Ab Initio Theory for Accurate Spectroscopic Constants and Molecular Properties

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1 INTRODUCTION

The accuracy that may be achieved in the theoretical prediction of spectroscopic constants and molecular properties has increased significantly over the past decade. Although this is in part due to the advances in computer hardware, it has really been made possible by the continuous development in ab initio methodologies and the resulting computational software. In particular, significant advances have been made in ab initio electronic-structure theory for computing potential energy surfaces (PESs) to very high accuracy. The quality of the electronic PES is probably the single largest limiting factor for obtaining an accurate theoretical prediction for spectroscopic constants and molecular properties. The accuracy of an ab initio PES is determined by the level to which the following physical effects are accounted for in the ab initio calculation:

- the electrostatic attraction between the electrons and the nuclei;
- the correlated motion of the electrons due to their Coulombic repulsion;
- relativistic effects; and
- the nonadiabatic coupling between the electronic and the nuclear motion.

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Generally speaking, the first two effects have, by far, the largest influence on the shape of a PES. A frequently adopted strategy for PES computation is, therefore, to solve the nonrelativistic Schrödinger equation for the electronic wave function as accurately as possible (within the Born–Oppenheimer approximation) and to add corrections for the influence of relativistic and nonadiabatic effects on the basis of a perturbational treatment. The quality of the PES is then determined by the accuracy of the approximate solution or solutions to the electronic Schrödinger equation, used to compute the nonrelativistic energy and the relativistic and nonadiabatic corrections.

There are many ab initio methods for computing electronic wave functions (Szabo and Ostlund 1989, Helgaker *et al*. 2000). In this article, we discuss exclusively those where the wave function is expanded as a linear combination of Slater determinants: Hartree–Fock (HF), Møller–Plesset perturbation theory (MP2, MP3, etc.), configuration interaction (CI), coupled-cluster (CC) methods, and their multireference (MR) equivalents. For these methods, the convergence toward the exact solution to the electronic Schrödinger equation is in two directions:

- The excitation level of the wave function M, which accounts for the effect of up to M electrons interacting simultaneously.
- The size of the one-particle basis N, which governs the accuracy to which each M-electron interaction is treated.

The excitation level is determined by the choice of ab initio method (e.g., for coupled-cluster singles and doubles (CCSD) $M = 2$). Concerning the convergence with respect to the one-particle basis, the series of correlation-consistent basis sets cc-pVXZ and aug-cc-pVXZ, with X = D, T, Q, 5 and 6, provide a smooth and systematic reduction in the basis set error (Dunning 1989, Kendall *et al*. 1992, Woon and Dunning 1993). However, the convergence with respect to the size of the one-particle basis is notoriously slow and extremely large basis sets are required for high accuracy. In this article, we discuss the recent developments in explicitly correlated approaches, which overcome this basis set problem.

To illustrate the importance of reducing the basis set error, we may consider the computations of Polyansky *et al*. (2003), who achieved spectroscopic accuracy for the rotation–vibration transitions of water. Polyansky *et al*. constructed a series of increasingly accurate PESs, using ab initio methods that provide successively accurate approximations to the nonrelativistic Schrödinger equation, as well as computing correction surfaces for relativistic, QED, and nonadiabatic effects. The nonrelativistic Schrödinger equation was solved using the multireference configuration interaction (MRCI) method, which was shown to very closely approximate the full CI (FCI) approach where simultaneous interactions between all 10 electrons are accounted for. MRCI calculations were performed using the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The standard deviations between the computed transitions and all known experimental values are listed in Table 1. Increasing the basis set from aug-cc-pV5Z to aug-cc-pV6Z reduced the standard deviation between theoretical and experimental values by $3\,\mathrm{cm}^{-1}$ and using the aug-cc-pV6Z basis in combination with corrections for relativistic, QED, and nonadiabatic effects gave errors with a standard deviation of $5.5\,\mathrm{cm}^{-1}$. Using the smooth convergence with respect to the basis size to extrapolate to the basis set limit (vide infra) further reduced the standard deviation to $1.9\,\mathrm{cm}^{-1}$. The error due to the incomplete basis set is clearly a limiting factor in calculations of this type. Indeed, Polyansky *et al*. reported that the remaining basis set error is still a dominant contribution to the $1.9\,\mathrm{cm}^{-1}$ standard deviation between theoretical and experimental values.

The basis set problem is by no means specific to the above example and must always be sufficiently accounted for when high accuracy is required. For further examples, we refer the reader to studies on H_2S (Tarczay *et al*. 2001), NH_3 and H_3O^+ (Rajamäki *et al*. 2003, Yurchenko *et al*. 2005), HeCO (Peterson and McBane 2005), BH_3 (Schuurman *et al*. 2005), MgH_2 (Li and Le Roy 2007), and the H_2O dimer (Salmi *et al*. 2008). In these examples, near spectroscopic accuracy was obtained only when extrapolation techniques were used to reduce the basis set error and corrections were included for higher order correlation, relativistic, and sometimes even nonadiabatic effects. The reliance on extrapolation techniques to reduce the basis set error meant that large orbital basis sets were necessary, usually cc-pV5Z quality or even aug-cc-pV5Z.

The necessity for large basis sets is problematic because of the way in which the required computational resources, such as memory, disk space, and CPU hours, increase with the size of the basis. For example, the CPU time required for a calculation scales (at least) as N_{AO}^4, where N_{AO} is the number of basis functions per atom. For the calculations on water described above, increasing the basis from aug-cc-pV5Z to aug-cc-pV6Z increased the CPU time by an order of magnitude, but only reduced the basis set error by a factor of 2. Clearly, a brute force approach to this problem,

Table 1 The standard deviations between predicted and experimental rotation–vibration transitions of water, using MRCI aug-cc-pV5Z, aug-cc-pV6Z and (Q56)[a] PESs with CV,[b] Rel.,[c] QED,[d] and BODC[e] correction surfaces.

PES	σ	max
MRCI/aug-cc-pV5Z	22.8	63
MRCI/aug-cc-pV6Z	19.7	52
MRCI/(Q56)	16.6	39
MRCI/(Q56) + CV	7.9	−13
MRCI/(Q56) + CV + Rel.	4.2	14
MRCI/(Q56) + CV + Rel. + QED	3.8	13
MRCI/aug-cc-pV6Z + CV + Rel. + QED + BODC	5.5	19
MRCI/(Q56) + CV + Rel. + QED + BODC	1.9	6

[a]Extrapolation of HF and correlation energies toward the basis set limit.
[b]Correction for core–valence correlation.
[c]The mass–velocity term, the one- and two-electron Darwin terms, and the Breit interaction.
[d]Correction for the one-electron Lamb shift.
[e]Diagonal Born–Oppenheimer correction and second-order (nonadiabatic) correction.

using larger basis sets, is both inefficient and impractical. In the following sections, we describe the recent developments in the R12 class of explicitly correlated methods, which are now capable of achieving very high accuracy with relatively small basis sets and correspondingly low computational resources. We highlight the utility of these new methods for computing spectroscopic constants and molecular properties through various numerical examples.

2 R12 AND F12 EXPLICITLY CORRELATED METHODS

2.1 The Correlation Cusp

The origin of the slow convergence of the electronic energy with the size of the one-particle basis is well known. It arises due to the use of atom-centered functions (atomic orbitals, AOs) to represent the form of the correlation hole, which is electron centered. The term *correlation hole* is used here to describe the decrease in the magnitude of the wave function, relative to the HF (mean field) wave function, whenever two or more electrons approach each other in space. More precisely, it may be defined as $\psi - \psi_{\mathrm{HF}}$, analogous to the correlation energy, $E - E_{\mathrm{HF}}$. The form of the correlation hole at short interelectronic distance, $r_{12} \to 0$, is determined by the universal coalescence conditions for the exact wave function. At the coalescence of two electrons with opposite spin, the exact wave function obeys the s-wave coalescence condition:

$$\psi = \left(1 + \tfrac{1}{2} r_{12}\right) \psi_{r_{12}=0} + \mathcal{O}\left(r_{12}^2\right) \tag{1}$$

Thus, the exact wave function has a derivative discontinuity at the point where two electrons meet, which is illustrated for helium in Figure 1. Equation (1) is known as *Kato's cusp condition* (Kato 1957). For two electrons that have the same spin, the wave function vanishes at $r_{12} = 0$ and in this case, the exact wave function obeys the p-wave coalescence condition (Pack and Byers Brown 1966, Tew 2008):

$$\psi = \left(1 + \tfrac{1}{4} r_{12}\right) \boldsymbol{r}_{12} \cdot \left.\frac{\partial \psi}{\partial \boldsymbol{r}_{12}}\right|_{r_{12}=0} + \mathcal{O}\left(r_{12}^3\right) \tag{2}$$

In the region of two-electron coalescence, the correlation hole has the general form $1 + cr_{12} + \mathcal{O}(r_{12}^2)$. In Figure 2, we have illustrated the basis set convergence of CCSD calculations toward the exact correlation hole for helium, together with the convergence in the energy. This plot clearly demonstrates the necessity for AOs with a large angular momentum quantum number. The use of an AO expansion to represent the region close to the cusp essentially amounts to a partial wave expansion of linear r_{12}, which is very slowly convergent (Schwartz 1962, Hill 1985, Kutzelnigg 1985).

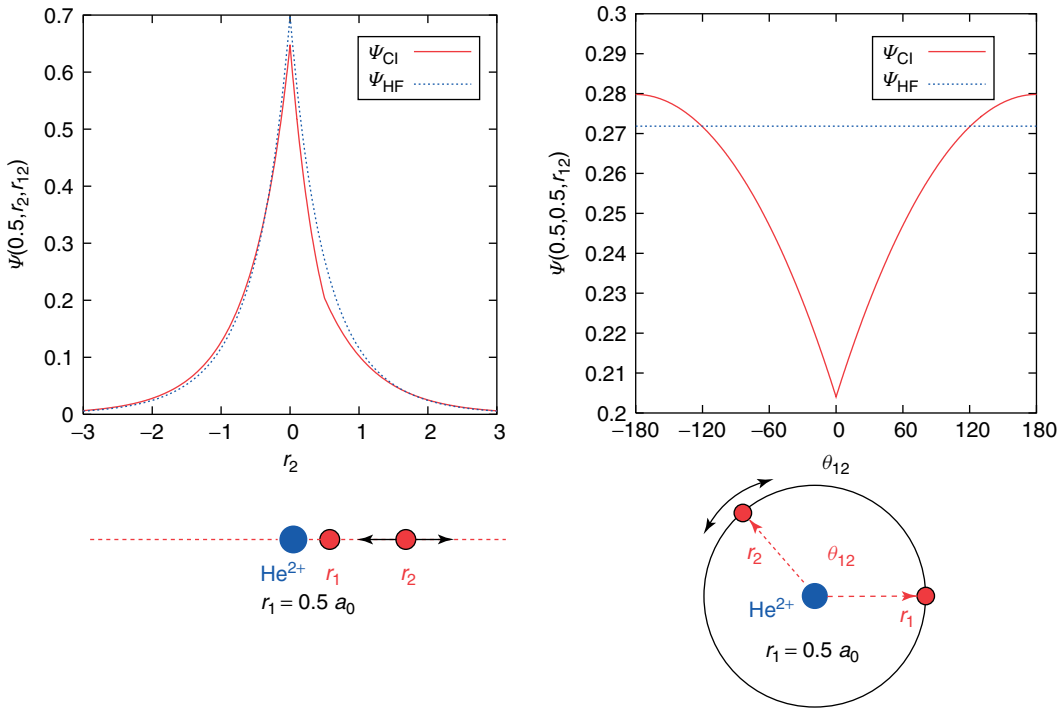


Figure 1 Radial and angular cuts of the Hartree–Fock and basis set limit FCI (CCSD) wave functions of helium. Electron 1 is kept fixed at a radius of 0.5 a_0 from the nucleus and electron 2 moves along radial or angular paths through electron 1.

