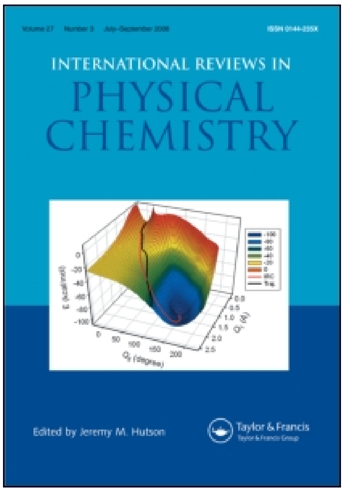

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R12 methods in explicitly correlated molecular electronic structure theory

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R12 methods in explicitly correlated molecular electronic structure theory

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The past few years have seen a particularly rich period in the development of the explicitly correlated R12 theories of electron correlation. These theories bypass the slow convergence of conventional methods, by augmenting the traditional orbital expansions with a small number of terms that depend explicitly on the interelectronic distance r_{12}. Amongst the very numerous discoveries and developments that we will review here, two stand out as being of particular interest. First, the fundamental numerical approximations of the R12 methods withstand the closest scrutiny: Kutzelnigg's use of the resolution of the identity and the generalized Brillouin condition to avoid many-electronic integrals remains sound. Second, it transpires that great gains in accuracy can be made by changing the dependence on the interelectronic coordinate from linear (r_{12}) to some suitably chosen short-range form (e.g., $\exp(-\alpha r_{12})$). Modern R12 (or F12) methods can deliver MP2 energies (and beyond) that are converged to chemical accuracy (1 kcal/mol) in triple- or even double-zeta basis sets. Using a range of approximations, applications to large molecules become possible. Here, the major developments in the field are reviewed, and recommendations for future directions are presented. By comparing with commonly used extrapolation techniques, it is shown that modern R12 methods can deliver high accuracy dramatically faster than by using conventional methods.

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Contents

1. Introduction

The slow convergence of electron correlation energies in orbital expansions limits the accuracy that can currently be achieved in wavefunction quantum chemistry. This slow convergence is coupled with a steep increase in computer resources as the orbital expansions become larger. Consider, for example, calculations in the popular correlation consistent basis sets of Dunning *et al.*, cc-pVnZ with $n = 2, 3, 4, \ldots$ for double-zeta, triple-zeta, quadruple-zeta, etc. [1–5]. These basis sets are constructed in a principal expansion, so that a double-zeta basis for a first-row atom consists of 3s2p1d, triple-zeta of 4s3p2d1f, and so on. The number of basis functions in these sets increases as $m = \mathcal{O}(n^3)$. Since conventional electronic structure methods need four-index two-electron integrals, the computational work associated with calculations in these basis sets increases (at least) as $t = \mathcal{O}(m^4)$ or $t = \mathcal{O}(n^{12})$.

Unfortunately the errors in correlation energies decay only like $\epsilon = \mathcal{O}(n^{-3})$ [6, 7], or, in terms of the number of basis functions, as $\epsilon = \mathcal{O}(m^{-1})$ [8]. This slow convergence coupled with the steep rise in cost of calculations in larger basis sets leads to the terrible relationship $\epsilon = \mathcal{O}(t^{-1/4})$ between error in correlation energies and computer time. Thus the rewards in terms of accuracy for increasing computational effort are extremely meagre: a 10 000-fold increase in computer resources gives only one order of magnitude improvement in accuracy. Explicitly correlated methods circumvent this very slow convergence by supplementing orbital expansions with terms that depend explicitly on interelectronic distances.

1.1. *The origin of the problem*

The slow convergence of configuration interaction (CI) expansions in orbital basis sets is linked to the presence of the correlation cusp in the wavefunction. As charged particles approach one another, the Coulomb interaction – which scales like the reciprocal of the interparticle distance – diverges. Nonetheless the local energy $E = \hat{H}\Psi/\Psi$ is constant everywhere for the exact wavefunction; thus the divergence in the Coulomb energy must be exactly cancelled by the kinetic energy operator. This can only be so if the wavefunction becomes linear in the interparticle distance as the particles coalesce because $-(1/2)\nabla^2 r = -1/r$. A more rigorous examination of the equations leads to the famous cusp condition of Kato [9],

$$\left(\frac{\partial\Psi(r_{12})}{\partial r_{12}}\right)_{r_{12}\to 0,\,\mathrm{av}} = \frac{1}{2}\Psi(r_{12} = 0) \tag{1}$$

('av' indicates spherical averaging) and to more general conditions by Pack and Brown [10]. It is the difficulty of reproducing this cusp feature in the wavefunction that makes convergence with respect to orbital expansions so difficult.

It has been argued (correctly) for quite some time that the actual contribution to the energy from a small sphere of configuration space around the coalescence point is negligible [11, 12]. So in fact it is not the cusp condition that is important for energies, but rather the overall shape and size of the Coulomb hole. There are some properties, nevertheless – notably the two-electron expectation value $\langle\delta(r_{12})\rangle$ that arises in the relativistic two-electron Darwin term [13] – for which the value at the cusp is the very quantity of interest, and then special care is required to reproduce the cusp accurately.

1.2. *Two-electron systems*

Hylleraas, frustrated by the slow convergence of his orbital expansions for helium [14], realized that the problem could be overcome by including terms in the wavefunction that depend explicitly on interelectronic coordinates [15]†.

Hylleraas used the coordinates $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$ to construct a wavefunction for the helium atom in the form

$$\Psi(s, t, u) = e^{-\alpha s} \sum_{k\ell m} c_{k\ell m} s^k t^{2\ell} u^m, \tag{2}$$

where only even powers of t appear to ensure the symmetry of the spatial wavefunction, leading to the correct antisymmetric singlet ground state (para-helium). Even with extremely small expansions of this kind, Hylleraas was able to reduce the discrepancy with the experimental value of the ionization energy of helium from 0.12 to 0.01 eV.

Extensions of the Hylleraas approach to H_2 were soon afterwards described by James and Coolidge [18], and later by Kołos and Wolniewicz [19], but attempts to apply such ideas to larger systems were hampered by the introduction of integrals over the coordinates of many electrons. These integrals are typically not solvable in analytic form, and, worse, they are so numerous that the computational effort involved grows very steeply with the size of the problem.

1.3. *Explicitly correlated MP2 methods*

For MP2 calculations is it conventional to take advantage of the decomposition of the second-order energy into a sum of pair contributions [20], a decomposition that requires that the first-order pair functions $|u_{ij}\rangle$ be strongly orthogonal to the occupied space. In orbital based methods this is trivially achieved by expanding $|u_{ij}\rangle$ in products of virtual orbitals. In general, though, it is necessary to use an explicitly projected form $\hat{Q}_{12}|u_{ij}\rangle$ where $\hat{Q}_{12}$ is a projection operator onto the (complete) virtual space. The Hylleraas functional [21]

$$H[u_{ij}] = \langle u_{ij}|\hat{Q}_{12}(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)\hat{Q}_{12}|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12} r_{12}^{-1}|ij\rangle \geq \epsilon_{ij}^{(2)} \tag{3}$$

can then be minimized for each pair to provide upper bounds for each MP2 pair energy. (Here, and throughout sections 1 and 2, we use a spin-orbital formalism, in which i and j denote spin-orbitals, and in which the functions $|u_{ij}\rangle$ and $|ij\rangle$ are understood to be properly antisymmetrized. $\hat{F}$ is the Fock operator and ϵ_i is an orbital energy. For simplicity, we assume that the spin-orbitals are canonical Hartree–Fock orbitals.)

In conventional MP2 calculations, the pair functions $|u_{ij}\rangle$ are built from one-electron orbital products. In explicitly correlated MP2 theory, however, these pair functions

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†See also [16] for a modern perspective on Hylleraas' achievements and [17] for an English translation.

also contain terms that depend on the interelectronic coordinate explicitly. If the pair function $|u_{ij}\rangle$ is an explicit two-electron function (i.e. a geminal), then the second term in equation (3) contains three-electron integrals, and the first contains both three- and four-electron terms. The number of four-electron integrals scales as $\mathcal{O}(m^8)$, and although the full integral transformation of these can be avoided, their evaluation still represents a formidable computational challenge for all but the smallest of cases.

Three basic strategies have been developed to avoid the need to compute the four-electron integrals in MP2 and other explicitly correlated theories: the transcorrelated method of Boys, the weak orthogonality functional of Szalewicz *et al.*, and the R12 approaches of Kutzelnigg and Klopper. The first two of these will be outlined in the following sections; the last forms the main focus of the rest of this review.

1.4. *Gaussian geminals*

Boys [22] and Singer [23] independently realized that it was possible to compute (analytically) all of the necessary integrals for explicitly correlated calculations on molecules, provided that both the one- and two-electron basis functions took the form of Gaussians. This being the case, all many-electron integrals that arise can be reduced exactly to expressions involving the Boys function $F_m(T)$. Although a most significant advance, the problem of the rapidly scaling number of many-electron integrals still obstructed applications to larger systems.

In the 1980s, Szalewicz, Jeziorski, Monkhorst and Zabolitzky introduced a scheme for performing MP2 calculations that capitalized on the advantages of the Gaussian geminals of Boys and Singer but, through an ingenious device, managed to avoid the need to compute any four-electron integrals at all [24, 25]. This is achieved through the weak orthogonality functional (WOF), which retains a strict upper bound to the second-order energy.

The WOF has the form

$$W[u_{ij}] = \langle u_{ij}|\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j|u_{ij}\rangle + 2\langle u_{ij}|\hat{Q}_{12}r_{12}^{-1}|ij\rangle \\ + \eta_{ij}\langle u_{ij}|\hat{O}_1 + \hat{O}_2|u_{ij}\rangle \geq \epsilon_{ij}^{(2)}, \quad (4)$$

where η_{ij} is a positive parameter satisfying $\eta_{ij} \geq (\epsilon_i + \epsilon_j)/2 - \epsilon_1$ and where ϵ_1 is the orbital eigenvalue of the lowest occupied orbital. The Ansatz used for the pair function in WOF studies has the form

$$|u_{ij}\rangle = \hat{\mathcal{A}}\left(\sigma(1)\sigma(2)\sum_p a_p e^{-\alpha_p|\vec{r}_1-\vec{A}_p|^2-\beta_p|\vec{r}_2-\vec{B}_p|^2-\gamma_p|\vec{r}_1-\vec{r}_2|^2}\right), \quad (5)$$

with full optimization of all linear coefficients a_p, all exponents α_p, β_p and γ_p, and of all function centres $\vec{A}_p$ and $\vec{B}_p$, which are not constrained to be coincident with nuclei ($\hat{\mathcal{A}}$ is an antisymmetrizer and σ is a spin function). All parameters are optimized individually for each pair function $|u_{ij}\rangle$. Szalewicz *et al.* were able to obtain highly converged MP2, MP3 and coupled-cluster results for a variety of small molecules and atoms [26–28].

One disadvantage of the WOF Gaussian geminals method as used by Szalewicz *et al.* is the need for expensive non-linear optimizations of basis set parameters. This is necessary to obtain extremely high accuracy, but if an efficient method to obtain MP2 energies converged to chemical accuracy is the target, one can imagine geminals theories that involve optimization of linear expansion coefficients only. This was exactly the approach of Persson and Taylor, who investigated the possibility of augmenting conventional MP2 calculations with a modest set of (say, six) Gaussian geminal functions $\exp(-\alpha r_{12}^2)$ [29–33]. This research suggested that high accuracy could be achieved in modest AO basis sets (of around triple-zeta quality) augmented by a small number of Gaussian geminal functions.

Despite the successes, it remains the case that Gaussian geminals calculations (with or without non-linear optimizations) with exact three-electron integral evaluation are limited to high accuracy studies of small systems. Furthermore, it seems that the penalty function $\eta_{ij}\langle u_{ij}|\hat{O}_1 + \hat{O}_2|u_{ij}\rangle$ in the WOF may lead to poor results if small basis sets are used. For example, a second-order MP2 correlation energy of only $-333.1\,\mathrm{m}E_\mathrm{h}$ is obtained for the neon atom if nine Gaussian geminal functions with even-tempered exponents in the range of 1/9 to $729a_0^{-2}$ are added to a conventional MP2 expansion in the aug-cc-pCVDZ basis (see table 7.10 of [32]; the basis set limit is $-388.1\ \mathrm{m}E_\mathrm{h}$ [34]). A similar calculation with six contracted Gaussian geminals, however not relying on the WOF but rather on the approximations discussed in section 3, yields $-376.5\ \mathrm{m}E_\mathrm{h}$.

Note that in this review, we distinguish between Gaussian geminals methods, in which the whole pair function is expanded in Gaussian geminals (cf. equation 6), and R12 (or rather F12) methods, in which the conventional expansion in terms of orbital products is supplemented with a few Gaussian geminals (cf. section 2). The methods of Szalewicz and coworkers [24–28] belong to the former, those of Taylor and coworkers [29–33] belong to the latter.

