refs 507, 509, and 349. [c] Included for ROHF references only.

and the one- and two-body U intermediate defined by

$$U^{i}_{a} = -\sum_{j>k,\,c'} g^{ic'}_{jk} r^{jk}_{ac'} \tag{411}$$

$$U^{ij}_{ab} = \sum_{kc'} (g^{ic'}_{ak} r^{jk}_{bc'} + g^{jc'}_{bk} r^{ik}_{ac'}) \tag{412}$$

We note that precomputing the above two intermediates is only possible in the SP approach. Furthermore, we define the "pure geminal" energy contribution to the MP2-F12 energy

$$\Delta E^{\text{geminal}}_{\text{MP2-F12}} = \sum_{i>j} \left(B^{ij}_{ij} - (\varepsilon_i + \varepsilon_j) X^{ij}_{ij} + 2V^{ij}_{ij} \right) \tag{413}$$

With these definitions we can write down the CCSD(F12*) equations, which are collected in Table 17. The actual expressions can be obtained by adding the pertinent conventional contributions, i.e., E_{CCSD}, $\Omega_{\mu_1,\text{CCSD}}$, and $\Omega_{\mu_2,\text{CCSD}}$. The other methods, CCSD[F12], CCSD-F12a, and CCSD-F12b, and CCSD$(2)_{\overline{\text{F12}}}$ use a subset of these terms as indicated by × in Table 17.

The main difference between CCSD(F12*) and CCSD[F12] is the neglect of the higher-order terms in the latter. The effect is well illustrated by the perturbational analysis in Table 14. The numerically most significant terms that make up the difference between the two methods are R2-5 and R2-6, Table 17. These are on order of $\lambda^2\mu^2$, and their contribution in the perturbational analysis amounts to +2.66 mE_h for F_2O using a cc-pVTZ-F12 basis set. Indeed, the difference between the self-consistent results of the CCSD(F12*) calculation (correlation energy −857.61 mE_h) and the CCSD[F12] calculation (− 860.17 mE_h) is +2.56 mE_h. The CCSD[F12] value is closer to the basis-set limit (−865.13 mE_h), but for larger basis sets there is a clear tendency of overshooting the limit, as shown by the inferior results for atomization energies.[509]

The CCSD-F12b method neglects the R2-5 and R2-6 terms as well. Out of the other terms neglected in CCSD-F12b, E-6 and R2-3 are the numerically most significant ones. They are on the order of $\lambda\nu^2$, and in the above F_2O example their contribution amounts to −3.85 mE_h. Thus, their effect nearly cancels that of the higher-order terms. Again, the perturbative analysis very well predicts the difference between CCSD-F12b (−856.535 mE_h using a variant with full evaluation of the V intermediate) and CCSD(F12*) which is 1.07 mE_h.

In CCSD-F12a, particularly, the term E-4 is neglected, which for F_2O gives a huge contribution of +11.10 mE_h (note that this is only one-half of the value listed in Table 14 as R2-2, the counterpart of E-4, is still included). In effect this lowers the total CCSD-F12a energy by 11 mE_h and brings it very close to the basis-set limit. For larger basis sets, however, CCSD-F12a grossly overshoots and use of CCSD-F12b has been recommended in this case.[427]

CCSD(F12*), on the other hand, is the most complete method with respect to CCSD(F12) and full CCSD-F12. For the present F_2O example, it differs by only 0.02 mE_h from the CCSD(F12) result and by around 0.3 mE_h from full CCSD-F12 (we recall that all calculations are based on the SP ansatz).[438] With respect to computational cost, one immediately sees that all additional terms with respect to conventional CCSD are either constant contributions to the residual or contractions with t^{i}_{a} or t^{ij}_{ab} which have analogous counterparts in the conventional part. In fact, for CCSD(F12*) as well as for all other methods discussed in this section implementations are feasible that have no noticeable additional operation count during the iterative solution of the coupled-cluster equations (noting that CCSD$(2)_{\overline{\text{F12}}}$ implies an unmodified CCSD run anyway).[510]

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The only difference between the methods lies in the noniterative step of calculating the various additional integrals and intermediates, as described in section 6.3. The major savings with CCSD-F12b, as compared to CCSD(F12*), are due to the approximate calculation of V_{ab}^{ij} according to eq 395, which effectively avoids computation of integrals of the type $g_{pq}^{ic'}$. For the usual sizes of auxiliary basis sets this approximately halves the operation count for formation of V. In principle, however, this approximate calculation is also compatible with CCSD(F12*). In addition, CCSD(F12*) requires computation of the U intermediate, which is less problematic as all the involved two-electron integrals have two occupied orbital indices.

For CCSD-F12a, precomputation of V_{ab}^{ij} can be avoided altogether as shown in ref 427, and the method hence is the computationally least demanding one. The perturbative correction of Valeev, on the other hand, has basically the same operation count as CCSD(F12*) as it also uses the full V_{ab}^{ij} intermediate. In a note of caution, it should be said that the actual runtime of the programs crucially depends on a number of other factors, e.g., the efficiency of the integral routines, and hence, the above formal considerations warrant a dedicated study that is presently not available in the literature. As a reference point, the overhead for the noniterative part in the present Turbomole implementation of CCSD(F12*) amounts to about 3−5 CCSD iterations, depending on the size of the CABS. Assuming around 10−15 iterations for a sufficiently converged CCSD result, this is an overhead of around 20−50%. If the calculation is followed by a calculation of a (T) correction, the overhead is much reduced, as due to its steeper computational scaling the latter will dominate the operation count for larger molecules.

With respect to accuracy, Hättig et al.[509] find that (F12*) > $(2)_{\overline{\text{F12}}}$ > F12b> F12a, where the CCSD basis-set errors for (F12*) are on average one-half those of F12b. However, for ground-state energies the differences are small (only a few kJ/mol) and the discussion mainly reduces to formal consistency versus fast computation (where we again note that the most time-saving approximation to V, eq 395, is also compatible with (F12*) and $(2)_{\overline{\text{F12}}}$). Considering coupled-cluster response theory, however, CCSD(F12*) is clearly the preferred choice. A closely related approximation was already shown to work well,[465] while some preliminary studies show that methods neglecting higher-order terms, like CCSD[F12], lead to inferior results for excitation energies.

As a general note on the performance of explicitly correlated coupled-cluster methods, we point out that the range of application of the approximate CCSD-F12 methods is not much different from the range of application of conventional CCSD calculations. In particular, use of local-correlation techniques (cf. section 7.8) has paved the way toward large-scale applications at the CCSD-F12a and -F12b levels (see, for example, refs 426 and 429). Since the domain error of local-correlation methods is reduced by the explicitly correlated geminals, the local CCSD-F12a and -F12b seem to be attractive, cost-efficient methods. As far as CCSD(F12) coupled-cluster calculations with canonical Hartree−Fock orbitals are concerned, an example from our own recent work[511] with the Turbomole program package is illustrated in Figure 16. CCSD(T)/cc-pVDZ and CCSD(F12)/cc-pVDZ-F12 calculations were performed on the transition-state structures for the hydrogen-abstraction reactions for a chemical reaction in which one phenyl radical abstracts a hydrogen atom from another phenyl radical to form benzene (C_6H_6) plus benzyne (C_6H_4). Depicted are the results for the "singlet" (M_S = 0)

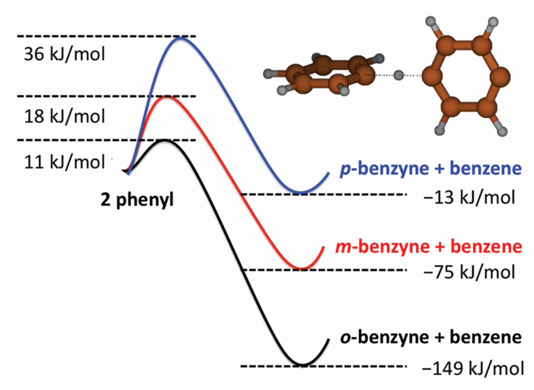

Figure 16. Barrier heights and reaction energies for three hydrogen abstraction reactions of two phenyl radicals toward benzene plus *o*-, *m*-, or *p*-benzyne. The energies include the vibrational zero-point energy. The optimized structure of the transition state for the reaction toward benzene + *p*-benzyne is also shown. Data taken from ref 511.

transition states, and all calculations were based on (broken-symmetry) UHF reference determinants. (The geometries and vibrational zero-point energies were computed at the DFT level.) The purpose of Figure 16 is to show the kind of calculations that can be performed at the CCSD(F12) level in an appropriate basis set (cc-pVDZ-F12), but this figure also nicely illustrates the Bell−Evans−Polanyi principle: exothermic reactions via lower barriers release more reaction energy than reactions via higher barriers.

