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RESEARCH ARTICLE

Explicitly correlated coupled cluster methods with pair-specific geminals

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Explicitly correlated MP2-F12 and CCSD(T)-F12 methods with orbital-pair-specific Slater-type geminals are proposed. The fixed amplitude ansatz of Ten-no is used, and different exponents of the Slater geminal functions can be chosen for core-core, core-valence, and valence-valence pairs. This takes care of the different sizes of the correlation hole and leads to improved results when inner-shell orbitals are correlated. The complications and the extra computational cost as compared to corresponding calculations with a single geminal are minor. The improved accuracy of the method is demonstrated for spectroscopic properties of Br₂, As₂, Ga₂, Cu₂, GaCl, CuCl, and CuBr, where the *d*-orbitals are treated as core.

1. Introduction

During the last few years efficient and robust explicitly correlated second-order Møller-Plesset (MP2-F12) and coupled-cluster [CCSD(T)-F12] methods have been developed, and it has been demonstrated in numerous benchmarks and applications that these lead to dramatically reduced basis set truncation errors. Typically, CCSD(T)-F12 with triple- ζ basis sets yields results that show at least the accuracy of conventional CCSD(T) calculations with quintuple- ζ basis sets. Even with double- ζ basis sets the intrinsic accuracy of CCSD(T) is often reached. Details and references to earlier work can be found in recent reviews[1–3].

A common feature of most CCSD(T)-F12 methods is that the amplitudes of the Slater-type geminal are determined from the wave function cusp conditions[4, 5], as proposed by Ten-no[6, 7]. Thus, no extra equations have to be solved to determine these amplitudes. A remaining parameter in the calculations is the exponent γ of the Slater function, $F_{12} = -\frac{1}{\gamma}e^{-\gamma r_{12}}$, which determines the size of the correlation hole modeled by the geminal. If the geminal amplitudes are fully optimized, the dependence of the energy on this parameter is rather weak; but it is more pronounced if the fixed amplitude approximation is used. For calculations in which just the valence orbitals are correlated this does not cause significant errors, and an average value of $\gamma = 1.0 a_0^{-1}$ has been found to work well for a large range of molecules and applications[8–11]. However, if inner shells are also correlated, it is not possible to define an exponent that is appropriate for all orbital pairs. For example, in calculations involving transition metals or other post-*d* elements, it is important to correlate the *d*-shell. Since the *d*-orbitals are much more compact

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than the outer valence orbitals, a larger geminal exponent is desirable. Using a single geminal, one can at best use a compromise value for valence and core-valence correlation, but this is not fully satisfactory.

In the current work we propose a simple method that makes it possible to use different Slater-type geminals, depending on the pair type. Different exponents can then be used for core-core, core-valence, and valence-valence correlating pairs. It should be noted that a MP2-F12 method with multiple Gaussian geminals has previously been proposed by Valeev[12]. In this method, which is much more complicated than what we propose here, several geminals were used for each pair, and the geminal amplitudes were fully optimized. In contrast, we use just one suitable geminal for each pair. This makes it possible to determine the geminal amplitudes from the wave function cusp conditions, and no additional amplitude equations have to be solved. This method can be transparently included in MP2-F12 and a number of approximate CCSD-F12 methods. Such approximate CCSD-F12 methods have been in the focus of recent development, since formally exact CCSD-F12 methods[13–16] are much more expensive than standard CCSD, place higher demands on the auxiliary basis set used for the resolution of the identity, and are basically only applicable for benchmarking purposes. Compared to full CCSD-F12, simpler methods like CCSD(F12)[17–20], CCSD-F12x (x=a,b)[8–10, 21], CCSD $_{\overline{R12}}$ [22–24], and CCSD(F12*)[25] offer a similar accuracy at a greatly reduced cost, and production level programs are already publicly available in MOLPRO and TURBOMOLE. Here we focus on the CCSD-F12x (x=a,b) methods, which are only marginally more expensive than conventional CCSD, and on the CCSD(F12*) method (in MOLPRO denoted as CCSD-F12c), which is about 20%–50% more expensive.

In section 2 we will outline the method for introducing multiple geminals. In section 3 we will present some illustrative examples.