1.5. *Exponentially correlated Gaussians*

The conclusion of the previous section that the Gaussian geminals method is limited to small systems also applies to the method of exponentially correlated Gaussians (ECGs) [35–38]: they are limited to high accuracy studies of extremely small systems. In the ECG method, an expansion similar to equation (5) is chosen for the whole N-electron full configuration interaction wavefunction,

$$\Psi = \hat{\mathcal{A}}\left(\Theta_{S,M_S}\hat{\mathcal{S}}\sum_{k=1}^{K} c_k\psi_k\right), \tag{6}$$

where $\hat{\mathcal{A}}$ and $\hat{\mathcal{S}}$ are permutational and spatial symmetry operators, respectively, and Θ_{S,M_S} is a proper spin eigenfunction. The N-electron basis functions $|\psi_k\rangle$ are of the form [39]

$$\psi_k(1,2,\ldots,N) = \exp\left[-\sum_{i=1}^{N}\sum_{j=1}^{N} A_{ij,k}(\vec{r}_i - \vec{s}_{i,k})\cdot(\vec{r}_j - \vec{s}_{j,k})\right]. \tag{7}$$

Each basis function for a system with N electrons contains $3N + N(N+1)/2$ non-linear variational parameters ($A_{ij,k}$, $\vec{s}_{i,k}$) and depends on the coordinates of all electrons. The resulting $3N$-dimensional integrals can, however, be computed in closed form [35, 40, 41]. For very small systems, the accuracy achieved with ECGs is unprecedented (cf. [42] and references therein). ECGs can also be applied straightforwardly to fully non-adiabatic computations [35, 43].

1.6. *The transcorrelated method*

Computations on fully correlated wavefunctions of the form

$$\Psi = C\Phi, \tag{8}$$

where Φ is some suitably constructed reference wavefunction, and where

$$C = \prod_{i<j} f(\vec{r}_i, \vec{r}_j), \tag{9}$$

are hampered by the introduction of coupled integrals over $3N$ dimensions for an N-electron system. On the lines of previous work by Hirschfelder [44] and Jankowski [45], Boys and Handy recognized that by using the non-Hermitian transcorrelated Hamiltonian $\tilde{H} = C^{-1}\hat{H}C$ they could formulate a set of approximate equations for the wavefunction and for the energy that involved integrals over no more than three particles at a time [46]. Furthermore, all of the three-electron operators that arise have the form $[\vec{\nabla}_1 f(\vec{r}_1, \vec{r}_2)] \cdot [\vec{\nabla}_1 f(\vec{r}_1, \vec{r}_3)]$ (cf. [47] and references therein). In the Boys–Handy work, they chose a flexible form for the correlation function $f(\vec{r}_1, \vec{r}_2)$, which does not lead to analytically solvable integrals. However, they noted that the nine-dimensional integrals over $[\vec{\nabla}_1 f(\vec{r}_1, \vec{r}_2)] \cdot [\vec{\nabla}_1 f(\vec{r}_1, \vec{r}_3)]$ could be evaluated as two analytic three-dimensional integrals followed by a three-dimensional quadrature. This idea has been used more recently by Ten-no [48] (see section 3.4 below).

The same author has also examined the use of transcorrelated Hamiltonians with frozen Gaussian geminal expansions for $f(\vec{r}_1, \vec{r}_2)$ [49, 50]. The method with a Gaussian geminal expansion fitted to satisfy the cusp condition around coalescence showed improved convergence in second-order perturbation theory and in the coupled-electron pair approximation [51, 52]. The use of the non-Hermitian Hamiltonian results in the loss of a strict upper bound to the exact energy, and more flexible one-electron basis sets are required for stable results in comparison with other explicitly correlated methods. Nevertheless, the transcorrelated formulation has been useful for relevant advances in density functional theory [53] and quantum Monte Carlo methods [54–56].

2. R12 wavefunctions

In the preceding section we have discussed various explicitly correlated methods based on Gaussian geminals, exponentially correlated Gaussians and transcorrelated wavefunctions. These approaches have in common that the whole wavefunction or the whole pair function $|u_{ij}\rangle$ is expanded in explicitly correlated basis functions. Kutzelnigg and Klopper proposed a different MP2 approach in the 1980s, in which the pair function is first and foremost expanded in a basis of products of virtual orbitals, as in conventional MP2 theory. This conventional expansion is then supplemented by only one explicitly correlated basis function or a small number of them [57–59]. In this review, we shall focus on this particular class of approaches, which are denoted R12 methods, and in which a conventional expansion in terms of orbital products is supplemented by one or a few explicitly correlated two-electron basis functions.

2.1. *Definition*

In R12 methods the pair function $|u_{ij}\rangle$ in the Hylleraas functional (equation (3)) has the form

$$|u_{ij}\rangle = |v_{ij}\rangle + |w_{ij}\rangle, \tag{10}$$

with

$$|v_{ij}\rangle = \sum_{k<l} c_{ij}^{kl} \hat{Q}_{12} f_{12} |kl\rangle \tag{11}$$

and

$$|w_{ij}\rangle = \sum_{a<b} t_{ij}^{ab} |ab\rangle. \tag{12}$$

Here and in the following, orbital indices i, j, k, l, m will be used for spin-orbitals occupied in the Hartree–Fock reference state; indices a, b, c, d for virtual spin-orbitals and p, q, r, s for any molecular spin-orbitals. We restrict ourselves to real functions and amplitudes c_{ij}^{kl} and t_{ij}^{ab}.

In practically all of the R12 work until now, the sum over k, l in equation (11) has been restricted to occupied orbitals, but Taylor, Persson and Dahle and coworkers have also considered sums over occupied and virtual indices k, b as well as over virtuals a, b [29–33]. Recently, Neiss and coworkers have added a few seminatural virtual orbitals to the sum over k, l in explicitly correlated coupled-cluster linear-response calculations [60].

It is only since publication of [61] that the sum in equation (11) runs over the occupied orbitals k and l. In the first implementations of R12 theory, the pair function was restricted to only the diagonal term

$$|v_{ij}\rangle = c_{ij} \hat{Q}_{12} f_{12} |ij\rangle, \tag{13}$$

with $c_{ij} \equiv c_{ij}^{ij}$. This 'diagonal' Ansatz is, however, not invariant with respect to unitary transformations of the occupied orbitals. For example, different energies were obtained with canonical or localized Hartree–Fock orbitals (or with extremal electron pairs [62]).

If localized MOs are used, the energies are close to those obtained with the pair function of equation (11), and equation (13) may become useful again in the future in the context of local correlation methods (cf. section 5.2).

The projection operator $\hat{Q}_{12}$ that appears in equation (11) was introduced in section 1.3 above; this operator ensures the strong orthogonality of the pair function $|u_{ij}\rangle$, and the various choices for the form of $\hat{Q}_{12}$ are discussed below. The factor f_{12} is the correlation factor, which is a function of r_{12}, the distance between the electrons 1 and 2. Until very recently, this factor was always chosen as $f_{12} = r_{12}$, but other functions have been used more recently, as we shall see below. Some researchers speak of F12 methods in place of R12 methods if other functions than $f_{12} = r_{12}$ are used, to highlight the fact that a particular correlation factor f_{12} is used instead of r_{12}.

2.2. *Correlation factors*

Practically all of the early work with the R12 methods has been based on the correlation factor

$$f_{12} = r_{12}, \tag{14}$$

which takes care of the correlation cusp (equation (1)) and the fact that the many-body wavefunction is linear in r_{12} for very small interelectronic distance. Calculations with the linear factor have been very successful, not only for very small molecules but also for larger systems such as the water tetramer [63], the hydrogen fluoride pentamer [64], ferrocene [65], [10] annulene [66], and the benzene dimer [67]. But there are also two disadvantages connected with this linear correlation factor. First, the three- and four-electron integrals involved in the electronic structure calculation are difficult and cannot be evaluated analytically for a many-centre problem (the four-electron integrals could be avoided by means of the WOF approach (see section 1.4), but the three-electron integrals remain an obstacle). Second, the linear r_{12} term yields a proper wavefunction for small interelectronic distance but shows the wrong long-range behaviour.

Persson and Taylor [29, 30] (see also [68, 69]) have addressed these two drawbacks by fitting an expansion in Gaussian geminals to the linear r_{12} term,

$$r_{12} \approx \sum_{v} b_v \left[1 - \exp(-\gamma_v r_{12}^2)\right]. \tag{15}$$

Using the WOF approach, only three-electron integrals occur in any molecular calculation, and these three-electron integrals can be computed analytically. They are, however, numerous.

Samson and coworkers [70] have tried to damp the linear r_{12} term by multiplication with a Gaussian function,

$$f_{12} = r_{12} \exp(-\gamma r_{12}^2) = r_{12} + \mathcal{O}(r_{12}^3), \tag{16}$$

so that the correlation factor vanishes for large interelectronic distances while retaining the linear form for small r_{12}. A correlation factor as in equation (16) seemed to open perspectives for prescreening techniques in large molecules and could possibly be used in local correlation methods. However, Samson [71] found that the exponent γ should have a rather small value in order to obtain results with the same quality as those obtained with the linear r_{12} term, and a single Gaussian-damped r_{12} term did not seem very promising at the time [71].

Recently, Ten-no [72] suggested the use of a Slater-type geminal of the form

$$f_{12} = 1 - \exp(-\gamma r_{12}) = \gamma r_{12} + \mathcal{O}(r_{12}^2). \tag{17}$$

Excellent results were obtained with this correlation factor, and the idea was quickly picked up by other researchers [73, 74]. As for equation (16), the correlation factor of equation (17) shows the correct asymptotes for $r_{12} \to 0$ and $r_{12} \to \infty$. The two-electron integrals that are required by the R12 methods can be computed analytically, as shown in [72], but alternatively, the Slater-type geminal can be expanded in terms of a few (3–6) Gaussian geminals [69, 73, 74], which gives rise to the correlation factor

$$\begin{aligned} f_{12} &= 1 - \sum_v b_v \exp(-\gamma_v r_{12}^2) \approx 1 - \exp(-\gamma r_{12}) \\ &= \gamma r_{12} - 1/2\gamma^2 r_{12}^2 + \mathcal{O}(r_{12}^3). \end{aligned} \tag{18}$$

The analogy with fitting STOs as expansions in GTOs, as done for the STO-3G and STO-6G basis sets, is clear. We emphasize that it has been found important to include not only a weighting function $\exp(-\beta r_{12}^2)$ but also a proper Jacobian with r_{12}^2 for the integration over r_{12} in the least-squares fit [73]. Tew and Klopper [73] have also investigated

$$\begin{aligned} f_{12} &= r_{12} \sum_v b_v \exp(-\gamma_v r_{12}^2) \approx r_{12} \exp(-\gamma r_{12}) \\ &= r_{12} - \gamma r_{12}^2 + \mathcal{O}(r_{12}^3). \end{aligned} \tag{19}$$

The results obtained with the correlation factors of equations (18) and (19) did not differ much. When optimizing the exponent γ, it was found that the optimum value for the correlation factor of equation (18) was twice as large as for that of equation (19), compensating the factor of a half in the quadratic term. Thus, it seems that the term quadratic in r_{12}, which is missing in equation (16), is important.

The first results obtained with these correlation factors (equations 17, 18 and 19) are very promising indeed. If a given accuracy is obtained with the linear r_{12} term using a correlation-consistent basis set of the type aug-cc-pV*n*Z, then the same accuracy can be obtained with the new correlation factors in the next smaller basis, that is, aug-cc-pV($n-1$)Z. Since an increase in the cardinal number n causes an increase in computing time by an order of magnitude, much computing time can be saved by the new correlation factors. Moreover, new basis sets of the correlation-consistent type (which one could denote 'explicitly-correlation-consistent') may be designed and optimized, leading again to significant savings in computing time.

2.3. *Projection operators*

In the first R12 work [58], the projection operator $\hat{Q}_{12}$ in the pair function equation (10) was chosen as

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2), \tag{20}$$

to ensure that the pair function is, by virtue of the Brillouin theorem, strongly orthogonal to the Hartree–Fock reference state. In equation (20), $\hat{O}_1$ is the projection operator onto the occupied Hartree–Fock orbitals,

$$\hat{O}_1 = \sum_i \big|\varphi_i(1)\big\rangle\big\langle\varphi_i(1)\big|. \tag{21}$$

Later, in [75], it was suggested to orthogonalize the two-electron basis function $\hat{Q}_{12} f_{12}|kl\rangle$ against all orbital products constructable in the given one-particle basis. This is achieved by the projection operator

$$\begin{aligned}\hat{Q}_{12} &= \left(1 - \hat{P}_1\hat{P}_2\right)\left(1 - \hat{O}_1\right)\left(1 - \hat{O}_2\right)\\ &= 1 - \hat{O}_1\left(1 - \hat{P}_2\right) - \left(1 - \hat{P}_1\right)\hat{O}_2 - \hat{P}_1\hat{P}_2,\end{aligned} \tag{22}$$

where

$$\hat{P}_1 = \sum_p \big|\varphi_p(1)\big\rangle\big\langle\varphi_p(1)\big| \tag{23}$$

is the one-electron projection operator onto the given one-particle basis, in which the calculation is carried out. Note that equation (22) is also obtained if the two-electron basis function $\hat{Q}_{12} f_{12}|kl\rangle$ is orthogonalized against all pairs of virtual orbitals $|ab\rangle$. By doing so, with

$$\hat{V}_1 = \sum_a \big|\varphi_a(1)\big\rangle\big\langle\varphi_a(1)\big|, \tag{24}$$

we obtain

$$\begin{aligned}\hat{Q}_{12} &= \left(1 - \hat{V}_1\hat{V}_2\right)\left(1 - \hat{O}_1\right)\left(1 - \hat{O}_2\right)\\ &= (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1\hat{V}_2\\ &= 1 - \hat{O}_1\left(1 - \hat{P}_2\right) - \left(1 - \hat{P}_1\right)\hat{O}_2 - \hat{P}_1\hat{P}_2,\end{aligned} \tag{25}$$

which is identical with equation (22). As long as all integrals and matrix elements are evaluated exactly and no approximations are invoked, the various approaches with the projection operators of equations (20), (22) and (25) are strictly equivalent. It makes no difference whether the r_{12}-dependent basis functions are orthogonalized against the conventional orbital products or not.

