

Explicitly correlated second-order perturbation theory calculations on molecules containing heavy main-group elements

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Abstract Slater-type geminals (STGs) have been used as explicitly correlated two-electron basis functions for calculations on the hydrides of N–As and Sb (as well as on the hydrides of O–Se and F–Br with similar, not reported results) in various one-electron basis sets of Gaussian atomic orbitals. The performance of the explicitly correlated theory has been assessed with respect to the exponent of the STG, for example, by using different exponents for individual pair correlation functions and pair energies. It is shown that a correlation factor with an exponent of $\gamma = 1.4 a_0^{-1}$ can give reliable results within 1% from the basis-set limit for all investigated molecules in an aug-cc-pVQZ basis set for the valence shells, using fixed amplitudes for the STGs in a diagonal orbital-invariant formulation of the theory. The use of relativistic effective core potentials (RECPs) in explicitly correlated second-order perturbation theory has been investigated.

1 Introduction

Since many years, one major problem of wavefunction-based quantum chemistry has been the slow convergence of electron-correlation contributions (to molecular energies and properties) to the basis-set limit. Approaches to overcome this slow-convergence problem include the use of wavefunctions that depend explicitly on the interparticle distances r_{ij} in the atom or molecule. Such an approach was first applied to the He atom by Hylleraas [1], and today, wavefunctions that are expanded in terms of two-particle basis functions

are referred to as explicitly correlated wave functions [2]. In modern approaches, explicitly correlated wavefunctions are used in quantum Monte Carlo methods [3], in electron-correlation methods based on second-order Møller–Plesset (MP2) perturbation theory or coupled-cluster theory using Gaussian geminals [4–6] as well as in full configuration-interaction calculations in terms of exponentially correlated Gaussians (ECGs) [7,8].

One of these approaches, the R12 method, has seen rapid development in recent times. Starting from the first formulation in 1985 by Kutzelnigg [9], the R12 method has emerged as a versatile tool in quantum chemistry [10,11]. Many of its initial shortcomings, for example, the need for very large basis sets to resolve the identity when calculating the complicated three- and four-electron integrals, have been improved by the use of auxiliary basis sets [12,13], general correlation factors [14,15] and commutator approximations [11,16]. When using a general, non-linear correlation factor, the method is often referred to as F12 to indicate the correlation factor to be a function $f(r_{12})$ rather than r_{12} itself [11]. Both names (R12 and F12) are found in the literature but we will use F12 throughout this article.

In the present work, we shall investigate the effect of the exponent of the Slater-type correlation factor on the basis set requirements for molecules with atoms from several rows of the periodic table of the elements. Furthermore, as in [11], we shall introduce the commutator approximation as proposed in [16] into the F12 theory as well as the use of relativistic effective core potentials (RECPs). This commutator approximation avoids the evaluation of two-electron integrals over the commutator between the kinetic energy operator and the correlation factor $f(r_{12})$.

The secondary purpose of the present article is to report the details of our current MP2-F12 implementation in TURBOMOLE [17].

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2 Theory

In this section, we shall recapitulate the R12 theory as described in [12]. Most changes are due to the use of CABS instead of ABS and F12 instead of a linear correlation factor. In F12 theory, the conventional first-order pair functions $\sum_{ab} t_{ij}^{ab} |ab\rangle$ are supplemented by geminal pair functions of the form

$$|u_{ij}\rangle = \sum_{kl} c_{ij}^{kl} \hat{Q}_{12} f_{12} |kl\rangle, \quad (1)$$

where $f_{12} = f(r_{12})$ is the correlation factor and \hat{Q}_{12} ensures the strong orthogonality of the pair functions on the occupied space [18]. The most successful Ansatz in F12 theory uses the strong-orthogonality operator \hat{Q}_{12} as

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

The operators \hat{O} and \hat{V} are the projectors onto the occupied and the virtual space, respectively. Pictorially, this operator projects out all contributions from the two-particle configuration space that belong to the general/general, occupied/complementary and complementary/occupied orbital pairs, where “general” refers to the finite one-electron basis set used for the calculation (decomposed into occupied and virtual orbitals) and “complementary” to the space complementary to this finite basis set. Hence, what remains in Eq. (1) can be understood as double excitations into the orbital pairs complementary/complementary, virtual/complementary and complementary/virtual. However, the projection operator \hat{Q}_{12} gives rise to three- and four-electron integrals. To avoid the calculation of these many-electron integrals, the projectors that occur alone (i.e., not in a product such as $\hat{O}_1 \hat{O}_2$) must be augmented with an additional projection operator for the other electron. Two possible approximations exist:

$$\hat{Q}_{12} \approx 1 - \hat{O}_1 \hat{P}_2'' - \hat{P}_1'' \hat{O}_2 - \hat{P}_1 \hat{P}_2, \quad (3a)$$

$$\hat{Q}_{12} \approx \hat{P}_1'' \hat{P}_2'' + \hat{V}_1 \hat{P}_2'' + \hat{P}_1'' \hat{V}_2. \quad (3b)$$

\hat{P} is the projector onto the whole finite orbital space (“general” = occupied + virtual), and \hat{P}'' is the projector onto a complementary auxiliary basis set (CABS). This finite CABS attempts to represent the true complementary space, and in the limit of a complete CABS, both approximations become exact and thus equivalent. Equation (3a) is used when the integrals that occur with the unity operator can be calculated analytically. If not, then Eq. (3b) is used, which only contains products of projection operators and thus always leads to a factorization of the many-electron integrals into products of two-electron integrals. It is in the spirit of F12 theory to use Eq. (3a) wherever possible, because the projector of Eq. (3b) does not truncate and eventually leads to a convergence similar to the conventional basis set expansion.