2. Theory

The MP2-F12 and CCSD(T)-F12x theory and the working equations as used in our programs have been presented in earlier work[3, 8, 21, 26, 27], and the details will not be repeated here. We will therefore just outline the ansatz, and explain how the method is extended to pair-specific geminals. In the following, occupied orbitals will be denoted by indices i, j, k, l, m, n, o, p ; virtual orbitals in the orbital basis set (OBS) by a, b ; any orbitals in the OBS by r, s ; and complementary auxiliary orbitals (CABS) by x, y . The occupied orbital indices $i \dots p$ exclude frozen core orbitals, unless indicated otherwise. The indices α, β run over the complete virtual space, which contains the virtual (a, b) and CABS (x, y) orbitals as subspaces. Summation over repeated dummy indices is always implied. For simplicity, we will first consider the closed-shell case, using a spin-free formulation. We will assume that canonical Hartree-Fock orbitals are used (i.e., that the Fock matrix is diagonal in the OBS). The extension to an orbital invariant formulation[26] and open-shell[8] cases is discussed at the end of this section.

The new wave function ansatz with pair specific geminals is best shown for the MP2-F12 method, which is also the first step of a CCSD(T)-F12x calculation. The MP2-F12 first-order wavefunction is defined as [28]

$$\Psi^{(1)} = \frac{1}{2} \left[\Phi_{ij}^{ab} T_{ab}^{ij} + \Phi_{ij}^{\alpha\beta} \langle \alpha\beta | \hat{Q}_{12} F_{12}^{(ij)} | kl \rangle T_{kl}^{ij} \right], \quad (1)$$

$$\Phi_{ij}^{\alpha\beta} = \hat{E}_i^\alpha \hat{E}_j^\beta \Phi_{\text{HF}}. \quad (2)$$

Here $\hat{E}_i^\alpha = \eta_\alpha^\dagger \eta_i + \bar{\eta}_\alpha^\dagger \bar{\eta}_i$ are spin-summed one-electron excitation operators, and $F_{12}^{(ij)}$ is the r_{12} -dependent correlation factor,

$$F_{12}^{(ij)} = -\frac{1}{\gamma} e^{-\gamma^{(ij)} r_{12}} \quad (3)$$

with $\gamma^{(ij)}$ a length-scale parameter. In contrast to previous F12 treatments, we assume here that this parameter can be pair dependent, as indicated by the superscript (ij) . As will be discussed later, we will only use two or three different values in practice, but for the sake of simplicity and generality, we make no such restrictions in the theory.

The projector \hat{Q}_{12} keeps the explicitly correlated terms strongly orthogonal to the Hartree-Fock (HF) reference function and orthogonal to the conventional singly and doubly excited configurations Φ_i^a and Φ_{ij}^{ab}

$$\hat{Q}_{12} = (1 - \hat{o}_1)(1 - \hat{o}_2) - \hat{v}_1 \hat{v}_2, \quad (4)$$

where the operators $\hat{o} = \sum_i^{\text{occ}} |i\rangle\langle i| \equiv |i\rangle\langle i|$, $\hat{v} = \sum_a^{\text{virt}} |a\rangle\langle a| \equiv |a\rangle\langle a|$ project onto the occupied orbital space (including frozen core orbitals) and virtual orbital space, respectively. The subscripts of \hat{o} and \hat{v} denote the electron coordinate on which they act. In order to avoid many-electron integrals, resolution of the identity (RI) approximations are used. If the RI is spanned by the union of the OBS and an auxiliary basis set (CABS approach[29]) the projector takes the form

$$\hat{Q}_{12} = 1 - |rs\rangle\langle rs| - |ix\rangle\langle ix| - |xi\rangle\langle xi|, \quad (5)$$

where i includes frozen core orbitals. The amplitudes T_{kl}^{ij} of the explicitly correlated terms are determined by the wave function cusp conditions[4, 5], as proposed by Ten-no[6, 7]

$$T_{kl}^{ij \text{ FIX}} \equiv \frac{3}{8} \delta_{ik} \delta_{jl} + \frac{1}{8} \delta_{jk} \delta_{il}. \quad (6)$$

This is denoted either fixed amplitude (FIX) or SP-ansatz. According to this definition, the indices k, l can only take the values i, j or j, i , i.e., the ansatz is “diagonal” in the pair indices. This should be kept in mind when considering the following expressions, in which it is always assumed that T_{kl}^{ij} is restricted in this way.