7.7. Density Fitting

At the MP2-F12 level a large fraction of the additional computational costs for the explicitly correlated terms arises from calculation of the additional two-electron integrals. This is, in particular, the case for the SP approach, which requires only the diagonal elements of the V, B, and X intermediates. These can be evaluated with $\mathcal{O}(\mathcal{N}^4)$ scaling costs once the required two-electron integrals are available in the MO basis. Computation of the two-electron integrals scales, however, with $\mathcal{O}(\mathcal{N}^5)$ and has a rather high prefactor if they are obtained by four-index transformations from AO two-electron integrals.

A standard technique to speed up evaluation of two-electron MO integrals is the density fitting (DF) approximation. Density fitting is in the literature also known as resolution of the identity (RI) approximation. However, in the context of F12 theory we reserve the term RI approximations for expansion of three- and four-electron integrals as products of two-electron integrals to avoid confusion. The idea behind the DF approximation is that in large orbital basis sets the products of orbitals appearing for electrons 1 and 2 in the expressions for four-index two-electron integrals

$$(pq|\hat{o}|rs) = \int\int \varphi_p(\mathbf{r}_1)\varphi_q(\mathbf{r}_1)\hat{o}_{12}\varphi_r(\mathbf{r}_2)\varphi_s(\mathbf{r}_2)\, d\tau_1 d\tau_2 \tag{414}$$

will soon become (numerically) highly linear dependent and can thus be expanded with good accuracy in a dedicated auxiliary basis of fitting functions $\{Q\}$

$$\varphi_p(\mathbf{r})\varphi_q(\mathbf{r}) \approx \sum_Q Q(\mathbf{r})c_{Q,pq} \tag{415}$$

For the Coulomb repulsion r_{12}^{-1}, which is a positive definite operator so that the matrix elements define a valid inner product, the coefficients can be calculated as

$$c_{Q,pq} = \sum_{Q} [\mathbf{V}^{-1}]_{PQ}(Q|pq) \tag{416}$$

where $V_{pq} = (Q|P)$ and $(Q|pq)$ are two- and three-index Coulomb integrals,

$$(Q|P) = \iint Q(\mathbf{r}_1) r_{12}^{-1} P(\mathbf{r}_2) \mathrm{d}\tau_1 \mathrm{d}\tau_2 \tag{417}$$

$$(Q|pq) = \iint Q(\mathbf{r}_1) r_{12}^{-1} \varphi_p(\mathbf{r}_2)\varphi_q(\mathbf{r}_2) \mathrm{d}\tau_1 \mathrm{d}\tau_2 \tag{418}$$

The four-index Coulomb integrals are then computed within the DF approximation as

$$\begin{aligned}(pq|r_{12}^{-1}|rs) &\approx (pq|r_{12}^{-1}|rs)^{\mathrm{DF}} \\ &= \sum_{PQ} (pq|P)[\mathbf{V}^{-1}]_{PQ}(Q|rs) = \sum_{Q} G_{Q,pq}G_{Q,rs}\end{aligned} \tag{419}$$

with

$$G_{Q,pq} = \sum_{P} [\mathbf{V}^{-1/2}]_{QP}(P|pq) \tag{420}$$

Evaluation of the two- and three-index AO integrals and their transformation to the MO basis is much cheaper than for four-center AO integrals. The only $O(N^5)$ scaling step is then the final contraction to form the target four-index MO integrals. If these integrals are only needed for a small subset of the whole MO space, for example, because two or more indices are restricted to occupied orbitals, as it is the case for the integrals needed for the intermediates in MP2-F12 calculations, the DF approximation reduces the computational costs often by more than an order of magnitude. With optimized auxiliary basis sets the additional error introduced by the DF approximation can be kept orders of magnitude smaller than the orbital basis-set error so that the overall accuracy of a calculation is not affected. Importantly for the performance of the DF approximation, the error in the integrals $(pq|r_{12}^{-1}|rs)^{\mathrm{DF}}$ is quadratic in the fitting error for the orbital products

$$R_{pq}(\mathbf{r}) = \varphi_p(\mathbf{r})\varphi_q(\mathbf{r}) - \sum_{Q} Q(\mathbf{r})c_{Q,pq} \tag{421}$$

as

$$(pq|r_{12}^{-1}|rs)^{\mathrm{DF}} - (pq|r_{12}^{-1}|rs) = (R_{pq}|r_{12}^{-1}|R_{rs}) \tag{422}$$

The same procedure can be used for other positive or negative definite operators for which inversion of the two-index integral matrix $(Q|\hat{o}_{12}|P)$ is numerically stable.

A generalization of the fitting formula in eq 419 for operators that are neither positive nor negative definite, which has the same property that errors in the integrals are quadratic in the fitting error R_{pq}, is the robust density-fitting formula proposed by Manby.[404] It can be cast into the form

$$(pq|\hat{o}_{12}|rs)^{\mathrm{DF}} = \sum_{Q} (G_{Q,pq}O_{Q,rs} + O_{Q,pq}G_{Q,rs}) \tag{423}$$

where

$$O_{Q,pq} = \sum_{P} [\mathbf{V}^{-1/2}]_{QP}\left((P|\hat{o}_{12}|pq) - \frac{1}{2}\sum_{RS}(P|\hat{o}_{12}|R)[\mathbf{V}^{-1}]_{RS}(S|pq)\right) \tag{424}$$

Computation of two-electron MO integrals for general operators is thus only twice as expensive as for electron repulsion integrals. Besides the lower operation count, another advantage of the DF approximation is that, in particular, at the MP2-F12 level, also the memory and disk requirements can be greatly reduced by avoiding storage of the various four-index two-electron integrals.

7.8. Local Correlation Methods

The enhanced basis-set convergence of explicitly correlated methods reduces dramatically the computational costs for accurate correlated wave function calculations. However, just as for conventional wave function methods, they suffer from a very steep scaling of the operation count with the system size, which hinders calculations on large systems. This problem can be alleviated by combining F12 theory with a local correlation approach, as has been shown by Werner and co-workers.[407,413,429] Local correlation methods exploit the short-range character of dynamic electron correlation using a local orbital basis and restricting for each localized occupied orbital i the excitations into the virtual space to a subset of projected atomic orbitals (PAOs) that are spatially close to i. This subset is called the domain for i and denoted as $[i]$. For each pair of occupied orbitals i, j double excitations are restricted to a pair domain $[ij]$ which is formed as the union of $[i]$ and $[j]$. Since the size of the domains is roughly independent of the molecular size and since the set P_s of so-called strong pairs i, j that contribute significantly to the correlation energy increases for large systems asymptotically only linearly with the system size, one can achieve with this ansatz a linear scaling in computational cost.

At the CCSD-F12 level the local correlation variant, LCCSD-F12, approximates the single- and double-excitation parts of the cluster operator as[429]

$$\hat{T}_1 = \sum_{i} \sum_{a \in [i]} t_a^i a_a^\dagger a_i \tag{425}$$

$$\hat{T}_2 = \sum_{i>j \in P_s} \sum_{a>b \in [ij]} t_{ab}^{ij} a_a^\dagger a_i a_b^\dagger a_j \tag{426}$$

$$\hat{T}_{2'} = \sum_{i>j \in P_s} \sum_{x>y} c_{xy}^{ij} \tau_{ij}^{xy} \tag{427}$$

where in the SP approach $c_{xy}^{ij} = \delta_{ix}\delta_{jy} - \delta_{iy}\delta_{jx}$. Since the conventional double excitations in eq 426 are restricted to the pair domains, the strong orthogonality projector for ansatz 2 is for the local correlation methods chosen such that it only projects out these excitations. The pair-specific projector becomes

$$\hat{Q}_{12}^{ij} = (1 - \hat{O}_1)(1 - \hat{O}_2)\left(1 - \sum_{cd \in [ij]} |cd\rangle\langle cd|\right) \tag{428}$$

Thereby the excitations into the geminals can compensate for most of the domain error caused by the restriction of the conventional double excitations into products of virtual or projected atomic orbitals. Some results which demonstrate how efficiently the geminal contribution can compensate for the domain errors at the CCSD level are shown in Table 18.