In [75], it was recognized that the many-electron integrals occurring due to the terms with the isolated projection operators onto the occupied space in equation (25), that is, the operators $\hat{O}_1$ and $\hat{O}_2$, can be approximated accurately using a resolution-of-the-identity (RI) approximation. This approximation implies that the operators $\hat{O}_1$ and $\hat{O}_2$ are replaced by the products $\hat{O}_1\hat{P}'_2$ and $\hat{P}'_1\hat{O}_2$, where

$$\hat{P}'_1 = \sum_{p'} |\varphi_{p'}(1)\rangle\langle\varphi_{p'}(1)| \tag{26}$$

is the projection operator onto an orthonormal auxiliary basis $\{\varphi_{p'}\}$ [76]. In this RI approximation, we write

$$\begin{aligned}\hat{Q}_{12} &= (1-\hat{V}_1\hat{V}_2)(1-\hat{O}_1)(1-\hat{O}_2)\\ &= 1-\hat{O}_1(1-\hat{P}_2)-(1-\hat{P}_1)\hat{O}_2-\hat{P}_1\hat{P}_2,\\ &\approx 1-\hat{O}_1(\hat{P}'_2-\hat{P}_2)-(\hat{P}'_1-\hat{P}_1)\hat{O}_2-\hat{P}_1\hat{P}_2.\end{aligned} \tag{27}$$

Of course, if the orbital basis set, in which the wavefunction is expanded, is used as auxiliary basis for the RI approximation, then $\hat{P}_1 = \hat{P}'_1$, and equation (27) reduces to

$$\hat{Q}_{12} \approx 1-\hat{P}_1\hat{P}_2. \tag{28}$$

So far in this section we have referred to equation (20), which is the original Ansatz of R12 theory and known today as Ansatz **2**. In comparison with other Ansätze, it yields by far the most accurate results. The form orthogonalized against the space of products of virtual orbitals (equation (25)) was advocated by Wind *et al.* [77] and Valeev [78], and is the method of choice for iterative approaches such as CC2-R12, CCSD(R12), and CCSD-R12 (see below).

There is an alternative Ansatz – Ansatz **1** – that is now known to be less accurate, but is of historical interest. In the early 1990s [79], it seemed more straightforward to derive the final working equations of the theory by starting from the projection operator

$$\hat{Q}_{12} = \left(1-\hat{P}_1\right)\left(1-\hat{P}_2\right) = 1-\hat{P}_1-\hat{P}_2+\hat{P}_1\hat{P}_2 \tag{29}$$

and if the RI is performed in the MO basis (always the case at that time) the results were identical to those obtained with equation (20). Invoking the RI we obtain

$$\hat{Q}_{12} \approx 1-\hat{P}_1\hat{P}'_2-\hat{P}'_1\hat{P}_2+\hat{P}_1\hat{P}_2, \tag{30}$$

and if the RI is performed in the orbital basis, this is clearly equivalent to equation (28).

By virtue of the projection operators, which can be either those of Ansatz **1** or those of Ansatz **2**, the Hylleraas functional equation (3) can be written as

$$H[u_{ij}] = \langle u_{ij}|\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j|u_{ij}\rangle + 2\langle u_{ij}|r_{12}^{-1}|ij\rangle \geq \epsilon_{ij}^{(2)}, \tag{31}$$

where $|u_{ij}\rangle = |v_{ij}\rangle + |w_{ij}\rangle$ is the pair function as defined in equation (10). The functional can furthermore be expressed as

$$H[u_{ij}] = H[v_{ij}] + H[w_{ij}] + 2H[v_{ij}, w_{ij}], \tag{32}$$

where $H[v_{ij}]$ and $H[w_{ij}]$ are Hylleraas-type functionals for the R12 and conventional expansions, respectively, and where

$$H[v_{ij}, w_{ij}] = \langle v_{ij}|\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j|w_{ij}\rangle \tag{33}$$

represents the coupling matrix elements between these two expansions. In Ansatz **1**, where the R12 functions $|v_{ij}\rangle$ are strongly orthogonal on all products of virtual orbitals in $|w_{ij}\rangle$, this coupling is zero. Hence, $H[v_{ij}]$ and $H[w_{ij}]$ can be minimized individually in Ansatz **1**, and the minimum of $H[w_{ij}]$ is just the conventional MP2 energy. The minimum of $H[v_{ij}]$ is a correction to this conventional energy due to the R12 functions and can be interpreted as a basis set incompleteness correction. In the limit of a complete basis, $H[v_{ij}]$ vanishes.

In Ansatz **2**, assuming canonical Hartree–Fock orbitals, the coupling becomes

$$H[v_{ij}, w_{ij}] = \sum_{k<l} c_{ij}^{kl} \sum_{a<b} t_{ij}^{ab} \langle ab|\Big(\hat{F}_1 + \hat{F}_2 - \epsilon_a - \epsilon_b\Big) r_{12}|kl\rangle. \tag{34}$$

The coupling in Ansatz **2** is not zero, except if we assume that the virtual orbitals φ_a and φ_b are exact eigenfunctions of the Fock operators $\hat{F}_1$ and $\hat{F}_2$. This assumption is equivalent with the assumption that the extended Brillouin condition (EBC) holds, that is, that the orbital space is closed under the Fock operator. In practical calculations in large basis sets, this is either assumed or the calculated matrix elements $\langle ab|(\hat{F}_1 + \hat{F}_2 - \epsilon_a - \epsilon_b) r_{12}|kl\rangle$ are very small. Using the projection operators of equation (22) or equation (25) for Ansatz **2** improves convergence of explicitly correlated coupled-cluster calculations such as CC2-R12 and CCSD(R12) calculations compared to those with the projection operators of equation (20), by virtue of this small coupling.

2.4. *Levels of theory*

Concerning single-reference methods, the R12 approach has not only been implemented at the level of second-order Møller–Plesset perturbation theory (MP2), but also at higher orders of perturbation theory as well as coupled-cluster theory.

Already in 1991, first results were reported for third-order Møller–Plesset theory (MP3) and the configuration-interaction approach with doubles (CID), the latter also in form of coupled-electron pair approximations (CEPA-0, CEPA-2) and the coupled-pair functional (CPF) [80]. At that time, an auxiliary basis set $\{\varphi_{p'}\}$ (see above) was not used, and in today's terminology, one would say that Ansatz **1** (e.g. equation (29)) was used.

Soon hereafter, Noga and coworkers developed and implemented explicitly correlated coupled-cluster methods with singles, doubles (CCSD-R12) and triples excitations (e.g. CCSD[T]-R12, CCSD(T)-R12, CCSDT-1a-R12, and CCSDT-1b-R12,) [81–88]. Today, these methods are available in the DIRCCR12 program [89], which has been parallelized and includes an efficient calculation of triples corrections [90]. This code has for instance been used to compute highly accurate atomization energies and heats of formation of small molecules [91, 92] or to compute highly accurate potential energy surfaces of molecules such as SiH_3^- [93], NH_3 [94], H_3O^+ [95], and $H_2 \cdots H_2O$ [96].

A comprehensive exposition of the explicitly correlated coupled-cluster theory is presented in [97], and the theory has been reviewed already on a few occasions. See [98–101] and references therein.

Until very recently, explicitly correlated basis functions had been used in coupled-cluster theory only in the framework of Ansatz **1**, on the basis of equation (29), without using an auxiliary basis set $\{\varphi_{p'}\}$. More precisely, in [97], the theory had been developed for the projection operator of equation (20), but due to the approximations and assumptions that are introduced when implementing the theory, the working equations that follow from equation (20) are equal to those that follow from equation (29). However, certain terms and diagrams are exactly zero with the projection operator of equation (29) while these terms and diagrams are zero only due to the approximations invoked in the theory based on equation (20) [101].

If an auxiliary basis set is used, as proposed for MP2-R12 theory by Klopper and Samson [76], then the coupled-cluster theories for Ansätze **1** and **2** differ. Currently, work is in progress to implement the coupled-cluster models CC2-R12 and CCSD(R12) in the DALTON [102] program (in conjunction with corrections for triples) for both Ansätze using the auxiliary-basis-set approach and the projection operators of equations (22) or (29), respectively. This implementation has already been completed for Ansatz **1**, where it can handle not only linear r_{12} correlation factors but also other, novel correlation factors such as those discussed in [73]. The implementation also addresses excitation energies and response properties [60, 103–105].

2.5. *Methods for open shells*

It is relatively straightforward to implement R12 methods for open-shell cases that can be described by coupled-cluster or Møller–Plesset perturbation theory based on a single-reference state, for example a state obtained from a spin-unrestricted Hartree–Fock (UHF) or a restricted open-shell Hartree–Fock (ROHF) calculation [106]. This has been accomplished in the DIRCCR12-OS program, where 'OS' indicates the possibility to perform calculations on open shells [89]. At the MP2-R12 level, calculations based on a spin-unrestricted Hartree–Fock reference are also possible with the R12 modules of the programs MPQC [107] and TURBOMOLE [108], the former using auxiliary basis sets for the resolution-of-the-identity approximation and the latter using density-fitting techniques [109, 110].

For multireference open-shell cases of ground and excited states, Gdanitz and coworkers [111, 112] have developed an explicitly correlated R12 theory at the level of multireference configuration interaction (MRCI) theory. This explicitly correlated MRCI approach is mostly applied in the size-extensive modified form of the multireference averaged coupled pair functional (ACPF) of Gdanitz and Ahlrichs [113], more recently also in a modified form denoted MR-ACPF-2 [114].

This explicitly correlated multireference approach has been made available through the AMICA program [115], and has been applied in a series of papers by Gdanitz and coworkers [116–122]. This method is particularly suited for computations of excited states such as the valence excited states of methylene [123] and for computations of globally accurate potential energy hypersurfaces for studies of chemical reactions. An example for the latter has been provided recently for the reaction $F + H_2 \rightarrow FH + H$ [124, 125].

3. Approximations of many-electron integrals

As we have seen, the slow convergence of dynamic correlation energies using conventional CI expansions is efficiently avoided in explicitly correlated electronic structure theory. The penalty is the introduction of many-electron integrals, which consist of one of the operators in the electronic Hamiltonian and a power of correlation factors. For instance, explicitly correlated MP2 methods involve the evaluation of three-electron integrals of the form

$$\langle ij|r_{12}^{-1}\hat{O}_2 f_{12}|kl\rangle = \sum_m \langle ijm|r_{12}^{-1}f_{13}|kml\rangle, \tag{35}$$

$$\langle ij|[\hat{T}_{12}, f_{12}]\hat{O}_2 f_{12}|kl\rangle = \sum_m \langle ijm|[\hat{T}_{12}, f_{12}]f_{13}|kml\rangle \tag{36}$$

in addition to new two-electron integrals over $f_{12}r_{12}^{-1}$, $[\hat{T}_{12}, f_{12}]$, f_{12}^2, and $[[\hat{T}_{12}, f_{12}], f_{12}]$, where $\hat{T}_{12} = \hat{T}_1 + \hat{T}_2$ is the sum of kinetic energy operators for electrons 1 and 2, respectively. Different treatments of the commutator between the exchange operator and the correlation factor require additional integrals over many-electron operators as $f_{13}r_{12}^{-1}f_{23}$ and $f_{13}r_{14}^{-1}f_{23}$. The success of the recent explicitly correlated methods is indebted to the progress of the ingenious treatment of many-electron integrals.

In equations (35) and (36), we no longer imply that the bra $\langle ij|$ and ket $|kl\rangle$ are antisymmetrized products of spin-orbitals. Rather, in this section, we are concerned with integrals over spatial orbitals, that is, $|kl\rangle \equiv \phi_k(1)\phi_l(2)$ and $|klm\rangle \equiv \phi_k(1)\phi_l(2)\phi_m(3)$. For the sake of brevity, we use a spin-orbital formalism to describe the wavefunctions (sections 1 and 2) but a simple spatial orbital picture to discuss the integrals (section 3).