The correlation energy of the electron pair (ij) with the multiplicity s can be expressed in several ways:

$$e_{ij}^s = - \left\{ \tilde{\mathbf{V}}^{(ij,s)} \right\}^T \left\{ \tilde{\mathbf{B}}^{(ij,s)} \right\}^{-1} \tilde{\mathbf{V}}^{(ij,s)}, \quad (4a)$$

$$e_{ij}^s = - (\tilde{\mathbf{V}}_{ij}^{(ij,s)})^2 / \tilde{\mathbf{B}}_{ij}^{(ij,s)}, \quad (4b)$$

$$e_{ij}^s = a^2 \tilde{\mathbf{B}}_{ij}^{(ij,s)} + 2a \tilde{\mathbf{V}}_{ij}^{(ij,s)}. \quad (4c)$$

Equation (4a) denotes the orbital-invariant formulation with fully optimized amplitudes [19] and Eq. (4b) is a variational diagonal approximation which is not orbital invariant [20]. The third equation (4c) is a diagonal, orbital-invariant formulation that uses Kato’s cusp condition [21] for fixing the amplitudes in the Hylleraas functional [22]. This condition states that the term linear in r_{12} carries a factor $a = 1/2$ for singlet pairs ($s = 0$) and $a = 1/4$ for triplet pairs ($s = 1$).

The spin-adapted matrices $\tilde{\mathbf{V}}$ and $\tilde{\mathbf{B}}$ are defined as

$$\tilde{\mathbf{V}}_{kl}^{(ij,s)} = (1 + \delta_i^j)^{-1/2} (1 + \delta_k^l)^{-1/2} \times \left(\tilde{v}_{kl}^{(ij)} + (1 - 2s) \tilde{v}_{lk}^{(ij)} \right), \quad (5)$$

$$\tilde{\mathbf{B}}_{kl}^{mn(ij,s)} = (1 + \delta_k^l)^{-1/2} (1 + \delta_m^n)^{-1/2} \times \left(\tilde{b}_{kl}^{mn(ij)} + (1 - 2s) \tilde{b}_{lk}^{mn(ij)} \right), \quad (6)$$

where the tilde indicates the inclusion of the coupling between the conventional and the F12 terms:

$$\tilde{v}_{kl}^{(ij)} = v_{kl}^{(ij)} - \sum_{ab} \frac{C_{kl}^{ab} g_{ab}^{ij}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (7)$$

$$\tilde{b}_{kl}^{mn(ij)} = b_{kl}^{mn(ij)} - \sum_{ab} \frac{C_{kl}^{ab} C_{ab}^{mn}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}. \quad (8)$$

The matrices \mathbf{V} , \mathbf{B} and \mathbf{C} are defined as

$$V_{kl}^{(ij)} = \langle kl | f_{12} \hat{Q}_{12} g_{12} | ij \rangle, \quad (9)$$

$$B_{kl}^{mn(ij)} = \langle kl | f_{12} \hat{Q}_{12} (\hat{F}_{12} - \epsilon_i - \epsilon_j) \hat{Q}_{12} f_{12} | mn \rangle, \quad (10)$$

$$C_{kl}^{ab} = f_{kl}^{aq''} F_{q''}^b + f_{kl}^{p''b} F_{p''}^a, \quad (11)$$

with $\hat{F}_{12} = \hat{F}_1 + \hat{F}_2$ the Fock operator for electrons one and two, f_{12} the correlation factor and g_{12} the interelectronic repulsion. We use the usual notation for different kinds of orbitals in agreement with the definition of the projection operators in (3): i, j, \dots denote occupied, a, b virtual, p, q general, p'', q'' complementary auxiliary and p', q' the union of general and complementary orbitals. Matrix elements are defined similarly. By rewriting the kernel of Eq. (10) as

$$\begin{aligned} & f_{12} \hat{Q}_{12} (\hat{F}_{12} - \epsilon_i - \epsilon_j) \hat{Q}_{12} f_{12} \\ &= \frac{1}{2} f_{12} \hat{Q}_{12} [\hat{F}_{12}, \hat{Q}_{12} f_{12}] + \frac{1}{2} [f_{12} \hat{Q}_{12}, \hat{F}_{12}] \hat{Q}_{12} f_{12} \\ &+ \frac{1}{2} f_{12} \hat{Q}_{12} f_{12} (\hat{F}_{12} - \epsilon_i - \epsilon_j) \\ &+ \frac{1}{2} (\hat{F}_{12} - \epsilon_i - \epsilon_j) f_{12} \hat{Q}_{12} f_{12} \end{aligned} \quad (12)$$

advantage can be taken of the generalized Brillouin condition (GBC) to evaluate the latter two terms:

$$\langle kl|f_{12}\hat{Q}_{12}f_{12}(\hat{F}_{12} - \epsilon_i - \epsilon_j)|mn\rangle \approx (\epsilon_m + \epsilon_n - \epsilon_i - \epsilon_j)X_{kl}^{mn}, \quad (13)$$

with \mathbf{X} being the overlap of the pair functions. The first two terms in Eq. (12) can be evaluated as

$$f_{12}\hat{Q}_{12}[\hat{F}_{12}, \hat{Q}_{12}f_{12}] = f_{12}\hat{Q}_{12}[\hat{F}_{12}, f_{12}] + f_{12}\hat{Q}_{12}[\hat{F}_{12}, \hat{Q}_{12}]f_{12}. \quad (14)$$