Recently, alternative approaches to combining F12 and localization ideas have been explored. Friedrich et al.[512] applied Stoll's incremental scheme to the CCSD(F12)-SP method using local occupied orbitals. Here, the CCSD(F12)-SP equations are solved independently for each domain, each pair of domains, each triplet of domains, and so on until the incremental expension of the energy converges. Smaller basis sets can be used for

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Table 18. Correlation Energies (in mH) Obtained with the cc-pVTZ-F12 Basis Set with Conventional CCSD, in CCSD-F12a, and Their Local Variants in Comparison to Extrapolated Basis Set Limits[a]

molecule	CCSD	LCCSD	CCSD-F12a	LCCSD-F12a	basis-set limit
C_2H_4O	−611.8	−609.2	−658.0	−658.1	−650.4
CH_3CHO	−606.1	−603.8	−651.6	−651.7	−643.9
C_2H_5OH	−648.2	−644.3	−697.3	−697.3	−689.1
NH_2CONH_2	−851.9	−847.6	−918.0	−917.9	−908.2
$HCOOCH_3$	−844.7	−841.1	−911.7	−911.7	−901.7

[a] All results adopted from ref 429.

the higher-order increments, and the study demonstrated that it was not necessary to include F12 terms beyond pair domains.

Tew et al.[513] very recently combined the MP2-F12-SP method with the pair natural orbital (PNO) approach of Meyer.[514−516] PNOs have recently been advocated by Neese[517,518] as an attractive way of reducing steep scaling through locality, without necessitating the definition of domains. In this aproach the set of virtuals used to expand each pair correlation function is transformed to PNOs by diagonalizing an approximate first-order pair density and then truncated on the basis of the occupation number. Tew et al. showed that these ideas can be used very effectively in F12 theory to reduce both the number of virtual and the CA orbitals to an average of only 40 orbitals per pair, without significant loss of accuracy.

7.9. Basis Sets

For the accuracy and efficency of calculations with F12 methods it is crucial that the orbital basis and the complementary auxiliary basis for the RI of the three- and four-electron integrals are chosen or optimized carefully.

7.9.1. Orbital Basis Sets. As discussed in previous sections, with basis sets saturated up to L_{max} the remaining basis-set error for conventional correlated wave function methods decreases only with $(L_{max} + b)^{-3}$. Orbital basis sets which have been optimized for calculations with these methods reflect the slow convergence by including already for small cardinal numbers (or ζ levels) high angular momentum functions, Table 19. Inclusion of the geminals in the F12 methods enhances the convergence with the angular momentum of the basis functions to $(L_{max} + b)^{-7}$. A balanced orbital basis for F12 calculations should thus contain less functions with high angular momenta compared to the number of functions with small angular momenta. The latter are also important to keep the basis-set error of the underlying Hartree−Fock (or, in the multireference case, MCSCF) calculation small enough so that it does not limit the overall accuracy of a calculation. Furthermore, the functions with higher angular momentum need not be as tight in F12 calculations as in standard orbital expansions.[447]

Orbital basis sets optimized for explicitly correlated calculations with F12 methods are (at the time this article has been written) available for the atoms H, He, Li−Ne, and Na−Ar from the work of Peterson and co-workers.[414,417,519] These cc-pVXZ-F12 basis sets are constructed in a similar manner to the correlation-consistent basis set for conventional correlated wave functions, cc-pVXZ, such that the remaining basis-set errors are approximately the same for each angular momentum. For the first-row atoms B−Ne this strategy led for the cc-pVDZ-F12 basis sets to the composition [5s5p2d] and for the triple- and quadruple-ζ basis sets cc-pVTZ-F12 and cc-pVQZ-F12 to the composition [6s6p3d2f] and [7s7p4d3f2g], respectively. This is somewhat less regular than the composition of the basis sets optimized for conventional correlated calculations. The accuracy achieved with these basis sets with respect to remaining basis-set errors has been tested in the literature, in particular, for MP2-F12 and several approximations to CCSD-F12.[520−523]

Table 19. Statistical Measures for the Remaining Basis Set Errors from the Orbital Basis in Frozen Core MP2-F12 Calculations (with optimized amplitudes) from a Benchmark Study on Set of 106 Small Molecules Containing H, C, N, O, and F[a]

correlation energies	mean	STD	MAD	rms	max
cc-pVDZ-F12	0.97	0.24	0.97	1.00	1.75
cc-pVTZ-F12	0.26	0.08	0.26	0.27	0.41
cc-pVQZ-F12	0.07	0.02	0.07	0.07	0.10
aug-cc-pVDZ	1.71	0.22	1.71	1.73	2.19
aug-cc-pVTZ	0.63	0.18	0.63	0.65	1.02
aug-cc-pVQZ	0.23	0.07	0.23	0.24	0.04
aug-cc-pV5Z	0.09	0.03	0.09	0.09	0.17
total energies	**mean**	**STD**	**MAD**	**rms**	**max**
cc-pVDZ-F12	1.90	0.30	1.90	1.92	3.00
cc-pVTZ-F12	0.48	0.12	0.48	0.49	0.73
cc-pVQZ-F12	0.10	0.03	0.10	0.10	0.16
aug-cc-pVDZ	2.93	0.36	2.93	2.95	3.90
aug-cc-pVTZ	1.30	0.26	1.30	1.33	1.91
aug-cc-pVQZ	0.39	0.11	0.39	0.41	0.66
aug-cc-pV5Z	0.12	0.04	0.12	0.13	0.22
atomization energies	**mean**	**STD**	**MAD**	**rms**	**max**
cc-pVDZ-F12	−0.33	0.34	0.35	0.47	−1.84
cc-pVTZ-F12	−0.02	0.04	0.03	0.04	−0.18
cc-pVQZ-F12	0.01	0.01	0.01	0.01	−0.03
aug-cc-pVDZ	−0.21	0.33	0.29	0.39	−2.10
aug-cc-pVTZ	0.02	0.10	0.08	0.11	−0.64
aug-cc-pVQZ	0.09	0.04	0.10	0.10	−0.16
aug-cc-pV5Z	0.05	0.01	0.05	0.06	0.08

[a] Listed are the mean error and standard (STD), mean absolute (MAD), root mean square (RMS), and maximum deviations for the correlation and total energies as well as for the atomization energies. All values are adopted from ref 521 and given in kJ mol^{-1} per valence electron.

An alternative to the cc-pVXZ-F12 basis-set families is the correlation-consistent basis sets augmented with diffuse functions, aug-cc-pVXZ, from the work of Dunning and co-workers.[524−527] The remaining basis-set errors are with these basis sets larger than with the optimized cc-pVXZ-F12 basis sets of the same cardinal number, but this is partially compensated by the smaller size of the aug-cc-pVXZ basis sets.[521]

For calculations with conventional correlated wave function methods and the correlation-consistent cc-pVXZ basis sets the remaining basis-set errors in the correlation energy follows in good approximation the idealized power law $E_X^{corr} = E_{limit}^{corr} + AX^{-3}$ (compare eq 94 in section 3.7.5). This is a consequence of the building principle of the cc-pVXZ basis sets and the fact that in conventional (i.e., not explicitly correlated) calculations the basis-set error is dominated by the error in the pair correlation

Table 20. Optimized Exponents for Extrapolating MP2-F12 Correlation Energies with Eq 96 from Ref 50[a]

basis sets	exponent	MAD	STD
MP2-F12/2C			
cc-pVDZ-F12/cc-pVTZ-F12	2.75	0.16	0.14
cc-pVTZ-F12/cc-pVQZ-F12	4.07	0.04	0.04
aug-cc-pVDZ/aug-cc-pVTZ	2.08	0.37	0.30
aug-cc-pVTZ/aug-cc-pVQZ	2.98	0.20	0.16
aug-cc-pVQZ/aug-cc-pV5Z	4.11	0.05	0.04
MP2-F12/2C(FIX)			
cc-pVDZ-F12/cc-pVTZ-F12	3.09	0.38	0.30
cc-pVTZ-F12/cc-pVQZ-F12	4.35	0.13	0.27
aug-cc-pVDZ/aug-cc-pVTZ	2.30	0.70	0.54
aug-cc-pVTZ/aug-cc-pVQZ	3.25	0.40	0.38
aug-cc-pVQZ/aug-cc-pV5Z	4.33	0.07	0.05

[a] The listed values refer to approximation 2C (in ref 50, denoted as "3C") with geminal coefficients determined by minimization of the Hylleraas functional (MP2-F12/2C) or from the *s*- and *p*-wave coalescence conditions at the interelectronic cusp (MP2-F12/2C(FIX)). The results for the mean absolute and standard deviations have been determined for set of 14 small molecules containing first- and second-row main-group elements.

energy due to the poor description of the electronic cusp. This relation is often employed to correct approximately for the remaining basis-set error by extrapolating the basis-set limit from the results obtained with two different cardinal numbers X and Y based on eq 95 as

$$E_{\mathrm{limit}}^{\mathrm{corr}} \approx (E_Y^{\mathrm{corr}} - E_X^{\mathrm{corr}})\frac{Y^3}{Y^3 - X^3} \tag{429}$$

For F12 methods the remaining incompleteness error follows such a simple power law only with specially constructed basis sets which, e.g., have been saturated up to a given angular momentum. With the basis-set families cc-pVXZ-F12 and aug-cc-pVXZ an extrapolation with AX^{-n}, where n is a fixed exponent, does not efficiently improve the results. The remaining incompleteness errors have for these sets a more complicated dependence on the cardinal number. As shown in ref 520 they can, however, successfully be improved by a Schwenke-type[50] extrapolation, eq 96, with exponents p optimized for the employed basis sets and cardinal numbers and the variant of F12 theory. Optimized exponents for MP2-F12/2C calculations with the geminal coefficients determined variationally or fixed by the *s*- and *p*-wave coalescence conditions (SP approach, "FIX") are listed in Table 20 together with some results for the remaining errors.