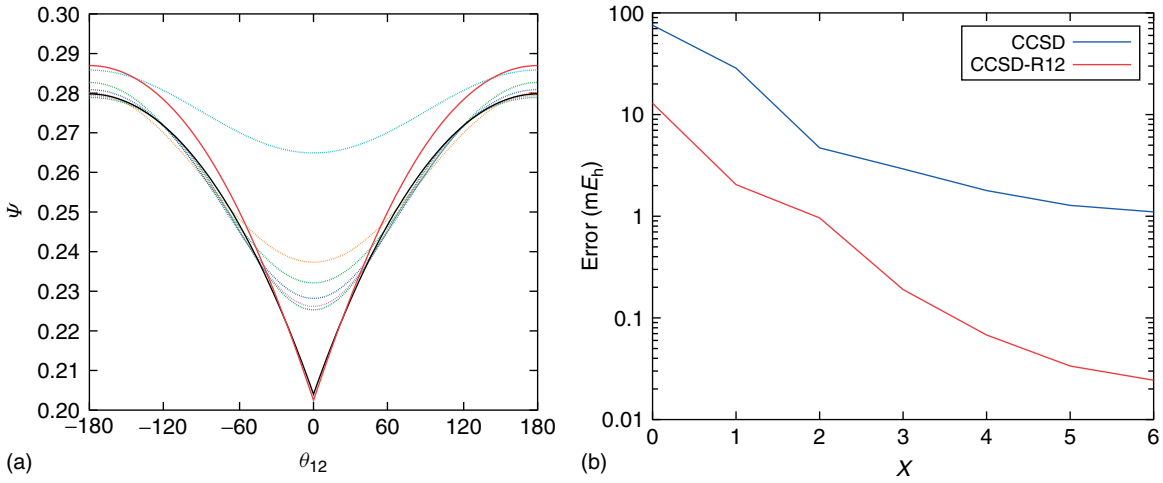


Figure 2 Results from CCSD calculations on helium using basis functions $r^n\,\mathrm{e}^{-2r}Y_{lm}(\theta,\phi)$, with $0 \le n \le X$ and $l \le n$. (a) Radial cuts of the CCSD wave functions compared with the basis set limit (black line) and a CCSD-R12 calculation using the basis $X = 1$ and an additional function r_{12} 1s1s (red line). (b) The error in the total electronic energy as a function of X for CCSD and CCSD-R12 calculations.

2.2 Extrapolation Methods

Although the basis set convergence is slow, it is smooth and fairly well defined and is, therefore, amenable to extrapolation. For a partial wave expansion, where the basis is first saturated using only s-type AOs, then saturated using s- and p-type AOs, etc., up to AOs with a maximum angular momentum l, the correlation energy increment for each angular set has been shown to be proportional to $(l+\frac{1}{2})^{-4}$ (Hill 1985). The total error for a set truncated at l is then proportional to $(l+1)^{-3}$. The standard basis sets of computational chemistry generally follow a principal quantum number expansion rather than a partial wave expansion. For example, the cc-pVDZ basis (cardinal number $X = 2$) contains 3s2p1d and the cc-pVTZ (cardinal number $X = 3$) contains 4s3p2d1f. Nonetheless, because of the way the correlation-consistent basis sets of Dunning and coworkers are optimized, the basis set error for the correlation energy is still well represented as (Kutzelnigg 2008)

$$E_\infty - E_X \approx AX^{-3} \tag{3}$$

The basis set error may be significantly reduced by computing the correlation energy using two basis sets with cardinal numbers Y and $X = Y + 1$ and eliminating AX^{-3} (Halkier *et al.* 1998):

$$E_\infty \approx \frac{E_X X^3 - E_Y Y^3}{X^3 - Y^3} \tag{4}$$

This two-point extrapolation is denoted as (YX). For example, (Q5) energies, computed using the cc-pVQZ and cc-pV5Z basis sets, are approximately as accurate as energies computed using a cc-pV6Z basis.[a] In other words, extrapolation reduces the basis set error by an amount equivalent to increasing the size of the basis by one cardinal number. Numerical examples for this are given in Section 3. In contrast to the correlation energy, the HF contribution to the electronic energy converges approximately exponentially to the basis set limit (the cusps in the HF wave function are centered only at the nuclei and are well described by AOs):

$$E_\infty - E_X \approx A\mathrm{e}^{-BX} \tag{5}$$

The basis set error in the HF energy may be reduced through a three-point extrapolation formula using basis sets with cardinal numbers Z, $Y = Z + 1$, and $X = Y + 1$ (Halkier *et al.* 1999):

$$E_\infty \approx \frac{E_X}{1-\mathrm{e}^{-B}} - \frac{E_Y \mathrm{e}^{-B}}{1-\mathrm{e}^{-B}} \tag{6}$$

$$\mathrm{e}^{-B} = \frac{E_X - E_Y}{E_Y - E_Z} \tag{7}$$

When both the HF and the correlation energy are extrapolated using equations (5) and (6), respectively, the energy is referred to as a *CBS* or a (ZYX) value. Although extrapolated energies are always an improvement over the raw energies, they often overshoot the basis set limit and high accuracy requires at least a (TQ5) or (Q56) extrapolation. The reduction in the basis set requirements is, thus, not as large as desired, since it is still necessary to use at least cc-pV5Z quality basis sets. In the following sections,

we describe the current status of the R12 class of explicitly correlated methods, which are an improvement over extrapolation methods, producing basis set limit correlation energies with cc-pVTZ quality basis sets.

2.3 Two-electron Basis Functions

From the discussion in Section 2.1, it is clear that one-electron basis functions are ill suited to describe the correlation hole. A more direct and far better way to represent the correlation hole is to use two-electron basis functions (geminals), chosen to explicitly contain the appropriate r_{12} dependence. In particular, a good description of the correlation cusp requires that the geminals depend linearly on r_{12} as $r_{12} \to 0$ and the basis functions

$$r_{12}|ij\rangle \tag{8}$$

are a good choice, where $|ij\rangle$ denotes a Slater determinant of two occupied HF spin orbitals (Kutzelnigg 1985). In Figure 2, we have plotted the basis set convergence of the correlation energy of helium when the orbital basis is augmented by this R12 geminal basis function. The description of the correlation hole is enormously improved and the problem of the slow basis set convergence has been removed. Methods that incorporate basis functions of this type into standard electronic-structure approaches are referred to as *R12 methods* (Klopper and Kutzelnigg 1987, Kutzelnigg and Klopper 1991, Noga *et al*. 1992).

Linear r_{12} dependence is appropriate only for the very short range features of the correlation hole and the basis functions (8) become unphysical at large r_{12}. An even better representation of the correlation hole is obtained by accounting for the effect of screening and using basis functions (Ten-no 2004b):

$$f_{12}|ij\rangle = \exp(-\gamma r_{12})|ij\rangle \tag{9}$$

These are referred to as *Slater-type geminals* (*STGs*). γ represents the extent of the correlation hole and is, thus, proportional to the effective nuclear charge experienced by the correlated electrons (Tew and Klopper 2005). For valence electrons, any value in the range 1–2 a_0^{-1} is a reasonable choice. R12 methods where these basis functions are used instead of equation (8) are referred to as *F12 methods*.

In terms of M-electron interactions, the R12/F12 geminal functions describe the interaction of two electrons, with the associated one-electron relaxation effects. In the standard methods of quantum chemistry, such as MPn, CC, or CI, the basis functions used to treat single excitations are orthogonal to those used to treat double excitations, as well as being orthogonal to the HF wave function. To incorporate the R12/F12 geminals into the standard methods, it is necessary to enforce this property and to project out the contribution to single excitations. Therefore, instead of the functions (9), we use

$$\hat{Q}_{12} \exp(-\gamma r_{12})|ij\rangle \tag{10}$$

where

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) \tag{11}$$

and $\hat{O}_1$ projects onto the space of occupied spin orbitals for electron 1. $\hat{Q}_{12}$ is called the *strong orthogonality operator*. The geminal basis functions (10) correspond to pure double excitations and enter the formulae for the approximate solution of the Schrödinger equation in a completely analogous way to that of conventional double orbital replacements.

The strong orthogonality operator of equation (11) is the operator that is currently in use and is known as *ansatz 2*. It is computationally advantageous to additionally project out all products of virtual orbitals (Wind *et al*. 2002, Valeev 2004), and ansatz 2 is, therefore, implemented in the most optimal manner using

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

where $\hat{V}_1$ projects onto the space of virtual spin orbitals for electron 1. With $-\hat{V}_1\hat{V}_2$ included, ansatz 2 is sometimes referred to as *ansatz 3*, but the two strong orthogonality operators are strictly equivalent as long as no approximations are introduced into the theory. At the MP2-F12 level of theory, approximations give rise to small differences between 2 and 3, but these are so insignificant that a distinction between 2 and 3 is not really needed (indeed, we make no such distinction). However, some approximate CC-F12 methods exploit the smallness of the explicitly correlated contribution and require ansatz 3. Ansatz 1, with $\hat{Q}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2)$ and $\hat{P}_1$ projecting onto the space of all spin orbitals for electron 1, is less accurate and has only historical significance.

2.4 MP2-F12

In second-order Møller–Plesset perturbation theory (MP2), the first-order wave function $|\Psi^{(1)}\rangle$ is determined by minimizing the Hylleraas functional

$$E^{(2)} \leq F = \langle\Psi^{(1)}|\hat{H}^{(0)} - E^{(0)}|\Psi^{(1)}\rangle + 2\langle\Psi^{(1)}|\hat{H}^{(1)}|\mathrm{HF}\rangle \tag{13}$$

Exactly the same is done in MP2-F12 theory. The only difference between the standard MP2 and MP2-F12 theories is that $|\Psi^{(1)}\rangle$ is expanded only in double orbital replacements $|\Phi_{ij}^{ab}\rangle$ in the former but in double orbital replacements *and* STGs (equation 10) in the latter. It is important to note that including the STGs in the first-order wave function improves the convergence of the MP2 energy to the basis set limit, but that it does not change the method as such or its properties. The same is true for CCSD(F12) and CCSD-F12. The basis set limit of CCSD theory is approached more rapidly with STGs, but the model itself just remains CC theory with singles and doubles. F12 theory is nothing else but choosing a particular (very efficient) basis set. For a recent review of MP2-F12 theory, see Klopper *et al*. (2006).

Minimizing the Hylleraas functional implies optimizing the amplitudes t_{ab}^{ij} and t_{kl}^{ij} of the functions used to expand the first-order wave function:

$$|\Psi^{(1)}\rangle = \tfrac{1}{4} t_{ab}^{ij} |{}_{ij}^{ab}\rangle + \tfrac{1}{4} t_{kl}^{ij} |{}_{ij}^{kl}\rangle \tag{14}$$

In equation (14), we adhere to the usual conventions that $i, j, \ldots$ refer to occupied and $a, b, \ldots$ to virtual spin orbitals. $|{}_{ij}^{kl}\rangle$ denotes a Slater determinant where the orbital pair ij has been replaced by the geminal $\hat{Q}_{12} f_{12} kl$. Summation over repeated dummy indices is assumed. It is also possible to keep the F12 amplitudes t_{kl}^{ij} fixed and to optimize only the standard amplitudes t_{ab}^{ij}. This is the fixed amplitude[b] or rational generator ansatz of Ten-no (2004a), where the STG is chosen such that the first-order coalescence conditions for s and p waves are fulfilled (therefore sometimes termed *SP ansatz*). Compared to the original unitary invariant ansatz, the SP ansatz has the advantage of better numerical stability and the absence of geminal basis set superposition errors (Tew and Klopper 2006).

Finally, we note that instead of restricting the ansatz by using only the "diagonal" amplitudes t_{ij}^{ij} and fixing these according to the coalescence conditions, it is also possible to extend the ansatz. Extensions are, for instance, required for explicitly correlated F12 CC response theory (Fliegl *et al*. 2006a, Neiss *et al*. 2006, Neiss and Hättig 2007, Köhn 2009b, Yang and Hättig 2009).

2.5 Resolution-of-the-identity Approximation

The difficulty with equation (13) is that the evaluation of the matrix elements with STGs leads to three- and four-electron integrals. These many-electron integrals are not only tedious to compute but also numerous. Note that in conventional MP2 calculations, only Coulomb-type two-electron integrals occur, which are relatively easy to compute. In the F12 methods, the three- and four-electron integrals are circumvented by inserting an approximate completeness relation, known as the *resolution-of-the-identity* (*RI*) *approximation*,

$$1 \approx |p''\rangle\langle p''| \tag{15}$$

into the many-electron integrals, such that they factorize into sums of products of two-electron integrals.[c] All three- and four-electron integrals are avoided and, thus, the F12 methods involve only two-electron integrals, as do standard electronic-structure methods. We note that it is also possible to achieve a decomposition of many-electron integrals into sums of products of lower index objects using numerical quadrature. This approach was applied by Ten-no in his early work on the transcorrelated method (Ten-no 2000a,b) and more recently in MP2-F12 theory (Ten-no 2004a). The method represents electron repulsion integrals, for example, as sums of two- and three-center objects over grid points,

$$\langle pq|r_{12}^{-1}|rs\rangle \approx \sum_g \overline{\phi}_p(\boldsymbol{r}_g)\overline{\phi}_r(\boldsymbol{r}_g)\langle q|r_{1g}^{-1}|s\rangle \tag{16}$$

where $\overline{\phi}_p(\boldsymbol{r}_g) = w_g \phi_p(\boldsymbol{r}_g)$ denotes the weighted value of the orbital ϕ_p at the quadrature grid point $\boldsymbol{r}_g$ (w_g is the weight of that grid point). Applied to three-electron integrals, numerical quadrature yields

$$\langle pqr|r_{12}^{-1} f_{13}|stu\rangle \approx \sum_g \overline{\phi}_p(\boldsymbol{r}_g)\overline{\phi}_s(\boldsymbol{r}_g)\langle q|r_{1g}^{-1}|t\rangle\langle r|f_{1g}|u\rangle \tag{17}$$

In the RI approximation, such three-electron integrals are (approximately) computed as

$$\langle pqr|r_{12}^{-1} f_{13}|stu\rangle \approx \sum_{p''}\langle pq|r_{12}^{-1}|p''t\rangle\langle p''r|f_{12}|su\rangle \tag{18}$$

where the sum runs over the orthonormal functions of the auxiliary basis set $\{\phi_{p''}\}$ (*ABS*) (Klopper and Samson 2002). How to choose such ABS is discussed below (Section 2.9.2).