Again using the GBC, and since $\hat{Q}_{12}\hat{V}_1\hat{V}_2 = 0$, matrix elements of the second term in Eq. (14) are computed as

$$\langle kl|f_{12}\hat{Q}_{12}[\hat{F}_{12}, \hat{Q}_{12}]f_{12}|mn\rangle = -C_{kl}^{ab}f_{ab}^{mn}, \quad (15)$$

with \mathbf{C} the coupling matrix of Eq. (11) and f_{ab}^{mn} matrix elements of the correlation factor. Matrix elements of the first term in Eq. (14) are split into

$$\langle kl|f_{12}\hat{Q}_{12}[\hat{F}_{12}, f_{12}]|mn\rangle = T_{kl}^{mn} + K_{kl}^{mn}, \quad (16)$$

$$K_{kl}^{mn} = Q_{kl}^{mn} - P_{kl}^{mn}. \quad (17)$$

For the operators contained in the Fock operator \hat{F}_{12} in Eq. (16), three different situations may occur. First, the commutator (16) may vanish, for example with the electron–nucleus potential $\hat{V}_{\text{nuc},12}$ and the Coulomb operator \hat{J}_{12} . Second, it does not vanish, but the unity operator in (3a) can be evaluated analytically, for example, with the kinetic energy \hat{T}_{12} . In this case, approximation (3a) can be used, which leads to the \mathbf{T} matrix. Third, the commutator neither vanishes nor the unity operator can be evaluated analytically, for example, for the exchange operator \hat{K}_{12} and the effective core potential $\hat{V}_{\text{RECP},12}$. In this last case, the commutator is split into its two summands and definitions (3a) and (3b) are used for the two terms \mathbf{Q} and \mathbf{P} . Finally, in matrices such as \mathbf{X} and \mathbf{V} , the integrals with the unity operator can be evaluated analytically and approximation (3a) can be used. The matrices are evaluated as

$$V_{kl}^{(mn)} = (fg)_{kl}^{mn} - f_{kl}^{p''j}g_{p''j}^{mn} - f_{kl}^{iq''}g_{iq''}^{mn} - f_{kl}^{pq}g_{pq}^{mn}, \quad (18)$$

$$X_{kl}^{mn} = (f^2)_{kl}^{mn} - f_{kl}^{p''j}f_{p''j}^{mn} - f_{kl}^{iq''}f_{iq''}^{mn} - f_{kl}^{pq}f_{pq}^{mn}, \quad (19)$$

$$T_{kl}^{mn} = (f'^2)_{kl}^{mn} - f_{kl}^{p''j}t_{p''j}^{mn} - f_{kl}^{iq''}t_{iq''}^{mn} - f_{kl}^{pq}t_{pq}^{mn}, \quad (20)$$

$$Q_{kl}^{mn} = (\bar{f}^2)_{kl}^{mn} - f_{kl}^{p''j}q_{p''j}^{mn} - f_{kl}^{iq''}q_{iq''}^{mn} - f_{kl}^{pq}q_{pq}^{mn}, \quad (21)$$

$$P_{kl}^{mn} = f_{kl}^{p''b}p_{p''b}^{mn} + f_{kl}^{aq''}p_{aq''}^{mn} + f_{kl}^{p''q''}p_{p''q''}^{mn}, \quad (22)$$

with

$$f'^2 = (\bar{\nabla}f)^2.$$

The matrix elements t , q , p and \bar{f}^2 are defined as follows:

$$t_{pq}^{mn} = T_q^{r'}f_{pr'}^{mn} - f_{pq}^{mr'}T_{r'}^n + T_p^{r'}f_{r'q}^{mn} - f_{pq}^{r'n}T_{r'}^m, \quad (23)$$

$$q_{pq}^{mn} = f_{pq}^{mr'}U_{r'}^n + f_{pq}^{r'n}U_{r'}^m, \quad (24)$$

$$p_{pq}^{mn} = U_p^{r'}f_{qr'}^{mn} + U_m^{r'}f_{r'n}^{mn}, \quad (25)$$

$$(\bar{f}^2)_{kl}^{mn} = (f^2)_{kl}^{mr'}U_{r'}^n + (f^2)_{kl}^{r'n}U_{r'}^m. \quad (26)$$

The transformation matrix U_p^q is the matrix representation of the exchange operator minus the effective core potential

$$U_p^q = K_p^q - (\hat{V}_{\text{RECP}})_p^q. \quad (27)$$

The definition of the t integrals is the major difference between previous implementations of the F12 theory, standard approximations A and B, and the present one (standard approximation C). In the standard approximations A and B, the commutator integrals are calculated exactly as