7.9.2. Complementary Auxiliary Basis Sets. From the expressions for the V and X intermediates in MP2-F12 calculations with ansatz 2, eqs 276 and 277, it follows that in a calculation on an atom, which has occupied orbitals with a maximum angular momentum L_{occ}, an accurate computation of V_{ij}^{kl} and X_{ij}^{kl} requires that the combined orbital plus CA basis is saturized up to $L = 3L_{\mathrm{occ}}$. For higher angular momenta the contributions from the CA basis functions to

$$-(1 + \hat{P}_{ij}^{kl}) \sum_{ma'} \langle ij|o_{12}|ma'\rangle\langle ma'|f_{12}|kl\rangle \tag{430}$$

where o_{12} and f_{12} are totally symmetric operators, vanish due to symmetry. However, for the C and B intermediates, which are calculated (partially) with the more approximate form of the strong orthogonality projector in eq 256, also higher angular momentum functions contribute to the resolution of the identity. Test calculations in refs 415 and 416 on molecules with the first- and second-row atoms H−Ar showed that CA basis sets with functions up to $L_{CA} = \max(3L_{\mathrm{occ}}, L_{\max}) + 1$, where $L_{\max}$ is the maximum angular momentum of the orbital basis set, are for these atoms sufficient to achieve very accurate results. Yousaf and Peterson[415,416] and Hill et al.[519] optimized such CA basis sets for the cc-pVXZ-F12, aug-cc-pVXZ, and cc-pCVXZ-F12 basis-set families by minimizing the functional

$$\Delta RI = \sum_{ij} \frac{\left(V_{ij}^{ij} - V_{ij}^{ij,\mathrm{ref}}\right)}{V_{ij}^{ij,\mathrm{ref}}} + \sum_{ij} \frac{\left(B_{ij}^{ij} - B_{ij}^{ij,\mathrm{ref}}\right)}{B_{ij}^{ij,\mathrm{ref}}} \tag{431}$$

With these CA basis sets the errors in total and reaction energies due the resolution of the identity approximation for the three- and four-electron integrals are about an order of magnitude smaller than the incompleteness error from the orbital basis. Table 21 shows some results from MP2-F12/2C calculations with the cc-pVXZ-F12 basis sets from ref 415 (therein referred to as "MP2-F12/3C"). For the first-row atoms B−Ne the CA basis sets are uncontracted and have the compositions (4s4p4d3f1g) for cc-pVDZ-F12, (4s4p4d3f2g) for cc-pVTZ-F12, and (4s4p4d3f2g1h) for cc-pVQZ-F12, while the orbital basis sets have the compositions (11s7p2d)/[5s5s2d] for cc-pVDZ-F12, (13s7p3d2f)/[6s6p3d2f] for cc-pVTZ-F12, and (15s9p4d3f2g)/[7s7p4d3f2g] for cc-pVQZ-F12. Thus, the size of the CA basis increases only slowly with the size of the orbitals basis set.

Table 21. Basis Set Errors in MP2-F12/2C Correlation Energies Due to Truncation of the Orbital and Complementary Auxiliary Basis Sets (in kcal/mol) for a Test Set of 42 Molecules with First- and Second-Row Atoms[a]

	orbital basis			CA basis		
	MAD	STD	MAX	MAD	STD	MAX
cc-pVDZ-F12	0.71	0.80	3.84	0.05	0.07	0.31
cc-pVTZ-F12	0.24	0.24	0.99	0.01	0.02	0.09
cc-pVQZ-F12	0.15	0.12	0.47	0.004	0.005	0.03

[a] All values have been adopted from ref 415 (therein referred to as MP2-F12/3C). Listed are mean absolute deviations (MAD), standard deviations (STD), and maximum deviations from reference results obtained with large reference basis sets.

7.9.3. Auxiliary Basis Sets for Density Fitting. Several implementations of F12 methods employ the density-fitting approximation described in section 7.7 for computation of the various two-electron integrals that enter in the expressions for the V, X, B, C, etc. intermediates. This necessitates a further auxiliary basis set in addition to the orbital and CA basis sets. For integrals $(pi|rs)$ with at least one occupied MO index i auxiliary basis sets with functions up to an angular momentum of $L_{\max} + L_{\mathrm{occ}}$ are sufficient to make the DF errors insignificantly small. F12 methods employ the DF approximation also for integrals of the type $(p'i|rs)$, where p' is a CA basis function. For these calculations the DF auxiliary basis should include functions up to an angular momentum of $\max(L_{\max}, L_{CA}) + L_{\mathrm{occ}}$, where L_{CA} is the maximum angular momentum of the CA basis set.

Not only the angular momenta but also the range of exponents that needs to be spanned by the DF basis set depend on the orbital products that are fitted. Auxiliary basis sets optimized for RI-MP2 calculations are tuned to accurately fit products of occupied and virtual orbitals $\varphi_a\varphi_i$. For integrals with products of two occupied orbitals $\varphi_i\varphi_j$ the fitting basis should contain somewhat tighter (i.e., larger) exponents, while the maximum angular momentum could be restricted to $2L_{occ}$. This led to development of method-specific auxiliary basis sets, for instance, the RI-J basis sets for fitting the Coulomb matrix in DFT calculations with functionals without exact exchange contribution, the RI-JK basis sets for a simultaneous fitting of the Coulomb and exchange matrices in DFT (with hybrid functionals) or Hartree−Fock calculations, or the RI-C basis sets for fitting $(p'i|rs)$ integrals in calculations with correlated wave function methods.

For F12 calculations the cc-pVXZ-F12 and aug-cc-pVQZ orbital basis sets with the respective optimized CA basis sets from Peterson and co-workers[414−416,519] can be combined with the aug-cc-pwCV(X+1)Z auxiliary RI-C basis sets from refs 528 and 529 for the DF of the integrals for V, X, B, C, etc. intermediates and the RI-JK basis sets cc-pV(X+1)Z from ref 530 for the DF in the computation of the Fock matrix elements $F_{pq'}$ and $F_{p'q'}$. The tight core−valence functions in the aug-cc-pwCV-(X+1)Z RI-C basis sets are included to accurately fit products of two occupied orbitals in the integrals for the F12 intermediates. With these basis sets the errors from the DF approximation in the correlation contribution are negligible in comparison to the incompleteness errors from the orbital basis sets. For example, for calculations in the cc-pVTZ-F12 basis sets the errors due to the DF approximations are with these auxiliary basis sets on the order of $1-2\,\mu E_h$ per valence electron compared to truncation errors on the order of $4-20\,\mu E_h$ and $100-400\,\mu E_h$ per valence electron from the CA and orbital basis sets.

8. PROPERTIES AND RESPONSE THEORY

The largest part of the development work in F12 theory has has been devoted to energy calculations, but as the methodology develops, other targets such as molecular properties come into focus. The main questions are as follows. How important are F12 corrections for the prediction of properties? Do the assumptions behind the approximations used in F12 theory carry over to the expressions to be evaluated for the calculation of properties?

One obvious next step is exploration of the Born−Oppenheimer potential energy surface (PES), in particular, in order to obtain equilibrium structures and vibrational frequencies. While for 2−4 atoms this still might be feasible by calculating the PES on a grid, for any larger system, the implementation of analytical geometric derivatives is required. Analytical derivatives of the energy not only give access to geometric gradients on the PES, but also provide access to molecular properties via generalization of the Hellmann−Feynman theorem to approximate wave functions.

