



## Calculation of the two-electron Darwin term using explicitly correlated wave functions

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### ABSTRACT

This article is concerned with the calculation of the two-electron Darwin term (D2). At the level of explicitly correlated second-order perturbation theory (MP2-F12), the D2 term is obtained as an analytic energy derivative; at the level of explicitly correlated coupled-cluster theory, it is obtained from finite differences. To avoid the calculation of four-center integrals, a density-fitting approximation is applied to the D2 two-electron integrals without loss of accuracy, even though the absolute value of the D2 term is typically about 0.1 mE<sub>h</sub>. Explicitly correlated methods provide a qualitatively correct description of the short-range region around the Coulomb hole, even for small orbital basis sets. Therefore, explicitly correlated wave functions remedy the otherwise extremely slow convergence of the D2 contribution with respect to the basis-set size, yielding more accurate results than those obtained by two-point basis-set extrapolation. Moreover, we show that the interference correction of Petersson's complete-basis-set model chemistry can be used to compute a D2 basis-set correction at the MP2-F12 level to improve standard coupled-cluster singles-and-doubles results.

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### 1. Introduction

Today, the general consensus is to include small energy contributions such as the diagonal Born–Oppenheimer correction (DBOC) [1,2] and scalar-relativistic effects when highly accurate reaction energies are calculated, even when only light elements are involved. In contrast to one-electron contributions such as the (one-electron) Darwin (D1) and mass-velocity (MV) terms, however, relativistic two-electron contributions are often neglected, even in highly accurate composite approaches such as the HEAT protocol [3].

Quiney and co-workers [4] have shown that the D2 correction needs to be taken into account for accurate computations of vibration-rotation levels of light molecules such as H<sub>2</sub>O. Moreover, the D2 term is the most-important two-electron relativistic correction: it completes the Coulomb–Pauli approximation for closed-shell systems when added to the D1 and MV terms and it allows for the computation (or estimation) of the two-electron spin–spin term and Lamb shift [5].

In case of the two-electron Darwin (D2) correction, the two major obstacles are the calculation of time-consuming two-electron

four-center integrals and the slow convergence to the basis-set limit with  $X^{-1}$ , where  $X$  is the cardinal number of the orbital basis set [6] or with  $(L + 1)^{-1}$ , where  $L$  is the maximum angular momentum quantum number contained in the orbital basis set. For two-electron atomic ions in a <sup>1</sup>S state, Kutzelnigg has analysed the partial-wave expansion of relativistic corrections and shown that the leading relativistic correction indeed converges as  $(L + 1)^{-1}$  [7].

For light systems ( $Z \leq 18$ ), the total D2 correction is of the same order of magnitude as the effect of electron correlation on the mass-velocity and one-electron Darwin terms [8]. Therefore, the D2 correction should be accounted for as soon as the effect of electron correlation on the (much larger) one-electron relativistic terms becomes significant. Furthermore, we note that other (small) two-electron terms such as the two-electron Lamb shift [9] and the two-electron spin–spin contribution [10] can easily be estimated or computed from the D2 value. Seen from this perspective, it seems worthwhile to implement the efficient calculation of the D2 term using explicitly correlated wave functions for rapid convergence to the basis-set limit. This implementation has been accomplished in the course of the present work, using density-fitting approximations to the two-electron Darwin integrals.

In 1959, Boys and Shavitt [11] expanded products of one-electron functions in an auxiliary one-electron basis set so as to reduce the number of centers in the two-electron integrals. Due to the much decreased prefactor for the integral evaluation, this technique has since then been applied not only to the density-functional and Hartree–Fock methods but also to correlation methods

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such as second-order Møller–Plesset (MP2) perturbation theory and coupled-cluster theory [12]. Today, the expansion of products of functions (densities) in auxiliary basis sets is known both as the “resolution-of-the-identity” (RI) approximation and as the “density-fitting” (DF) approximation. In our work with explicitly correlated wave functions, we prefer the name “density-fitting approximation”, because other types of resolutions of the identity are inserted into certain matrix elements in another context. For operators other than  $1/r_{12}$ , robust density fitting seems appropriate [13,14] because there is then no first-order error due to fitting.