2.6 Other Approximations

Approximations for increasing the efficiency may be applied to MP2-F12 theory in much the same manner as for standard MP2 theory. For example, density fitting (DF) to reduce four-index quantities to sums of products of

three-index quantities can be applied to MP2-F12 theory (Manby 2003). Furthermore, the RI approximation of F12 theory may be reformulated when applying DF (Ten-no and Manby 2003), and DF may, of course, be combined with the local-correlation (LMP2) approach (Werner and Manby 2006, Manby *et al*. 2006, Adler *et al*. 2009).

A few other approximations are also currently in use in F12 theory. Most of these approximations are concerned with the evaluation of the matrix elements for $\langle \Psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle$, leading to the letters A, B, or C being appended to the acronym for the method. Approximation A involves the neglect of all but the dominant kinetic energy contribution, whereas B denotes that all terms are included (Kutzelnigg and Klopper 1991). Approximation C is essentially the same as B (indeed we make no distinction) except that integrals involving the single commutator $[\hat{T}_1, f_{12}]$ are avoided by a further RI insertion, where $\hat{T}_1$ is the operator of kinetic energy (Kedžuch *et al*. 2005). Approximation A neither saves a substantial amount of computation time nor is more accurate than B. It may, nevertheless, be worthwhile to compute both MP2-F12/2A and MP2-F12/2B because A tends to overestimate and B to underestimate the magnitude of the MP2 basis set limit correlation energy. In this sense, the average (or something like 60% of A plus 40% of B) of the two results is often a good approximation to the basis set limit and the two values may provide an estimate of the final accuracy (Samson and Klopper 2004). For CC theory, it is recommended that the most accurate method, namely, B should be used.

Other general decisions to make are whether the generalized Brillouin condition (GBC) and extended Brillouin condition (EBC) are assumed to be satisfied (Kutzelnigg and Klopper 1991). The GBC holds if one assumes that the set of occupied HF orbitals is closed under the Fock operator, that is,

$$\hat{F}|\phi_j\rangle = \sum_\mu |\phi_\mu\rangle f_{\mu j} \approx \sum_i |\phi_i\rangle f_{ij} \tag{19}$$

where the orbitals ϕ_μ form a complete basis. It is safe to assume the GBC to simplify or eliminate certain terms in $\langle \Psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle$, except perhaps for MP2-F12 calculations in very small (i.e., of double-zeta quality) HF basis sets. The EBC is more problematic. Assuming this condition to be satisfied means that one assumes that the whole HF basis set is closed under the Fock operator, that is,

$$\hat{F}|\phi_q\rangle = \sum_\mu |\phi_\mu\rangle f_{\mu q} \approx \sum_p |\phi_p\rangle f_{pq} \tag{20}$$

When the EBC is assumed, it is a common practice to attach an asterisk to the method's acronym, which then, for example, is denoted as MP2-F12/2A* or MP2-F12/2B* (Klopper and Samson 2002). Application of the EBC is not recommended (May *et al*. 2005), and in modern applications of MP2-F12 theory, the MP2-F12/2A or MP2-F12/2B approaches are used, that is, without asterisk, that is, without assuming the EBC.

Further approximations are also possible, for example, "hybrid" approaches, where the RI basis is reduced for certain Fock matrix contributions, and also there are various choices for partitioning the Hamiltonian in perturbation theory. For further details, we refer the reader to the original literature (Klopper 2004, Werner *et al*. 2007, Noga *et al*. 2007) and a recent review on the MP2-F12 method (Klopper *et al*. 2006).

2.7 CCSD-F12

Compared with the standard CCSD wave function, the CCSD-F12 wave function is obtained by adding an extra cluster operator $T_{2'}$ to the singles and doubles cluster operator $T = T_1 + T_2$. Hence,

$$|\Psi_{\text{CCSD-F12}}\rangle = \exp(T_1 + T_2 + T_{2'})|\text{HF}\rangle \tag{21}$$

$|\text{HF}\rangle$ is the HF reference wave function and $T_{2'}$ is the "F12 doubles cluster operator". Here, we assume that STGs are used, but note that exactly the same models and equations are obtained with other correlation factors such as linear r_{12} terms (such as CCSD-R12 and CCSD(R12) theories). In particular, the F12 doubles cluster operator reads (Noga *et al*. 1992, Noga and Kutzelnigg 1994)

$$T_{2'} = \tfrac{1}{8} t_{kl}^{ij} R_{\alpha\beta}^{kl} a_{ij}^{\alpha\beta}, \qquad T_{2'}|\text{HF}\rangle = \tfrac{1}{4} t_{kl}^{ij} |{}_{ij}^{kl}\rangle \tag{22}$$

The STGs are introduced via the "contraction coefficients" $R_{\alpha\beta}^{kl} = \langle \alpha\beta | \hat{Q}_{12} \, \mathrm{e}^{-\gamma r_{12}} | kl \rangle$, where the indices $\alpha, \beta, \ldots$ refer to virtual spin orbitals of a formally complete basis.

By defining $\overline{H} = \exp(-T) H \exp(T)$ with $T = T_1 + T_2$, we can write the CCSD-F12 energy and amplitudes equations as

$$E = \langle \text{HF} | \overline{H} + [\overline{H}, T_{2'}] | \text{HF} \rangle \tag{23}$$

$$0 = \langle {}_{i}^{a} | \overline{H} + [\overline{H}, T_{2'}] | \text{HF} \rangle \tag{24}$$

$$0 = \langle {}_{ij}^{ab} | \overline{H} + [\overline{H}, T_{2'}] + \tfrac{1}{2} [[\overline{H}, T_{2'}], T_{2'}] | \text{HF} \rangle \tag{25}$$

$$0 = \langle {}_{ij}^{kl} | \overline{H} + [\overline{H}, T_{2'}] + \tfrac{1}{2} [[\overline{H}, T_{2'}], T_{2'}] | \text{HF} \rangle \tag{26}$$

The only difference with conventional CCSD theory is that commutators with $T_{2'}$ occur with one extra set of amplitude equations (equation 26).

Using ABSs, CCSD-F12 theory can be implemented as given by the above equations, without further approximations (Köhn *et al*. 2008, Shiozaki *et al*. 2008a, b). However, it is worthwhile to consider various simplifications that make the implementation more cost efficient without notable loss of accuracy. Before we do so, we first note that the removal of all terms within a particular commutator ensures that the remaining equations are still size extensive. Hence, we can "linearize" the CCSD-F12 equations in the sense that we remove all terms quadratic in $T_{2'}$, that is, all double commutators in equations (25) and (26). This results in the CCSD-F12(lin) method (Köhn *et al*. 2008), with

$$0 = \langle {}^{ab}_{ij} | \overline{H} + [\overline{H}, T_{2'}] | \mathrm{HF} \rangle \tag{27}$$

$$0 = \langle {}^{kl}_{ij} | \overline{H} + [\overline{H}, T_{2'}] | \mathrm{HF} \rangle \tag{28}$$

replacing equations (25) and (26). These approximate methods require ansatz 3 (or 1) since they assume that the F12 amplitudes are small and vanish in the limit of an infinite orbital basis. In the CCSD(F12) model of Fliegl *et al*. (2005, 2006b) and Bokhan *et al*. (2009), one goes a step further and, in addition to the above linearization, replaces equation (28) by

$$0 = \langle {}^{kl}_{ij} | \overline{H} + [F, T_{2'}] | \mathrm{HF} \rangle \tag{29}$$

where F is the Fock operator. The rationale for this approach is that one wishes to avoid the evaluation of very small terms via multiple RI approximations (for details, see the work by Noga *et al*. (2008, 2009a) and Köhn *et al*. (2008)). Table 2 shows that the CCSD(F12) model is a good approximation of the full CCSD-F12 model. The differences between the two models are of the order of a few tenths of a millihartree and smaller than the remaining basis set error. Since a few years, the CCSD(F12) model has become an established method, and the results presented later in this article were all obtained from "(F12)" calculations. One should also remember that ultimately, in an infinite and complete basis, both models yield the same CCSD basis set limit.

When solving the amplitudes equations by the usual iterative procedures, CCSD(F12) iterations require roughly three times as much computation time as standard CCSD iterations. Because the basis set convergence is significantly improved by F12 methods, this factor of 3 certainly does not pose any problems in practical applications. Much smaller basis sets (e.g., of triple-zeta quality) can be used at the CCSD(F12) level to achieve the same accuracy as at the CCSD level in a much larger basis (e.g., of quintuple-zeta quality) (Tew *et al*. 2007c, 2008). The difference in computation time between those basis sets is roughly 2 orders of magnitude. Furthermore, CCSD(F12) calculations are usually combined with (much more involved) CC calculations of contributions from higher excitations, that is, from connected triples, quadruples, and so on.

Nevertheless, it is possible to simplify the CCSD(F12) model even further toward methods in which there are no extra costs (compared to CCSD) except those that are required to evaluate the integrals that contribute to the MP2-F12 functional and energy. Methods of this type have been developed by Adler *et al*. (i.e., CCSD-F12a and CCSD-F12b models) and Valeev (i.e., CCSD(2)$_{\overline{\mathrm{R12}}}$ or, in terms of our F12 notation, CCSD(2)$_{\overline{\mathrm{F12}}}$ model). Concerning these models, we refer the reader to the original literature (Adler *et al*. 2007, Knizia *et al*. 2009, Valeev 2008, Torheyden and Valeev 2008, Valeev and Crawford 2008).

Finally, we note that all of the above methods can be formulated and applied with fixed F12 doubles amplitudes instead of optimized amplitudes t^{ij}_{kl}. This fixed-amplitudes approach is often dubbed "diagonal, orbital-invariant" approach (e.g., d-CCSD(2)$_{\overline{\mathrm{F12}}}$ model). Then, of course, there are no F12 doubles amplitude equations to solve, but the energy must be computed from an appropriate Lagrangian (Hylleraas functional).

Table 2 Valence-shell CCSD correlation energy of H_2O (in mE_h). A Slater-type geminal was used with exponent 1.3 a_0^{-1}.[(a)]

Basis	CCSD(F12)	CCSD-F12(lin)	CCSD-F12
aug-cc-pVDZ	−291.005	−291.300	−291.190
aug-cc-pVTZ	−296.097	−295.959	−295.950
aug-cc-pVQZ	−297.820	−297.655	−297.654

[(a)]Taken from the work of Köhn *et al*. 2008. A basis of composition 19s14p10d8f6g4h2i, denoted as "K4", was used as CABS.

2.8 CCSD(T)-F12 and Higher Order Excitations

For most applications in the area of high-resolution molecular spectroscopy, CC theory restricted to single and double orbital replacements is not accurate enough. Fortunately, the explicitly correlated CCSD(F12) and related models described in the previous section can all be combined with a calculation of the (T) contribution of connected triples. Usually, any couplings via the F12 doubles in the triples amplitudes equations are neglected and the (T) contribution is simply computed from the converged singles and doubles amplitudes in the usual manner. This procedure defines the CCSD(T)(F12) model, and similar approaches are taken in the CCSD(T)-F12a, CCSD(T)-F12b, and CCSD(T)$_{\overline{\mathrm{F12}}}$ methods. All results presented later in this article are obtained from the CCSD(T)(F12) model, in which the (T) contribution is computed in the usual manner from singles and doubles amplitudes.

There is, however, a need to go beyond this approach. Because the CCSD(F12) method only requires a comparably small basis set to yield results close to the basis set limit of CCSD theory, one may be tempted to use only small (e.g., of triple-zeta quality) basis sets in CCSD(T)(F12) calculations. The basis set convergence of the (T) contribution, however, is rather slow. Hence, with extremely efficient methods at hand to obtain the CCSD basis set limit, one has to address the basis set convergence behavior of higher connected excitations such as triples, quadruples, and so on. Work on these lines is in progress (Shiozaki *et al*. 2008a, 2009, Köhn 2009a).