To demonstrate how the proposed pair-specific geminal ansatz of Eq. (3) can be incorporated into MP2-F12 and CCSD-F12 methods, we will now recapitulate the relevant equations of such methods and show which changes have to be made. In MP2-F12, the conventional amplitudes T_{ab}^{ij} for the double excitations into virtual orbitals are computed as

$$T_{ab}^{ij} = -\frac{K_{ab}^{ij} + C_{ab}^{ij}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (7)$$

where ϵ_r are the Hartree-Fock (HF) orbital energies. The MP2-F12 energy is given by the Hylleraas functional

$$\mathcal{E}_{\text{MP2-F12}} = \left[\tilde{T}_{ab}^{ij} (K_{ab}^{ij} + C_{ab}^{ij}) + 2\mathcal{V}^{ij} + \mathcal{B}^{ij} - (\epsilon_i + \epsilon_j) \mathcal{X}^{ij} \right]. \quad (8)$$

with $\tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ab}^{ji}$. The matrix elements are defined as

$$K_{ab}^{ij} = \langle ab|r_{12}^{-1}|ij\rangle, \quad (9)$$

$$C_{ab}^{ij} = \langle ab|(\hat{f}_1 + \hat{f}_2)\hat{Q}_{12}F_{12}|kl\rangle T_{kl}^{ij}, \quad (10)$$

$$\mathcal{V}^{ij} = \tilde{T}_{kl}^{ij}\langle kl|F_{12}^{(ij)}\hat{Q}_{12}r_{12}^{-1}|ij\rangle, \quad (11)$$

$$\mathcal{B}^{ij} = \tilde{T}_{kl}^{ij}\langle kl|F_{12}^{(ij)}\hat{Q}_{12}\hat{f}_{12}\hat{Q}_{12}F_{12}^{(ij)}|mn\rangle T_{mn}^{ij}, \quad (12)$$

$$\mathcal{X}^{ij} = \tilde{T}_{kl}^{ij}\langle kl|F_{12}^{(ij)}\hat{Q}_{12}F_{12}^{(ij)}|mn\rangle T_{mn}^{ij}. \quad (13)$$

where $\hat{f}_{12} = \hat{f}_1 + \hat{f}_2$ are the Fock operators acting on the electron coordinates 1 and 2, and $\tilde{T}_{kl}^{ij} = 2T_{kl}^{ij} - T_{kl}^{ji}$. Explicit expressions to evaluate these quantities can be found, for example, in Ref. [26].

In the CCSD-F12a and F12b methods, the standard CCSD singles and doubles residuals r_a^i and R_{ab}^{ij} , respectively, are augmented by a few additional terms

$$r_a^{i,F12a} = r_a^i + \sum_k (2\mathcal{V}_{ak}^{ik} - \mathcal{V}_{ak}^{ki}) \quad (14)$$

$$R_{ab}^{ij,F12a} = R_{ab}^{ij} + \mathcal{V}_{ab}^{ij} + C_{ab}^{ij} - \mathcal{V}_{ak}^{ij}t_b^k - t_a^k\mathcal{V}_{bk}^{ij} \quad (15)$$

where

$$\mathcal{V}_{rs}^{ij} = \langle rs|r_{12}^{-1}\hat{Q}_{12}F_{12}^{(ij)}|kl\rangle T_{kl}^{ij}. \quad (16)$$

In order to simplify the evaluation of the latter quantity, the projector can be approximated by $\hat{Q}_{12} = 1 - |rs\rangle\langle rs|$, that is, the CABS contributions are neglected[21]. In MOLPRO, this approximation is made by default, even though the full projector can also be used[8]. The CCSD singles and doubles amplitudes t_a^i and T_{ab}^{ij} are optimized by solving the amplitude equations $r_a^{i,F12a} = 0$ and $R_{ab}^{ij,F12a} = 0$. The CCSD-F12a energy is then evaluated in analogy to eq. (8)

$$\mathcal{E}_{\text{CCSD-F12a}} = \left[\tilde{D}_{ab}^{ij}K_{ab}^{ij} + \tilde{T}_{ab}^{ij}C_{ab}^{ij} + 2\mathcal{V}^{ij} + \mathcal{B}^{ij} - (\epsilon_i + \epsilon_j)\mathcal{X}^{ij} \right]. \quad (17)$$

where

$$D_{rs}^{ij} = \sum_{ab} \delta_{ra}\delta_{rb}(T_{ab}^{ij} + t_a^i t_b^j) + \delta_{ri} \sum_b \delta_{sb} t_b^j + \delta_{sj} \sum_a \delta_{ra} t_a^i, \quad (18)$$

and $\tilde{D}_{ab}^{ij} = 2D_{ab}^{ij} - D_{ab}^{ji}$. The CCSD-F12b energy is defined as

$$\mathcal{E}_{\text{CCSD-F12b}} = \mathcal{E}_{\text{CCSD-F12a}} + \tilde{D}_{rs}^{ij}\mathcal{V}_{rs}^{ij}. \quad (19)$$