3.1. *Exact evaluation*

The introduction of correlation factors directly dependent on r_{12} [14, 18] shows very rapid convergence. Nevertheless a generalization to polyatomic molecules with more than two electrons seemed almost impractical due to the difficulties of the mathematical treatment of the complex integrals. The only reasonable expansion with explicit formulas was developed by Boys and Singer [22, 23] in terms of correlated Gaussian functions of the form

$$G = \exp\left[-\sum_{iA} a_i r_{iA}^2 - \sum_{ij} c_{ij} r_{ij}^2\right] \tag{37}$$

(see section 1.4). It was shown that all relevant integrals that arise in the use of the correlated Gaussian functions can be evaluated [22, 23, 126] in forms that involve at most one Boys function, defined as

$$F_m(T) = \int_0^1 u^{2m} \exp(-Tu^2) du. \tag{38}$$

Indeed, explicitly correlated Gaussian functions have been employed successfully in adiabatic [126, 127] and non-adiabatic [35, 36, 128] electronic structure calculations involving a few correlated particles. The mathematical features of the functions have also been useful in many-body perturbation theories based on GTGs with various orthogonal projectors [24–28, 129–134].

The correlated Gaussian functions are handicapped by the inability to describe cusps in the wavefunction. Although the volume element $4\pi r_{12}^2$ ensures that the cusp behavior does not contribute to the correlation energy at coalescence, yet the exact Coulomb hole obeys the cusp conditions at finite r_{12}. Furthermore, the methods with correlated Gaussians involve full optimization of non-linear parameters. More recently, Persson and Taylor showed that the linear r_{12} behavior in a suitable range can be represented by a few terms of GTGs and that tedious non-linear optimization can be avoided by using a frozen GTG expansion [29]. The requirement of four-electron integrals in explicitly correlated MP2 theory can be sidestepped by the simplified WOF energy functional of Szalewicz and coworkers [24, 25] (see section 1.4).

However, the evaluation of three-electron integrals is still expensive. This is especially so for the integrals over $[\hat{T}_{12}, f_{12}]f_{23}$, because they are inherently more complicated than the others, and because the number scales quadratically in the number of terms in the GTG fit. To maximize the efficiency, integral recurrence relations that work on the object after taking the double summation over GTGs have been proposed [50]. It is also noted that the most important three-electron integrals of the linear r_{12} Ansatz can be calculated explicitly for atoms [77, 135]. Anyhow, since the three-electron integrals are so numerous, the applications of these methods are restricted to atoms and small molecules. Exact evaluation is nevertheless useful to examine the accuracy of approximations of many-electron integrals.

3.2. Approximations: GBC, EBC and $[\hat{K}_1, r_{12}] \approx 0$

The high computational cost of the 'exact' treatment of three- and four-electron integrals that appear in explicitly correlated theories prevents application to chemically interesting systems. Kutzelnigg's breakthrough idea was to approximate such integrals using an approximate resolution of the identity (RI) and to use partial wave analysis to establish requirements on the RI basis [57] (see section 3.3 for a discussion of the RI approach).

Direct application of the RI approximation to the matrix elements of the zeroth-order operator

$$B_{ij}^{kl} = \langle v_{ij} | \hat{F}_{12} | v_{kl} \rangle, \tag{39}$$

which appear in the Hylleraas functional (equation (31)), is not possible because of its slowly convergent partial wave expansion. (In equation (39), $\hat{F}_{12} = \hat{F}_1 + \hat{F}_2$ is the sum of the Fock operators of electrons 1 and 2.) The manipulations of this term to make accurate RI approximations possible are therefore the key to the success of linear R12 methods.

The original scheme for handling equation (39), due to Kutzelnigg and Klopper [58] and in use by most researchers today, is referred to as 'standard approximation' (SA). They rewrote the elementary matrix element of the zeroth-order Hamiltonian

$$B_{ij}^{kl} = \langle ij | \hat{v}_{12}^{\dagger} \hat{F}_{12} \hat{v}_{12} | kl \rangle, \tag{40}$$

where

$$\hat{v}_{12} = \hat{Q}_{12} f_{12}, \tag{41}$$

as

$$B_{kl}^{ij} = \langle ij | \hat{v}_{12}^{\dagger} \hat{v}_{12} \hat{F}_{12} | kl \rangle + \langle ij | \hat{v}_{12}^{\dagger} \left[\hat{F}_{12}, \hat{v}_{12} \right] | kl \rangle. \tag{42}$$

The first term on the right-hand side is easy to evaluate if the standard,

$$\hat{V} \hat{F} \hat{O} \overset{\mathrm{BC}}{\approx} 0, \tag{43}$$

and generalized,

$$(1 - \hat{P}) \hat{F} \hat{O} \overset{\mathrm{BC}}{\approx} 0, \tag{44}$$

Brillouin conditions are assumed [59], to obtain

$$\langle ij | \hat{v}_{12}^{\dagger} \hat{v}_{12} \hat{F}_{12} | kl \rangle \overset{\mathrm{GBC}}{\approx} (\epsilon_k + \epsilon_l) \langle ij | \hat{v}_{12}^{\dagger} \hat{v}_{12} | kl \rangle. \tag{45}$$

The commutator in the second term of equation (42) is more tricky because of the commutator of the Fock operator with the projector $\hat{Q}_{12}$,

$$\left[\hat{F}_{12}, \hat{v}_{12}\right] = \left[\hat{F}_{12}, \hat{Q}_{12}\right] f_{12} + \hat{Q}_{12}\left[\hat{F}_{12}, f_{12}\right]. \tag{46}$$

The explicit evaluation of all of the terms that appear due to the first term is possible [74, 136], but it can be avoided by making additional assumptions so that the $[\hat{F}_{12}, \hat{Q}_{12}]$ commutator vanishes. In Ansatz **2** (the practically important case) this assumption relies only on the generalized Brillouin condition if the projector of equation (20) is used. If the modified projector of equation (25) is used, the more stringent extended Brillouin condition is required as well:

$$(1 - \hat{P})\hat{F}\hat{V} \overset{\text{EBC}}{\approx} 0. \tag{47}$$

The impact of this approximation is significant [74], but can in any case be avoided.

The second commutator in equation (46) is decomposed into two parts,

$$\left[\hat{F}_{12}, f_{12}\right] = \left[\hat{T}_{12}, f_{12}\right] - \left[\hat{K}_{12}, f_{12}\right]. \tag{48}$$

The matrix elements for the kinetic energy commutator are usually evaluated analytically using a number of published algorithms [137–139], whereas the exchange commutator ($\hat{K}_{12} = \hat{K}_1 + \hat{K}_2$) is approximated via RI using a double completeness insertion.

Kutzelnigg and Klopper also suggested a useful practical variant of the standard approximation, where the exchange commutator is omitted altogether. This so-called standard approximation A is simpler technically, because its matrix elements require only single RI insertions and the cost of the integral evaluation scales linearly with the size of the RI basis. The cost of integrals in standard approximation B, in which the exchange commutator is computed rigorously, scales quadratically with the size of the RI basis (see, however, [140] for a formulation of standard approximation B that scales linearly with the RI basis set size). Energies computed in standard approximation A approach the basis set limit from below and also converge asymptotically slower than the results obtained with approximation B, $\mathcal{O}(L^{-5})$ and $\mathcal{O}(L^{-7})$, respectively. The MP2-R12/A energies computed with small Hartree–Fock basis sets, however, are closer to the basis set limit than the corresponding MP2-R12/B energies. It seems therefore that the standard approximation A can be useful in practical computations using non-iterative methods, such as MP*n*, as long as only medium accuracy is sought.

Note that the EBC and GBC approximations become more accurate as the Hartree–Fock basis approaches completeness. The effect of EBC and GBC on MP2-R12 energies computed with small basis sets was investigated by May *et al.* [74]. These authors found that EBC and $[K_{12}, r_{12}] \approx 0$ had an appreciable effect on the energies, although the magnitude was significantly smaller than the residual basis set incompleteness error. The assumption of GBC was found to have an even smaller effect on the energies. The recommendation of the authors was to avoid the use of EBC and commutator approximation in the MP2-R12 methods.

Recently, Noga *et al*. suggested a significantly simpler method to deal with the matrix elements of equation (39), which they dubbed standard approximation C [141]. They noted that if one expands the projectors in equation (40) explicitly, then the only term that cannot be evaluated via RI is $\langle ij|f_{12}\hat{F}_{12}f_{12}|kl\rangle$. The idea of standard approximation C is to separate exchange from the rest of the Fock operator,

$$\begin{aligned}\langle ij|f_{12}\hat{F}_{12}f_{12}|kl\rangle = {} & \langle ij|f_{12}(\hat{F}_{12}+\hat{K}_{12})f_{12}|kl\rangle \\ & - \langle ij|f_{12}\hat{K}_{12}f_{12}|kl\rangle. \end{aligned} \tag{49}$$

The second term can be evaluated accurately via a double RI insertion because the partial wave series for this integral converges quickly, as $\mathcal{O}(L^{-7})$. The first term in equation (49) is evaluated via the commutator identity

$$\begin{aligned} f_{12}(\hat{F}_{12}+\hat{K}_{12})f_{12} &= \frac{1}{2}\left[f_{12},\left[\hat{F}_{12}+\hat{K}_{12},f_{12}\right]\right] + \frac{1}{2}\left[\hat{F}_{12}+\hat{K}_{12},f_{12}^{2}\right]_{+} \\ &= \frac{1}{2}\left[f_{12},\left[\hat{T}_{12},f_{12}\right]\right] + \frac{1}{2}\left[\hat{F}_{12}+\hat{K}_{12},f_{12}^{2}\right]_{+} \end{aligned} \tag{50}$$

The second term can be accurately approximated by the RI approach. The double commutator is not evaluated in the linear R12 method ($f_{12} = r_{12}$), since

$$\frac{1}{4}\left[r_{12},\left[\hat{T}_{12},r_{12}\right]\right] = 1. \tag{51}$$

The double commutator can be evaluated analytically for other correlation factors [69].

Not only is standard approximation C more rigorous than the original schemes because no approximations are necessary other than RI, it is also simpler to implement, because no integrals $[\hat{T}_{12},f_{12}]$ need to be evaluated. Finally, the results presented by the authors using a single basis formalism indicate that the MP2-R12/C energies always lie closer to the basis set limit than the corresponding MP2-R12/A and MP2-R12/B energies. There is no reason to believe, however, that this result is a consequence of superior convergence properties of the MP2-R12/C model. Because the effect of GBC on MP2-R12 energies is completely negligible, MP2-R12/C energies are very close to the MP2-R12/B energies computed without the assumption of EBC, provided that the RI basis (or orbital basis in the single basis formalism) is nearly complete [136].

3.3. *Resolution of the identity*

The three- and four-electron integrals that appear in matrix elements can be most easily simplified via an approximate resolution of the identity (RI). For example, the following three-electron integral, which appears in all linear R12 methods

$$\langle ijm|r_{12}r_{13}^{-1}|kml\rangle \approx \sum_{p'} \langle ij|r_{12}|p'm\rangle\langle p'm|r_{12}^{-1}|kl\rangle, \tag{52}$$

is reduced to products of two-electron integrals. For reasons of technical simplicity, an RI basis of atom-centred Gaussian functions is most often used.

Kutzelnigg realized [57] that the partial wave analysis of the RI error in atoms can establish basic requirements on the RI basis $\{p'\}$ for atoms and possibly also for molecules. The three-electron integral in equation (52), for example, has a partial wave expansion that truncates at angular momentum $3L_{\mathrm{occ}}$ for atoms. Therefore the RI for such an integral is exact if the RI basis is saturated to $3L_{\mathrm{occ}}$. Standard approximations B and C also involve three-electron integrals such as

$$\langle ijm|r_{12}r_{13}^{-1}r_{23}|mkl\rangle \approx \sum_{p'q'r'} \langle ij|r_{12}|p'q'\rangle\langle p'm|r_{12}^{-1}|mr'\rangle\langle q'r'|r_{12}|kl\rangle, \tag{53}$$

whose partial wave expansion does not truncate but converges quickly [59]. The RI basis for approximations B and C must include functions of all angular momenta, but in practice the RI error due to omission of *h*-functions and higher is rather small [141].

The original implementation of R12 methods utilized the Hartree–Fock basis (or orbital basis) set for the RI. This technical simplification meant that the Hartree–Fock basis set had to be very large. Klopper and Samson were the first to implement a version of MP2-R12 theory using a separate RI basis, the 'auxiliary basis set' (ABS) method [76]. The ABS method involves the replacement

$$1 \rightarrow \hat{P}', \tag{54}$$

where $\hat{P}'$ is a projector on an orthonormal RI basis.

The RI error in the ABS method can be made as small as desired by increasing the completeness of the ABS. Unfortunately, when the ABS is not sufficiently complete, the RI error can quickly become too large. A key requirement on the RI basis set is that it spans the Hartree–Fock basis set exactly,

$$\hat{P}\hat{P}' = \hat{P}. \tag{55}$$

When this condition does not hold, the ABS approximation (equation (27)) can break down,

$$\text{exact}: \hat{P}(1-\hat{P}) = 0, \tag{56}$$

$$\text{ABS}: \hat{P}(\hat{P}'-\hat{P}) \neq 0, \quad \text{if } \hat{P}\hat{P}' \neq \hat{P}. \tag{57}$$

The errors can be significant, especially when small Hartree–Fock basis sets are used [78]. It is recommended in such situations to include the Hartree–Fock basis set into the ABS, since then the condition of equation (55) holds automatically. This approach is labelled ABS+ and has a smaller RI error than the ABS method [78], at the expense of a larger auxiliary basis and therefore increased computation times.