2.9 F12 Basis Sets

2.9.1 Optimized Basis Sets (cc-pVXZ-F12)

In principle, MP2-F12 and CCSD(F12) calculations can be performed in standard basis sets for electron correlation methods, for example, in the standard augmented correlation-consistent aug-cc-pVTZ basis, in which roughly aug-cc-pV5Z quality results are obtained. As a general rule, however, it has been found that for F12 theory, the exponents of the polarization functions should be smaller than in standard electron correlation calculations. For example, improved results are obtained by scaling the exponents of cc-pVXZ polarization functions by a factor of 0.6 (Tew and Klopper 2005) or by using the augmented sets (aug-cc-pVTZ). So far, basis sets optimized explicitly for F12 calculations exist for the atoms H, He, B–Ne, and Al–Ar. These sets are denoted as *cc-pVXZ-F12* and are available with X = D, T, and Q (Peterson *et al*. 2008). We recommended the use of these basis sets in F12 calculations. In a recent assessment of aug-cc-pVXZ and cc-pVXZ-F12 basis sets for F12 calculations, it was found that "the cc-pVQZ-F12 and aug-cc-pV5Z basis sets are the preferred basis sets for highly accurate calculations using F12 methodology. If such high accuracy is not needed, then the basis sets aug-cc-pVQZ, cc-pVTZ-F12, and def-QZVPP may be used almost interchangeably" (Bischoff *et al*. 2009). For a molecule such as benzene, 99.4 and 99.9% of the valence-shell second-order correlation energy are obtained in the cc-pVDZ-F12 and cc-pVTZ-F12 basis sets, respectively (Table 3). Note that at the conventional MP2 level, not even 99% is obtained in the large aug-cc-pV6Z basis with 1896 contracted basis functions (Yamaki *et al*. 2007). Further advantages of the cc-pVXZ-F12 sets are that the exponent of the STG has been optimized for each set and that corresponding complementary auxiliary basis sets (CABSs), see next subsection) have also been provided.

Finally, we note that at the time of writing, there had been little experience with F12 calculations on molecules containing d elements and/or calculations that include core orbitals in the correlation treatment. Hence, the reader should search the current literature or perform a careful basis set study when performing calculations of this type.

2.9.2 Complementary Auxiliary Basis Set (CABS)

Researchers applying the F12 methods must be aware of the fact that a quadrature grid or an ABS must be chosen and may effect the accuracy and reliability of the results. To illustrate this point, let us consider two of the matrix elements that occur in F12 methods:

$$\langle \mathrm{HF}|r_{12}\hat{Q}_{12}r_{12}^{-1}|\mathrm{HF}\rangle \quad \text{and} \quad \langle \mathrm{HF}|r_{12}\hat{Q}_{12}r_{12}|\mathrm{HF}\rangle \quad (30)$$

where $|\mathrm{HF}\rangle$ is a two-electron determinant representing the $1s^2$ ground-state configuration. Let us take the example

Table 3 Valence-shell second-order correlation energy of benzene (in mE_h), obtained at the standard MP2 and explicitly correlated MP2-F12 levels.

Basis[a]	N[b]	γ[c]	Hartree–Fock[d]	MP2[e]		MP2-F12[e]	
aug-cc-pVDZ	192	1.5	−230.727652	−811.92	(76.8)	−1040.67	(98.4)
aug-cc-pVTZ	414	1.5	−230.779990	−964.48	(91.2)	−1053.36	(99.6)
aug-cc-pVQZ	756	1.5	−230.793044	−1016.44	(96.1)	−1056.51	(99.9)
aug-cc-pV5Z	1242	1.5	−230.795863	−1035.78	(97.9)	−1057.32	(100.0)
aug-cc-pV6Z	1896	1.5	−230.796248	−1044.58	(98.8)	−1057.58	(100.0)
cc-pVDZ-F12	234	0.9	−230.769267	−885.23	(83.7)	−1051.62	(99.4)
cc-pVTZ-F12	426	1.0	−230.792162	−982.29	(92.9)	−1056.07	(99.9)
cc-pVQZ-F12	726	1.1	−230.795785	−1019.62	(96.4)	−1057.18	(100.0)

[a]A def2-QZVPP exchange fitting basis was used as CABS in the aug-cc-pVXZ calculations. The cc-pVXZ-F12 calculations used the optimized CABS of Yousaf and Peterson 2008.
[b]Number of contracted basis functions.
[c]Exponent of the STG in a_0^{-1}.
[d]Hartree–Fock energy in E_h.
[e]Percentage of the basis set limit (-1057.5 ± 0.5 mE_h) (Yamaki *et al*. 2007) between parentheses.

of He and expand |HF⟩ in a cc-pVTZ basis or rather in its subset of s-type functions. The exact values for the above matrix elements are −0.147 806 6 (dimensionless) and 0.150 750 9 a_0^2, respectively, which are easy to compute in this one-center case. Table 4 shows the values obtained for these integrals using the RI approximation, for the correlation factor $f_{12} = r_{12}$. As an auxiliary basis $\{\phi_{p''}\}$, we have chosen the HF basis $\{\phi_p\}$ supplemented by an orthonormal basis set $\{\phi_{p'}\}$, which is orthogonal on the HF basis,

$$\{\phi_{p''}\} = \{\phi_p\} \cup \{\phi_{p'}\} \tag{31}$$

The basis set $\{\phi_{p'}\}$ is denoted as *complementary auxiliary basis set* (*CABS*). Recent work has shown that the CABS approach is the method of choice for invoking the RI approximation in F12 theories. Table 4 shows that the matrix element $\langle \mathrm{HF}|r_{12}\hat{Q}_{12}r_{12}^{-1}|\mathrm{HF}\rangle$, which involves three-electron integrals of the type $\langle pqr|r_{12}^{-1}r_{13}|stu\rangle$, is more easy to compute accurately than the matrix element $\langle \mathrm{HF}|r_{12}\hat{Q}_{12}r_{12}|\mathrm{HF}\rangle$, which involves three-electron integrals of the type $\langle pqr|r_{12}r_{13}|stu\rangle$. This is one of the reasons for the success of the RI approximation in F12 theories, because the three-electron integrals $\langle pqr|r_{12}^{-1}r_{13}|stu\rangle$ directly contribute to the correlation energy. Another observation from Table 4 is that the error of the RI approximation is relatively large for the primitive 4s CABS taken from the cc-pVTZ basis, which is also the basis used for the orbitals. This is understandable, because the CABS functions are required to be orthogonal to the orbital basis functions, and thus to construct an orthonormal CABS, functions of the primitive 4s basis that are linearly dependent on the HF basis (to within some threshold) are removed. The remaining CABS is rather poor in this particular case. In general, the CABS functions should be chosen so that they are different from the HF basis (different exponent and/or angular momentum). Optimized CABS are available for the cc-pVXZ-F12 (Peterson *et al*. 2008) as well as for the aug-cc-pVXZ and aug-cc-pV(X+d)Z sets for the atoms H, He, B–Ne, and Al–Ar (Yousaf and Peterson 2008, 2009).

2.9.3 Other Auxiliary Basis Sets

If DF is used, as, for example, in the F12 methods as implemented in the TURBOMOLE package (TURBOMOLE V6.0 2009), then also MP2 fitting basis sets and exchange fitting basis sets are required. We recommend to use fitting basis sets of the types aug-cc-pwCV($X+1$)Z (Hättig 2005) and aug-cc-pV($X+1$)Z (Weigend 2007), respectively, for calculations in the cc-pVXZ-F12 sets. For the hydrides BH_3, CH_4, NH_3, H_2O, HF, AlH_3, SiH_4, PH_3, H_2S, and HCl, the mean absolute deviation (MAD) between CCSD(F12) calculations with and without DF amounts to 32, 36, and 13 μE_h for the sets cc-pVDZ-F12, cc-pVTZ-F12, and cc-pVQZ-F12, respectively. These deviations are comparable with the usual DF errors in standard MP2 calculations.

2.10 CABS Singles

When F12 calculations are performed using the CABS approach, then additional basis functions are available that, in principle, could be used to improve the HF reference wave function. An HF calculation could, for instance, be performed in the union of the HF and CABS basis sets, $\{\phi_{p''}\} = \{\phi_{p'}\} \cup \{\phi_p\}$. However, such HF calculations would be much more time consuming and would also make the subsequent MP2-F12 of CCSD(F12) calculation much more time consuming than in the basis $\{\phi_p\}$ alone. However, it is relatively straightforward to improve the HF description by perturbation theory, that is, by allowing for single excitations from occupied HF spin orbitals $\{\varphi_i\}$ into the CABS spin orbitals $\{\varphi_{p'}\}$. This leads to the "CABS singles" energy correction:

$$\Delta E_{\mathrm{CABS}} = \sum_{i,p'} \frac{f_{ip'}^2}{\epsilon_i - \epsilon_{p'}} \tag{32}$$

where it is understood that the HF basis set as well as the CABS have been rotated among themselves in such a manner that the HF...HF and CABS...CABS blocks of the Fock matrix are diagonal (with diagonal elements

Table 4 Errors in the approximate calculation of matrix elements for the He atom ground state using the CABS approach.

CABS[a]	$\langle \mathrm{HF}\|r_{12}\hat{Q}_{12}r_{12}^{-1}\|\mathrm{HF}\rangle$	Error (%)	$\langle \mathrm{HF}\|r_{12}\hat{Q}_{12}r_{12}\|\mathrm{HF}\rangle/a_0^2$	Error (%)
4s (cc-pVDZ)	−0.147 828 9	0.015	0.150 872 1	0.080
6s (cc-pVTZ)	−0.147 858 3	0.035	0.154 384 5	2.4
7s (cc-pVQZ)	−0.147 812 4	0.004	0.150 771 1	0.013
8s (cc-pV5Z)	−0.147 808 6	0.001	0.150 766 9	0.011
10s (cc-pV6Z)	−0.147 808 6	0.001	0.150 760 4	0.006
Exact	−0.147 806 6		0.150 750 9	

[a]Primitive set of s-type functions taken from the cc-pVXZ basis.

ϵ_i and $\epsilon_{p'}$, respectively). The HF...CABS off-diagonal block, however, is nonzero ($f_{ip'} \neq 0$). The $f_{ap'}$ off-diagonal elements are also nonzero and give rise to a coupling term to the above equation (Adler *et al*. 2007, Knizia *et al*. 2009, Knizia and Werner 2008), but they can be neglected if the EBC is assumed to hold. The computational results presented in this article include CABS singles contributions from equation (32). It is important to note that care must be taken when using the CABS singles correction to compute PESs. If the threshold for linear dependence between CABS and orbital basis functions is chosen to be too loose, the number of CABS functions used in equation (32) can vary across the surface, leading to steps. In general, it is usually safe to choose a threshold of 10^{-8} or even 10^{-10} in the singular value decomposition of the overlap matrix.

3 POTENTIAL ENERGY SURFACES WITH F12 METHODS

The computation of a PES to high accuracy requires an adequate treatment of basis set effects, many-electron interactions, and relativistic and nonadiabatic effects. As discussed previously, an accurate solution to the nonrelativistic Schrödinger equation within the Born–Oppenheimer approximation frequently forms the basis for such a calculation. However, except for very small molecules, it is not possible to perform a single calculation that is sufficiently converged with respect to both the treatment of many-electron interactions and the basis set employed. Instead, the energy is often decomposed into contributions that account for successively higher order M-electron interactions:

$$E = E_{\mathrm{HF}} + \Delta E_{\mathrm{CCSD}} + \Delta E_{\mathrm{CCSD(T)}} + \Delta E_{\mathrm{CCSDT(Q)}} + \cdots \tag{33}$$

These contributions decrease in magnitude with the order M and the series may be truncated when the effect of the remaining terms is smaller than the target accuracy or the errors made in approximating the larger terms. Since the computational cost of a calculation rises exponentially with M, each term can only be computed in a basis set where the calculation becomes feasible, and often the frozen-core (fc) approximation is also made, where core and core–valence electron correlation is neglected. We have seen from the examples described in the Introduction that the reduction of the basis set error for each of these terms is essential for high accuracy, and that the large basis set requirements of standard approaches are a limiting factor in the final accuracy, even when extrapolation techniques are employed. The R12/F12 approach may be applied to any of the correlated wave functions in equation (33) to reduce the basis set requirements, so that either a much higher accuracy can be achieved than would otherwise be possible or a given accuracy can be obtained at a reduced computational cost.