In the CCSD(F12*) approximation[25] some further terms, which involve CABS orbitals, are added to the CCSD residuals. In our spin-free closed-shell formulation

these read

$$R_{ab}^{ij,(F12^*)} = R_{ab}^{ij,F12a} + \mathcal{V}_{kl}^{ij} D_{ab}^{kl} - \mathcal{V}_k^i T_{ab}^{kj} - T_{ab}^{ik} \mathcal{V}_k^j + U_{ab}^{ij} + U_{ba}^{ji} \quad (20)$$

$$r_a^{i,(F12^*)} = r_a^{i,F12a} + u_a^i + \mathcal{F}_{ax}^{ik} f_x^k - \mathcal{V}_k^i t_a^{lk} \quad (21)$$

$$U_{ab}^{ij} = \tilde{\mathcal{F}}_{ax}^{ik} (K_{xb}^{kj} - \frac{1}{2} J_{xb}^{kj}) - \frac{1}{2} \mathcal{F}_{ax}^{ki} J_{xb}^{kj} - \mathcal{F}_{bx}^{ki} J_{xa}^{kj} \quad (22)$$

$$u_a^i = -\mathcal{F}_{ax}^{kl} l_x^{lk}, \quad (23)$$

where $\mathcal{V}_k^i = \sum_l \mathcal{V}_{kl}^{il}$ and $l_x^{kli} = 2K_{xi}^{kl} - K_{xi}^{lk}$. In this case the full projector is used to compute \mathcal{V}_{rs}^{ij} , which actually causes the largest part of the additional computational effort. Furthermore, the integrals $J_{xa}^{kl} = \langle kx | r_{12}^{-1} | lb \rangle$ need to be evaluated, which are not required in CCSD-F12a,b.

The (F12*) correction to the energy reads

$$E_{\text{CCSD}(F12^*)} = E_{\text{CCSD-F12b}} + U_{ab}^{ij} \tilde{T}_{ab}^{ij} + 2u_a^i t_a^i. \quad (24)$$

It should be noted that our CCSD(F12*) implementation in MOLPRO[30] differs from the CCSD(F12*) one of Hättig et al.[25] in TURBOMOLE by different density fitting approximations. In TURBOMOLE most integrals classes in the CCSD program are approximated by density fitting, while in MOLPRO they are computed exactly, and only the integrals involving F_{12} or CABS orbitals are density fitted. For this reason the two programs yield exactly the same results only in the limit of very large density fitting basis sets.

For all three CCSD-F12 approximations, the triples (T) energy correction is computed as in standard CCSD(T). It is not explicitly correlated. While a genuine F12 treatment for (T) has been proposed by Köhn[16], it has not yet been implemented in a production-level program.

Due to the “diagonal” ansatz with canonical orbitals used, the MP2-F12 expressions for different pairs ij are entirely decoupled, and for each pair only one $F_{12}^{(ij)}$ is needed. The B and X matrices are diagonal in the pair indices, i.e., only $B_{ij,ij}$ and $B_{ij,ji}$ are needed. The matrix elements for different ij may involve integrals over different geminals, but there are no integrals needed which involve two different geminals for a single ij , and there is only one B and one X matrix. This means that the MP2-F12 and CCSD(T)-F12x formalisms remains completely unchanged, once the integrals have been evaluated. However, the integrals involving $F_{12}^{(ij)}$ have to be computed for each value of $\gamma^{(ij)}$. We use density fitting approximations, and then only two-center and three center integrals are needed. The computational effort for their evaluation and transformation is roughly proportional to the number of different $\gamma^{(ij)}$ values. The most expensive step is the assembly of the 4-index integrals from 3-index quantities, which scales with $\mathcal{O}(N^5)$. The cost for this step is not affected by the pair-specific geminal treatment, since the number of final transformed integrals remains unchanged. Thus, the additional computational effort is small. It mainly depends on the efficiency of the 3-index integral evaluation, which is only a $\mathcal{O}(N^3)$ process.

In the current work a new integral code written by one of us (GK) has been employed. This code, denoted as *adaptive integral core* (AIC), is overall around 5–10 times faster for F12 integrals than our previous one[31, 32]. For the integration, the F12 Slater geminal of eq. (3) is approximated by a linear combination of six Gaussian geminals[26]. The integrals are evaluated with a variant of the Obara-Saika scheme[33–35] in Ahlrichs’ three-center solid harmonic modification[36]. The

integral kernel functions $G_m(\rho, T)$ necessary for contracted Gaussian geminals are documented in Ref. [37]. For some F12 integral classes, up to 70% of the total integration time are spent evaluating the scalar $G_m(\rho, T)$ kernels, and in these cases some computational savings (up to around 20%) are possible by employing generally contracted Gaussian geminals with shared exponents. These are supported in the new integral code. In this work, however, the Slater geminals are fitted independently to six Gaussians each, as described in Ref. [26], with non-shared exponents. In this case the cost of the raw F12 integral evaluation rises in proportion to the number of exponents used.