Explicitly correlated methods were originally introduced almost together with quantum chemistry in 1929 by Hylleraas and many flavors of the explicitly correlated methodology have followed. These approaches, however, suffered from the requirement to compute a large number of very expensive (in terms of computer resources) many-electron integrals and could only be applied to few-electron systems. A promising ansatz was introduced by Kutzelnigg and Klopper, in which the very expensive many-electron integrals are avoided entirely [15]. Their approach developed into what today is known as MP2-F12 theory (when applied to MP2 theory). It consists of supplementing the conventional expansion of the first-order MP2 wave function with geminals of the type

$$|\chi_{kl}\rangle = \hat{Q}_{12} f_{12} |kl\rangle, \quad (1)$$

which depend explicitly on the inter-electronic distance  $r_{12}$ . In the above notation,  $\hat{Q}_{12}$  denotes a projection operator,  $f_{12} = f(r_{12})$  is the correlation factor, and  $|kl\rangle$  is an anti-symmetrized product of occupied Hartree–Fock orbitals. In the present work, the projection operator is

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1 \hat{V}_2), \quad (2)$$

where  $\hat{O}$  projects onto the occupied orbitals and  $\hat{V}$  onto the virtual orbitals. The use of the geminals in Eq. (1) yields a significantly improved description of the inter-electronic cusp region and is applicable to arbitrary wave functions. The inclusion of geminals—that is, explicit two-electron basis functions—in the wave function is particularly efficacious when electronic properties are to be computed to high accuracy. In the literature, a variety of examples exist—not only regarding the electronic energy itself [16] but also concerning dipole moments and (hyper) polarizabilities [17–19]. Another example is the one-electron Darwin term [20].

The present article focuses on the D2 term. The article is organized as follows. First, we outline the robust-density fitting approach and the explicitly correlated MP2 method, which are subsequently applied to compute the D2 term. Second, we present the results and show that the approach is numerically stable and efficient. Summary and conclusions are given in Section 5.

## 2. Theory

The operators for computing scalar relativistic corrections are commonly derived from a four-component many-body Dirac–Coulomb–Breit description [21], which can be reduced by means of the Foldy–Wouthuysen transformation [22,23] to a two-component equation with quasi-relativistic many-body operators. In this treatment, not only the usual one-electron mass–velocity and spin–orbit operators arise but also the (one- and two-electron) Darwin operators and the two-electron spin–spin, spin–orbit and orbit–orbit operators.

To compute the D2 correction, it is introduced as a perturbation of perturbation strength  $\lambda$ ,

$$\hat{H}_{\text{tot}}(\lambda) = \hat{H} + \lambda \hat{H}_{\text{D2}}, \quad (3)$$

where  $\hat{H}$  is the conventional non-relativistic Hamiltonian and

$$\hat{H}_{\text{D2}} = -\frac{\pi}{c^2} \sum_{i<j} \delta(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i<j} \hat{\delta}(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i<j} \hat{\delta}_{ij}. \quad (4)$$

Note that we have absorbed the prefactor  $-\pi/c^2$  into the operator  $\hat{\delta}$  for convenience, where  $c$  is the velocity of light in atomic units. To obtain the D2 contribution to the energy, the energy is differentiated with respect to  $\lambda$ . Since this formulation is closely related to analytic derivative techniques for molecular properties, the working expressions are straightforwardly obtained by substituting the differentiated two-electron integrals over  $1/r_{12}$  with the (undifferentiated) D2 integrals in the gradient expression of an arbitrary wave function, as suggested in Ref. [24]. The D2 integrals themselves are easily calculated [24], not only in the McMurchie–Davidson scheme [25] but also in the Obara–Saika framework [26].

### 2.1. Integral evaluation by density fitting

To avoid the explicit calculation of expensive four-center integrals, we apply a density-fitting approximation to the D2 integrals. Our main objective is to investigate whether it is possible to use approximated integrals without loss of accuracy, using standard auxiliary basis sets. Following the general procedure of Ref. [13], the density-fitted D2 integrals can be written as

$$(\mu\nu|\hat{\delta}_{12}|\kappa\tau)_{\text{DF}} = \sum_Q \left( \tilde{D}_{\mu\nu}^Q G_Q^{\kappa\tau} + G_{\mu\nu}^Q \tilde{D}_Q^{\kappa\tau} \right), \quad (5)$$

where

$$\tilde{D}_{\mu\nu}^Q = D_{\mu\nu}^Q - \frac{1}{2} \sum_R G_{\mu\nu}^R U_R^Q, \quad (6)$$

$$G_{\mu\nu}^Q = \sum_R (\mu\nu|g_{12}|R)(R|g_{12}|Q)^{-\frac{1}{2}}, \quad (7)$$

$$D_{\mu\nu}^Q = \sum_R (\mu\nu|\hat{\delta}_{12}|R)(R|g_{12}|Q)^{-\frac{1}{2}}, \quad (8)$$

$$U_P^Q = \sum_{RS} (Q|g_{12}|R)^{-\frac{1}{2}} (R|\hat{\delta}_{12}|S)(S|g_{12}|P)^{-\frac{1}{2}}, \quad (9)$$

as demonstrated in Refs. [27,28]. Here,  $\mu, \nu, \kappa$  and  $\tau$  denote atomic basis functions, while  $P, Q, R$  and  $S$  denote auxiliary density-fitting basis functions. The expression in Eq. (5) is robust in the sense that errors in the integral are quadratic in the errors in the density fitting.