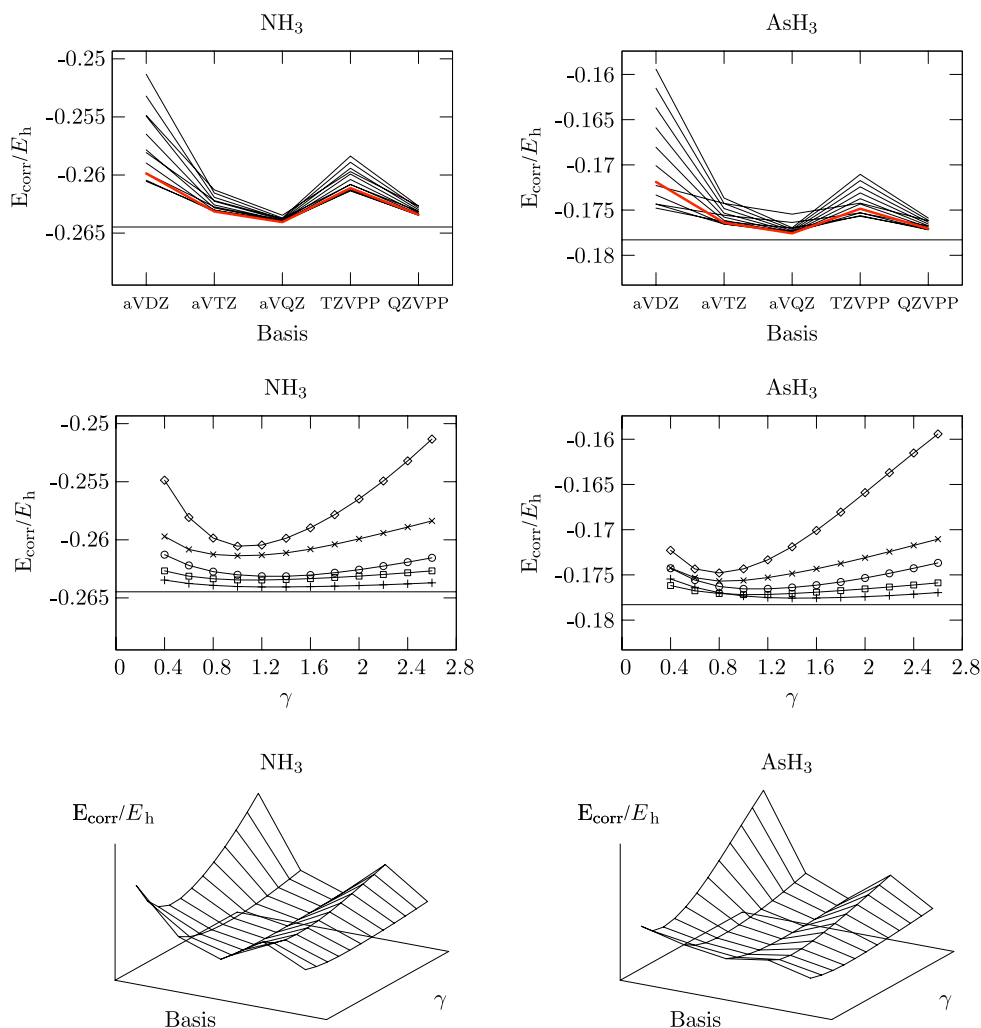
$$t_{kl}^{pq} = \langle kl|[\hat{T}_{12}, f_{12}]|pq\rangle. \quad (28)$$

In standard approximation C used here, however, these integrals are computed according to Eq. (23), with the transformation matrix \mathbf{T} given as the matrix representation of $\hat{F} + \hat{K}$. Of course, one could simply use the matrix representation of the kinetic energy operator \hat{T} instead of the sum $\hat{F} + \hat{K}$, but our experience showed that the direct use of the matrix elements of \hat{T} is numerically unstable for linear R12 theory (without using a CABS). The reason for this is that the matrix commutator is not equal to the operator commutator in a finite basis representation. If a Slater function is used as correlation factor in conjunction with a sufficiently large CABS, the matrix commutator is very accurate and any transformation matrix of the series (\hat{T}) , $(\hat{T} + \hat{V})$ or $(\hat{T} + \hat{V} + \hat{J}) = (\hat{F} + \hat{K} - \hat{V}_{\text{RECP}})$ can be applied. In the present work, we use the matrix representation of the core Hamiltonian $(\hat{T} + \hat{V})$.

Using either of the commutator approximations, only simple g , f and f^2 AO-integrals have to be calculated over the finite orbital basis and the CABS as well as the integrals (fg) and $(\bar{\nabla}f)^2$ over the finite orbital basis. All these integrals are available via the Obara–Saika scheme [23–25]. The integrals over $(\bar{\nabla}f)^2$ are essentially identical with those over f . They would be strictly identical when an analytic STG were used [26]. The operator identity does not hold for an STG represented by a linear combination of Gaussian geminals, but when a good fit is used, it may be worthwhile to assume that the identity holds. However, this is not done in the present work.

The four-index quantities can be calculated efficiently in the resolution-of-the-identity (RI) approximation of RI-MP2 theory, for which in other works the alternative name “density-fitting (DF) approximation” is used [27,28].

Fig. 1 Correlation energy with respect to the basis set and Slater exponent γ for NH_3 (left) and AsH_3 (right). Key for the second graph. Diamond aVDZ, Circle aVTZ, Plus aVQZ, Cross def2-TZVPP, Square def2-QZVPP



3 Computational details

All calculations were performed with the TURBOMOLE program package [17, 29, 30]. The molecules were optimized at the MP2 level of theory using a def2-TZVP basis set [31]. As correlation factor a linear combination of six Gaussians was used to fit a Slater function with a given exponent γ [32]. Basis sets and RECPs were taken from [31, 33–38]. As complementary auxiliary basis set (CABS) for the molecules N to F, P to Cl and As to Br, a cc-pVQZ Coulomb fitting basis was used [39, 40]. This is the auxiliary basis used in RI-MP2 calculations in the cc-pVQZ basis. The density-fitting RI was done with a cc-pV5Z Coulomb fitting basis, which is sufficient for covering the CABS as well as all orbital basis sets. For the correlation of the 3d electrons of AsH_3 , a (13s12p11d9f7g5h1i) CABS was used for As with a (40s29p24d19f19g15h13i11k) Coulomb fitting basis. For Sb, the Coulomb fitting basis of As was used as CABS, whereas for the density-fitting RI, a union of the basis sets