In order to keep the integral evaluation cost to a minimum, we only distinguish core-core, core-valence, and valence-valence pairs. One can either use three different geminal exponents for these classes, or treat core-core and core-valence pairs with the same geminal exponent. As will be shown later this is justified, since the core-core pairs usually have a negligible effect on energy differences and molecular properties.

A final note concerns the use of non-canonical orbitals or open-shell cases using spin-restricted Hartree-Fock (RHF) reference functions. In these cases the Fock matrix is not diagonal any more, and the MP2-F12 equations have to be solved iteratively[8, 26]. In the energy expression of Eq. (17), only the term containing eigenvalues needs to be modified, according to

$$-(\epsilon_i + \epsilon_j)\mathcal{X}^{ij} \rightarrow -(\mathcal{X}_{ik}^{ij} f_{kj} + f_{ik}\mathcal{X}_{kj}^{ij}) \quad (25)$$

with

$$\mathcal{X}_{kl}^{ij} = T_{mn}^{ij} \langle mn | F_{12}^{(ij)} \hat{Q}_{12} F_{12}^{(kl)} | op \rangle T_{op}^{kl}. \quad (26)$$

Using the projector in eq. (5) the matrix elements are evaluated as

$$\begin{aligned} \langle mn | F_{12}^{(ij)} \hat{Q}_{12} F_{12}^{(kl)} | op \rangle &= \langle mn | F_{12}^{(ij)} F_{12}^{(kl)} | op \rangle \\ &\quad - \langle mn | F_{12}^{(ij)} | rs \rangle \langle rs | F_{12}^{(kl)} | op \rangle \\ &\quad - \langle mn | F_{12}^{(ij)} | ix \rangle \langle ix | F_{12}^{(kl)} | op \rangle \\ &\quad - \langle mn | F_{12}^{(ij)} | xi \rangle \langle xi | F_{12}^{(kl)} | op \rangle. \end{aligned} \quad (27)$$

Thus, in this case we need the integrals $\langle mn | F_{12}^{(ij)} F_{12}^{(kl)} | op \rangle$ involving two different geminals. Using robust density fitting these are computed as[31, 38]

$$\begin{aligned} \langle mn | F_{12}^{(ij)} F_{12}^{(kl)} | op \rangle &= (mn | F_{12}^{(ij)} F_{12}^{(kl)} | A) d_{op}^A + d_{mn}^A (op | F_{12}^{(ij)} F_{12}^{(kl)} | A) \\ &\quad - d_{mn}^A \langle A | F_{12}^{(ij)} F_{12}^{(kl)} | B \rangle d_{op}^B, \end{aligned} \quad (28)$$

where d_{mn}^A are the fitting coefficients obtained by solving the linear equations

$$(A | r_{12}^{-1} | B) d_{mn}^B = (mn | r_{12}^{-1} | A), \quad (29)$$

and the integrals for a kernel \hat{O} are defined as

$$(A|\hat{O}|B) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_A(\mathbf{r}_1) \hat{O} \chi_B(\mathbf{r}_2), \quad (30)$$

$$(mn|\hat{O}|A) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_m(\mathbf{r}_1) \chi_n(\mathbf{r}_1) \hat{O} \chi_A(\mathbf{r}_2). \quad (31)$$

Note that the fitting coefficients are independent of the geminal exponent and need to be computed only once.

The method described above is orbital-invariant within the core, closed-shell valence, and open-shell valence subspaces. Of course, due to the different geminal exponents, it is not invariant with respect to orbital rotations between the core and valence orbitals.