An alternative to the ABS is to approximate the orthogonal projector $1 - \hat{P}$ directly,

$$\hat{X} \equiv 1 - \hat{P} \approx \hat{X}' = \sum_{p_\perp} |p_\perp\rangle\langle p_\perp|. \tag{58}$$

$\hat{X}'$ is an approximate projector on the orthogonal complement to the given basis. This is the crux of the 'complementary' ABS approach (CABS) [78]. A numerically robust method to construct $\hat{X}'$ applies a singular value decomposition to the overlap matrix between the ABS and the given basis to construct $\hat{X}'$ directly [78]. Other methods of construction have been described as well [73]. The main advantage of the CABS approach is its smaller RI error relative to the ABS approach for the same auxiliary basis [78]. It should in principle also permit computations with smaller auxiliary basis sets than required by the ABS method, because only the complementary space to the given basis needs to be spanned by the auxiliary basis. Of course, it is hard to ensure *a priori* (near)-orthogonality of Gaussian basis sets (except in some atomic computations).

By analogy with the ABS+ method, the RI error of the CABS method can be reduced by including the Hartree–Fock basis into the ABS. This approach, known as CABS+, has a higher computational cost than CABS and yields energies in almost complete numerical agreement with the ABS+ method [78].

3.4. *Numerical quadrature*

The methods that have transcended the restriction of small molecules break up many-electron integrals into sums of products of two-electron objects. The simplest way to achieve such a decomposition is based on numerical quadrature, which was applied in the early work on the transcorrelated method [46] and more recently in explicitly correlated MP2 theory [48]. The method represents electron repulsion integrals as sums of two- and three-centre objects over grid points,

$$(pq|rs) = \langle pr|r_{12}^{-1}|qs\rangle = \sum_g \bar{\phi}_p(\vec{r}_g)\phi_q(\vec{r}_g)\langle r|r_{1g}^{-1}|s\rangle, \tag{59}$$

where $\bar{\phi}_p(\vec{r}_g)$ denotes a weighted orbital of the quadrature,

$$\bar{\phi}_p(\vec{r}_g) = w(\vec{r}_g)\phi_p(\vec{r}_g), \tag{60}$$

and $\langle p|r_{1g}^{-1}|q\rangle$ are Coulomb integrals for the interaction with a unit point charge at the grid point $\vec{r}_g$,

$$\langle p|r_{1g}^{-1}|q\rangle = \int d\vec{r}_1 \phi_p(\vec{r}_1)\phi_q(\vec{r}_1)|\vec{r}_1 - \vec{r}_g|^{-1}. \tag{61}$$

The expansion of equation (59) involves at most three-index objects. Thus, the scaling of for instance the first integral transformation in an MP2 calculation is reduced from N^4O to N^2OG for the numbers of occupied and general functions, O and N, respectively, and that of grid points, G. This reduction is advantageous if $G \ll N^2$. For a suitable numerical quadrature, we can make use of the recent developments in DFT, that is, the invention of the fuzzy Voronoi polyhedra [142]. (See also the later refinements to gridding [143–146].) It is noted that the pseudospectral methods use the same type of expansion with different choice of weights [147–149], and similar quadratures occur in discrete variable representation (DVR) methods [150–152].

Similarly, all two-electron integrals in explicitly correlated electronic structure theory can be evaluated by numerical integration. For instance, the integrals over $[\hat{T}_1, f_{12}]$ are estimated as

$$\langle pq|\Big[\hat{T}_1, f_{12}\Big]|rs\rangle = \sum_g \bar{\phi}_p(\vec{r}_g)\Big[\phi_r(\vec{r}_g)\langle q|A_{1g}|s\rangle + \vec{g}_r(\vec{r}_g)\cdot\langle q|\vec{B}_{1g}|s\rangle\Big], \tag{62}$$

$$A_{1g} = -(\nabla_1^2 f_{1g}) - (\vec{\nabla}_1 f_{1g})\cdot\vec{\nabla}_1, \tag{63}$$

$$\vec{B}_{1g} = -(\vec{\nabla}_1 f_{1g}), \tag{64}$$

$$\vec{g}_p(\vec{r}_g) = \Big[\vec{\nabla}\phi_p(\vec{r}_g)\Big]. \tag{65}$$

In explicitly correlated MP2 methods, two-electron integrals involve at least two occupied orbitals. Thus the grid in the expressions of two-electron integrals should exactly integrate the spherical harmonics at least up to $\ell = 2(L_{\mathrm{occ}} + L_{\mathrm{bas}})$ for the maximum angular momentum quantum numbers of the occupied shells and given basis set, L_{occ} and L_{bas}, respectively.

The most important feature of using the numerical quadrature is that the three-electron integrals can also be calculated directly,

$$\langle ijm|r_{12}^{-1}f_{13}|kml\rangle = \sum_g \bar{\phi}_i(\vec{r}_g)\phi_k(\vec{r}_g)\langle j|r_{1g}^{-1}|m\rangle\langle m|f_{1g}|l\rangle, \tag{66}$$

$$\langle ijm|[\hat{T}_1, f_{12}]f_{12}|kml\rangle = \sum_g \bar{\phi}_i(\vec{r}_g) \times \Bigg[\phi_k(\vec{r}_g)\langle j|A_{1g}|m\rangle + \vec{g}_i(\vec{r}_g)\cdot\langle j|\vec{B}_{1g}|m\rangle\Bigg]\langle m|f_{1g}|l\rangle. \tag{67}$$

For this, the grids should integrate the spherical harmonics accurately up to $\ell = 6L_{\mathrm{occ}}$, which is usually smaller than the requirement for two-electron integrals, $2(L_{\mathrm{occ}} + L_{\mathrm{bas}})$, for a molecule without heavy atoms. If the outer-most occupied shell is filled completely, just the spherical average over m survives, reducing the requirement to $\ell = 4L_{\mathrm{occ}}$. The orbital indices in an integral are coincident in the MP2 method with the IJIJ (diagonal) Ansatz, i.e. $(ij) = (kl)$ in the above equations. In this case, the accumulation involving the three-electron integrals scales as O^3G, which is cheaper than the integral transformation of the four-centre objects. Previous work showed that the required number of grid points ranges from 1 to 30 thousand per atom for a reasonable accuracy (in the order of 1 microhartree) [48].

3.5. *Density fitting*

Explicitly correlated calculations based on the RI approximation with ABS or CABS are rather expensive in comparison with the usual orbital-based expansion because of the size of the ABS and the requirement of new types of two-electron integrals. Manby has mitigated this situation by introducing the density fitting (DF) technique in explicitly correlated theory [69, 153]. DF approximates four-centre integrals by two- and three-centre objects representing orbital products in terms of auxiliary basis functions,

$$\phi_p(\vec{r})\phi_q(\vec{r}) \simeq \sum_A C^A_{pq} \Xi_A(\vec{r}). \tag{68}$$

The technique has been implemented for *ab initio* methods involving SCF [154, 155], MP2 [156, 157], MCSCF [158, 159] and CCSD [160] besides the original use in DFT [161, 162]. DF has also been termed RI in recent years (see for instance the review of Kendall and Früchtl [163]). In this article, we use the label DF to avoid the confusion with the RI that is used for the decomposition of many-electron integrals.

In the explicitly correlated DF-MP2-R12 theory [69, 153], robust fitting has been employed. (See [164] for an account of robust fitting.) In what follows, the property is explained for electron repulsion integrals. For a given set of coefficients C^A_{pq}, the integrals can be estimated by the approximate formulas,

$$(\widetilde{pq}|\widetilde{rs}) = \sum_{AB} C^A_{pq} J_{AB} C^B_{rs}, \tag{69}$$

$$(\widetilde{pq}|rs) = \sum_A C^A_{pq} J^A_{rs}, \tag{70}$$

where $J_{AB} = (A|B)$ and $J^A_{pq} = (A|pq)$. The errors in the approximate products,

$$\Delta_{pq} = \widetilde{pq} - pq, \tag{71}$$

appear to first order in the error of the approximate integrals. Nevertheless, the robustly fitted expression eliminates them to leave only quadratic errors,

$$\begin{aligned}(pq|rs)_{\mathrm{robust}} &= (\widetilde{pq}|rs) + (pq|\widetilde{rs}) - (\widetilde{pq}|\widetilde{rs}) \\ &= (pq|rs) - (\Delta_{pq}|\Delta_{rs}).\end{aligned} \tag{72}$$

It is convenient to determine the coefficients by minimizing the diagonal elements $(\Delta_{pq}|\Delta_{pq})$. If the auxiliary basis is uniform to all products $\phi_p(\vec{r})\phi_q(\vec{r})$, the expression reduces to

$$(pq|rs)_{\text{robust}} = \sum_A \bar{J}^A_{pq} J^A_{rs}, \tag{73}$$

where $\bar{J}^A_{pq}$ are expansion coefficients based on the Coulomb criterion,

$$C^A_{pq} = \bar{J}^A_{pq} = \sum_B (\mathbf{J}^{-1})_{AB} J^B_{pq}. \tag{74}$$

It has been shown that the SCF energy using this expression is more accurate than other approximate formulas with the overlap metric by 1–2 orders of magnitude [155].

The explicitly correlated DF-MP2-R12 methods replace all necessary two-electron integrals in MP2-R12 by robustly fitted expressions [69, 153]. In this work, the coefficients of the Coulomb criteria $\bar{J}^A_{pq}$ were employed for all classes of integrals. For instance, the integrals over f_{12} are estimated as

$$(pq|f_{12}|rs)_{\text{robust}} = \sum_A (\bar{J}^A_{pq} F^A_{rs} + F^A_{pq} \bar{J}^A_{rs}) - \sum_{AB} \bar{J}^A_{pq} F^A_B \bar{J}^B_{rs} \tag{75}$$

where $F^A_{pq} = (pq|f_{12}|A)$ and $F_{AB} = (A|f_{12}|B)$. This allows us to utilize the robust fitting for integrals over indefinite operators. The integrals over the commutator $[\hat{T}_1, f_{12}]$ can be rearranged using the Hermiticity of $\hat{T}_1$ as

$$(pq|[\hat{T}_1, f_{12}] = (\{\hat{T}_1 p\} q - p\{\hat{T}_1 q\}| f_{12}. \tag{76}$$

Then the robustly fitted formula is given by

$$(pq|[\hat{T}_1, f_{12}]|rs)_{\text{robust}} = \sum_A (\bar{Y}^A_{pq} X^A_{rs} + X^A_{pq} \bar{Y}^A_{rs}) - \sum_{AB} \bar{Y}^A_{pq} F_{AB} \bar{Y}^B_{rs} \tag{77}$$

with the definitions

$$X^A_{pq} = \left(pq\middle|\left[\hat{T}_1, f_{12}\right]\middle|A\right), \tag{78}$$

$$\bar{Y}^A_{pq} = \sum_B (\mathbf{J}^{-1})_{AB} \left(pq\middle|\left[\hat{T}_1, r_{12}^{-1}\right]\middle|B\right). \tag{79}$$

The density-fitted MP2-R12 (DF-MP2-R12) theory has essentially the same numerical properties as the original MP2-R12 formulation at a fraction of the cost.

3.6. *DF combined with RI*

The framework of RI is not altered by the use of DF in the previous section, that is, there remains the requirement of $3L_{\mathrm{occ}}$ in the RI basis. Ten-no and Manby introduced another use of DF, which improves the convergence of the RI [165]. For a local operator (eg r_{12}^{-1}), one can move an orbital from the ket to the bra to give the integral identity

$$\langle ijm|r_{12}^{-1}f_{13}|kml\rangle = \langle (ik)jm|r_{12}^{-1}f_{13}|1ml\rangle, \tag{80}$$

which can then be resolved using the RI to give

$$\langle ijm|r_{12}^{-1}f_{13}|kml\rangle = \sum_{p'}\langle (ik)j|r_{12}^{-1}|p'm\rangle F_{ml}^{p'}, \tag{81}$$

where $F_{ml}^{p'} = \langle p'm|f_{12}|1l\rangle$. The symbol 1 in place of an orbital index indicates that the orbital is made unity. Applying density fitting to avoid the 5-index integral in equation (81), the three-electron integrals can be expressed as

$$\langle ijm|r_{12}^{-1}f_{13}|kml\rangle = \sum_{Ap'} C_{ik}^{A}(Ap'|jm)F_{ml}^{p'}. \tag{82}$$

As $F_{ml}^{p'}$ in equation (82) involves just two occupied orbitals besides the RI index, p', the maximum angular momentum required for the RI is reduced from $3L_{\mathrm{occ}}$ to $2L_{\mathrm{occ}}$ in the atomic limit. Thus, for s-, p- and d-occupied shells, we require s-, d-, and g-functions instead of s-, f-, and i-functions in the RI expansion.