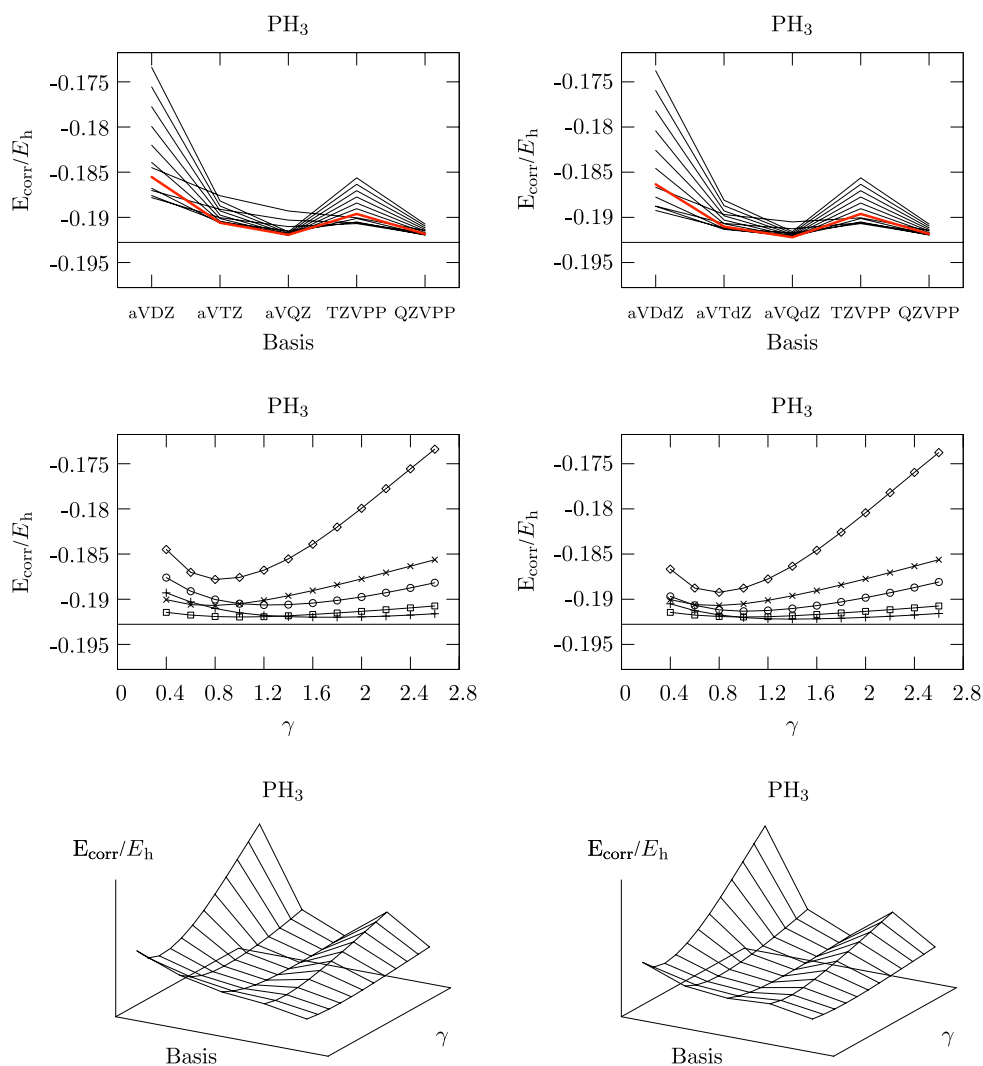
def2-QZVPP of Sb and cc-pV5Z of As was used for all orbital basis sets. When using RECPs, a small core of 10 was used for As and a core of 28 for Sb. The basis-set limits were obtained with RI-MP2-F12 calculations using a very large basis (aug-cc-pV6Z, aug-cc-pV(6+d)Z or specially designed for As to Br [39]) with an exponent of $\gamma = 1.4$ for the Slater-type geminal.

4 Results and Discussion

4.1 Main group element hydrides without RECPs

The figures show three graphs for each element (Figs. 1, 2) in group 15. Results for groups 16 and 17 were very similar and are not reported here (these data can be obtained from the authors). The first graph shows the energy as a function of the basis for various values of γ . Each curve corresponds to one particular value of γ . The thick red line corresponds

Fig. 2 Correlation energy with respect to basis set and Slater exponent γ for PH_3 , with (right) and without (left) steep d functions. Key for the second graph. Diamond aVDZ, Circle aVTZ, Plus aVQZ, Cross def2-TZVPP, Square def2-QZVPP



to $\gamma = 1.4$, which was proposed to be a good universal exponent for the valence shell correlation using augmented correlation-consistent basis sets [41]. The second graph shows the energy as a function of γ for several basis sets. Each curve corresponds to one particular basis set. The solid straight lines are the basis-set limits. A 3D-projection of the union of the two plots is given in the third graph.