3. Applications

In order to test the method, we have computed energies and spectroscopic constants for a number of diatomic molecules, namely Br_2 ($X^1\Sigma_g^+$), As_2 ($X^1\Sigma_g^+$), Ga_2 ($X^3\Pi_u$), Cu_2 ($X^1\Sigma_g^+$), GaCl ($X^1\Sigma^+$), CuCl ($X^1\Sigma^+$), and CuBr ($X^1\Sigma^+$). In all these cases core-valence correlation effects are significant, in particular on the equilibrium bond lengths. Here we define “core” to be the $3d$ orbitals; correlation of the $3s$ and $3p$ orbitals in Br, As, Ga, and Cu has a very small effect on the results and has therefore not been included. For Br, As, and Ga we used newly optimized cc-pVnZ-F12-PP orbital basis sets of Peterson and Hill[39], along with their associated OPTRI sets for CABS construction and MP2FIT sets for density fitting. All OPTRI basis sets include basis functions up to $l = 6$ (i), as required to treat the correlation of d -electrons. However, the relative energies were found to be rather insensitive to the high angular momentum functions, and 1-2 i functions are sufficient (the VDZ-F12/OPTRI sets contain one i , the VTZ-F12/OPTRI and VQZ-F12/OPTRI sets two i functions). Similar basis sets for treating core-valence correlation effects were recently published by Hill et al. for lighter atoms[40]. For simplicity, these basis sets will be denoted VnZ-F12 in the following. For Cu we used the aug-cc-pVnZ-PP basis[41] sets along with their OPTRI counterparts[42]. In this case Hättig’s MP2FIT sets[43] were used. Finally, for Cl the aug-cc-pV($n + d$)Z OBSs (with additional steep d -functions[44]) and the corresponding OPTRI basis sets[45] were employed. Robust density fitting approximations[31, 32] were used to compute all F_{12} -dependent integrals, as well as all other integrals involving CABS orbitals. In all cases the Fock matrix in the combined OBS/CABS basis, which is needed in MP2-F12, was density fitted using the QZVPP/JKFIT basis sets of Weigend[46]. All other integrals that occur in the MP2-F12 and CCSD-F12x equations (including the Fock matrix in the OBS) were computed exactly without density fitting. The small-core pseudopotentials (ECP10MDF) of Stoll, Dolg and co-workers[47–49] were used for the heavy atoms (not for Cl). Since the pseudopotentials do not commute with the correlation factor, they were treated in the MP2-F12 exactly as the exchange contribution, as noted by Bischoff *et al.* [50]. In the open-shell coupled-cluster calculations we used the partially spin-restricted RCCSD(T) method[8, 51], using spin restricted open-shell Hartree-Fock reference functions.

In the case of GaCl, a slight complication arises because the Cl ($3s$) orbital mixes significantly with the Ga ($3d_0$) one. This causes poor results if either just the valence orbitals (without $3d$) are correlated, or when valence and $3d$ orbitals

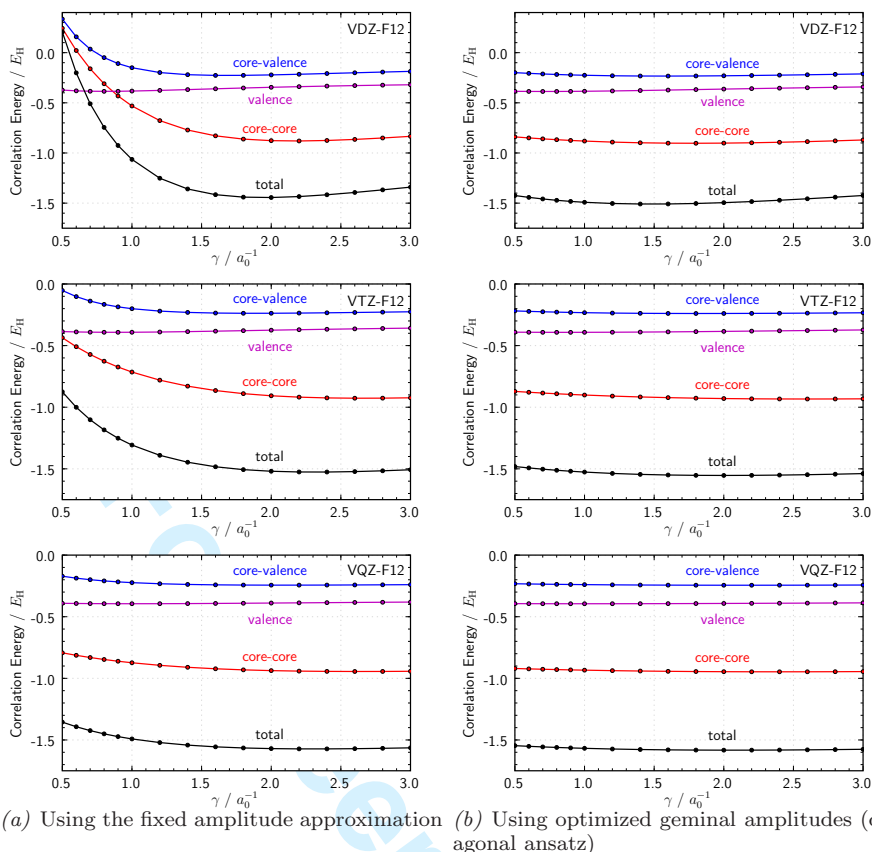


Figure 1. Dependence of the MP2-F12 core-core, core-valence and valence energy contributions of the correlation energy of Br_2 ($r=2.281 \text{ \AA}$) on the parameter γ .

are treated with different geminal exponents. This problem can be avoided by a 2×2 Boys localization of the Cl ($3s$) and Ga ($3d_0$) orbitals. One must then use the orbital invariant form of the MP2-F12 equations (c.f. previous section). Before computing the perturbative (T) triples correction, the orbitals are re-canonicalized, and the CCSD amplitudes are transformed accordingly. A similar problem occurs for CuCl and CuBr, but in these cases the Cl ($3p$) and Ga ($3d$) orbitals mix. Again, localization was used to reduce the mixing as much as possible.