Higher-order derivatives of the energy then give rise to nonlinear response properties such as polarizabilities (or, more general, susceptibilities). The time-dependent or frequency-dependent generalization of response theory can also be used to consistently derive equations for electronically excited states in the case of theories like coupled-cluster theory, which originally is a ground-state theory only.

We note that for Hy-CI, ECG-type calculations, and similar methods a rich literature on molecular property calculations exists (see, for example, ref 531). Here, we will only point to some recent results for the biggest systems that presently are in reach for these methods. Potential energy curves were reported for LiH (ground and excited states) using the free complement local Schrödinger equation approach (FC LSE)[176] and with an ECG expansion.[236] Excited states computed with the Hy-CI method were recently reported for lithium,[135] and with an ECG expansion beryllium[165,532] and boron[167] have been feasible. Dynamic dipole polarizabilities (up to second hyperpolarizabilities) have been computed for Be and Be-like ions with the ECG method.[533,534] Furthermore, nonadiabatic effects as well as relativistic and quantum electrodynamic effects were calculated for several systems, for example, for He_2.[241]

For R12 and F12 theory a number of exploratory works exist that use finite differences for calculation of geometry- or electric-field-dependent properties, as summarized in section 8.1. The encouraging results have triggered development of analytical techniques, like implementation of geometric analytical gradients, section 8.2, and implementation of response theory for treatment of excited states, section 8.3, and higher-order response properties, section 8.4.

8.1. Finite Difference Approaches

In this section we summarize calculations of molecular properties using R12 or F12 methods which were based on finite differences or evaluation of a Born−Oppenheimer surface on a grid.

Computing the spectroscopic constants of diatomics is rather straightforward, and a first example, concerned with N_2 at different levels of pair theory, was published by Klopper et al.[352] as early as 1991. Further examples, including Be_2, LiH, HF, etc. can be found in other work, e.g., refs 46, 366, 369, 484, 488, and 491. One of the first examples for application to a polyatomic molecule is possibly the work on SiH_3^- by Aarset et al.,[377] which also includes calculation of the quartic force field at the CCSD(T)-R12 level.

High-accuracy benchmarks using CCSD(T)-R12 (still in the standard approximation using large basis sets) have later been published for evaluation of composite methods for obtaining structures[386] and harmonic vibrational frequencies[387] of diatomics and small polyatomic molecules. More recently, a study of equilibrium structures and harmonic and anharmonic frequencies of polyatomics appeared which uses Slater-type correlation factors within the CCSD(T)-F12a and CCSD(T)-F12b approach.[535] The reported examples comprised, for example, CH_2NH and 1,2-$C_2H_2F_2$. Another recent study evaluates equilibrium structures and force fields up to quartic level using the CCSD(T)$_{F12}$ approach in comparison to extrapolation schemes.[349]

With respect to electric properties the literature becomes rather sparse. Magnetic properties have, to our knowledge, not been considered to date. A first finite-difference-based study of the dipole polarizability and second hyperpolarizability of the beryllium atom was published by Tunega et al.[536] in 1997. A number of R12 augmented coupled-cluster methods have been employed, including CCSD(T)-R12. The study was followed by work on LiH, which included up to the static second dipole hyperpolarizability and the quadrupole hyperpolarizability.[537] As at most basis sets with f functions were feasible at that time, very little improvement with the linear correlation factor was seen. CCSD(T)-R12 was also used as a benchmark for a basis-set convergence study of the BH and HF molecular dipole moment.[538]

Other work based on CCSD(T)-R12 in the standard approximation scheme and finite difference calculations includes investigation of interaction-induced changes in the dipole polarizability of helium[539] and a study of static electrical response properties of F^-, Ne, and HF.[456] The latter included the static

Table 22. Intermolecular Distance and Binding Energy of the Ammonia−Water Complex Calculated at the MP2 Level (with density fitting)[a]

basis	MP2-F12 + CABS singles $r(\mathrm{N}\cdots\mathrm{H})^c$	MP2-F12 + CABS singles ΔE^d	MP2 $r(\mathrm{N}\cdots\mathrm{H})^c$	MP2 ΔE^d	MP2 + CP correction[b] $r(\mathrm{N}\cdots\mathrm{H})^c$	MP2 + CP correction[b] ΔEc
aug-cc-pVDZ	196.56	−10.10	196.78	−11.07	201.98	−9.31
aug-cc-pVTZ	195.96	−10.40	195.74	−10.69		
aug-cc-pVQZ	196.07	−10.41	195.83	−10.55		
aug-cc-pV5Z	196.09	−10.40	196.01	−10.45	196.74	−10.26
aug-cc-pV6Z			196.03	−10.42		

[a] All values taken from ref 543. [b] Counterpoise-corrected results. [c] Intermolecular distance in pm. [d] Binding energy in mE_h.

dipole polarizability and second hyperpolarizability; for HF also the static dipole moment and the hyperpolarizability were reported.

8.2. Analytical Gradients

Analytical first derivatives are the essential ingredient for efficient determination of equilibrium structures and transition-state structures of polyatomic molecules. As compared to conventional orbital expansions, the main complication in F12 theory arises from the larger number of two-particle integrals for which effective two-particle densities and integral derivatives need to be calculated. Development of methods is still in its beginnings; analytical gradient codes have so far been reported for MP2-R12[540,541] using conventional four-index integrals and MP2-F12[542,543] using density fitting. In both works approximation A was used for the B matrix (see section 6.3) which reduces the number of necessary integral derivatives to a minimum. Accordingly, we will restrict the following discussion to this case, as this suffices to show the basic principles.

The starting point is a stationary Lagrange functional. To this end, the MP2-Hylleraas functional, eq 300, is augmented with the constraints for fulfillment of the Brillouin condition, $f_i^a = f_a^i = 0$, and canonical frozen orbitals, $f_J^i = f_i^J = 0$, where for J runs over all core orbitals that are excluded from the correlation treatment. The Lagrange functional thus reads

$$L = H_{\mathrm{MP2\text{-}F12}} + \sum_{ai} z_i^a f_a^i + \sum_{iJ} z_i^J f_J^i - \frac{1}{2}\sum_{rs} x_r^s (S_s^r - \delta_s^r) \qquad (432)$$

where the last term stems from the orthonormality condition, S_s^r being the overlap matrix of the orbitals.

The Lagrange multiplier z_i^a can be calculated by solving a set of coupled-perturbed Hartree−Fock equations, also known as z-vector equations.[544] As compared to the conventional case, the right-hand side of these equations has a few additional terms that originate from the orbital gradient of the F12 contributions. Once z_i^a is determined, the multipliers z_i^J and x_r^s can be calculated directly from the pertinent expressions, again with corresponding additional F12 terms.

The first derivative with respect to a geometric distortion ξ, expressed in the AO basis, has the general structure

$$\frac{\mathrm{d}E_{\mathrm{MP2\text{-}F12}}}{\mathrm{d}\xi} = \frac{\partial L}{\partial \xi} = \sum_{\mu\nu} D_{\mu\nu}^{\mathrm{rel}} \frac{\partial h_{\mu\nu}}{\partial \xi} - \sum_{\mu\nu} X_{\mu\nu}\frac{\partial S_{\mu\nu}}{\partial \xi} + \sum_{\mathscr{K}}\sum_{\mu\nu\kappa\lambda} d_{\mu\nu\kappa\lambda}^{\mathscr{K}} \frac{\partial\langle\mu\nu|\hat{O}_{12}^{\mathscr{K}}|\kappa\lambda\rangle}{\partial\xi} \qquad (433)$$

The derivatives of the one-electron Hamiltonian $(\partial/\partial\xi)h_{\mu\nu}$ are associated with the relaxed density $D_{\mu\nu}^{\mathrm{rel}}$, into which the contributions from z_i^a and z_i^J have been absorbed. The overlap matrix derivatives $(\partial/\partial\xi)S_{\mu\nu}$ come along with the Lagrange multipliers $X_{\mu\nu}$ which are the AO representation of x_r^s. The index $\mathscr{K}$ runs over all two-electron operators $\hat{O}_{12}^{\mathscr{K}}$. In the case of MP2-F12/A this comprises r_{12}^{-1}, $f(r_{12})$, $f(r_{12})r_{12}^{-1}$, and $|\nabla_1 f(r_{12})|^2$. All these integral derivatives are joined with the respective two-electron density matrices.