For the numerical finite-difference calculations, we have used an alternative (non-robust) density fitting. A “symmetric” density fitting is obtained by splitting the integral into two equal contributions and expanding each side with the help of the auxiliary basis set,

$$(\mu\nu|(g_{12} + \lambda\hat{\delta}_{12})|\kappa\tau)_{\text{SDF}} = \sum_Q \left( \tilde{G}_{\mu\nu}^Q G_Q^{\kappa\tau} + G_{\mu\nu}^Q \tilde{G}_Q^{\kappa\tau} \right), \quad (10)$$

$$\tilde{G}_{\mu\nu}^Q = \frac{1}{2} \sum_R (\mu\nu|(g_{12} + \lambda\hat{\delta}_{12})|R)(R|g_{12}|Q)^{-\frac{1}{2}}. \quad (11)$$

### 2.2. Analytic calculation of the D2 term using DF-MP2 theory

We start by noting that the Hartree–Fock contribution is very easy to calculate analytically since the molecular-orbital coefficients are optimized variationally. Hence, the contribution is simply equal to the expectation value of the two-electron operator,

$$E_{\text{D2}}^{\text{HF}} = \sum_{i<j} \langle ij|\hat{\delta}_{12}|ij\rangle, \quad (12)$$

where  $i$  and  $j$  denote occupied spin orbitals. Note that the two-electron ket notation  $|ij\rangle$  refers to an anti-symmetrized pair of spin orbitals—that is, a two-electron Slater determinant.

For non-variational wave functions, the Lagrangian approach [29,30] is used. In the framework of time-independent properties

such as the D2 perturbation, it is common to account for the relaxation of the Hartree–Fock orbitals, which is mandatory if finite-difference results are to be reproduced. As indicated above, we use the (orbital-relaxed) analytic gradient expression of the corresponding conventional method—for example, DF-MP2 [31]—and obtain for the D2 term

$$E_{D2}^{\text{ADF-MP2}} = \frac{1}{2} \sum_{\mu\nu} D_{\mu\nu}^{\text{eff,DF,ao}} G_{\mu\nu}(\hat{\delta}_{12}) + \frac{1}{2} \sum_{ijab} t_{ij}^{ab,DF} \langle ij | \hat{\delta}_{12} | ab \rangle^{\text{DF}}, \quad (13)$$

where the  $t_{ij}^{ab,DF}$  are the amplitudes of the double excitations in the DF-MP2 calculation and  $D^{\text{eff,DF,ao}}$  is the conventional back-transformed relaxed DF-MP2 density matrix, obtained by solving the Z-vector equation [32,33]. Note that  $\mathbf{G}(\hat{\delta}_{12}) = \mathbf{2J} - \mathbf{K}$  is computed from exact four-index integrals over  $\hat{\delta}(r_{12})$  unless a DF-approximated Hartree–Fock calculation is performed. An analogous equation is obtained for the full MP2 method without density fitting, by substituting the approximated integrals in the correlation contribution with the exact integrals. Clearly, it is possible to compute the integrals in the second term of Eq. (13) exactly, without recourse to density fitting, but density fitting is consistent with Eq. (3).

### 2.3. Analytic calculation of the D2 term using DF-MP2-F12 theory

As indicated above, in F12 theory, the conventional expansion of doubly-excited determinants is augmented with explicitly correlated two-electron basis functions, also known as geminals, yielding additional terms—for example, in the MP2 Hylleraas functional and in the coupled-cluster equations [34]. Note that these terms arise not from the use of a different Hamiltonian but from the use of an augmented wave function. Therefore, in the calculation of the D2 contribution using the perturbed Hamiltonian in Eq. (3), not all two-electron integrals are perturbed. In the MP2-F12 Hylleraas functional, for example, only the Coulombic electron-repulsion integrals originating from the Hamiltonian are perturbed; the two-electron integrals that originate in the explicitly correlated two-electron basis functions are unaffected. In particular, in the framework of the MP2-F12 ansatz 2\* in conjunction with approximation A, only a small number of terms are affected by the perturbation (in ansatz 2\*, the extended Brillouin condition is assumed to hold, which means that it is assumed that the orbital basis set is closed under the Fock operator; see Ref. [28] for details). Using ansatz 2\*, the perturbed F12 Hylleraas functional reads

$$\mathcal{H}^{\text{F12}}(\lambda) = 2 \sum_{i<j} \sum_{\mathbf{k}<\mathbf{l}} c_{ij}^{\mathbf{kl}} V_{\mathbf{kl}}^{ij}(\lambda) + \sum_{i<j} \sum_{\mathbf{k}<\mathbf{l}} \sum_{\mathbf{m}<\mathbf{n}} c_{ij}^{\mathbf{kl}} c_{ij}^{\mathbf{mn}} B_{\mathbf{kl},\mathbf{mn}}, \quad (14)$$