We will first consider the core-core (cc), core-valence (cv) and valence (vv) correlation contributions as function of the geminal exponent. A similar analysis has been performed by Bischoff *et al.* at the level of MP2-F12 theory[50]. Since the MP2-F12 pair energies are uncoupled, the exponents for the different classes can be optimized independently (in the cases with localized orbitals and in the open-shell case of Ga_2 this is only approximately true). The dependence of the correlation energy contributions on the geminal exponent is shown for Br_2 in Fig. 1.

It is strongest for the cc energy contribution. For small exponents γ and the cc-pVDZ-F12 basis set, the energy contribution even becomes positive. This is a consequence of the fixed amplitude approximation and the fact that the energy is computed using the variational Hylleraas functional. The dependence on γ is very much reduced if the geminal coefficients T_{ij}^{ij} and T_{ji}^{ij} are optimized, as is demonstrated in Fig. 1. This optimization is easy at the MP2-F12 level, but difficult and expensive for CCSD-F12. One way out is to use the optimized MP2-F12 amplitudes as fixed parameters in the CCSD-F12. Even though this approximation is more pragmatic than well justified, it works quite well, as will be shown in another forthcoming publication[52]. In the current work we will stick to the fixed

Table 1. Comparison of MP2-F12 correlation energy contributions for Br₂, $r=2.281$ Å

β^a	E_{cc}	E_{cv}	E_{vv}	E_{corr}
cc-pVDZ-F12:				
none	-0.348225	-0.106380	-0.286396	-0.741001
1.25	-0.704926	-0.205413	-0.374249	-1.284588
0.8,1.7	-0.847970	-0.227079	-0.385674	-1.460722
0.8,1.7,2.2	-0.880350	-0.227079	-0.385674	-1.493103
cc-pVTZ-F12:				
none	-0.615204	-0.174067	-0.330602	-1.119874
1.4	-0.829053	-0.230702	-0.386580	-1.446335
0.9,1.9	-0.899375	-0.237835	-0.392111	-1.529321
0.9,1.9,2.6	-0.926908	-0.237835	-0.392111	-1.556854
cc-pVQZ-F12:				
none	-0.758205	-0.207960	-0.362500	-1.328665
1.4	-0.910334	-0.238061	-0.393400	-1.541795
1.0,2.1	-0.939559	-0.243764	-0.394562	-1.577885
1.0,2.1,2.7	-0.944325	-0.243764	-0.394562	-1.582652

^aThe first, second, and third values are for vv , cv , cc pairs, respectively. If less than 3 values are given, the last value is also used for the missing ones.

amplitude ansatz.

In Tables 1–4 we present the correlation energies computed with up to 3 different geminal exponents for the vv , cv , and cc pairs, respectively. In case with 2 exponents, the cc and cv pairs are treated with the same exponent. The exponents were roughly optimized for each class by running MP2-F12 calculations for a range of γ values between 0.5 and 3.0 a_0^{-1} , as shown in Fig. 1 for Br₂. If only a single exponent is used for all pairs, an average value for the vv and cv is employed. Note that the chosen values do not maximize the total correlation energy, which is dominated by the cc contribution. The latter does not have a large effect on the molecular properties, and it is therefore more important to choose appropriate geminals for the vv and cv contributions. An exception is Cu₂. Due to the diffuse nature of the 4s "valence" orbital the corresponding optimized exponent is very small. If only a single geminal exponent is used, the results for the spectroscopic constants are rather sensitive to its choice, and we found that larger exponents, which are more appropriate for correlation of the d -shell, improve the results. For simplicity, we used the exponent optimized for the cv energy contribution in this case.

The results show the expected trends: The optimized geminal exponents are smallest for the vv and largest for the cc correlation contributions. They increase with increasing nuclear charge, i.e. from left to right in the periodic table. They also increase with increasing OBS, since for large basis sets the role of the geminals is mainly to improve the cusp region for small r_{12} , while for small basis sets they also help to model a larger range of the correlation hole. We note that the geminal exponents should not be optimized using the CCSD-F12x approximations. Since in these methods an approximate Lagrangian is used to compute the energy, which is not variational as the Hylleraas functional for MP2-F12, artificial results may result.