In the MO representation these density matrices possess two occupied and two general indices (including frozen and CABS orbitals). Storage of these matrices and their subsequent back-transformation and contraction with integral derivatives is likely to pose a severe bottleneck, in particular, as for certain integral types up to two indices will also include the CABS. This problem is removed when using density fitting (see section 7.7). This approximation replaces the terms with four-index integral derivatives by terms involving three-index and two-index integrals and corresponding density matrices

$$\sum_{\mu\nu\kappa\lambda} d_{\mu\nu\kappa\lambda}^{\mathscr{K}} \frac{\partial\langle\mu\nu|\hat{O}_{12}^{\mathscr{K}}|\kappa\lambda\rangle}{\partial\xi} \rightarrow \sum_{\mu\kappa P} \Delta_{P,\mu\kappa}^{\mathscr{K}} \frac{\partial(\mu\kappa|\hat{O}_{12}^{\mathscr{K}}|P)}{\partial\xi} + \sum_{PQ} \gamma_{PQ}^{\mathscr{K}} \frac{\partial(P|\hat{O}_{12}^{\mathscr{K}}|Q)}{\partial\xi} \qquad (434)$$

As in section 7.7 the indices P and Q run over the auxiliary basis employed for density fitting. The quantities $\Delta_{P,\mu\kappa}^{\mathscr{K}}$ and $\gamma_{P,Q}^{\mathscr{K}}$ are the effective three- and two-index two-particle density matrices.

An example application is shown in Table 22 for the ammonia−water complex. Using MP2-F12 in the structure determination, for both the intermolecular distance and the resulting interaction energy basically converged results are obtained at the triple-ζ level, and even using a double-ζ basis set only little deviation from the putative basis-set limit is found. In contrast, conventional calculations are plagued by basis-set superposition errors, which in the present case fortuitously compensate for the basis-set error in the correlation contribution. The results including the counterpoise correction[545] reveal a much larger uncertainty in the conventional results, for example, for the hydrogen bond which is 6 pm longer for the counterpoise-corrected double-ζ calculation (see also ref 546).

8.3. Excited States

Multireference approaches (section 6.9) can treat excited states rather naturally. Nevertheless, only the most recent works have actually moved beyond the ground state, for example, different low-lying states of methylene were considered by Flores and Gdanitz[493] using the MRACPF-R12 approach. Similarly, in his initial work on F12 corrections for MR-MP2 Ten-no[430] applied his method to the excited states of carbon atom and silane. Shiozaki and Werner reported CASPT2-F12 excitation energies for pyrrole[431] and MRCI-F12 excited-state potential energy curves for LiF, O_3, and the H_2 + OH reaction.[433] In all cases the correlation factors significantly improve the convergence of excitation energies toward the basis-set limit, as expected from the good performance for ground-state energies.

Single-reference theories, as coupled-cluster theory, are also capable of describing excited states, for example, by use of response theory.[547] The basic principle of this approach is as follows: Formulate the time-dependent coupled-cluster equations and obtain the response functions and equations. In this procedure it is important to take care of a physically correct pole structure of the response functions. If this is the case, one may identify the position of the poles as excitation energies and devise equations to directly calculate these. In the case of coupled cluster, one finds that the excitation energies can be obtained as the eigenvalues of the Jacobian **A** which is the first derivative of the coupled-cluster residual $\Omega_\mu = \langle\mu|e^{-T}He^{T}|\mathrm{HF}\rangle$ (cf. section 6.5) with respect to the cluster amplitudes

$$A_{\mu\nu} = \frac{\partial\Omega_\mu}{\partial t_\nu} = \langle\mu|e^{-\hat{T}}[\hat{H},\hat{\tau}_\nu]e^{\hat{T}}|\mathrm{HF}\rangle \tag{435}$$

For excitation energies, the procedure turns out to be equivalent to the equation of motion coupled-cluster (EOM-CC) method. Some differences, however, occur for calculation of transition moments and excited-state properties, which only for response theory are strictly size consistent. The particular appeal of response theory is the fact that any (approximate) method can be fully defined by its ground-state energy Lagrange functional. All other equations can be derived from that by the response formalism.

A straightforward application of response theory to CC2-R12 was reported in Fliegl et al.[457] CC2 is a simplification of CCSD which truncates the doubles equations such that excitation energies remain correct through second order in the fluctuation potential.[548] Fliegl et al. obtained a general eigenvalue problem of the form

$$\mathbf{A}\mathscr{E} = \mathbf{S}\mathscr{E}\omega \tag{436}$$

where **S** is the metric matrix with elements

$$S_{\mu\nu} = \langle\mu|\hat{\tau}_\nu|\mathrm{HF}\rangle \tag{437}$$

The geminal–geminal block $S_{\mu_{2'}\nu_{2'}}$ is equivalent to the X intermediate, eq 268, while for conventional excitations the metric is unity. Analogous to the cluster amplitudes, the vector $\mathscr{E}$ consists of a singles, $\mathscr{E}_1$, doubles, $\mathscr{E}_2$, and geminal part, $\mathscr{E}_{2'}$.

Contrary to initial expectations, the excitation energies were not found to improve by including the correlation factor in CC2-R12. On the contrary, for certain cases a significantly worse convergence was observed.[457] It was found that this problem is caused by the ansatz for the geminal contribution which is inherently biased toward the ground state. The geminal contribution to the excited state can be written as the operator

$$\mathscr{E}_{2'} = \sum_{\substack{i>j\\a>b}} \mathscr{E}^{ij}_{kl} \sum_{\alpha>\beta} w^{kl}_{\alpha\beta} a^{\alpha\beta}_{ij} \tag{438}$$

The $\mathscr{E}^{ij}_{kl}$ amplitudes just include occupied indices, and the correlation factor effectively only contains basis functions of the type $f(r_{12})|ij\rangle$. Hence, the expansion misses contributions

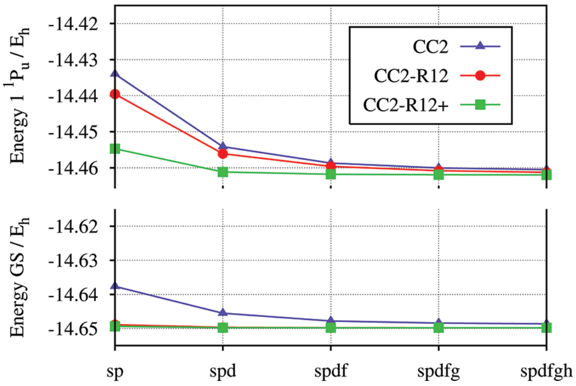

Figure 17. Partial wave expansion of the ground- and ^{1}P excited-state energy of the Be atom using CC2 and a 20s17p14d11f8g5h basis and subsets thereof. R12 denotes the usual ansatz for the linear correlation factor, the extended ansatz (R12+) includes virtual p orbitals in the generating space of the geminal. Figure based on the values from ref 458.

from the virtual orbitals. Even worse, in certain cases it might even not contain any geminal contributions. This happens if no occupied orbitals of the appropriate symmetry are present. Consider, for example, the P state of the Be atom, whose ground state features occupied *s*-type orbitals only. This is illustrated by Figure 17: The ground-state converges quickly with CC2-R12, but the excited state remains nearly unaffected by the correlation factor.

The finding is supported by a numerical analysis[457,458] which indicates that the geminal fails to describe excited-state correlation effects. It was therefore suggested to extend the generating space of the geminal to include virtual orbitals[458] (see also section 6.6.4). Computational feasibility and numerical stability demands, however, restricting these additional orbitals to a minimal set. Neiss et al.[458] therefore performed a selection based on MP2 natural orbitals. The approach, termed R12+, indeed leads to the expected improvements, as indicated in Figure 17.

Yang and Hättig[460] later generalized the approach to F12 correlation factors. However, they adhered to the original geminal factor with occupied orbitals only but found that excited-state structures and vibrational frequencies are nevertheless well described.