where

$$V_{\mathbf{kl}}^{ij}(\lambda) = \langle \mathbf{kl} | f_{12} \hat{Q}_{12} (g_{12} + \lambda \hat{\delta}_{12}) | ij \rangle \quad (15)$$

$$B_{\mathbf{kl},\mathbf{mn}} = \hat{P}_{\mathbf{mn}}^{\mathbf{kl}} \langle \mathbf{kl} | f_{12} \hat{Q}_{12} [\hat{T}_{12}, f_{12}] | \mathbf{mn} \rangle, \quad (16)$$

with  $\hat{P}_{\mathbf{mn}}^{\mathbf{kl}}$  being a symmetrizer that interchanges  $\mathbf{mn}$  with  $\mathbf{kl}$ ,

$$\hat{P}_{\mathbf{mn}}^{\mathbf{kl}} A_{\mathbf{kl},\mathbf{mn}} = \frac{1}{2} (A_{\mathbf{kl},\mathbf{mn}} + A_{\mathbf{mn},\mathbf{kl}}), \quad (17)$$

and where  $\hat{T}_{12}$  denotes the sum of the kinetic operators of electrons 1 and 2. Note that orbital relaxation causes an indirect perturbation of the matrix  $\mathbf{B}$  through its dependence on the molecular orbitals even though the matrix elements contain no D2 integrals. The excellent cost/accuracy ratio of DF-MP2-F12/2\* A model for properties [35,36] can be traced back to the very judicious choices of the projection operator  $\hat{Q}_{12}$  [37] in Eq. (2) and of the correlation factor  $f_{12}$  as a linear combination of an exponential function in  $r_{12}$  in Gaussians [38,39],

$$f_{12} = \sum_i c_i \exp(-\omega_i r_{12}^2) \approx -\frac{1}{\gamma} \exp(-\gamma r_{12}). \quad (18)$$

In passing, we note that the term in  $f_{12} \hat{Q}_{12} \hat{\delta}_{12}$  of Eq. (15) arising from the “1” in the projection operator  $\hat{Q}_{12}$ ,

$$f_{12} \times 1 \times \hat{\delta}_{12} = \hat{\delta}_{12} \sum_i c_i \approx -\frac{\hat{\delta}_{12}}{\gamma} \quad (19)$$

is nothing but the standard Darwin integral times the sum of the expansion coefficients of the geminal.

For the analytic calculation of the D2 term, we differentiate the MP2-F12 Hylleraas functional in Eq. (14) and obtain:

$$E_{D2}^{\text{AF12}} = \frac{\partial \mathcal{H}^{\text{F12}}(\lambda)}{\partial \lambda} = 2 \sum_{i<j} \sum_{\mathbf{k}<\mathbf{l}} c_{ij}^{\mathbf{kl}} \langle \mathbf{kl} | f_{12} \hat{Q}_{12} \hat{\delta}_{12} | ij \rangle. \quad (20)$$

We emphasize the role of the Z-vector equation, which not only contains contributions from the matrix  $\mathbf{B}$  but also couples the MP2 and F12 contributions due to the orbital relaxation. Therefore, in the notation

$$E_{D2}^{\text{DF-MP2-F12}} = E_{D2}^{\text{HF}} + E_{D2}^{\text{ADF-MP2}} + E_{D2}^{\text{AF12}}, \quad (21)$$

the term  $E_{D2}^{\text{ADF-MP2}}$  is not the usual MP2 contribution, as obtained without explicit correlation. Rather, it differs numerically from Eq. (13) by the effect of the explicitly correlated contributions to the relaxed density. For a detailed description of the gradients and first-order properties of the DF-MP2-F12/2\* A model, the reader is referred to Refs. [35,36,40].

## 3. Computational details

We have implemented the numerical and analytic treatments of the D2 contribution in a local version of the Turbomole program package [41]. Both treatments were implemented for Hartree–Fock theory in `DSCF` [42], for MP2 theory in `MPGRAD` [43], and for DF-MP2 and DF-MP2-F12 theories in `RICC2` [12], respectively. Furthermore, we have implemented the numerical treatment for the MP2-F12 and CCSD(F12) models [44] in a local version of `DALTON` [45].

We have used Dunning’s orbital basis sets aug-cc-pVXZ with  $X = D, T, Q, 5$ , and 6 [46–48] together with the MP2 fitting basis sets C-aug-cc-pwCV(X+1)Z. For the 5Z and 6Z orbital basis sets, owing to the lack of a C-aug-cc-pwCV6Z auxiliary basis, we have used the C-aug-cc-pV6Z fitting basis. For the `DALTON` calculations, subsets of the 20s14p11d9f7g5h3i basis in conjunction with an auxiliary basis set of the form 32s24p18d15f12g9h6i have been employed. Both basis sets are described in Ref. [49].

There exist two approaches to obtain the amplitudes of F12 theory: the orbital-invariant approach [50] and the fixed-amplitudes approach [51]. All analytic MP2-F12 results were obtained using the fixed-amplitudes approach, ansatz 2\* and approximation A. The `DALTON` calculations were performed with the orbital-invariant approach, ansatz 2 and approximation B.