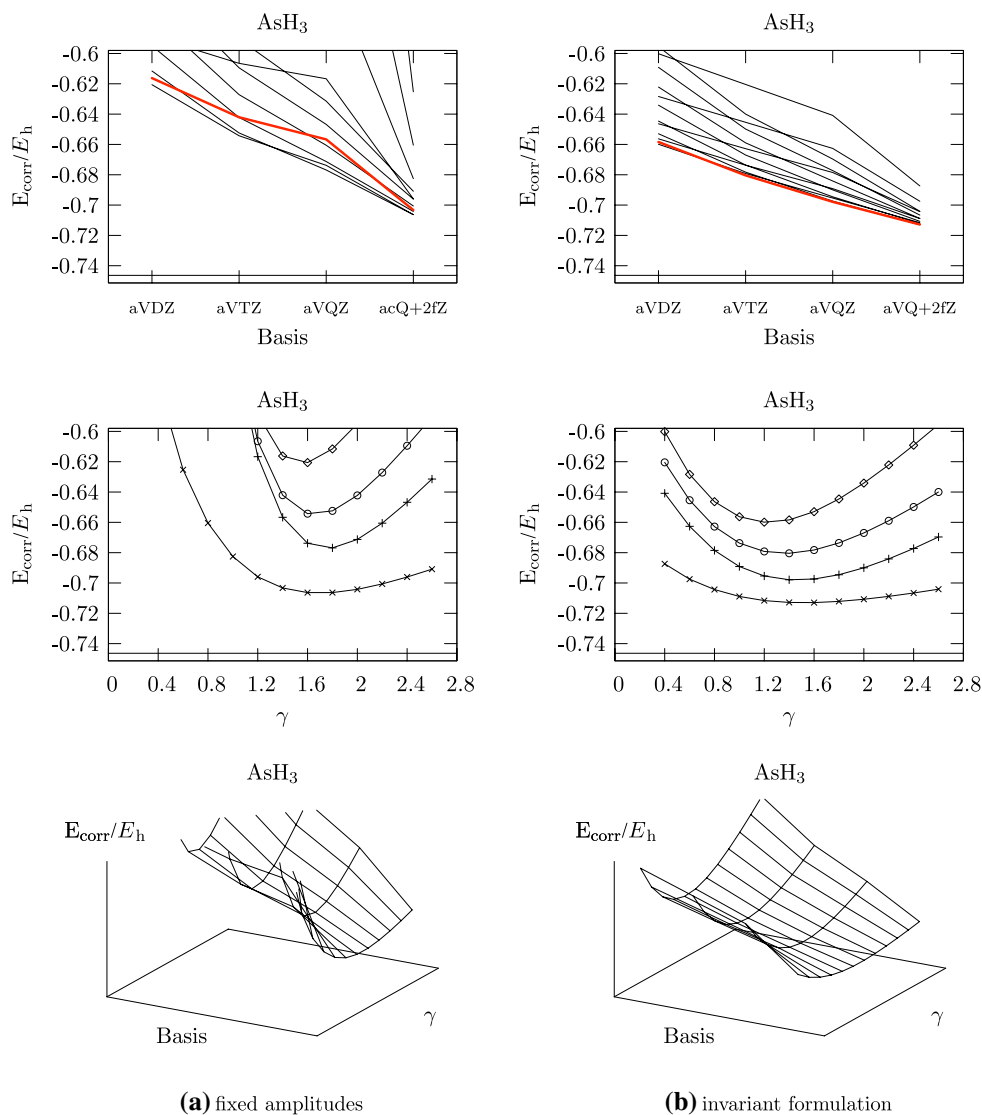
The calculations of the main-group-element hydrides correlating eight electrons show a rapid convergence to the basis-set limit. This is true not only for the first-row elements, where this behaviour has been shown before, but also for their heavier counterparts in the homologous series. The optimal γ is close to 1.4 for the larger basis sets in the molecules, which confirms that the corresponding Slater-type geminal is a good universal correlation factor. Smaller basis sets require a smaller γ , as discussed in [41].

Comparing the two types of basis sets, for first row elements, the augmented correlation-consistent (aug-cc) basis sets perform slightly better than the TURBOMOLE ones for

a given cardinal number. The TURBOMOLE basis sets give results similar to or better than the non-augmented cc basis sets. The reason for the superior performance of the aug-cc basis sets compared to the TURBOMOLE sets is the augmentation, which is very important in F12 theory [41]. The augmented correlation-consistent basis sets have a significantly larger number of contracted basis functions than the TURBOMOLE sets, but nevertheless, the TURBOMOLE sets (such as TZVPP) give lower SCF energies than the aug-cc sets (such as aug-cc-pVTZ).

The second-row elements usually require an additional steep d -function to polarize the core in molecular calculations [35], which also lowers the Hartree–Fock energy considerably (1.4–4.4 mE_h) for the aug-cc basis sets. The conventional MP2 correlation energies are only slightly changed (0.07–0.21 mE_h , 0.03–0.1%), whereas the F12 calculations benefit more by the new d -function (0.2–1.4 mE_h , 0.1–1%). Without the d -function, the γ -dependence is more pronounced for the triple- and quadruple-zeta aug-cc basis sets, and

Fig. 3 Correlating 18 electrons in AsH_3 , invariant formulation. Key for the second graph. Diamond aVDZ, Circle aVTZ, Plus aVQZ, Cross aVQZ+2f



also the optimal exponents tend to be larger, especially for H_2S and HCl . This can be understood with the poorer description of the short-range part of the correlation hole without using tight d -functions. This tight function is already included in the TURBOMOLE basis sets, and therefore, these sets perform as well as the X+d sets. When adding the d -function to the aug-cc basis set, it again outperforms the TURBOMOLE basis sets slightly.