The expression of the integrals over $[\hat{T}_1,f_{12}]$ is slightly more complicated because of the presence of the kinetic energy operator. The fact that $[\hat{T}_1,f_{12}]$ differentiates at most one function of $\vec{r}_1$ leads to the relations

$$\begin{aligned}
&\langle ijm|[\hat{T}_1,f_{12}]f_{13}|kml\rangle + \langle kjm|[\hat{T}_1,f_{12}]f_{13}|iml\rangle \\
&\quad = \langle 1jm|[\hat{T}_1,f_{12}]f_{13}|(ik)ml\rangle + \langle (ik)jm|[\hat{T}_1,f_{12}]f_{13}|1ml\rangle \\
&\quad = \sum_{p'A} C_{ik}^{A}\Big\{ Y_{jm}^{p'}\langle p'm|f_{12}|Al\rangle + \langle Aj|[\hat{T}_1,f_{12}]|p'm\rangle F_{ml}^{p'}\Big\},
\end{aligned} \tag{83}$$

where

$$Y_{jm}^{p'} = \langle 1j|[\hat{T}_1,f_{12}]|p'm\rangle. \tag{84}$$

Then, we obtain the desired expressions of direct and exchange components within the framework of explicitly correlated MP2 theory by substituting the indices,

$$\langle ijm|[\hat{T}_1,f_{12}]f_{13}|imj\rangle = \frac{1}{2}\sum_{p'A} C_{ii}^{A}\Big\{ Y_{jm}^{p'}\langle p'm|f_{12}|Aj\rangle + \langle Aj|[\hat{T}_1,f_{12}]|p'm\rangle F_{mj}^{p'}\Big\}, \tag{85}$$

and

$$\langle ijm|[\hat{T}_1, f_{12}]f_{13}|jmi\rangle = -\sum_{p'}\langle jj|[\hat{T}_1, f_{12}]|p'm\rangle\langle p'm|f_{12}|ii\rangle + \sum_{p'A} C^{A}_{ij}\left\{ Y^{p'}_{jm}\langle p'm|f_{12}|Ai\rangle + \langle Aj|[\hat{T}_1, f_{12}]|p'm\rangle F^{p'}_{mi}\right\}. \quad (86)$$

The first term of the exchange integral in equation (86) has the form of a standard RI decomposition. However, the convergence of the RI is much faster since the integrals have the same occupied indices. For atoms saturated in degenerate shells, the vector coupling coefficients survive just for $\ell = 0$ in the total energy because of the independent summation over the coincident orbitals. As a result, the RI in this term requires only L_{occ} for a saturated energy.

It was shown that the improved RI with DF turned out to be more accurate by one order of magnitude than the original RI method [165]. The four-index integrals remaining in the combined DF-RI expression equation (82) suggests that there is room for further improvement, that is, these integrals can be replaced by DF expressions. At any rate, it is evident from the different applications of DF that the technology enhances the efficiency and accuracy of explicitly correlated calculations.

4. Examples from second-order perturbation theory

Today, MP2-R12 calculations in large basis sets (comprising ca. 75 basis functions on the hydrogens and 150–200 basis functions on the non-hydrogens, which is significantly more than the minimum requirement of ca. 100 functions for non-hydrogens as suggested by Bearpark and Handy [166]) can routinely be performed on molecules with up to five non-hydrogens and five hydrogens, that is, of the size of thiophene, urea and methyl formate (figure 1). Calculations in such large basis sets can yield second-order correlation energies of benchmark quality to within 1 mE_h of the basis-set limit. Note that 1 mE_h corresponds to 2.6255 kJ/mol, which in turn roughly corresponds to RT at 25°C. This level of accuracy is often referred to as 'chemical accuracy' (see [167] for a recent review on the *a priori* calculation of molecular properties to chemical accuracy).

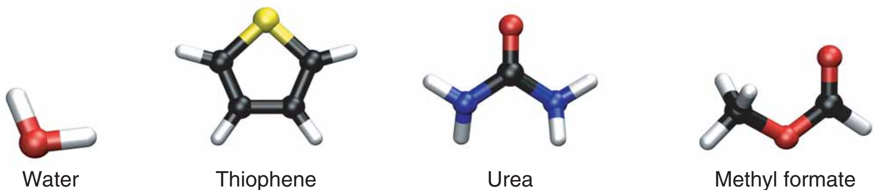

Figure 1. [Color online] Selected small molecules for which MP2-R12 calculations were carried out. See table 2 for the Cartesian coordinates of the MP2(FC)/aug-cc-pV(T+d)Z optimized geometries.

Calculations on much larger molecules and clusters are possible at the MP2-R12 level if the density-fitting technique is invoked [69, 153], in particular in a local-correlation framework [168, 169]. For example, accurate calculations in large basis sets (of approximately augmented quadruple-zeta quality) of hydrogen-bonded and π-stacked weakly bound complexes of 2-pyridone and tetra-, penta- and hexafluorobenzene are possible at this level of theory [170].

In the present review, we focus on absolute correlation energies at the MP2-R12 and MP2-F12 levels, using linear r_{12} and exponential (Slater-type) correlation factors, respectively. Slater-type geminals yield superior results, but in very large basis sets [73], the differences between the linear r_{12} and Slater-type correlation factors become less important in comparison with the other approximations in the theory. The new correlation factors are particularly helpful for calculations in comparably small basis sets (of double- or triple-zeta quality).

4.1. *Technical details*

The calculations reported in section 4.2 were performed with the DALTON [102] and MPQC programs [107]. The basis sets for the R12 calculations were derived in a manner that is typical for highly accurate explicitly correlated calculations in a single basis (i.e. one basis that is used both as orbital basis and as auxiliary basis for the RI approximation of R12 theory). In such calculations, the basis sets are often derived from rather large augmented correlation-consistent basis sets of at least quadruple-zeta quality. Typically, such basis sets are used uncontracted and supplemented with polarization functions with large exponents (tight functions). Since convergence with angular momentum is fast with the R12 methods, polarization functions with very high angular momentum functions can safely be omitted. The basis sets given below were derived from the augmented quintuple-zeta basis, which was used without contractions and without the h-type Gaussian functions. Recently, Noga and coworkers [171–173] have designed and optimized universal R12 suited basis sets for the first row atoms Li–Ne, but further research is required in this area to enable accurate, numerically stable and balanced calculations on molecules containing heavier atoms.

In detail, the basis sets were constructed as follows: the 21s13p9d7f5g basis set for S was derived from the primitive 21s13p6d4f3g set of the aug-cc-pV(5+d)Z basis of Dunning and coworkers [174] by adding a 3d3f2g set of tight polarization functions. Its exponents are given in table 1. Similarly, the 15s9p7d6f4g basis sets for C, N and O were derived from the primitive 15s9p5d4f3g sets of the aug-cc-pV5Z basis of Dunning and coworkers [175] by adding 2d2f1g sets of tight polarization functions (cf. table 1 for the exponents). For H, a 1p1d set of tight polarization functions with exponents 11.91 and 7.216, respectively, was added to the 9s5p4d3f primitive subset of the aug-cc-pV5Z basis [175] to yield the final 9s6p5d3f basis used in the present work. The basis sets for H, C, N and O are very similar to the basis sets of [176], but not identical.

The calculations reported in section 4.3 were performed with the DALTON [102] and the F12 program at Nagoya University. The present F12 method will be made available to the public in the Gellan program package [177]. MP2-R12 calculations were performed for Ansatz **2** in the standard aug-cc-pV(Q+d)Z (for S) and aug-cc-pVQZ

Table 1. Exponents of the tight polarization functions that were added to primitive subsets of the aug-cc-pV5Z (for H, C, N and O) and aug-cc-pV(5+d)Z (for S) basis sets.

Type	S	C	N	O	H
p					11.91
d	26.6	20.25	30.53	38.18	7.216
	13.17	7.966	11.91	14.98	
	3.217				
f	9.747	11.49	17.57	26.82	
	4.705	4.802	7.189	10.38	
	2.271				
g	5.731	4.532	6.693	9.439	
	2.477				

(for C, N, O, and H) basis sets, using the ABS approach of Klopper and Samson [76], for approximation B as proposed in [140]. The uncontracted aug-cc-pV5Z basis (uncontracted aug-cc-pV(5+d)Z for S) was used as auxiliary basis. MP2-F12 calculations were performed for Ansatz **2** in the standard augmented correlation-consistent basis sets with $n = 2, 3, 4$, using a Slater-type geminal with exponent $1.5\, a_0^{-1}$ and numerical quadrature with a medium-sized grid (13824 points per atom). We used the analytic scheme for the Slater objects [72], and the hybrid RI and numerical quadrature method was employed for four-electron integrals [178]. Results are reported for calculations with explicitly correlated basis functions chosen according to equation (11) or (13). In some calculations, the explicitly correlated amplitudes (c_{ij}^{kl} or c_{ij}) were optimized by minimizing the Hylleraas functional, in other calculations they were kept fixed to the derivative values 0.5 and 0.25 for singlet and triplet pairs, respectively [48], to fulfill the cusp conditions explicitly [9, 10, 179].

All of the calculations were performed at fixed geometries of the molecules studied. These geometries, which were optimized at the MP2(FC)/aug-cc-pV(T+d)Z level, are given in table 2. Only the valence orbitals were correlated in the MP2-R12 calculations, the core and semicore orbitals (1s for C, N and O; 1s, 2s and 2p for S) were kept frozen.

4.2. *R12 results in comparison with extrapolated values*

The results of our MP2-R12 calculations are summarized in table 3. In similar work on benchmark calculations on the molecules ethylene and ethane [180], in which localized orbitals were used, it was found that the best estimate of the basis-set limit for the valence-shell MP2 correlation energy was obtained by taking the weighted average of the MP2-R12/A and MP2-R12/B values (cf. figure 1 of [180]). As in [180], we take 60% of the MP2-R12/A and 40% of the MP2-R12/B value.

The MP2-R12 results in table 3 are compared with the conventional MP2 correlation energies that are obtained in the standard correlation-consistent cc-pVnZ and augmented aug-cc-pVnZ basis sets with $n = 2, 3, 4, 5, 6$. Note that even in the largest basis sets with $n = 6$, the errors in the valence-shell correlation energies of the four molecules under study range from 5 to 15 mE_h. For example, the cc-pV6Z value for thiophene is in error by ca. 14 mE_h. Even the corresponding aug-cc-pV6Z value is still in error

Table 2. Fixed Cartesian coordinates (in Å) of a few selected small molecules.

Molecule	Atom	x	y	z
Water	O	0.000 000 000 0	0.000 000 000 0	−0.057 338 488 5
	H	0.758 133 054 3	0.000 000 000 0	0.533 819 244 2
	H	−0.758 133 054 3	0.000 000 000 0	0.533 819 244 2
Thiophene	S	0.000 000 000 0	0.000 000 000 0	1.127 828 284 1
	C	1.232 062 131 6	0.000 000 000 0	−0.050 916 134 8
	C	−1.232 062 131 6	0.000 000 000 0	−0.050 916 134 8
	C	0.706 479 827 2	0.000 000 000 0	−1.326 340 960 3
	C	−0.706 479 827 2	0.000 000 000 0	−1.326 340 960 3
	H	2.268 374 951 2	0.000 000 000 0	0.245 304 904 9
	H	−2.268 374 951 2	0.000 000 000 0	0.245 304 904 9
	H	1.318 157 068 8	0.000 000 000 0	−2.216 370 776 9
	H	−1.318 157 068 8	0.000 000 000 0	−2.216 370 776 9
Methyl formate	O	1.273 199 887 5	0.576 301 036 0	0.000 000 000 0
	O	−0.613 263 982 2	−0.680 960 014 5	0.000 000 000 0
	C	0.713 863 063 4	−0.494 258 897 2	0.000 000 000 0
	C	−1.375 822 642 7	0.539 998 900 1	0.000 000 000 0
	H	1.214 674 372 5	−1.466 132 204 7	0.000 000 000 0
	H	−2.414 508 165 9	0.231 159 101 7	0.000 000 000 0
	H	−1.145 350 316 3	1.125 149 089 3	0.886 598 447 1
	H	−1.145 350 316 3	1.125 149 089 3	−0.886 598 447 1
Urea	O	0.000 000 000 0	0.000 000 000 0	1.305 566 819 5
	N	1.156 642 341 1	0.058 840 693 8	−0.670 526 405 7
	N	−1.156 642 341 1	−0.058 840 693 8	−0.670 526 405 7
	C	0.000 000 000 0	0.000 000 000 0	0.086 396 293 1
	H	1.138 831 668 4	−0.386 381 510 0	−1.573 056 571 6
	H	−1.138 831 668 4	0.386 381 510 0	−1.573 056 571 6
	H	1.986 961 026 8	−0.122 500 782 7	−0.130 660 879 0
	H	−1.986 961 026 8	0.122 500 782 7	−0.130 660 879 0

Table 3. Valence-shell second-order Møller–Plesset energies (in $\mathrm{m}E_\mathrm{h}$) of a few selected small molecules.