Numerical investigations were carried out using the finite-field perturbation approach. We studied different finite perturbations and found that the results are rather insensitive to the strength of the perturbation, yielding six significant digits. Since all results (i.e., the analytic versus numerical results and the density-fitting versus non-density-fitting results) are in good agreement, we conclude that our calculations are hampered neither by numerical instabilities nor by density-fitting errors.

## 4. Results

### 4.1. Frozen-core approximation

In correlated methods, the core orbitals are often omitted from the correlation treatment. This “frozen-core” (FC) approximation may be justified by noting that the innermost orbitals are insensi-

tive to the chemical environment. Consequently, core correlation is rather insensitive to changes in the environment—for example, during a chemical reaction. In many cases, therefore, the effects of core correlation cancel to a large extent. Only for high accuracy should core correlation be taken into account (e.g., as done in the HEAT protocol). For scalar relativistic effects, the region close to the nucleus is important and core-correlation corrections may thus be significant. Therefore, we report both all-electron (AE) and frozen-core calculations in the following.

#### 4.2. Density fitting

All-electron MP2 (without density fitting) and DF-MP2 (with density fitting) results are listed and compared in Table 1 for the HF molecule. All results were obtained from analytic gradients and only the density-fitting error needs to be considered. This error is largest for the largest orbital basis, probably because it is more difficult to construct a high-quality auxiliary basis for a large orbital basis than for a small one. Nevertheless, the error remains below 1%, which is negligible for all practical purposes.

#### 4.3. Convergence

The dramatic improvement in basis-set convergence obtained with F12 theory for the D2 term is clearly seen in Tables 2–6 and in Fig. 1. Since the D2 term samples the wave function at the points where two electrons coalesce (i.e., at the bottom of the Coulomb hole), it is very difficult to describe with conventional methods due to the absence of linear  $r_{12}$  terms. Accordingly, the basis-set convergence of the D2 term is extremely slow in conventional correlated theories but much improved by the F12 geminals. It is noteworthy that, for all systems considered by us (He, Ne, H<sub>2</sub>, HF, H<sub>2</sub>S, C<sub>6</sub>H<sub>6</sub>), the conventional aug-cc-pV6Z result is much poorer than the F12 result in the aug-cc-pVDZ basis, testifying to the remarkable efficiency of the F12 technique.

Like the correlation energy itself, the D2 value can be decomposed into contributions from singlet and triplet spin-adapted pairs. However, unlike for the correlation energy, we would expect the D2 triplet contribution to vanish since same-spin electrons cannot occupy the same point in space. Nevertheless, as seen from the MP2 and CCSD results for the Ne atom in Tables 7 and 8, respectively, the triplet pairs do make a small contribution, about two orders of magnitude smaller than the singlet contribution. The triplet contribution is non-zero because of orbital relaxation—without this relaxation, it would be exactly zero, because the corresponding D2 integrals are zero for triplet pairs in the last term of Eq. (13). Since the small orbital-relaxation effect converges very fast, the D2 convergence is dominated by the singlet contribution. In Table 10, we have listed the corresponding MP2-F12 results together with the total CCSD(F12) D2 values.

The slow basis-set convergence of the conventional MP2 and CCSD methods observed in Tables 2–6 and also in Fig. 1 is a manifestation of the  $X^{-1}$  convergence of the singlet contribution to the D2 term, when calculated without explicit correlation. We have verified the  $X^{-1}$  convergence by plotting the error in the singlet-

**Table 1**

Analytic D2 correlation contributions (in mE<sub>h</sub>) with (DF-MP2) and without (MP2) the density-fitting approximation for the HF molecule ( $R_{\text{HF}} = 0.917 \text{ \AA}$ ) from all-electron calculations.

Basis set	$\Delta\text{MP2}$	$\Delta\text{DF-MP2}$	DF error in %
aug-cc-pCVDZ	0.2195	0.2192	0.1
aug-cc-pCVTZ	0.3244	0.3240	0.1
aug-cc-pCVQZ	0.4051	0.4050	0.0
aug-cc-pCV5Z	0.4531	0.4506	0.6

**Table 2**

Analytic D2 corrections to the ground-state energy of He in mE<sub>h</sub>.

Basis set	SCF	$\Delta\text{DF-MP2}$	$\Delta\text{DF-MP2-F12/2}^*\text{A}$
aug-cc-pVDZ	−0.0316	0.0060	0.0166
aug-cc-pVTZ	−0.0319	0.0093	0.0164
aug-cc-pVQZ	−0.0319	0.0112	0.0161
aug-cc-pV5Z	−0.0319	0.0123	0.0161
aug-cc-pV6Z	−0.0319	0.0131	–
(56) <sup>(a)</sup>	–	0.0167	–

<sup>(a)</sup>  $X^{-1}$  extrapolation from the aug-cc-pV5Z and aug-cc-pV6Z results.