The fc-CCSD(T) contribution to the energy is in many cases dominant and the core–valence, higher M-electron interaction and relativistic terms are often similar in magnitude and partially cancel. It is, thus, far more important to reduce the basis set error in the fc-CCSD(T) contribution than in the remaining terms. In the following sections, we discuss the performance, that is, the remaining deviation from the basis set limit, of the fc-CCSD(T)(F12) method, in comparison with standard fc-CCSD(T) and extrapolation techniques. We examine three measures of the quality of the PES: equilibrium geometries, r_e, harmonic wavenumbers, ω_e, and barrier heights. Wherever possible, we compare the basis set errors with the magnitude of post-CCSD(T) corrections and discuss accuracy in terms of agreement with experimental data. As our test, we use the 12 closed-shell molecules, HF, H_2O, NH_3, $CH_2(^1A_1)$, CH_4, F_2, N_2, CO, HCN, HNC, CO_2, and C_2H_2, for which the basis set limit fc-CCSD(T) equilibrium geometries and harmonic wavenumbers are known to spectroscopic accuracy. In Section 3.4, we discuss the accuracy of fc-CCSD(T) and fc-CCSD(T)-F12a anharmonic PESs, comparing computed fundamental frequencies with observed ro-vibrational band origins.

3.1 Stationary Points

The positions of the stationary points, the minima and saddle points, are basic measures for the accuracy of a PES. For the 12 molecules in our set, a systematic study of the convergence of the structural parameters with respect to the treatment of electron correlation and basis set effects has been performed by Heckert *et al*. (2005, 2006). Ruden *et al*. have performed a similar study for the four diatomics in our set (Ruden *et al*. 2004). These works provide the necessary information regarding the dependence of the structural parameters on the basis set and higher order correlation effects, relevant to our discussion on the performance of the CCSD(T)(F12) method.

In Heckert *et al*. (2006), benchmark fc-CCSD(T)-R12 equilibrium geometries were used to assess the basis set error in fc-CCSD(T)/cc-pVXZ optimized structures and we use these data here to compare the performance of the fc-CCSD(T)(F12) method to that of standard CCSD(T) and extrapolation techniques. The benchmark basis set limit fc-CCSD(T)-R12 calculations are taken from Tew *et al*. (2007a) and were performed using the DIRCCR12-OS program (Noga *et al*. 2009b) and using the large uncontracted basis sets of Klopper and Samson (2002) (i.e.,

Table 5 Frozen-core CCSD(T) geometries (in picometers and degrees), computed using cc-pVXZ basis sets and extrapolation techniques.

Molecule	Parameter	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	(TQ5)	(Q56)
HF	r(HF)	91.724	91.622	91.675	91.704	91.746	91.738
H_2O	r(OH)	95.943	95.789	95.804	95.818	95.840	95.836
	∠(HOH)	103.582	104.116	104.372	104.421	104.596	104.476
NH_3	r(NH)	101.410	101.242	101.206	101.204	101.188	101.206
	∠(HNH)	105.644	106.183	106.514	106.585	106.817	106.641
CH_2 ($^1A_1$)	r(CH)	111.050	110.862	110.812	110.807	110.781	110.806
	∠(HCH)	101.614	101.895	102.004	102.034	102.083	102.064
CH_4	r(CH)	108.900	108.790	108.758	108.755	108.734	108.753
F_2	r(FF)	141.577	141.294	141.103	141.024	140.941	140.956
N_2	r(NN)	110.376	110.029	109.943	109.919	109.874	109.889
CO	r(CO)	113.571	113.139	113.073	113.050	113.028	113.021
HCN	r(CN)	116.009	115.644	115.564	115.537	115.494	115.502
	r(CH)	106.684	106.684	106.659	106.658	106.636	106.658
HNC	r(NC)	99.642	99.614	99.623	99.629	99.631	99.638
	r(NH)	117.547	117.200	117.133	117.108	117.076	117.077
CO_2	r(CO)	116.629	116.263	116.207	116.185	116.167	116.156
C_2H_2	r(CC)	120.970	120.648	120.570	120.546	120.495	120.513
	r(CH)	106.370	106.336	106.302	106.301	106.269	106.302
	MAD	0.332	0.113	0.041	0.021	0.027	0.007
H_2O (TS)	r(OH)	93.247	93.240	93.339	93.369	93.457	93.400
NH_3 (TS)	r(NH)	99.520	99.487	99.520	99.534	99.570	99.549

19s14p8d6f4g3h2i for C, N, O, and F and 9s6p4d3f2g for H) and approximation B. Since analytic gradients were not available, the minima were determined by fitting 4th order polynomials to grids of 5 points per degree of freedom, centered at the fc-CCSD(T)/cc-pV6Z optimized geometries. The geometries resulting from this procedure are within 0.0001 pm of an analytic geometry optimization with tight convergence criteria. The residual basis set error of the reference fc-CCSD(T)(F12) structural parameters is estimated to be 0.001 pm for bond lengths and 0.001° for bond angles.

The structural parameters of the 12 molecules of our set, optimized at the fc-CCSD(T)/cc-pVXZ level of theory, were reported in Heckert *et al*. (2006) and are listed in Table 5, together with the MAD of the bond lengths from the basis set limit values. The structural parameters for the stationary points on the PESs constructed from (TQ5) and (Q56) extrapolations of fc-CCSD(T) energies are also tabulated. The geometries resulting from fc-CCSD(T)(F12)/cc-pVXZ-F12 calculations are presented in Table 6, together with the benchmark values. The CCSD(T)(F12) energies were computed using the cc-pVXZ-F12 CABS basis sets and the aug-cc-pV(X + 1)Z MP2- and JK-fitting basis sets, as discussed in Section 2.9.3. Approximation B was used and the geminal amplitudes were optimized during the CC iterations. The CABS singles correction to the HF energy was also included. Since analytic gradients were not available, the grid-based optimization strategy was applied to determine the equilibrium structures.

Comparing Tables 5 and 6 one sees that, with respect to the basis set error, the fc-CCSD(T)(F12)/cc-pVDZ-F12 and fc-CCSD(T)/cc-pV5Z methods are equivalent in accuracy (MAD 0.04 pm) and that the fc-CCSD(T)(F12)/cc-pVTZ-F12 structures are almost as accurate as the fc-CCSD(T)/(Q56) values (MAD 0.01 pm). However, care must be taken when comparing standard and F12 methods. In particular, the F12 methods include a correction to the HF energy and the basis set error in the HF energy is a large contribution to the total CCSD(T) basis set error. Without CABS singles, the MADs for the basis set errors are 0.207, 0.039, and 0.009 pm for X = D, T, and Q, respectively. The reduction in the HF error is clearly very important for high accuracy. An alternative to CABS singles is to compute a correction from a separate accurate HF calculation. The use of a large basis to compute the HF energy is less problematic than for the correlation energy. Using a HF correction computed from the (Q56) HF energy reduces the mean absolute basis set errors for the fc-CCSD(T)/cc-pVXZ bond lengths to 0.191, 0.079, 0.035, and 0.020 pm for X = T, Q, 5, and 6, respectively, while the corresponding fc-CCSD(T)(F12)/cc-pVXZ-F12 MADs are 0.045, 0.008, and 0.003 pm, for X = D, T, and Q, respectively. With respect to the correlation contribution to the PES, the CCSD(T)(F12)/cc-pVTZ-F12 method is, thus, as accurate as the (Q56) extrapolation method.

Table 6 Frozen-core CCSD(T)(F12) geometries (in picometres and degrees), computed using cc-pVXZ-F12 orbital basis sets, compared to benchmark CCSD(T)-R12 calculations.

Molecule	Parameter	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12	R12[(a)]
HF	r(HF)	91.712	91.733	91.720	91.722
H_2O	r(OH)	95.816	95.836	95.825	95.824
	∠(HOH)	104.419	104.429	104.456	104.463
NH_3	r(NH)	101.208	101.212	101.204	101.201
	∠(HNH)	106.603	106.604	106.619	106.614
CH_2 ($^1A_1$)	r(CH)	110.837	110.812	110.800	110.797
	∠(HCH)	101.827	101.996	102.042	102.064
CH_4	r(CH)	108.755	108.760	108.749	108.747
F_2	r(FF)	140.857	140.937	140.897	140.912
N_2	r(NN)	109.939	109.888	109.881	109.881
CO	r(CO)	113.084	113.024	113.018	113.016
HCN	r(CN)	115.547	115.501	115.497	115.497
	r(CH)	106.647	106.659	106.658	106.656
HNC	r(NC)	117.128	117.076	117.073	117.074
	r(NH)	99.641	99.639	99.636	99.635
CO_2	r(CO)	116.191	116.161	116.153	116.150
C_2H_2	r(CC)	120.565	120.512	120.509	120.511
	r(CH)	106.294	106.302	106.299	106.299
	MAD	0.042	0.011	0.003	
H_2O (TS)	r(OH)	93.387	93.394	93.383	
NH_3 (TS)	r(NH)	99.527	99.543	99.540	

[(a)] Basis set limit CCSD(T)-R12 values of Tew *et al*. 2007a.

One further consideration when comparing F12 and conventional calculations is the size of the cc-pVXZ and cc-pVXZ-F12 basis sets—the F12 sets are slightly larger than the cc-pVXZ sets. Indeed, the cc-pVXZ-F12 sets contain almost the same number of functions as the cc-pV($X+1$)Z sets. Nonetheless, the computational effort involved in an fc-CCSD(T)(F12)/cc-pVTZ-F12 calculation is significantly less than that of an fc-CCSD(T)/cc-pV6Z calculation. The CCSD(T)(F12) method is thus a highly efficient means of reducing the basis set error to 0.01 pm for structural parameters.

The comprehensive studies of Heckert *et al*. and Ruden *et al*. provide the data necessary to compare the fc-CCSD(T) basis set error with the magnitude of contributions beyond CCSD(T) theory and to assess the agreement with experimental structures. Table 7 is taken from Heckert *et al*. (2005, 2006) and lists various statistical measures for the deviation of the computed bond lengths from those derived from spectroscopy. The fc-CCSD(T) method, even at the basis set limit, predicts bond lengths that differ from experimental values by 0.2–0.3 pm. To improve agreement to 0.04 pm, it is necessary to account for core–valence

Table 7 Statistical measures (in pm) for bond lengths computed using various additivity schemes with and without basis set extrapolation in comparison with experiment.

		$\overline{\Delta}$	$\overline{\Delta}_{abs}$	Δ_{max}	Δ_{std}
HF-SCF/cc-pV6Z		−2.318	2.318	8.595	1.936
HF-SCF/(Q56)		−2.318	2.318	8.600	1.937
CCSD(T)/cc-pVQZ		0.183	0.192	0.330	0.116
CCSD(T)/cc-pV5Z		0.135	0.155	0.263	0.107
CCSD(T)/cc-pV6Z		0.122	0.151	0.238	0.112
CCSD(T)/(Q56)		0.107	0.145	0.284	0.117
CCSD(T)/cc-pV6Z	+ core/cc-pCVQZ	−0.041	0.056	0.353	0.094
	+ T/cc-pVTZ	−0.062	0.072	0.387	0.101
	+ Q/cc-pVDZ	−0.002	0.031	0.094	0.040
CCSD(T)/(Q56)	+ HLC[(a)]	−0.017	0.033	0.162	0.062

[(a)] HLC = core/cc-pCVQZ + T/cc-pVTZ + Q/cc-pVDZ.

correlation and the effect of four-electron interactions. Both Heckert *et al*. and Ruden *et al*. report that the effect of five-electron interactions is in the range of 0.001–0.002 pm for single bonds and 0.02 pm for multiple bonds, and that relativistic effects are of the order of 0.01 pm for our set of molecules. To compute structural parameters to high accuracy, it is thus essential to account for many-body electron correlation effects. It is, however, remarkable that the basis set error from fc-CCSD(T)(F12)/cc-pVTZ-F12 calculations is already below many of these computationally more demanding higher order contributions. Indeed, the remaining errors beyond the fc-CCSD(T)(F12)/cc-pVDZ-F12 predictions are so small that they are currently only important when comparing with experimental bond lengths for small and semirigid molecules.

3.2 Harmonic Wavenumbers

A more demanding test for the quality of a PES is the accuracy of the second derivatives at the stationary points. In Table 8, we have listed the harmonic wavenumbers predicted by the fc-CCSD(T) method using

Table 8 Frozen-core CCSD(T) equilibrium harmonic wavenumbers (in cm^{-1}), computed using cc-pVXZ orbital basis sets and extrapolated values.