Method	Basis	Water	Thiophene	Methyl formate	Urea
MP2	cc-pVDZ[a]	−0.201 959	−0.664 691	−0.638 743	−0.645 700
	cc-pVTZ[a]	−0.261 802	−0.814 987	−0.800 801	−0.809 833
	cc-pVQZ[a]	−0.283 131	−0.869 792	−0.859 000	−0.868 952
	cc-pV5Z[a]	−0.291 843	−0.891 720	−0.882 413	−0.892 497
	cc-pV6Z[a]	−0.295 543	−0.901 954	−0.892 930	−0.902 952
	aug-cc-pVDZ[a]	−0.219 730	−0.692 007	−0.674 261	−0.683 809
	aug-cc-pVTZ[a]	−0.268 710	−0.828 347	−0.815 959	−0.826 392
	aug-cc-pVQZ[a]	−0.286 258	−0.876 422	−0.866 169	−0.876 592
	aug-cc-pV5Z[a]	−0.293 246	−0.895 428	−0.886 111	−0.896 352
	aug-cc-pV6Z[a]	−0.296 296	−0.904 152	−0.895 104	−0.905 161
	Uncontracted[b]	−0.291 757	−0.889 648	−0.880 918	−0.891 102
MP2-R12/A	Uncontracted[b]	−0.300 928	−0.917 468	−0.908 925	−0.918 681
MP2-R12/A′	Uncontracted[b]	−0.300 936	−0.917 538	−0.908 933	−0.918 697
MP2-R12/B	Uncontracted[b]	−0.300 271	−0.914 760	−0.906 713	−0.916 545
Best estimate[c]		−0.300 7(4)	−0.916 4(16)	−0.908 0(13)	−0.917 8(13)

[a] (aug-)cc-pV($n+d$)Z for S, (aug-)cc-pVnZ for C, N, O, and H.

[b] 21s13p9d7f5g for S, 15s9p7d6f4g for C, N, and O, 9s6p5d3f for H.

[c] Estimated by taking 60% of MP2-R12/A and 40% of MP2-R12/B (see text). The number in parentheses indicates the uncertainty in the last digits.

by ca. $12\,\mathrm{m}E_\mathrm{h}$. We observe that the uncertainty in our best estimates is roughly one order of magnitude smaller than the errors obtained in the plain and augmented sextuple-zeta basis sets. In the last decade, there has been much interest in the systematic behavior of the correlation-consistent basis sets with respect to increasing n. By carrying out calculations for several values of n, this behavior can be exploited to extrapolate to the basis-set limit, denoted here as E_∞. While convergence to this limit is fast (i.e. of the type $E_n = E_\infty + A\exp(-bn)$) at the Hartree–Fock and multireference (complete active space) self-consistent-field levels of theory [181–183], dynamic correlation energies such as the MP2 second-order energy converge rather slowly, that is, with an inverse-power law with respect to the cardinal number n of the correlation-consistent basis sets.

Early attempts to extrapolate correlation energies from correlation-consistent basis sets utilized the exponentional form that is appropriate for uncorrelated wavefunctions [4, 184], and in 1996, Martin [185, 186] proposed an extrapolation formula of the form

$$E_\ell = A + B/(\ell + 1/2)^4 + D/(\ell + 1/2)^6, \tag{87}$$

with ℓ the maximum angular momentum in the basis set.

Martin's formula was motivated by the energy increments of partial-wave expansions of atomic correlation energies [179, 187, 188], and similar expressions can be derived from the convergence behaviour of the principal expansion [189, 190], in which the principal quantum number n (or cardinal number n) is used to define an extrapolation formula. Various extrapolation formulae of the general form

$$E_n = A + B/(n + C)^\gamma \tag{88}$$

have been proposed and investigated for various values of C and γ [6, 191–196]. Lee and coworkers, in particular, have used various extrapolation formulae of this general type for calculations on weakly bound complexes [197–201].

In the framework of the principal expansion, the simplest two-point extrapolation formula is [6]

$$E_n = E_\infty + Bn^{-3}. \tag{89}$$

Results from calculations in two basis sets are required to solve equation (89) for the two unknowns B and E_∞. Usually, two subsequent basis sets of the correlation-consistent hierarchy are chosen, and the results are commonly denoted cc-pV(DT)Z if the double- and triple-zeta basis sets were used, cc-pV(TQ)Z if the triple- and quadruple-zeta basis sets were used, and so on.

Although it is not the topic of the present review, a comment on other extrapolation formulae that are currently in the literature seems in order. Equation (89) appears to perform extremely well, in particular for larger basis sets, but one could argue that formulae with other values for C and γ might perform even better. Firstly, MP2 basis-set errors tend to be larger than the basis-set errors at higher levels of perturbation theory and higher levels of excitation in the Møller–Plesset or coupled-cluster hierarchies [103, 189, 198, 202]. Hence, different formulae for MP2 and, for example, CCSD(T) extrapolations seem appropriate [195, 198, 202]. Secondly, the value of C can be chosen such that the next term (i.e. n^{-4}) in the expansion of E_n around $n = \infty$ is taken into account [193]. Thirdly, basis-set errors of energies related to correlations between electrons with like and unlike spin behave differently. While the leading term of the basis-set error of singlet-coupled pairs is n^{-3}, it is n^{-5} for triplet-coupled pairs [195, 203, 204]. These issues were first addressed 25 years ago when Petersson and Nyden investigated the convergence behavior of electron correlation energies with respect to the number of natural orbitals [205, 206]. To obtain higher-order corrections for basis-set incompleteness, MP2 basis-set errors were multiplied with an 'interference factor' [207] to account for the fact that this error tends to be overestimated at the MP2 level, and moreover, Petersson and coworkers [208] applied different extrapolation formulae of the types n^{-3} and n^{-5} to the $\alpha\beta$ and $\alpha\alpha$ pair energies of MP2 theory.

Extrapolated MP2 correlation energies obtained using several popular extrapolation schemes based on equation (88) are compared against our best explicitly correlated values in tables 4–6. All extrapolated correlation energies obtained using the quintuple and sextuple-zeta basis sets are in agreement with our best estimates to within the uncertainty in these estimates. Thus, the quality of our estimates derived from MP2-R12 theory is fully supported by the extrapolated values. Differences between the extrapolation schemes are relatively minor but remarkable nevertheless. It has been noted before [180, 195] that MP2 energies extrapolated using equation (88) with $C = 1/2$ (table 6) tend to be more accurate than the values obtained with $C = 0$ (tables 4 and 5). Indeed, the aug-cc-pV(TQ)Z values in table 6 already agree with our explicitly correlated estimates. The quality of our extrapolated values obtained with double- and triple-zeta basis sets is, however, rather low. Perhaps one should expect much better performance for small basis sets from other recent extrapolation schemes [196].

Table 4. Valence-shell second-order Møller–Plesset energies (E_∞ in mE_h) obtained from the two-point extrapolation formula $E_n = E_\infty + Bn^{-3}$ [6].

Extrapolation	Water	Thiophene	Methyl formate	Urea
cc-pV(DT)Z	−0.286 998	−0.878 269	−0.869 036	−0.878 942
cc-pV(TQ)Z	−0.298 696	−0.909 785	−0.901 468	−0.912 092
cc-pV(Q5)Z	−0.300 984	−0.914 726	−0.906 977	−0.917 201
cc-pV(56)Z	−0.300 624	−0.916 011	−0.907 376	−0.917 313
aug-cc-pV(DT)Z	−0.289 334	−0.885 754	−0.875 621	−0.886 427
aug-cc-pV(TQ)Z	−0.299 063	−0.911 504	−0.902 809	−0.913 225
aug-cc-pV(Q5)Z	−0.300 577	−0.915 368	−0.907 033	−0.917 084
aug-cc-pV(56)Z	−0.300 486	−0.916 136	−0.907 457	−0.917 262
Best estimate[a]	−0.300 7(4)	−0.916 4(16)	−0.908 0(13)	−0.917 8(13)

[a] See table 3.

Table 5. Valence-shell second-order Møller–Plesset energies (E_∞ in mE_h) obtained from the two-point extrapolation formula $E_n = E_\infty + Bn^{-\gamma}$, where γ is 3 and 5 for singlet and triplet pair energies, respectively [203].

Extrapolation	Water	Thiophene	Methyl formate	Urea
cc-pV(DT)Z	−0.281 823	−0.866 238	−0.855 218	−0.864 906
cc-pV(TQ)Z	−0.296 742	−0.905 308	−0.896 290	−0.906 776
cc-pV(Q5)Z	−0.300 109	−0.912 878	−0.904 888	−0.915 070
cc-pV(56)Z	−0.300 305	−0.915 269	−0.906 567	−0.916 503
aug-cc-pV(DT)Z	−0.285 571	−0.875 667	−0.864 568	−0.875 266
aug-cc-pV(TQ)Z	−0.297 761	−0.907 977	−0.898 895	−0.909 307
aug-cc-pV(Q5)Z	−0.300 061	−0.913 958	−0.905 497	−0.915 593
aug-cc-pV(56)Z	−0.300 288	−0.915 589	−0.906 855	−0.916 683
Best estimate[a]	−0.300 7(4)	−0.916 4(16)	−0.908 0(13)	−0.917 8(13)

[a] See table 3.

Table 6. Valence-shell second-order Møller–Plesset energies (E_∞ in mE_h) obtained from the two-point extrapolation formula $E_n = E_\infty + B(n + 1/2)^{-\gamma}$, where γ is 3 and 5 for singlet and triplet pair energies, respectively [195].

Extrapolation	Water	Thiophene	Methyl formate	Urea
cc-pV(DT)Z	−0.289 487	−0.885 757	−0.876 028	−0.885 972
cc-pV(TQ)Z	−0.299 794	−0.913 244	−0.904 644	−0.915 252
cc-pV(Q5)Z	−0.301 409	−0.916 195	−0.908 415	−0.918 613
cc-pV(56)Z	−0.300 878	−0.916 867	−0.908 204	−0.918 131
aug-cc-pV(DT)Z	−0.291 977	−0.893 606	−0.883 052	−0.893 855
aug-cc-pV(TQ)Z	−0.300 325	−0.915 007	−0.906 197	−0.916 607
aug-cc-pV(Q5)Z	−0.301 127	−0.916 856	−0.908 531	−0.918 604
aug-cc-pV(56)Z	−0.300 767	−0.916 960	−0.908 264	−0.918 065
Best estimate[a]	−0.300 7(4)	−0.916 4(16)	−0.908 0(13)	−0.917 8(13)

[a] See table 3.

4.3. *Comparison between R12 and F12 results*

For a set of calculations in the aug-cc-pVQZ basis (aug-cc-pV(Q+d)Z for S and Cl) on 28 small molecules, the MP2-R12/**2**A*, A, B* and B approaches yield 98.7 ± 0.6, 98.8 ± 0.9, 98.4 ± 0.6 and 98.4 ± 0.8%, respectively, of the estimated basis set limits for the valence-shell MP2 energies, which were estimated in the same manner as in the previous section for water, thiophene, methyl formate and urea. The set of 28 molecules comprises the 21 molecules investigated by Werner and Manby and coworkers in [168] and [169] plus the molecules SO_2, SO_3, H_2S, CS_2, Cl_2, $COCl_2$ and thiophene. The average percentages for these 28 molecules are similar but slightly (0.3%) below the values of 99.0 and 98.7% reported in [76] for the MP2-R12/**2**A and B methods, respectively, for a much smaller set of molecules in the same aug-cc-pVQZ basis. In [76], the MP2-R12/2B value increases to 99.5% in the aug-cc-pV5Z basis and to 99.8% in the aug-cc-pV6Z basis. Although the MP2-R12 methods perform very well, yielding 99% of the correlation energy or more, the results are even better if Slater-type geminals are used in place of the linear r_{12} correlation factor. For example, Tew and Klopper report that in the aug-cc-pVQZ basis, the percentage of correlation energy is increased from 98.7% (MP2-R12/2B) to 99.6% (MP2-F12/2B) if a Slater-type geminal (represented by six contracted Gaussians) with exponent $1.2a_0^{-1}$ is used in place of the linear r_{12} term. This corresponds to a reduction of the error by a factor of three.

Table 7 shows the results obtained with Slater-type geminals for the four molecules water, thiophene, methyl formate and urea. The results obtained from Slater-type geminals are reported for calculations with pair functions of the form of equation (13), in which only diagonal amplitudes c_{ij} occur. The differences between the results obtained with the pair functions of equations (11) and (13) are expected to be significantly smaller with a Slater-type geminal than with the linear r_{12} factor. The Ansatz of equation (11) is able to correct for errors that occur if short- and long-range linear r_{12} terms occur at the same time in one and the same pair function that involves spatially extended, delocalized orbitals. In conjunction with linear r_{12} factors, the long-range terms are harmful, but they are taken care of by the orbital-invariant approach of equation (11). Note that there is a large difference (5–8 mE_h) between the results obtained from equations (11) and (13) for thiophene, methyl format and urea, whereas this difference is much smaller (ca. 0.3 mE_h) for the comparably compact H_2O molecule. With the Slater-type geminals, the long-range terms do not contribute from the very beginning, and equation (13) seems appropriate with these geminals. The orbital-invariance is nevertheless an important property to avoid ambiguous results. The defects of equation (13) originate from the use of different amplitudes for different pairs. Thus it is preferred to use the fixed amplitudes from the cusp conditions [9, 10, 179] to retain the unitary invariance when equation (13) is used. Anyway, the differences between equations (11) and (13) become very small when we approach the basis set limit. This becomes clear when we compare the large-uncontracted-basis MP2-R12 results of table 3, which are based on equation (11), with the corresponding MP2-R12 results of table 7, which are based on equation (13). The differences amount to only a few tenths of a millihartree in the large uncontracted basis.