**Table 3**

Analytic D2 corrections (FC) to the ground-state energy of Ne in mE<sub>h</sub>.

Basis set	SCF	$\Delta\text{DF-MP2}$	$\Delta\text{DF-MP2-F12/2}^*\text{A}$
aug-cc-pVDZ	−7.1050	0.0442	0.1464
aug-cc-pVTZ	−7.1124	0.0586	0.1372
aug-cc-pVQZ	−7.1163	0.0754	0.1357
aug-cc-pV5Z	−7.1170	0.0864	0.1356
aug-cc-pV6Z	−7.1171	0.0944	–
(56) <sup>(a)</sup>	–	0.1345	–

<sup>(a)</sup>  $X^{-1}$  extrapolation from the aug-cc-pV5Z and aug-cc-pV6Z results.

**Table 4**

Analytic D2 corrections (FC) to the ground-state energy of the HF molecule ( $R_{\text{HF}} = 0.917 \text{ \AA}$ ) in mE<sub>h</sub>.

Basis set	SCF	$\Delta\text{DF-MP2}$	$\Delta\text{DF-MP2-F12/2}^*\text{A}$
aug-cc-pVDZ	−5.0131	0.0311	0.0978
aug-cc-pVTZ	−5.0153	0.0410	0.0927
aug-cc-pVQZ	−5.0186	0.0523	0.0919
aug-cc-pV5Z	−5.0191	0.0597	0.0920
aug-cc-pV6Z	−5.0191	0.0649	–
(56) <sup>(a)</sup>	–	0.0910	–

<sup>(a)</sup>  $X^{-1}$  extrapolation from the aug-cc-pV5Z and aug-cc-pV6Z results.

**Table 5**

Analytic D2 corrections (FC) to the ground-state energy of the H<sub>2</sub>S molecule ( $R_{\text{SH}} = 1.337 \text{ \AA}$ ,  $\angle(\text{H-S-H}) = 92.295^\circ$ ) in mE<sub>h</sub>.

Basis set	SCF	$\Delta\text{DF-MP2}$	$\Delta\text{DF-MP2-F12/2}^*\text{A}$
aug-cc-pVDZ	−34.1147	0.0058	0.0180
aug-cc-pVTZ	−34.1178	0.0082	0.0200
aug-cc-pVQZ	−34.1196	0.0109	0.0205
aug-cc-pV5Z	−34.1191	0.0130	0.0213
aug-cc-pV6Z	−34.1186	0.0144	–
(56) <sup>(a)</sup>	–	0.0214	–

<sup>(a)</sup>  $X^{-1}$  extrapolation from the aug-cc-pV5Z and aug-cc-pV6Z results.

**Table 6**

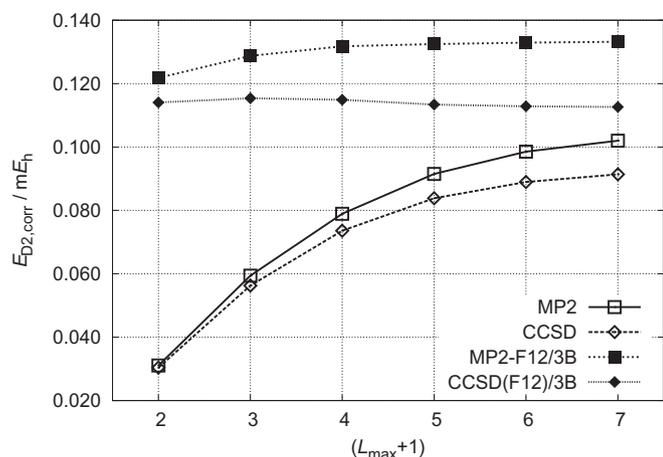
Analytic D2 corrections (FC) to the ground-state energy of the C<sub>6</sub>H<sub>6</sub> molecule ( $R_{\text{CC}} = 1.339 \text{ \AA}$ ,  $R_{\text{CH}} = 1.041 \text{ \AA}$ ) in mE<sub>h</sub>.