A different route was taken by Köhn[463] with the intention of combining response theory and the SP ansatz. As a pure fixed-amplitude geminal does not contribute to the response, an extension is needed. The extended SP (XSP) ansatz, as described in section 6.6.4, leads to the desired amplitudes, which are obtained as the response of $[\hat{R}^{(hp)},\hat{T}_1]$

$$\hat{\mathscr{E}}_{2'} = \left[\hat{R}^{(hp)},\hat{\tilde{\mathscr{E}}}_1\right] = \sum_{\substack{i>j\\\alpha>\beta}} \left(\sum_c \tilde{\mathscr{E}}^{i}_{c} w^{cj}_{\alpha\beta} + \sum_c \tilde{\mathscr{E}}^{j}_{c} w^{ic}_{\alpha\beta} \right) a^{\alpha\beta}_{ij} \tag{439}$$

Clearly, this ansatz incorporates geminals of the type $f(r_{12})|ia\rangle$, that is, a correlation factor times a singly excited determinant. Two choices are possible for the above parametrization: One can either fix $\hat{\tilde{\mathscr{E}}}_1 = \hat{\mathscr{E}}_1$ (as it naturally results from the expansion, eq 339, where $[\hat{R}^{(hp)}, \hat{T}_1]$ appears) or allow $\tilde{\mathscr{E}}_1$ as an additional free parameter. The first choice is numerically more stable, but a small bias toward the ground state remains. Better results for excitation energies are obtained with the second choice; for excited-state structures and vibrational frequencies, however, both choices work equally well.[463]

Table 23. Comparison of the CCSD Values for the Frequency-Dependent ESHG Hyperpolarizabilities $\gamma_{||}(\omega)$ of N_2 (in atomic units) Using Conventional CCSD and Different Explicitly Correlated Variants[a]

	CCSD[b]		CCSD(R12)[b]			CCSD(F12)[c]	CCSD(F12′)-XSP[d]	
λ/nm	TZ	QZ	TZ	QZ	est. limit[e]	TZ	TZ	QZ
∞	903.0	882.7	882.4	872.7	864.5	872.4	864.3	865.2
1055.0	959.2	936.9	936.7	925.9	917.2	918.2[e]e	916.9	917.7
694.3	1041.1	1015.6	1015.7	1003.2	993.8	995.6[e]	993.4	993.9
457.9	1273.4	1238.1	1239.1	1221.5	1210.0	1214.0[e]	1208.9	1209.0

[a] The t-aug-cc-pVXZ basis sets have been used in all calculations, unless indicated otherwise. [b] Values from ref 459. [c] Values from ref 461. [d] Values from ref 465. [e] $\lambda = \infty$: CCSD(R12)/t-aug-cc-pV6Z value, for nonzero frequency estimated as $\gamma(\omega) = \gamma_{(R12)/QZ}(\omega) \times \gamma_{(R12)/6Z}(0)/\gamma_{(R12)/QZ}(0)$. [f] Obtained with the d-aug-cc-pVTZ basis set.

Closely related to this approach is the work of Bokhan and Ten-no, who recently showed that ionization potentials can be accurately calculated within the SP approach.[549] In this case, one electron is removed upon excitation, and hence, no extension of the generating space for the geminal is required.

8.4. Analytical Calculation of Higher-Order Response Properties

Response theory not only provides a framework for calculating excited states, as discussed in the previous section, but also gives access to linear and nonlinear optical properties. Except for the static limit, calculation of coupled-cluster response properties is not compatible with including the response of the SCF orbitals (also known as "relaxed properties"). The reason for that is the occurrence of additional poles due to the response of the SCF wave function.[547] Instead, one relies on the capability of the coupled-cluster wave function to approximately treat orbital relaxation through the $\hat{T}_1$ operators. Often the term "unrelaxed properties" is used in this context, but it should be understood that the term unrelaxed merely refers to the absence of SCF contributions to the response.

For R12 and F12 wave functions the issue of orbital relaxation leads again to the question of an appropriate ansatz for the geminal. In all studies that include orbital relaxation contributions, the geminal generating space is adapted to the perturbation, and hence, no problems occur. This holds for all finite-difference studies mentioned in section 8.1 and the analytical relaxed first-order properties discussed in refs 540 and 542.

In the orbital-unrelaxed ansatz the geminal generating space is not adapted to the perturbation, as $\hat{T}_1$ does not directly modify $T_{2'}$. Neiss and Hättig[459] derived and implemented analytical response properties up to second hyperpolarizabilities for the CCSD(R12) approach. In most cases, the response of the c_{kl}^{ij} was found to be sufficiently flexible, and an improved basis-set convergence of the calculated properties was observed. In addition to static properties, also the dispersion of the electric-field-induced second-harmonic generation (ESHG) hyperpolarizability of N_2 was presented. For cases analogous to those giving problems for excitation energies, however, a slowed-down convergence was found, for example, for the polarizability of BH perpendicular to the molecular axis. In this case, the extended R12+ ansatz is needed. Yang and Hättig[461,462] recently extended the work to Slater-type correlation factors.

Hanauer and Köhn[465] investigated the SP and XSP ansatz; see section 8.3 for a definition. They found best results for the XSP ansatz with optimized expansion coefficients in the geminal. In addition, they also considered a simplified method which is analogous to CCSD(F12*) and a correction for the error in one-electron contributions which is an iterative extension of the (S2) correction discussed in section 6.7. Apart from static nonlinear response properties of BH, LiF, and N_2, they also investigated the frequency dispersion of ESHG second hyperpolarizabilities of N_2 and the optical rotation of H_2O_2 at fixed values for the dihedral angle.

In Table 23 we compare the results for the dynamic ESHG hyperpolarizability of N_2 obtained with the different approaches that were presented in this section. The results clearly indicate that using Slater-type correlation factors converged results can already be obtained at the triple-ζ level, that is, with at most f functions in the basis set, while a conventional calculation must use i functions, and higher, in order to achieve this accuracy.[550] This is particularly important as properties like γ are relatively demanding with respect to the convergence of the one-electron basis set, requiring three sets of diffuse functions in the present example. In other words, in conventional calculations the choice of the basis is largely dictated by the interelectronic cusp rather than by the property under consideration. F12 methods relax the requirement to include high-angular momentum and allow adding those functions to the basis set which really are needed for accurate prediction of the property.

As a final remark, we note that the developments reported in the last two sections are restricted to CCSD theory. Quantitative comparison with the experiment requires inclusion of connected triply excited clusters. Work on this issue is in progress but not yet documented in the literature.

9. SUMMARY AND OUTLOOK

In the present review we have presented the basics and historical background of present-day R12 and F12 theories for nonrelativistic electronic wave functions. Fundamental properties of correlated electronic wave functions have been discussed as well as the explicitly correlated wave functions for few-electron atoms and molecules that were developed in the early days of quantum mechanics. Hylleraas-type and Hy-CI wave functions including variants for linear molecules (James–Coolidge- and Kołos–Wolniewicz-type wave functions) have proven to be very useful for accurate electronic-structure calculations ever since their conception in the 1920s and 1930s. The corresponding computational methods remain highly relevant to contempory numerical quantum chemistry and physics today, for example, for calculation of non-Born–Oppenheimer corrections, of various relativistic effects including those described by quantum electrodynamics, and of electronically excited states and for calculation of molecular properties such as rovibrational energy levels (e.g., for H_3^+).

Gaussian functions are very well suited to the represention of electronic wave functions of atoms and molecules with very high accuracy, despite their inability to satisfy the electronic cusp conditions. Exponentially correlated Gaussians have been used in variational calculations on systems with up to six electrons such as the carbon atom but as is also true for the Hylleraas-type and Hy-CI wave functions, progress toward more-electron systems is slow due to the very high computational costs involved. Gaussian geminals are exponentially correlated Gaussians for two electrons, either for a two-electron system or for the two-electron pair functions in pair theories for description of electron correlation, and they have been used successfully in the framework of second-order perturbation theory as well as coupled-cluster theory. However, due to the occurrence of six-center three-electron integrals, their range of application has remained rather limited. Nevertheless, when applied to few-electron systems, impressive results can be obtained, which was, for example, achieved for the four-electron problem of the helium pair potential.

R12 theories were introduced to quantum chemistry in 1985, and they have been actively developed ever since. Before 2004 linear r_{12} terms were used in the electronic wave functions, but thereafter, more general functions $f(r_{12})$ of the interelectronic distance have been considered. For this reason the newer methods are today known as F12 methods. Development of the R12 and F12 methods has been a breakthrough in explicitly correlated theories for general many-electron, polyatomic molecules, because the very challenging calculations of many-electron integrals (more than two) is entirely avoided. This was achieved by insertion of a resolution of the identity (also know as completeness relation) into the many-electron integrals such that only products of two-electron integrals remained. In particular, after it was proposed to use an auxiliary basis set for the completeness relation in 2002 and after the change to the functions $f(r_{12})$, that is, Slater-type geminals, further development of the R12/F12 methods has been vary rapid. These methods have now reached a high level of maturity, and they have been implemented in a number of noncommercial as well as commercial program packages of numerical quantum chemistry.