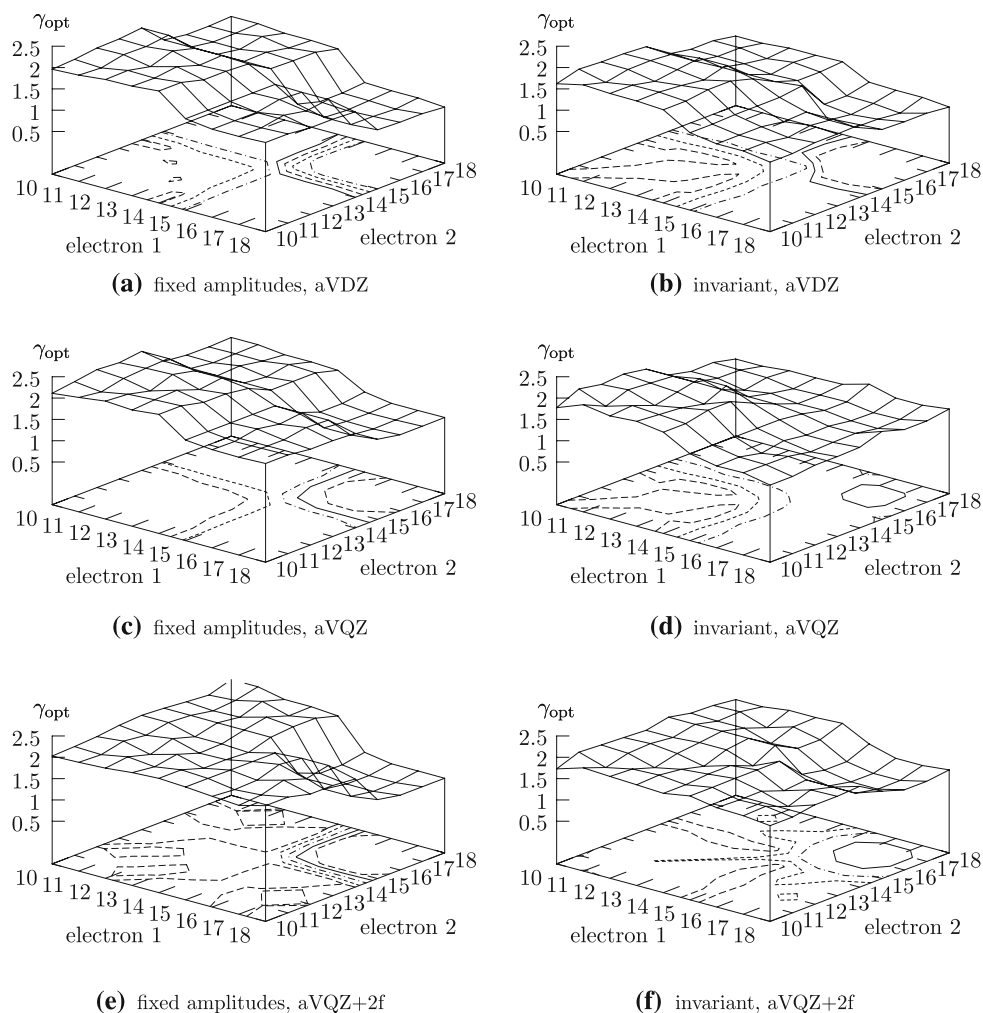
Also for third-row elements, we observe only marginal differences between the TURBOMOLE and correlation-consistent basis sets.

For all the molecules, the basis-set limit can be reached reliably to within 1% using an aug-cc-pVQZ basis and an exponent of $\gamma = 1.4$. This statement is true when correlating the valence shell, for which the basis sets have been designed. The situation may be different when the correlation of the outer core orbitals is also taken into account.

4.2 Analysis of γ

The correlation factor may serve different purposes. Either it can take care of the short-range correlation, which results in the need for a rather large γ , or it can take care of the intermediate correlation range, leading to a smaller value. In the invariant variational formulation, much flexibility is provided by the large number of amplitudes, making the results rather insensitive to the precise value of γ . In order to investigate the dependence on γ further, we have studied the orbital-invariant, fixed-amplitudes formulation, which is more sensitive to the exponent of the correlation factor. A series of calculations with different γ ranging from 0.4 to 2.6 a_0^{-1} were performed, and its best value was selected for each pair energy, using a local polynomial fit. This scheme does not optimize the correlation factor completely, as was done in the work by Valeev [42], but rather picks out an optimal γ for

Fig. 4 Dependence of γ with respect to basis and singlet pair for AsH₃



each pair of occupied orbitals. When optimizing the exponent γ for individual orbital pairs, however, the diagonal, fixed-amplitudes approach is no longer invariant with respect to rotations among the occupied orbitals. Furthermore, similar results can be obtained by optimizing the coefficients of the linear combination of Gaussians that represents the STG instead of the exponent.

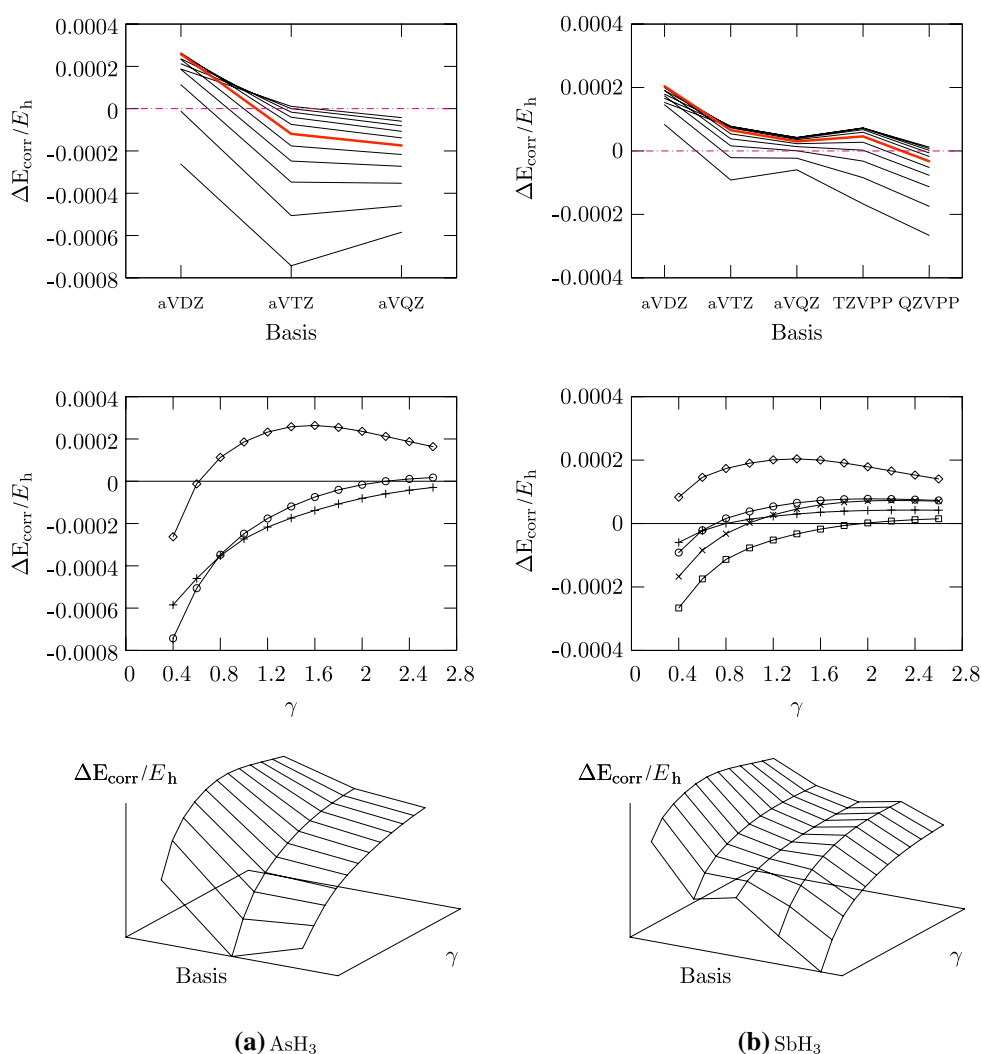
As an example, we consider the AsH₃ molecule in the aug-cc-pVXZ basis correlating 18 orbitals. The basis set is not designed for correlating core d -electrons, and its performance is quite poor due to missing f -functions [31]. The invariant F12 results are closer to the basis-set limit, but the γ -dependence is pronounced, especially for the smaller basis sets. Adding two steep f -functions improves the results significantly and the dependence of the energy on γ is reduced (Fig. 3).