Molecule		ω_e	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z	TQ5	Q56
HF	σ		4 177.4	4 162.3	4 151.0	4 145.5	4 140.0	4 139.3
H_2O	a_1	(bend)	1 668.9	1 659.3	1 653.4	1 651.4	1 647.8	1 648.4
	a_1	(s-stretch)	3 840.9	3 844.5	3 840.0	3 837.3	3 834.2	3 833.7
	b_2	(a-stretch)	3 945.5	3 951.4	3 949.3	3 947.4	3 946.4	3 944.6
NH_3	a_1	(s-bend)	1 109.2	1 084.0	1 067.5	1 060.5	1 050.8	1 055.1
	e	(a-bend)	1 687.9	1 679.6	1 677.9	1 676.1	1 676.9	1 674.6
	a_1	(s-stretch)	3 471.9	3 480.5	3 481.9	3 481.0	3 482.2	3 479.5
	e	(a-stretch)	3 597.5	3 608.8	3 612.6	3 612.6	3 615.8	3 611.9
CH_2 ($^1A_1$)	a_1	(bend)	1 406.6	1 402.9	1 401.0	1 400.1	1 399.8	1 399.2
	a_1	(s-stretch)	2 912.0	2 922.2	2 925.0	2 925.0	2 926.5	2 924.5
	b_2	(a-stretch)	2 983.1	2 996.1	2 999.4	2 999.8	3 001.3	2 999.9
CH_4	t_2	(bend)	1 344.4	1 345.4	1 345.2	1 344.7	1 345.0	1 344.0
	e	(bend)	1 570.8	1 570.4	1 570.3	1 570.1	1 570.1	1 569.9
	a_1	(s-stretch)	3 034.6	3 036.1	3 036.1	3 035.5	3 035.7	3 034.6
	t_2	(a-stretch)	3 154.0	3 157.0	3 157.8	3 157.6	3 158.2	3 157.4
F_2	σ_g		920.0	921.1	926.6	928.5	932.2	929.9
N_2	σ_g		2 346.0	2 356.2	2 359.8	2 360.9	2 363.5	2 362.4
CO	σ		2 153.8	2 164.4	2 165.1	2 165.8	2 165.8	2 166.8
HCN	π	(bend)	715.7	721.8	726.2	726.4	730.8	727.0
	σ	(CN stretch)	2 111.4	2 123.1	2 125.3	2 126.1	2 127.6	2 127.3
	σ	(CH stretch)	3 443.4	3 435.5	3 437.5	3 437.8	3 439.6	3 438.0
HNC	π	(bend)	472.5	466.6	464.3	465.3	461.8	467.6
	σ	(NC stretch)	2 045.4	2 054.3	2 054.4	2 054.6	2 054.9	2 055.2
	σ	(NH stretch)	3 824.5	3 820.6	3 816.7	3 814.3	3 813.3	3 811.4
CO_2	π_u	(bend)	660.3	670.5	672.2	673.4	673.7	675.2
	σ_g^+	(s-stretch)	1 346.2	1 351.9	1 352.6	1 353.0	1 353.2	1 353.5
	σ_u^-	(a-stretch)	2 396.3	2 396.5	2 394.3	2 394.8	2 393.9	2 395.8
C_2H_2	π_g	(bend)	577.6	595.3	614.8	617.1	633.1	620.5
	π_u	(bend)	746.3	746.4	748.4	748.3	750.8	748.5
	σ_g^+	(CC-stretch)	2 000.7	2 005.7	2 007.5	2 008.1	2 009.9	2 009.1
	σ_u^-	(a-stretch)	3 409.7	3 409.7	3 411.7	3 411.6	3 413.4	3 411.4
	σ_g^+	(s-stretch)	3 510.7	3 501.8	3 503.6	3 503.4	3 506.0	3 503.1
		MAD	12.1	5.6	2.3	1.2	1.7	1.1
H_2O (TS)	π_u	(bend)	i1 725.3	i1 705.2	i1 689.2	i1 685.2	i1 672.9	i1 680.2
	σ_g^+	(s-stretch)	4 101.7	4 085.2	4 067.8	4 060.4	4 047.7	4 052.4
	σ_u^-	(a-stretch)	4 504.7	4 479.8	4 462.6	4 456.7	4 446.4	4 450.7
NH_3 (TS)	a_1''	(inverse)	i900.4	i874.7	i857.0	i848.8	i838.1	i840.8
	e_1'	(bend)	1 587.1	1 585.6	1 584.2	1 584.0	1 582.7	1 583.8
	a_1'	(s-stretch)	3 654.2	3 647.7	3 605.4	3 637.9	3 632.8	3 634.4
	e_1'	(a-stretch)	3 864.0	3 858.4	3 853.2	3 850.9	3 848.2	3 847.9

the cc-pVXZ basis with X = T, Q, 5, and 6. These values are computed from second-derivative calculations performed at the stationary points on the corresponding fc-CCSD(T)/cc-pVXZ PES. Note that we have used the 2002 CODATA recommended values of the fundamental physical constants (Mohr and Taylor 2005), with $E_h = 4.359\,744\,17 \times 10^{-18}$ J, $a_0 = 0.529\,177\,210\,8 \times 10^{-10}$ m, and $m_e = 9.109\,382\,6 \times 10^{-31}$ kg. We have furthermore used the atomic mass constant $m_u = 1.660\,538\,86 \times 10^{-27}$ kg and the relative atomic masses 1.007 825 032 1 (H), 12.0 (^{12}C), 14.003 074 005 2 (^{14}N), 15.994 914 622 1 (^{16}O), and 18.998 403 20 (^{19}F).

The basis set limit fc-CCSD(T) harmonic vibrational frequencies of the 12 molecules in our set are known from the work in Tew *et al*. (2007a). fc-CCSD(T)-R12 calculations identical to those used to determine the equilibrium structures were used to compute the electronic Hessian at the basis set limit fc-CCSD(T) equilibrium geometries. The Hessian matrix was evaluated by finite difference, using a seven-point formula with a step size of 0.05 a_0 such that the finite difference error was reduced below 0.01 cm^{-1}. An identical procedure has been applied to obtain the harmonic wavenumbers predicted by the fc-CCSD(T)(F12)/cc-pVXZ-F12 method, for X = D, T, and Q, using the same ABSs and approximations as for the equilibrium geometries. Note that the CABS singles correction is assumed to form part of the CCSD(T)(F12) energy. The harmonic fc-CCSD(T)(F12)/cc-pVXZ-F12 wavenumbers, together with benchmark fc-CCSD(T)-R12 values, are presented in Table 9. The use of the finite difference procedure also enables us to straightforwardly compute the equilibrium harmonic wavenumbers on the extrapolated (TQ5) and (Q56) fc-CCSD(T) PESs. These are presented in Table 8.

The convergence of the fc-CCSD(T)/cc-pVXZ equilibrium harmonic wavenumbers with basis set is rather slow. The mean absolute basis set error halves with every successive increase in X and an MAD of 1 cm^{-1} remains even for the cc-pV6Z basis. In contrast to the equilibrium structures, extrapolation does not seem to improve matters significantly. The accuracy of the fc-CCSD(T)(F12)/cc-pVXZ-F12 harmonic wavenumbers, on the other hand, is impressive. The MAD for the fc-CCSD(T)(F12)/cc-pVTZ-F12 method is below 1 cm^{-1}, more accurate than (Q56) extrapolation, and the MAD for the cc-pVQZ-F12 basis is only 0.4 cm^{-1}.

At the time of writing, the only molecules within our test set where a thorough study of the post-CCSD(T) contributions to the harmonic wavenumbers has been performed are the diatomic molecules HF, N_2, F_2, and CO. For these molecules, very accurate harmonic wavenumbers have been derived from the ro-vibrational spectra (Huber and Herzberg 1979). The work of Ruden *et al*. provides CV corrections and higher level excitations up to CCSDTQ5, computed, for example, as the difference in the equilibrium harmonic wavenumber computed using the CCSDTQ5 and CCSDTQ levels of theory in a cc-pVDZ basis. Although the resulting wavenumbers do not formally correspond to those of the PES obtained from the corresponding additivity scheme (due to the differing equilibrium structures at which the second derivatives are evaluated), the corrections give reliable indications of the importance of the various contributions. Table 10 is taken from Tew *et al*. (2007a) and details post-fc-CCSD(T) corrections computed by Ruden *et al*. (2004) in combination with the basis set limit fc-CCSD(T)-R12 values of Tew *et al*. (2007a) and the deviation with experimental values.

The fc-CCSD(T)-R12 harmonic wavenumbers are only 4.1, 4.8, and $-2.5\,cm^{-1}$ away from the experimental values for HF, N_2, and CO, respectively, and 15.3 cm^{-1} away for the difficult F_2 molecule. However, this close agreement arises from a high degree of cancellation between the higher order terms. To improve the agreement with experiment to within 1 cm^{-1} it is necessary to take into account higher order excitations even up to $M = 5$, as well as core–valence correlation and relativistic effects. For example, the effect of higher order excitations is as much as 13 cm^{-1} for N_2 and F_2. After adding the above post-CCSD(T) corrections to the basis set limit fc-CCSD(T)-R12 harmonic wavenumbers, the ab initio predictions deviate by 0.1, 0.3, and $-0.4\,cm^{-1}$ for HF, N_2, and CO, respectively, and 3.2 cm^{-1} for F_2. The primary contribution to the large deviation for F_2 is considered to be the basis set error for the quadruples correction.

The basis set error for the fc-CCSD(T)(F12) method, when either the cc-pVTZ-F12 or cc-pVQZ-F12 basis sets are used, is an order of magnitude smaller than the error implicit in the neglect of post-CCSD(T) contributions. Indeed, with this method, the fc-CCSD(T) basis set error has been reduced to the same order of magnitude as the basis set error in post-CCSD(T) corrections.

3.3 Barrier Heights and Shapes

One further measure of the quality of a PES is the accuracy of the heights of any saddle points on the surface, together with their positions and shapes. The accuracy of a PES at a transition state is often poorer than at the equilibrium due to a slower convergence of the energy with respect to the level of electron correlation treatment. The barriers to linearity and planarity of water and ammonia, respectively, have been computed to high accuracy using R12 methods, extrapolation techniques, and focal point analysis, also including post-CCSD(T)

Table 9 Frozen-core CCSD(T)(F12) equilibrium harmonic wavenumbers (in cm^{-1}), computed using cc-pVXZ-F12 orbital basis sets, compared to benchmark CCSD(T)-R12 calculations.

Molecule		ω_e	cc-pVDZ-F12	cc-pVTZ-F12	cc-pVQZ-F12	R12
HF	σ		4 153.3	4 144.3	4 144.0	4 142.53
H_2O	a_1	(bend)	1 652.6	1 650.7	1 649.9	1 649.39
	a_1	(s-stretch)	3 847.9	3 837.2	3 836.8	3 835.89
	b_2	(a-stretch)	3 956.5	3 947.5	3 947.4	3 946.65
NH_3	a_1	(s-bend)	1 058.7	1 056.5	1 056.5	1 056.98
	e	(a-bend)	1 679.3	1 675.6	1 675.2	1 674.71
	a_1	(s-stretch)	3 486.9	3 481.1	3 480.8	3 480.64
	e	(a-stretch)	3 618.2	3 612.9	3 613.0	3 612.77
CH_2 ($^1A_1$)	a_1	(bend)	1 405.8	1 402.4	1 401.4	1 400.55
	a_1	(s-stretch)	2 923.8	2 926.1	2 925.8	2 925.61
	b_2	(a-stretch)	2 996.9	3 000.5	3 000.6	3 000.66
CH_4	t_2	(bend)	1 349.4	1 345.4	1 344.7	1 344.63
	e	(bend)	1 574.0	1 570.6	1 570.4	1 570.29
	a_1	(s-stretch)	3 037.8	3 036.1	3 035.9	3 035.75
	t_2	(a-stretch)	3 159.0	3 158.0	3 158.1	3 158.02
F_2	σ_g		936.3	932.5	932.3	931.86
N_2	σ_g		2 364.3	2 364.4	2 363.6	2 363.36
CO	σ		2 167.4	2 168.1	2 167.5	2 167.29
HCN	π	(bend)	732.8	727.4	728.4	728.33
	σ	(CN-stretch)	2 128.6	2 129.0	2 128.3	2 128.01
	σ	(CH-stretch)	3 440.1	3 438.7	3 438.3	3 438.10
HNC	π	(bend)	469.9	459.8	462.1	463.23
	σ	(NC-stretch)	2 055.8	2 057.1	2 056.3	2 055.93
	σ	(NH-stretch)	3 816.8	3 813.7	3 813.7	3 813.66
CO_2	π_u	(bend)	679.2	674.2	673.9	673.92
	σ_g^+	(s-stretch)	1 354.0	1 354.5	1 354.2	1 354.04
	σ_u^-	(a-stretch)	2 400.3	2 397.8	2 396.7	2 396.17
C_2H_2	π_g	(bend)	621.5	616.6	619.4	620.45
	π_u	(bend)	749.4	748.5	748.6	748.65
	σ_g^+	(CC-stretch)	2 009.8	2 010.2	2 009.7	2 009.41
	σ_u^-	(a-stretch)	3 412.4	3 412.4	3 412.3	3 412.09
	σ_g^+	(s-stretch)	3 505.6	3 504.7	3 504.2	3 503.86
		MAD	3.5	0.9	0.4	
H_2O (TS)	π_u	(bend)	i1 689.8	i1 687.6	i1 687.5	
	σ_g^+	(s-stretch)	4 064.9	4 058.1	4 058.1	
	σ_u^-	(a-stretch)	4 463.0	4 455.1	4 455.0	
NH_3 (TS)	a_1''	(inverse)	i859.7	i851.1	i846.9	
	e_1'	(bend)	1 587.4	1 585.1	1 584.7	
	a_1'	(s-stretch)	3 644.1	3 638.1	3 636.9	
	e_1'	(a-stretch)	3 856.9	3 850.9	3 850.4	

corrections, which allow us to assess the performance of conventional and explicitly correlated coupled-cluster methods and to compare the basis set error to the magnitude of post-CCSD(T) contributions.