In this review we have provided many details of F12 theory and many convincing arguments in favor of the applicability of F12 methods for obtaining reliable and accurate results in a cost-efficient manner. However, it is undeniably true that "*all the proof of the pudding is in the eating*". In other words, to actually find out how well they work the methods should be applied to chemical problems of current interest, where it is important to describe electron-correlation effects near the limit of a complete one-particle basis set. In our own work at the CCSD(F12) level, for example, we recently computed the enthalpies of formation of the radicals $HOSO_2$[551] and $HOSO_4$,[552] we studied the thermochemistry of the $HOSO_2 + O_2$ association reaction,[552] and we used the CCSD(F12) model to compute accurate reaction rate constants for two reactions between the CH_4 molecule and the CH_3 radical.[553] F12 methods are particularly useful for benchmarking, as shown in ref 554, where the hydrogenation of benzene and naphthalene was carefully studied by means of F12 methods to test more approximate methods for calculation of the hydrogenation products of fullerenes. These applications show the potential of the explicitly correlated methods in the field of computational thermochemistry.[522] With regard to larger systems, we refer to our own large-scale MP2-F12 calculations on the trimerization of the pyrazine ($C_4H_4N_2$)-molecule[555] or the recent study of complexes of argon with *n*-propanol.[556]

Feller et al.[557] performed a calibration study of the CCSD(T)-F12a/b methods for C_2 and small hydrocarbons, and Lane and others[444,558−560] assessed the performance of F12 with respect to weak intermolecular interaction (e.g., hydrogen bonds). Patkowski and Szalewicz[561] investigated the CCSD(T)-F12a/b methods on the Ar pair potential, but these authors note that "*the CCSD-F12 method cannot yet compete with the orbital basis calculations and extrapolations*." In this regard, we note that first and foremost the F12 methods have been developed to accomplish a rapid convergence toward the limit of a complete basis and to get a very good answer very quickly, but it appears that for extreme accuracy at the limits of what is technically feasible still more experience must be gained with the various approximations—F12/a or F12/b or (F12*)—and (auxiliary) basis sets in such calculations.

In a series of papers Botschwina and co-workers[562−567] performed explicitly correlated coupled-cluster calculations on astrochemically relevant molecules such as polyynes, their anions, the propargyl radical (H_2C_3H), etc. In particular, in the field of high-resolution spectroscopy and also for the study of molecular reaction dynamics, use of explicitly correlated coupled-cluster methods may be advantageous for the accurate calculation of the necessary potential energy hypersurfaces (see, for example, refs 535, 568, and 569).

Concerning larger systems or even solids, we note that the explicitly correlated MP2 and coupled-cluster theories not only have been implemented in terms of the local-correlation methods but also can be applied in the framework of Stoll's incremental scheme[512,570] or in the framework of quantum mechanics/molecular mechanics (QM/MM) strategies.[571,572] Preliminary results have been obtained for MP2-F12 calculations on systems with periodic boundary conditions,[573] where Slater-type geminals may be particularly important: in solids, the large one-particle basis sets required for accurate electron-correlation calculations can often not be used due to near linear dependencies, and explicit correlation may solve this problem.

Concerning heavy-element computational chemistry, we note that scalar relativistic corrections and scalar relativistic effective core potentials have been implemented[437,442,574] and that a two-component MP2-F12 theory with spin orbit relativistic effective core potentials has been developed.[442,575] However, with respect to applying F12 methods in four-component methods, for example, on the basis of the Dirac−Coulomb many-electron Hamiltonian, we note that the problems related to the Brown−Ravenhall[576] disease become rather subtle and difficult. Since fully relativistic calculations are beyond the scope of the present review, we refer the interested reader to very recent work by Pestka and co-workers.[577−580]

We expect that in the near future explicitly correlated coupled-cluster calculations in small basis sets will replace conventional coupled-cluster calculations in very large one-electron basis sets, because the explicitly correlated calculations will be more economical. The computer programs will be developed further toward including explicitly correlated higher excitations, methods for excited states, multireference methods, and analytical derivatives. These programs will then have the potential to become very useful tools for numerical quantum chemistry with a broad range of applicability.

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Christof Hättig studied Chemistry at the University Bonn, Germany, where he received his Ph.D. degree in Theoretical Chemistry in 1995. His thesis on the development of a correlated wavefunction method of dispersion coefficients for intermolecular interactions was supervised by Professor Bernd A. Hess. In 1996 he joined as a postdoctoral research associate and since 1997 as Forskningsadjunkt (Assistant Research Professor) in the theoretical chemistry group at Aarhus University, Denmark, where he worked with Poul Jørgensen on the development of an integral-direct coupled-cluster response code for the calculation of nonlinear optical properties such as first and second hyperpolarizabilities and two- and multiphoton transition moments. From 1999 to 2000 he has been a researcher at the Institute of Nanotechnology (INT) of the Forschungszentrum Karlsruhe, Germany, in the group of Professor Reinhart Ahlrichs. In 2000 he became head of an independent junior research group at the INT, and in 2003 he received his habilitation (venia legendi) in theoretical chemistry at the Universität Karlsruhe (TH). During that time he started to work on the development of approximate coupled-cluster response methods for electronic spectra and excited states in large molecules and became involved in the TURBOMOLE program package. In 2004 he was awarded the Hans G. A. Hellmann Prize of the Arbeitsgemeinschaft Theoretische Chemie. Since 2006, he has been Associate Professor for Theoretical Chemistry at the Ruhr-University Bochum, Germany.

Wim Klopper was born in Opperdoes, The Netherlands, in 1961. He studied Chemistry at the University of Leiden (1979–1982) and at the Ruhr-Universität Bochum (1982–1985). He received his Ph.D. degree in 1989 from the Ruhr-Universität Bochum under the supervision of Werner Kutzelnigg. He was a postdoctoral research associate in the groups of Jan Almlöf (University of Minnesota, 1991) and Hans Peter Lüthi (ETH Zurich, 1993–1996) and he spent three years (1996–1999) at the University of Oslo as Førsteamanuensis (Associate Professor) and three years (1999–2002) at the University of Utrecht as Akademie Onderzoeker of the Royal Netherlands Academy of Arts and Sciences (KNAW). In September 2002 he accepted the position of Professor of Theoretical Chemistry at the Universität Karlsruhe (TH), and in 2003 he became Group Leader at the Institute of Nanotechnology at the Forschungszentrum Karlsruhe. (Since 2009, the Universität Karlsruhe (TH) and the Forschungszentrum Karlsruhe have merged into the Karlsruhe Institute of Technology.) He has received the Venia Legendi for Theoretical Chemistry (ETH Zurich, 1998), the Hans G. A. Hellmann Prize of the Arbeitsgemeinschaft Theoretische Chemie (1999), and the Medal of the International Academy of Quantum Molecular Science (1999). He became Member of the International Academy of Quantum Molecular Science in 2011. His research interests include further development of explicitly correlated electronic structure methods and accurate computation of molecular energies as well as properties.

Born in 1974 in Germany, Andreas Köhn received his Ph.D. degree in Chemistry in 2003 under the supervision of Professor R. Ahlrichs at the University of Karlsruhe. After postdoctoral work with Christof Hättig at the Forschungszentrum Karlsruhe (2003) and Professor J. Olsen and Professor P. Jørgensen at the University of Aarhus, Denmark (2003–2005), he moved in 2005 to the University of Mainz, where he started an independent young researcher's group in theoretical chemistry and received in 2011 the venia legendi in physical chemistry. Since 2011 he has been a Heisenberg fellow of the German Research Foundation (Deutsche Forschungsgemeinschaft). His research interests are the development of advanced coupled-cluster methods, particularly with respect to explicit electron-correlation and multireference extensions, and development and application of methods for photophysical and photochemical problems. For his research he recently received the Hans G. A. Hellmann prize of the Arbeitsgemeinschaft Theoretische Chemie (2010) and the medal of the International Academy of Quantum Molecular Sciences (2011).

David P. Tew was born in the United Kingdom in 1977. He studied Natural Sciences at Trinity College, Cambridge, where he later also received his Ph.D. degree for work on wide amplitude motion in quantum molecular dynamics under the supervision of Professor N. C. Handy (2003). In 2004 he moved to the Univeristy of Karlsruhe, Germany, to work with Professor W. Klopper on explicitly correleted coupled-cluster theory, first as a Marie-Curie Fellow and then as an independent researcher. After 5 years in Karlsruhe he obtained a Royal Society University Research Fellowship and moved to the Centre for Computational Chemistry at Bristol University, U.K., where he now continues to persue his research interests, developing accurate and efficient methods for both electronic structure and quantum molecular dynamics.

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