Comparing valence correlation energies obtained with MP2-R12/2B (optimized amplitudes c_{ij}^{kl}) and MP2-F12/2B (optimized amplitudes c_{ij}) in aug-cc-pVQZ, we observe that in the latter method, errors are reduced by factors of 4.9 (H_2O), 7.5 (thiophene), 5.5 (methyl formate) and 5.7 (urea) by the MP2-F12/2B approach. The average proportions of the correlation energy recovered for the 28 molecules are 95.8, 99.0, and 99.7% at the MP2-F12/2B (fixed) and 96.8, 99.1, and 99.7% at the MP2-F12/2B (optimized) level for the double-, triple-, and quadruple zeta basis, respectively. It should be noted that the MP2-F12/2B (either with fixed or optimized amplitudes c_{ij}) approach in the triple-zeta basis appears to be superior to the MP2-R12/2B approach in the quadruple-zeta basis. Even in the double-zeta basis, the MP2-F12/2B approach yields reasonably accurate energies, although the difference between the approximations A and B is comparably large in this basis. Also the effect of optimizing the amplitudes c_{ij} is much larger in this basis than in the larger triple- and quadruple-zeta basis sets. The aug-cc-pVDZ basis is perhaps too small for highly accurate calculations (also the underlying Hartree–Fock results have not converged yet in this basis), but the Slater results obtained in this basis with fixed amplitudes are remarkably accurate (conventional MP2 requires a basis set of quadruple-zeta quality to yield similar results, cf. table 3).

Table 7. Valence-shell second-order Møller–Plesset energies (in mE_h) of a few selected small molecules. Comparison between MP2-F12[a] and MP2-R12[b] results for Ansatz **2**, with the explicitly correlated basis functions chosen according to equation (11) or (13).

Method	Equation	Basis	Water	Thiophene	Methyl formate	Urea
Fixed c_{ij}						
MP2-F12/**2**A*	(13)	aVDZ[c]	−0.300 877	−0.889 208	−0.901 240	−0.909 362
MP2-F12/**2**A			−0.298 633	−0.888 723	−0.898 220	−0.907 137
MP2-F12/**2**B*			−0.292 500	−0.872 737	−0.879 032	−0.887 824
MP2-F12/**2**B			−0.290 513	−0.872 350	−0.876 375	−0.885 870
MP2-F12/**2**A*	(13)	aVTZ[c]	−0.301 109	−0.913 987	−0.908 855	−0.918 378
MP2-F12/**2**A			−0.300 618	−0.913 234	−0.907 846	−0.917 681
MP2-F12/**2**B*			−0.298 514	−0.907 942	−0.901 642	−0.911 357
MP2-F12/**2**B			−0.298 055	−0.907 207	−0.900 681	−0.910 655
MP2-F12/**2**A*	(13)	aVQZ[c]	−0.300 801	−0.916 732	−0.908 500	−0.918 403
MP2-F12/**2**A			−0.300 658	−0.916 396	−0.908 190	−0.918 098
MP2-F12/**2**B*			−0.299 991	−0.914 422	−0.906 128	−0.916 102
MP2-F12/**2**B			−0.299 826	−0.914 048	−0.905 763	−0.915 746
Optimized c_{ij}						
MP2-F12/**2**A*	(13)	aVDZ[c]	−0.306 227	−0.923 614	−0.920 746	−0.930 238
MP2-F12/**2**A			−0.303 411	−0.923 385	−0.917 042	−0.927 558
MP2-F12/**2**B*			−0.293 929	−0.887 941	−0.885 394	−0.894 875
MP2-F12/**2**B			−0.291 742	−0.887 751	−0.882 508	−0.892 774
MP2-F12/**2**A*	(13)	aVTZ[c]	−0.301 423	−0.918 874	−0.910 433	−0.920 170
MP2-F12/**2**A			−0.300 916	−0.918 040	−0.909 390	−0.919 470
MP2-F12/**2**B*			−0.298 602	−0.909 805	−0.902 033	−0.911 766
MP2-F12/**2**B			−0.298 141	−0.909 028	−0.901 063	−0.911 071
MP2-F12/**2**A*	(13)	aVQZ[c]	−0.300 858	−0.917 513	−0.908 736	−0.918 663
MP2-F12/**2**A			−0.300 715	−0.917 123	−0.908 423	−0.918 354
MP2-F12/**2**B*			−0.300 037	−0.914 662	−0.906 226	−0.916 185
MP2-F12/**2**B			−0.299 881	−0.914 260	−0.905 874	−0.915 838
Optimized c_{ij}						
MP2-R12/**2**A*	(13)	aVQZ[c]	−0.297 251	−0.895 865	−0.893 909	−0.904 565
MP2-R12/**2**A			−0.297 644	−0.895 833	−0.895 145	−0.905 695
MP2-R12/**2**B*			−0.296 157	−0.893 236	−0.889 580	−0.900 532
MP2-R12/**2**B			−0.296 352	−0.893 074	−0.890 263	−0.901 119
Optimized c_{ij}^{kl}						
MP2-R12/**2**A*	(11)	aVQZ[c]	−0.297 647	−0.903 188	−0.898 843	−0.909 136
MP2-R12/**2**A			−0.297 968	−0.903 405	−0.899 826	−0.910 029
MP2-R12/**2**B*			−0.296 541	−0.900 396	−0.895 702	−0.906 123
MP2-R12/**2**B			−0.296 679	−0.900 402	−0.896 216	−0.906 543
Optimized c_{ij}						
MP2-R12/A[d]	(13)	Uncont.[e]	−0.300 926	−0.917 083	−0.908 724	−0.918 497
MP2-R12/B[d]			−0.300 260	−0.914 159	−0.906 338	−0.916 189
Best estimate[f]			−0.300 7(4)	−0.916 4(16)	−0.908 0(13)	−0.917 8(13)

[a] Using a Slater-type geminal with exponent 1.5 a_0^{-1} and numerical quadrature on a medium-sized grid (13824 points/atom).

[b] Using the ABS approach, with the uncontracted aug-cc-pV(5+d)Z basis as auxiliary basis set (uncontracted aug-cc-pV(5+d)Z for S and uncontracted aug-cc-pV5Z for C, N, O, and H).

[c] aug-cc-pV(n+d)Z for S, aug-cc-pVnZ for C, N, O, and H.

[d] Calculation without ABS. See table 3 for the corresponding energies with the explicitly correlated pair functions of equation (12).

[e] See table 3.

[f] Taken from table 3.

5. Perspectives

We first provide brief summaries of two important fields of current activity, aiming for higher accuracy and larger systems, then offer our final conclusions on the recent developments in the field.

5.1. *Higher level methods*

The highly accurate CC-R12 methods of Noga, Klopper, Kutzelnigg and coworkers can readily be extended to make use of more realistic correlation factors. Work of this kind is underway in the group of Klopper. The correlation factors of [73] can also be exploited at the coupled-cluster level. In particular in the CCSD(R12) and CCSD(T)(R12) models as developed by Fliegl *et al.* [103], the only minor complication in the theory due to using a correlation factor f_{12} other than r_{12} occurs in the vector components

$$V^{(ij)}_{\mu\nu} = \langle \mu\nu | f_{12} r_{12}^{-1} | ij \rangle - \langle \mu\nu | f_{12} \hat{Q}_{12} r_{12}^{-1} | ij \rangle, \tag{90}$$

where μ and ν are AO indices, i, j refer to occupied orbitals, and $\hat{Q}_{12}$ is a projection operator. The CCSD(R12) and CCSD(T)(R12) models have been implemented for all of the correlation factors of [73] for Ansatz **1** of R12 theory in the DALTON program.

5.2. *Local approximations*

The steep scaling of electronic structure methods with respect to system size is well known to arise partly from the delocalized nature of the HF canonical orbitals. The problem can be avoided through a variety of approaches that have in common the use of localized orbitals [209–215].

In the local formulation of Werner, Schütz and coworkers, based on the earlier work of Pulay and Saebø [209–213], it has proven possible to attain linear or near-linear scaling for a variety of electronic structure methods including MP2 [216, 217], CCSD [218, 219] and coupled-cluster triples [220–222].

It has also proven exceptionally advantageous to combine density fitting and local approximations to create methods with low scaling with respect to system size coupled with low prefactors and excellent performance in larger AO basis sets. This approach has been applied in MP2 [223], MP2 gradients [224], HF theory [225] and in coupled-cluster theory [226, 227].

For highly accurate calculations on very large (say, biological) problems, it is necessary to couple explicitly correlated electronic structure methods with local techniques. Work in this direction has already proven fruitful. Werner and Manby recently implemented a local form of MP2-R12 theory in which the explicitly correlated calculation is performed only for strongly correlated electron pairs [168]. Localization of the resolution of the identity and of density fitting was investigated. The success of the method was tempered slightly by the fact that poor asymptotic form of the correlation factor r_{12} leads to non-negligible errors in extended systems.

However, as detailed above, one of the key advances in R12-like methods of recent years is the use of short-range correlation factors. This not only brings vastly improved accuracy, but also makes local approximations easier to apply. Manby *et al.* therefore implemented a local variant of MP2-F12 theory using a frozen linear combination of Gaussian geminals to represent the correlation factor [169]. This theory, implemented in the Molpro package [228], can be applied to large systems of fifty atoms or more, and is very accurate. Using an aug-cc-pVTZ atomic orbital basis set, the correlation energies for a test set of small first-row chemical reactions are converged to within 1 kJ/mol, about half of the remaining error in the Hartree–Fock reaction energies in this basis set.

5.3. *Conclusions*

The fruitful recent history in the development of explicitly correlated electronic structure methods leaves us with some clear conclusions, as well as some clear directions for future work.

Applications of explicitly correlated methods to chemical problems are only viable if the three- and four-electron integrals are computed approximately. The R12-type methods, which approximate such integrals systematically, are presently the only practical approach. Published R12-type methods are a combinatorial manifold, owing to a number of explored correlation factors, Ansätze, and approximations. The non-specialist can therefore find it difficult to compare the results found in the literature and to decide which method to implement. Using the recent results as a guideline, we recommend the following features of linear R12-type methods as optimal from performance and implementation perspective.

5.3.1. Correlation factor. Although the precise form of the correlation factor is not as important in highly accurate computations of small systems, correlation factors other than linear r_{12} are essential to approach chemical accuracy in modest basis sets. Bounded correlation factors are also desirable for numerical reasons. It appears that a single Slater-type geminal factor $\exp(-\zeta r_{12})$ is very close to optimal. The required two-electron integrals can be computed in closed form, and it is sufficiently universal to attain 99% accuracy for valence correlation energies of light molecules using a triple-zeta basis. Proper description of heavier elements, as well as intracore and core-valence correlation, will likely require a set of a few correlation factors.

5.3.2. Projection operator. Ansatz **2** for the strong-orthogonality projector should be used in the form of equation (22) or equation (25). These projectors minimize the coupling between conventional and R12-dependent amplitudes and thus improve convergence of CC-R12 methods. The coupling matrix should be included in the zeroth-order Hamiltonian and evaluated rigorously without the assumption of extended Brillouin condition.

5.3.3. Formulation of intermediate B. Approximation C offers the most compact expression for intermediate B and may become the approximation to be preferred over the standard 'commutator'-based approach. The additional benefit is that the more difficult integrals over the $[\hat{T}_i, f_{12}]$ operator are not necessary. It is safe to assume the generalized Brillouin condition to simplify or eliminate certain terms in intermediate **B**. However, all of the approximations currently in use fail to guarantee to yield an intermediate **B** that is positive definite, as is

$$B_{ij}^{kl}(mn) = \langle ij | \hat{v}_{12}^{\dagger}(\hat{F}_{12} - \epsilon_m - \epsilon_n)\hat{v}_{12} | kl \rangle. \tag{91}$$

For computations of response properties and excitation energies, it is very important to guarantee the positive definiteness [60].

5.3.4. Approximating integrals. The three- and four-electron integrals can be approximated well using the RI in atom-centred Gaussian basis sets, especially using the CABS approach. The RI will likely become impractical for heavy elements when the demands on the auxiliary basis become too extreme. Numerical quadrature, or the hybrid RI-DF will likely be the preferred approach for such systems. In all methods, the integrals with two RI indices can be avoided.

5.3.5. Efficiency improvements. Density fitting can be used to enhance computational efficiency with practically no impact on the final accuracy of the results. Local methods can be used to extend the methods to much larger systems, with small and controllable errors.

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