Basis set	SCF	$\Delta\text{DF-MP2}$	$\Delta\text{DF-MP2-F12/2}^*\text{A}$
aug-cc-pVDZ	−7.9452	0.0384	0.1169
aug-cc-pVTZ	−7.9352	0.0559	0.1171
aug-cc-pVQZ	−7.9379	0.0701	0.1174
aug-cc-pV5Z	−7.9384	0.0791	0.1180
(Q5) <sup>(a)</sup>	–	0.1151	–

<sup>(a)</sup>  $X^{-1}$  extrapolation from the aug-cc-pVQZ and aug-cc-pV5Z results.

pair correlation contribution (relative to the explicitly-correlated basis-set limit) against  $L_{\text{max}} + 1$ , where  $L_{\text{max}}$  is the maximum angular-momentum quantum number in the basis:

$$\ln(\Delta E_{\text{D2,MP2}}) = \ln(E_{\text{D2,MP2-F12}}(\text{spdfghi}) - E_{\text{D2,MP2}}(L_{\text{max}} + 1)). \quad (22)$$



**Fig. 1.** Calculated relaxed MP2, CCSD, MP2-F12/2B and CCSD(F12)/2B correlation contribution to the D2 term for Ne (note that 3B in the figure refers to ansatz 2B in the text). The results were computed in subsets of the 20s14p11d9f7g5h3i basis with  $L_{\max} = 1, 2, 3, 4, 5, 6$ .

**Table 7**

Relaxed (FC) MP2 singlet and triplet two-electron Darwin contributions (D2) of the Ne atom (in  $mE_h$ ) computed in subsets of the 20s14p11d9f7g5h3i basis.

Basis set	Singlet	Triplet	Total
sp	0.0322	-0.0012	0.0311
spd	0.0611	-0.0017	0.0594
spdf	0.0806	-0.0017	0.0789
spdfg	0.0932	-0.0017	0.0915
spdfgh	0.1002	-0.0017	0.0985
spdfghi	0.1037	-0.0017	0.1020

**Table 8**

Relaxed (FC) CCSD singlet and triplet two-electron Darwin contributions (D2) of the Ne atom (in  $mE_h$ ) computed in subsets of the 20s14p11d9f7g5h3i basis.

Basis set	Singlet	Triplet	Total
sp	0.0355	-0.0053	0.0304
spd	0.0628	-0.0063	0.0563
spdf	0.0799	-0.0063	0.0736
spdfg	0.0900	-0.0062	0.0838
spdfgh	0.0952	-0.0061	0.0890
spdfghi	0.0976	-0.0063	0.0914

**Table 9**

Relaxed (FC) MP2-F12 and and CCSD(F12) two-electron Darwin contributions (D2) of the Ne atom (in  $mE_h$ ) computed in subsets of the 20s14p11d9f7g5h3i basis.

Basis set	MP2-F12			CCSD(F12)
	Singlet	Triplet	Total	Total
sp	0.1233	-0.0015	0.1218	0.1141
spd	0.1305	-0.0017	0.1287	0.1154
spdf	0.1335	-0.0017	0.1318	0.1149
spdfg	0.1342	-0.0017	0.1325	0.1134
spdfgh	0.1346	-0.0017	0.1329	0.1128
spdfghi	0.1349	-0.0017	0.1332	0.1126

**Table 10**

D2 interference factors  $F_{D2,X}^{ij}$  for the  $\alpha\beta$  pairs of the Ne atom computed in subsets of the 20s14p11d9f7g5h3i basis.

Pair	sp	spd	spdf	spdfg	spdfgh	spdfghi
2s <sup>2</sup>	0.8384	0.7396	0.6977	0.6740	0.6588	0.6498
2s2p	0.8992	0.8177	0.7454	0.7163	0.6979	0.6883
2p2p'	0.8820	0.7697	0.7284	0.7045	0.6903	0.6830
2p <sup>2</sup>	0.7909	0.6483	0.5914	0.5671	0.5528	0.5453

Fig. 2 shows the log-log plots for the MP2 and MP2-F12/2B models. The expected power law is observed for conventional MP2 theory (the slope of the fitted line is  $-0.987$ ). A linear regression reveals a dramatically improved convergence for explicitly correlated MP2-F12 theory (slope  $\approx -3.345$ ).

#### 4.4. Interference correction

It has recently been shown that the CCSD(T) basis-set truncation error can be accurately estimated by scaling down the (larger) basis-set truncation error at the MP2 level [52]. We here investigate whether it is possible to scale down the MP2 basis-set truncation error of the D2 term in order to obtain a good estimate of the corresponding coupled-cluster truncation error. We use the interference-corrected explicitly-correlated perturbation theory of Ref. [52] to estimate the CCSD basis-set limit:

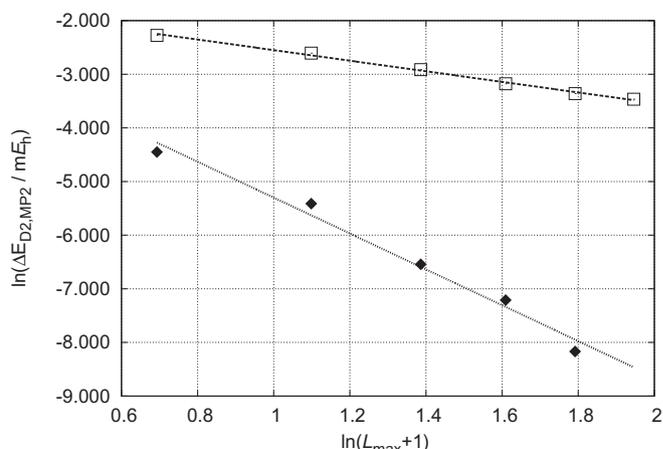
$$E_{\text{CCSD}/\infty} \approx E_{\text{CCSD}/X} + \Delta E_{\text{MP2}/\infty} + E_{\text{Int}/X}, \quad (23)$$