In Table 11, the barrier heights to planarity of ammonia, predicted by the fc-CCSD(T)/cc-pVXZ, fc-CCSD(T)(CBS), and fc-CCSD(T)(F12)/cc-pVXZ-F12 methods, are listed and the corresponding barriers to linearity for water are listed in Table 12. The fc-CCSD(T) contributions are decomposed into HF and correlation contributions, and the CCSD and (T) correlation contributions to the barrier are given separately. To simplify the discussion of the rate of convergence of these individual contributions, these calculations have been performed at the stationary points on the PES defined by the (Q56) HF energy plus the fc-CCSD(T)(F12)/cc-pVQZ-F12 correlation energy. This is necessary because, although the total barrier height is insensitive to minor shifts in the geometry, the individual contributions vary linearly with the geometry (the error in the total is quadratic in the structural parameters). The barrier height predicted by each method at its own stationary point and the deviation from the best estimate of the basis set limit are given in the last two columns in Tables 11 and 12.

Table 10 Post-CCSD(T) corrections to equilibrium harmonic wavenumbers of HF, N_2, F_2 (cm^{-1}), and CO, with the deviation from the experimental values in parentheses.

Contribution	HF		N_2		F_2		CO	
CCSD(T)-R12[a]	4 142.5	(4.1)	2 363.4	(4.8)	931.9	(15.3)	2 167.3	(−2.5)
CV correlation[b]	4.0	(8.1)	9.8	(14.6)	1.6	(16.9)	9.9	(7.4)
CCSDTQ–CCSD(T)[c]	−4.5	(3.6)	−9.1	(5.5)	−12.2	(4.7)	−6.5	(0.9)
CCSDTQ5–CCSDTQ[d]	−0.1	(3.5)	−3.9	(1.6)	−0.8	(3.9)	0.0	(0.9)
Rel. DPT correction[e]	−2.8	(0.7)	−0.8	(0.8)	−0.4	(3.5)	−0.9	(0.0)
Breit correction[e]	−0.6	(0.1)	−0.5	(0.3)	−0.3	(3.2)	−0.4	(−0.4)
Experiment[f]	4 138.4		2 358.6		916.6		2 169.8	

[a]Frozen-core, taken from Tew *et al*. 2007a.
[b]From ae- and fc-CCSD(T)/aug-cc-pCV5Z calculations, taken from Ruden *et al*. 2004.
[c]Frozen-core cc-pVTZ level, taken from Ruden *et al*. 2004.
[d]Frozen-core cc-pVDZ level, taken from Ruden *et al*. 2004.
[e]All electron CCSD(T)/aug-cc-pCVQZ level, taken from Tew *et al*. 2007a.
[f]Huber and Herzberg 1979. See Müller *et al*. 1998 for HF.

Table 11 HF, ΔCCSD, and Δ(T) contributions to $E^{\#}$, the barrier to planarity of ammonia (in cm^{-1}), at the basis set limit geometry and at the optimized geometries.

Basis	$E^{\#}_{HF}$	$\Delta E^{\#}_{CCSD}$	$\Delta E^{\#}_{(T)}$	$E^{\#}_{CCSD(T)}$	$E^{\#-opt}_{CCSD(T)}$	Error
cc-pVTZ	1854	307	65	2226	2238	407
cc-pVQZ	1739	232	53	2023	2026	195
cc-pV5Z	1651	198	44	1894	1894	63
cc-pV6Z	1632	181	41	1854	1854	23
TQ5	1570	164	36	1769	1770	−61
Q56	1628	158	35	1821	1821	−10
cc-pVDZ-F12[a]	1661	163	47	1871	1882	51
cc-pVTZ-F12[a]	1632	177	41	1849	1848	17
cc-pVQZ-F12[a]	1628	171	40	1838	1838	7
Limit[b]					1831	±11

[a]Using the fc-CCSD(T)(F12) method.
[b]Klopper *et al*. 2001.

Table 12 HF, ΔCCSD, and Δ(T) contributions to $E^{\#}$, the barrier to linearity of water (in cm^{-1}), at the basis set limit geometry and at the optimized geometries.

Basis	$E^{\#}_{HF}$	$\Delta E^{\#}_{CCSD}$	$\Delta E^{\#}_{(T)}$	$E^{\#}_{CCSD(T)}$	$E^{\#-opt}_{CCSD(T)}$	Error
cc-pVTZ	11 527	281	53	11 862	11 866	702
cc-pVQZ	11 360	74	16	11 451	11 451	287
cc-pV5Z	11 258	−16	−6	11 236	11 236	72
cc-pV6Z	11 254	−50	−13	11 191	11 191	27
TQ5	11 180	−110	−30	11 040	11 039	−125
Q56	11 256	−97	−23	11 135	11 135	−29
cc-pVDZ-F12[a]	11 309	−73	29	11 265	11 281	117
cc-pVTZ-F12[a]	11 267	−42	1	11 226	11 222	58
cc-pVQZ-F12[a]	11 257	−59	−5	11 193	11 193	29
Limit[b]					11 164	±30

[a]Using the fc-CCSD(T)(F12) method.
[b](TQ5) using augmented and counterpoise corrected basis sets. See Tarczay *et al*. 1999.

Concerning the positions and shapes of the barriers, the optimized structures of the saddle points are presented in Tables 5 and 6 for the conventional and F12 methods, respectively. The corresponding harmonic wavenumbers evaluated at the optimized saddle points are presented in Tables 8 and 9. The convergence patterns of both the bond lengths and the harmonic wavenumbers follow those observed for the equilibrium structures, as discussed in Sections 3.1 and 3.2. The rate of convergence of the F12 methods is much faster than that of conventional CCSD(T) and it is safe to conclude that the CCSD(T)(F12)/cc-pVTZ-F12 method is more accurate than (Q56) extrapolation.

The heights of the barriers form a more rigorous test for the quality of a PES. Examining first Table 11 for ammonia, one sees that the convergence of the barrier height with basis size for the conventional fc-CCSD(T) method is slow, in all three contributions listed. One also sees that although the contributions follow $E_{\mathrm{HF}} > \Delta E_{\mathrm{CCSD}} > \Delta E_{(\mathrm{T})}$, the HF and correlation basis set errors are similar in magnitude. At the cc-pV5Z and cc-pV6Z levels, total basis set errors of 63 and 23 cm^{-1} remain, respectively. Extrapolation provides a small reduction in the basis set errors, but tends to overshoot. This is partly due to the application of equation (4) for both the singlet and triplet pair contributions to the CCSD energy. The triplet pair energies converge more rapidly than the singlet pair energies, due to the Fermi node at the coalescence of electrons with the same spin, and should be extrapolated using X^{-5} rather than X^{-3} (Klopper 2001). Using a separate extrapolation for singlet and triplet pair contributions results in a (Q56) basis set error of $-7\,\mathrm{cm}^{-1}$. The CCSD(T)(F12) method affords a significantly faster convergence to the basis set limit than the conventional CCSD(T) method, and the CCSD(T)(F12)/cc-pVTZ-F12 method is more accurate than the CCSD(T)/cc-pV6Z method, but not as accurate as the Q56 extrapolation. The improvement of F12 over conventional methods is not only due to the reduction in the basis error of the CCSD correlation contribution. The F12 basis sets also provide a much improved description of the HF wave function and the basis set error in the barrier height from the HF contribution is below $5\,\mathrm{cm}^{-1}$ at the cc-pVTZ-F12 level, even without the CABS singles correction.

The studies in Klopper *et al*. (2001) and Császár *et al*. (1998) provide information about the post-CCSD(T) contributions to the barrier height of ammonia. Core–valence correlation acts to decrease the barrier by $64\,\mathrm{cm}^{-1}$, while the effect of higher excitations is only a few cm^{-1}. The diagonal Born–Oppenheimer correction for $^{14}NH_3$ decreases the barrier by $10\,\mathrm{cm}^{-1}$. For high accuracy, it is also important to include relativistic corrections because they differ between the equilibrium and transition state due to the rehybridization of the lone pair. The effect of special relativity is to increase the barrier by $20\,\mathrm{cm}^{-1}$ and the post-CCSD(T) corrections sum to $-54\,\mathrm{cm}^{-1}$, with an estimated uncertainty of $5\,\mathrm{cm}^{-1}$. To reduce the fc-CCSD(T) basis set errors to this accuracy using conventional calculations, it is necessary to do (Q56) extrapolation with separate extrapolations for singlet and triplet pairs, but this level of accuracy is already obtained with the CCSD(T)(F12) method and a cc-pVQZ-F12 basis.

The barrier to linearity for water is a more difficult case. From Table 12, one can see that the relative convergence of the conventional, extrapolation, and F12 methods is the same as observed for the barrier for ammonia. However, the basis set error for the correlation contribution is in this case more important than the basis set error for the HF contribution and is particularly slowly convergent. Indeed, it is rather difficult to obtain converged values for the basis set limit correlation contribution to the barrier height. Because of the high symmetry of the linear structure, many basis functions do not contribute, which leads to an unbalanced treatment of the electron correlation at the equilibrium and transition state structures, requiring counterpoise corrected approaches. This effect is seen even for the F12 methods and, although it is less than for the conventional calculations, it slows down the convergence toward the basis set limit. The F12 methods are nevertheless a great improvement over conventional calculations and the fc-CCSD(F12)/cc-pVTZ-F12 method is almost as accurate as the fc-CCSD/cc-pV6Z method. This is not true of the respective fc-CCSD(T) methods, however, and the basis set error for the (T) correction limits the accuracy currently obtainable with the CCSD(T)(F12) method. This problem can be overcome by the introduction of explicitly correlated treatments of the triples correction. The best estimate of the basis set error of the (Q56) and CCSD(T)(F12)/cc-pVQZ-F12 methods is $30\,\mathrm{cm}^{-1}$.

The post-CCSD(T) corrections have been reported in Császár *et al*. (1998) and Tarczay *et al*. (1999). Core–valence correlation decreases the barrier by $98\,\mathrm{cm}^{-1}$, the effect of higher M-electron interactions increases the barrier by $22\,\mathrm{cm}^{-1}$, while the effect of special relativity is to increase the barrier by $58\,\mathrm{cm}^{-1}$. Nonadiabatic effect decreases the barrier by $17\,\mathrm{cm}^{-1}$ and the total contribution from post-CCSD(T) effects is $-55\,\mathrm{cm}^{-1}$. Thus, for the difficult case of the barrier to linearity of water, the predominant uncertainty is due to the basis set error in the fc-CCSD(T) barrier height. In the (Q56) energies, the error is predominantly due to the CCSD correlation contribution, which is only improved by $5\,\mathrm{cm}^{-1}$ when extrapolating singlet and triplet pairs separately. For CCSD(T)(F12), the uncertainty is mostly due to the (T) basis set error, which can be reduced by further developments in F12 theory.

3.4 Anharmonic Vibrational Frequencies

Many practical applications of ab initio theory for the prediction of molecular properties are performed at the fc-CCSD(T) level, neglecting higher order contributions. This is particularly true for studies requiring semiglobal representations of the anharmonic PES, such as the determination of ro-vibrational transitions. For molecules with more than four atoms, the high dimensionality of the PES necessitates thousands or tens of thousands of energy evaluations and the large computational expense restricts the size of the feasible basis to aug-cc-pVTZ quality. Indeed, a wide range of PESs have been constructed from fc-CCSD(T)/aug-cc-pVTZ calculations.

In the previous sections, we have seen that the basis set error at the fc-CCSD(T)/cc-pVTZ and cc-pVQZ levels is the dominant contribution to the deviation between the ab initio predictions and experimentally derived values for equilibrium and harmonic wavenumbers. The use of explicitly correlated F12 methods effectively removes the basis set error such that the accuracy is limited only by that of neglecting effects beyond those treated by fc-CCSD(T). The work of Rauhut *et al*. provides a clear demonstration of this and of the accuracy obtainable with such an approach (Rauhut *et al*. 2009). Rauhut *et al*. used the fc-CCSD(T)/aug-cc-pVTZ and fc-CCSD(T)-F12a/aug-cc-pVTZ methods to compute two semiglobal anharmonic PESs for each of the molecules H_2O, HCN, CO_2, H_2CO, H_2O_2, H_2C_2, CH_2NH, C_2H_2O, and C_2H_2F. The construction of these surfaces followed the M-body (multimode) expansion in normal coordinates (Carter *et al*. 1998) and three-body anharmonicity was accounted for through fitting one-, two-, and three-dimensional cuts of the PESs (Rauhut 2004). For C_2H_2, four-body terms were found to be important and were also included. The fundamental frequencies were then computed using vibrational SCF and CI calculations with selected single through quadruple excited state configurations, sufficient to obtain converged energy levels accounting for all three-body couplings. All the important Coriolis coupling terms were included in the calculation and the predominant error between the ab initio fundamental $J = 0$ transitions and experimentally observed band centers was the quality of the PES.