The optimal γ 's for each singlet pair are depicted in Fig. 4. Orbitals 10 through 14 are the core d -orbitals, 15 through 18 are the valence orbitals forming the bonds to the hydrogens. In all cases it can be seen that the valence shells are described in a way different from the core shells. The val-

ues of γ are distinct for both types: intrashell and intershell pairs. The situation is slightly improved by adding two steep f -functions to the aug-cc-pVQZ basis. The description of the valence electrons is hardly affected by changing the basis. Comparing the fixed-amplitudes and the invariant results, it can be seen that the invariant results depend much less on the value of γ , as there is more flexibility through the larger number of geminals. The optimal γ 's for the triplet pairs are nearly constant for all orbital pairs and basis sets and differ at most by about $\Delta\gamma = 0.6 a_0^{-1}$.

The question remains whether γ should be large (>1) or small (<1) in general. For weak intermolecular interactions (e.g. van-der-Waals interactions), the STG with a small γ may be able to describe the long-range part of the correlation well [32]. In other cases, it may be important to describe the intraatomic correlation accurately, in which case γ should be larger. It is perhaps more important, however, that the optimal γ should have more or less the same value for all pairs. If not, contributions from certain pairs may be heavily underestimated and biased results may be obtained.

Fig. 5 Effect of neglecting $[f_{12}, \hat{V}_{\text{RECP}}]$ for AsH_3 and SbH_3 , that is, neglecting \hat{V}_{RECP} in Eq. 27. Key for the second graph. Diamond aVDZ, Circle aVTZ, Plus aVQZ, Cross def2-TZVPP, Square def2-QZVPP



4.3 RECPs

Moving down the 15th group, one arrives at antimony. Standard basis sets for that element are available only with relativistic effective core potentials (RECPs), and the question therefore arises, how RECPs can be used in F12 theory and what influence they have on the F12 results. Until now, no F12 calculations with RECPs have been performed, and this is the first time that F12 calculations take into account the commutator $[f_{12}, \hat{V}_{\text{RECP}}]$. The RECPs are non-local potentials, since they contain projection operators onto spherical harmonics, and for that reason, their commutator with the correlation factor does not vanish. The RECPs affect the orbital energies, and in that sense their influence is present in Eqs. (12) and (16). Therefore, neglecting their commutators only in Eq. (16) would lead to an unbalanced description. Neglecting the RECP commutator would be comparable to neglecting the commutator with the exchange operator in standard approximation A.

We have observed that the effect of the neglect of the commutators (as done in standard approximation A) is similar for RECPs and exchange. The contribution to the energy is small, but not negligible. No systematic behaviour is observed when comparing different basis sets (Fig. 5), but fortunately, there are no additional costs when taking the commutator into account and there is therefore no reason to neglect it.

Usually the use of RECPs is motivated by physical reasons (scalar relativistic effects) as well as by efficiency considerations. In F12 theory, the gain in efficiency is not as large as one might wish, since the standard approximation of F12 theory required a large CABS. This is especially true when correlating core orbitals. In the atomic case, the CABS must be saturated up to at least the angular momentum $L = \max(L_{\text{max}}, 3L_{\text{occ}})$, with L_{occ} the highest occupied angular momentum and L_{max} the highest angular momentum in the finite basis set [12]. For first-row elements, it seems to be sufficient to use a fairly small CABS [25], but for heavier elements, one must consider carefully the angular momenta of

the functions in the basis set. Moreover, the size of the CABS in turn has a bearing on the requirements for the density-fitting basis, since this fitting basis must not only describe products of orbitals of the finite basis but also those containing CABS.

5 Summary

RECPs are commonly used in heavy-element quantum chemistry. Fortunately, they can easily be used in F12 theory. This could be shown by calculating a series of molecules containing heavy main-group elements. A correlation factor with an exponent of $\gamma = 1.4 a_0^{-1}$ can give reliable results to within 1% of the basis-set limit for all molecules in an aug-cc-pVQZ basis set. When correlating core *d*-orbitals, it is essential to saturate the CABS to get meaningful results, due to the $3L_{\text{occ}}$ -rule. To achieve a balanced description of all pairs using a single γ it is helpful to use the invariant formulation of F12 theory with much flexibility in the pair functions.

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