$$\Delta E_{\text{MP2}/\infty} + E_{\text{Int}/X} = \sum_{i<j} F_X^{ij} \left( E_{\text{MP2}/\text{spdfghi}}^{ij} + E_{\text{F12}/\text{spdfghi}}^{ij} - E_{\text{MP2}/X}^{ij} \right), \quad (24)$$

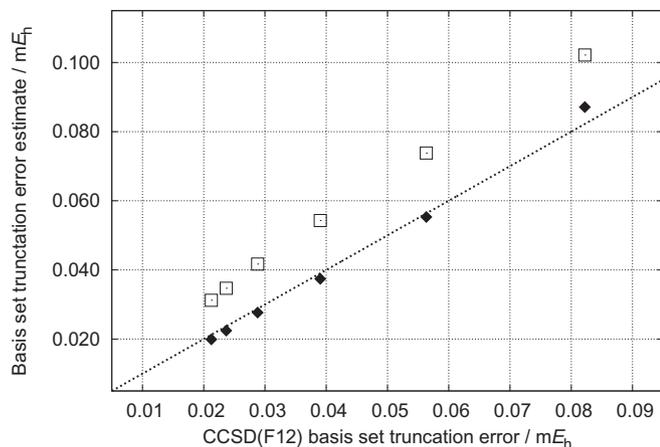
where the  $F_X^{ij}$  is the interference factor of the electron pair  $ij$  computed with cardinal number  $X$ , while the  $E^{ij}$  are second-order pair energies.

In Fig. 3, we have plotted the MP2-F12/2B basis-set truncation error with and without the interference factor against the CCSD (F12)/2B basis-set error for the Ne atom, demonstrating that interference-corrected explicitly correlated theory provides an accurate estimate of the CCSD truncation error. The raw MP2-F12 truncation error overestimates the CCSD error by 10–20  $\mu E_h$ , whereas the interference-corrected error agrees within 2–4  $\mu E_h$ . Table 9 shows the calculated interference factors for the different electron pairs and basis sets; they become smaller in larger basis sets but seem to converge to a limiting value.

The above result is perhaps unexpected in view of the very different convergence rates of the correlation energy ( $X^{-3}$ ) and the D2 term ( $X^{-1}$ ). However, the reason for the slower basis-set convergence in MP2 theory relative to CCSD theory stems from the non-iterative nature of perturbation theory, which means that contribution from high-energy states (here pair functions) is overestimated. In the iterative optimization of the CCSD wave functions, the first iteration yields the MP2 amplitudes. In each subsequent iteration, the contribution from amplitudes corresponding to large virtual excitation energies relative to those of low excitation energies is reduced by division of orbital-energy differences. As a result,



**Fig. 2.**  $\ln(\Delta E_{D2,MP2}/mE_h)$  ( $\square$ ) and  $\ln(\Delta E_{D2,MP2-F12}/mE_h)$  ( $\blacklozenge$ ) as a function of  $\ln(L_{\max} + 1)$  for the Ne atom in all subsets of the 20s14p11d9f7g5h3i basis. The dotted lines are obtained by linear regression of the  $\ln(\Delta E_{D2,MP2(-F12)}/mE_h)$  results.



**Fig. 3.** Basis-set truncation error (in  $mE_h$ ) of the D2 correlation contribution computed at the MP2-F12/2B level with ( $\blacklozenge$ ) and without ( $\square$ ) interference correction plotted against the basis-set truncation error computed at the CCSD(F12) level for the Ne atom in all subsets of the  $20s14p11d9f7g5h3i$  basis.

the contributions from orbitals of high principal quantum numbers is overestimated in MP2 theory relative to CCSD theory.

## 5. Conclusions

We have shown that it is possible to include the two-electron Darwin correction D2 easily into existing codes, given that analytic first-order properties are already available. Furthermore, robust density-fitting schemes can be straightforwardly applied to the D2 correction, and explicitly-correlated methods provide a fast convergence to the D2 basis-set limit. For future applications, the interference correction is a promising tool for providing good estimates of the D2 basis-set limit in the coupled-cluster theory. Therefore, we propose to perform conventional coupled-cluster calculations of the D2 term in medium-sized basis sets and to correct these energies with interference-corrected explicitly-correlated perturbation-theory values obtained from MP2-F12 calculations. For the proposed approach, only analytic derivatives at the levels of conventional MP2, conventional coupled-cluster, and MP2-F12 theories are required, which are available to us for open- as well as closed-shell systems.

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