Rauhut *et al*. reported that the MAD between the ab initio and best available experimental fundamental frequencies for the nine molecules (60 modes) investigated was $9.0\,\mathrm{cm}^{-1}$ for the fc-CCSD(T)/aug-cc-pVTZ method and $4.0\,\mathrm{cm}^{-1}$ when the fc-CCSD(T)-F12a/aug-cc-pVTZ method was used to determine the PES. Apart from the basis set error, two other sources of error enter the calculations of Rauhut *et al*., namely, the neglect of four-body and higher order couplings in the PES expansion and the neglect of post-CCSD(T) contributions.

As we have discussed in the previous sections, although the magnitude of individual post-CCSD(T) contributions can be significant, they often cancel to a large extent. For example, the basis set limit fc-CCSD(T) harmonic wavenumbers for HF, N_2, and CO agree with experimentally derived values by 4.1, 4.8, and $-2.5\,\mathrm{cm}^{-1}$, respectively, which correspond to the magnitude of the post-CCSD(T) contributions. Neglecting four-body couplings in the form of the PES for polyatomic molecules typically leads to errors of 2–3 cm^{-1}. For the conventional CCSD(T) method, the basis set error at the aug-cc-pVTZ is clearly the dominant contribution to the discrepancies between theoretical and experimental values. For the F12 method with the same basis, it is safe to conclude that the basis set error does not limit the accuracy of the calculation and is probably well below that due to the other missing contributions to the PES. These findings for the anharmonic PES are in full accord with the discussion in Section 3.2 for the equilibrium harmonic wavenumbers. Rauhut *et al*. also reported that the increase in computational time for the CCSD(T)-F12a calculation over that of the CCSD(T) calculation was only a few percent (using the same basis) and thus that the F12 methods remove the basis set error at very little additional computational expense.

4 EXAMPLE APPLICATIONS

The CCSD(T)-F12 methods capable of delivering high accuracy with relatively small basis sets and low computational effort, as discussed in the previous sections, appeared only a year or two before this article was written. Indeed, the progress in F12 methodologies continues to be rapid and the reader is advised to check the current literature for the most recent developments and applications. Nevertheless, in this section, we present a short review of the literature to date where R12 and F12 methods have been used in the context of molecular spectroscopy.

Following the pioneering analysis of Kutzelnigg 1985, the R12 methodology was first applied at the level of MP2 theory (Klopper and Kutzelnigg 1987, Klopper and Kutzelnigg 1990, 1991, Termath *et al*. 1991, Klopper 1991). By 1993, the R12 methodology had been extended to the level of CISD (Röhse *et al*. 1993), which provides results very close to the exact solutions to the nonrelativistic Born–Oppenheimer Schrödinger equation for two-electron systems. Röhse *et al*. applied the CISD-R12 method to compute a ground-state potential energy surface of H_3^+ up to $20\,000\,\mathrm{cm}^{-1}$ above the minimum (Röhse *et al*. 1994). Computed rovibronic frequencies agreed with those of experiment to within a few tenths of a cm^{-1} for singly excited vibrational states and rotational excitation up to $J = 10$ and an error of 1–2 cm^{-1} for highly excited vibrational

states (Jaquet and Röhse 1995). The accuracy of the CISD-R12 calculations was such that the primary source of error was the neglect of nonadiabatic effects.

In 1995, an efficient integral direct implementation of the CCSD(T)-R12 method appeared in the form of the DIRCCR12 program (Noga *et al*. 2009b). At that time, it was still necessary to use large orbital basis sets for R12 methods, because the orbital basis was used for the RI approximation of the three- and four-electron integrals. However, the CCSD(T)-R12 method, as implemented in the DIRCCR12 program, was highly suited for the computation of near basis set limit CCSD(T) energies of small molecules and many applications have resulted. For example, Müller *et al*. computed the potential curve of the HF molecule at the basis set limit all-electron (ae) CCSD(T)-R12 and also at a simplified ae-CCSDT-R12 level (Müller *et al*. 1998). After also accounting for relativistic effects, the deviation between the computed vibrational frequencies and experimental values was only $0.1\,\mathrm{cm}^{-1}$ for $\nu_{1\leftarrow 0}$, rising to $6\,\mathrm{cm}^{-1}$ for $\nu_{5\leftarrow 0}$. The principal source of error was the neglect of correlation effects arising from the simultaneous interaction of four electrons.

One of the main uses of the CCSD(T)-R12 method has been to benchmark the relative energies of stationary points, enabling assessment of the accuracy of PESs computed at lower levels of theory. The barriers to planarity of NH_3 (Klopper *et al*. 2001) and linearity of H_2O (Tarczay *et al*. 1999) have been discussed in Section 3.3. Other examples include H_5^+ (Müller and Kutzelnigg 2000), CH_5^+ (Müller *et al*. 1997), and the CO–H_2 complex (Wernli *et al*. 2006, Noga *et al*. 2006), as well as reaction barriers for hydrogen abstraction by the hydroperoxyl radical from methane (Aguilera-Iparraguirre *et al*. 2008).

The CCSD(T)-R12 method has also been applied to compute accurate PESs of several polyatomic molecules. The first such application was SiH_3^-, where the quadratic anharmonic PES in symmetry adapted internal coordinates was computed at the CCSD(T)-R12 level (Aarset *et al*. 2000). Rajamäki *et al*. have computed full six-dimensional PESs of H_3O^+ and NH_3, applying the same approach to the isoelectronic systems and combining CCSD(T)-R12 and extrapolated CCSD(T) energies (Rajamäki *et al*. 2004a, 2004b). In both cases, the six-dimensional surface was represented as a Taylor series expansion about a two-dimensional surface for the symmetric modes. The CCSD(T)-R12 method was used only for the two-dimensional surface (143 points), and the parameters for the Taylor series expansion covering the remaining degrees of freedom were taken from extrapolated CCSD(T)/aug-(TQ) values. The effects of core–valence and first- and second-order relativistic corrections were also included in the six-dimensional surface. For NH_3, the effects of higher order M-electron interactions and diagonal Born–Oppenheimer corrections were also included and the maximum deviation of calculated and experimental $J = 0$ rotation–vibration frequencies was less than $2\,\mathrm{cm}^{-1}$ for the fundamentals, overtones, and combination bands below $7000\,\mathrm{cm}^{-1}$, including the tunneling splitting for the inversion motion (Rajamäki *et al*. 2004a).

A similar application to a slightly larger system has been performed by Valiron *et al*., for the H_2O–H_2 complex (Valiron *et al*. 2008). The nine-dimensional PES was constructed from 350 000 single point energies computed at the CCSD(T) level with a carefully chosen basis of triple-ζ quality and a five-dimensional correction surface computed from 812 CCSD(T)-R12 energies. The accuracy of the resulting PES was approximately $3\,\mathrm{cm}^{-1}$ in the van der Waals region, predominantly arising from neglected post-CCSD(T) effects. At the time of writing, the dynamics calculations for the quenching of the low vibrational frequencies of water using the surface had not yet been published.

The computational expense involved in large basis set CCSD(T) calculations has so far prevented the CCSD(T)-R12 method from being more widely applied to compute high-dimensional PESs of polyatomic molecules. Indeed, in the above examples, the CCSD(T)-R12 method was used only to compute the most important low-dimensional cuts of the PES, so that relatively few expensive calculations were required. The application of R12 methods to whole PESs has until recently been restricted to the MP2 level of theory. For example, 3284 MP2-R12 calculations were used in the construction of a six-dimensional PES for the HF dimer (Klopper *et al*. 1998). The effect of correlation beyond a second-order treatment was accounted for by scaling and stretching the PES and although the resulting surface is semiempirical, it is highly useful for investigating the dynamics of this hydrogen-bonded system, particularly with respect to the mode selectivity in the vibrational predissociation process (Manca *et al*. 2008). The largest example to date is that of malonaldehyde, $C_3O_2H_4$, where the 21-dimensional PES was fit to over 11 000 fc-CCSD(T) energies (Wang *et al*. 2008). A triple-ζ quality basis was used and at every point a correction for the basis set error was included, computed at the MP2-F12 level of theory. This was the first time that a computed zero-point tunneling splitting for the internal hydrogen transfer of malonaldehyde was reliably computed to within $1\,\mathrm{cm}^{-1}$ of the experimental value.

5 SUMMARY AND OUTLOOK

The computation of accurate spectroscopic constants and molecular properties has been made possible by the development of ab initio methodologies that provide an accurate description of electron correlation. For traditional

computational approaches, where the wave function is expanded on the basis of HF Slater determinants, large orbital basis sets in combination with extrapolation techniques are required, making the calculations extremely costly. In this article, we have reviewed the current status of explicitly correlated CC approaches, which greatly reduce the basis set error for a given CC model, without the necessity of large basis sets. Indeed, CCSD(T)-F12 methods emerge as very accurate and cost-efficient computational methods for the calculation of PESs from which accurate spectroscopic constants and molecular properties are derived.

We have presented an analysis of the basis set errors in PESs computed at the CCSD(T) level of theory, focusing on stationary points, frequencies, and barrier heights, and have demonstrated that the basis set error for the CCSD(T)(F12) method using the cc-pVTZ-F12 basis is smaller than that of CCSD(T)/cc-pV6Z, and comparable to (Q56) extrapolation. Furthermore, the remaining basis set error is typically an order of magnitude smaller than the contributions from post-CCSD(T) corrections and often comparable in magnitude to the basis set error in the post-CCSD(T) corrections.

The computational effort of the CCSD(T)(F12) method is not significantly greater than that of a CCSD(T) calculation in the same basis and for the case of the CCSD(T)-F12a approach, the additional computational effort for the F12 contributions is only a few percent of the CCSD(T) calculation. It is, therefore, now possible to compute global PESs at the basis set limit CCSD(T) level of theory, using CCSD(T)-F12 methods and a cc-pVTZ-F12 basis, as demonstrated by the work of Rauhut *et al.*. The promise of high accuracy with low computational effort will certainly inspire many more applications of the CCSD(T)-F12 methods to high-resolution spectroscopy in the future.

It is important to note, however, that the CCSD(T)-F12 methods presented in this article improve only the basis set convergence of the CCSD contribution. The F12 functions improve the convergence of the energy contributions due to double excitations and the HF energy is improved through CABS singles. The basis set error of the triples correction (T), however, may not always be computed accurately enough when a relatively small basis such as cc-pVTZ-F12 is used. To improve the convergence of the (T) term or post-(T) terms, explicitly correlated connected triple and higher excitations should be included. Work is already in progress in this direction (Köhn 2009a) and it is likely that F12 methods returning near basis set limit accuracy for higher order CC models will soon be available.

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END NOTES

[a.] We use X to denote D, T, Q, 5, or 6, referring to the name of the basis and *X* to denote the corresponding cardinal number, 2, 3, 4, 5, or 6, respectively.

[b.] For historical interest, we mention that the MP2-R12 method as proposed by Kutzelnigg used fixed amplitudes. See equation (6.10a) of Kutzelnigg (1985). However, in the first implementation of the method, the amplitudes were treated as variational parameters (Klopper and Kutzelnigg 1987).

[c.] An alternative approach goes back to work by Szalewicz *et al*. (1982), who proposed to use a functional called *weak orthogonality* (*WO*) functional instead of the Hylleraas functional. At most three-electron integrals arise when the WO functional is used. We refer to the recent original literature concerning methods based on this functional (Polly *et al*. 2006, Patkowski *et al*. 2007, Dahle *et al*. 2007, Tew *et al*. 2007b, Dahle *et al*. 2008).

ABBREVIATIONS AND ACRONYMS

ABS	auxiliary basis set
ae	all-electron
AOs	atomic orbitals
CABSs	complementary auxiliary basis sets
CC	coupled-cluster
CCSD	coupled-cluster singles and doubles
CI	configuration interaction
DF	density fitting
EBC	extended Brillouin condition
fc	frozen-core
FCI	full CI
GBC	generalized Brillouin condition
HF	Hartree–Fock
MAD	mean absolute deviation
MR	multireference
MRCI	multireference configuration interaction
PESs	potential energy surfaces
RI	resolution-of-the-identity
STGs	Slater-type geminals
WO	weak orthogonality

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