The effect of the explicit correlation treatment on the correlation energies is quite dramatic, in particular for the double- ζ basis set. For Br₂ and As₂ the standard MP2 with the VDZ-F12 basis set recovers less than 40% of the cc correlation energies. This is due to the fact that these bases were not devised for cv and cc correlation without including F12; they contain only very few additional functions for correlating the d -shell. For a proper treatment of cc and cv effects without F12, the much larger aug-cc-pwCVnZ-PP basis sets[53] would be needed. In contrast

Table 2. Comparison of MP2-F12 correlation energy contributions for As₂, r=2.094 Å

β^a	E_{cc}	E_{cv}	E_{vv}	E_{corr}
cc-pVDZ-F12:				
none	-0.365514	-0.098149	-0.237425	-0.701089
1.20	-0.761724	-0.172542	-0.282661	-1.216927
0.75,1.50	-0.862881	-0.181837	-0.290339	-1.335056
0.75,1.50,2.0	-0.904589	-0.181837	-0.290339	-1.376764
cc-pVTZ-F12:				
none	-0.569346	-0.138765	-0.262744	-0.970856
1.2	-0.796320	-0.179895	-0.291208	-1.267423
0.8,1.6	-0.895576	-0.188822	-0.293300	-1.377698
0.8,1.6,2.2	-0.936038	-0.188822	-0.293300	-1.418160
cc-pVQZ-F12:				
none	-0.788728	-0.171469	-0.277584	-1.237780
1.4	-0.927424	-0.191992	-0.293235	-1.412650
1.0,2.1	-0.953087	-0.194372	-0.294394	-1.441854
1.0,2.1,2.7	-0.961590	-0.194372	-0.294394	-1.450356

^a The first, second, and third values are used for *vv*, *cv*, *cc* pairs, respectively. If less than 3 values are given, the last value is also used for the missing ones.

Table 3. Comparison of MP2-F12 correlation energy contributions for Ga₂, r=2.65 Å

β^a	E_{cc}	E_{cv}	E_{vv}	E_{corr}
cc-pVDZ-F12:				
none	-0.436434	-0.076403	-0.087732	-0.600570
1.00	-0.758908	-0.123747	-0.100080	-0.982734
0.7,1.30	-0.892358	-0.132306	-0.101460	-1.126123
0.7,1.3,1.75	-0.939597	-0.132305	-0.101460	-1.173363
cc-pVTZ-F12:				
none	-0.613708	-0.1075658	-0.094895	-0.816168
1.1	-0.843933	-0.133778	-0.102076	-1.079786
0.8,1.40	-0.930319	-0.138097	-0.102507	-1.170924
0.8,1.4,2.0	-0.974577	-0.138097	-0.102507	-1.215183
cc-pVQZ-F12:				
none	-0.771407	-0.126497	-0.098796	-0.996700
1.3	-0.941749	-0.140226	-0.102655	-1.184630
0.9,1.7	-0.982998	-0.141579	-0.102879	-1.227457
0.9,1.7,2.3	-0.998691	-0.141579	-0.102879	-1.243150

^a The first, second, and third values are used for *vv*, *cv*, *cc* pairs, respectively. If less than 3 values are given, the last value is also used for the missing ones.

to standard MP2, the MP2-F12 method recovers with just one geminal exponent about 75-80% and with the optimized exponent for core correlation 93-94% of the *cc* correlation energies, using the small VDZ-F12 basis (as compared to the best MP2-F12/VQZ-F12 energies). For Cu₂ the effect is less dramatic, since the aug-cc-pVnZ-PP basis set used in this case includes functions for *d*-correlation. Nevertheless, there is still a significant improvement by the F12-treatment, and using optimized geminal exponents for *vv*, *cv*, and *vv* leads to quite impressive energy lowerings. Of course, these effects become less pronounced for the larger triple- ζ and quadruple- ζ basis sets.

The computed equilibrium distances, harmonic and anharmonic vibrational frequencies ω_e as well as dissociation energies D_e of the homonuclear diatomics are presented in Tables 5–8. These were obtained from polynomial fits of 8th degree to 9 points in the range $r_e - 0.4$ Å to $r_e + 0.7$ Å. The core-valence correlation effects reduce the equilibrium distances and increase the harmonic wavenumbers significantly. As for the energies, the convergence with the basis set size is slow without

Table 4. Comparison of MP2-F12 correlation energy contributions for Cu_2 , $r=2.22$ Å

β^a	E_{cc}	E_{cv}	E_{vv}	E_{corr}
cc-pVDZ-F12:				
none	-0.897994	-0.066005	-0.018568	-0.982567
1.0	-1.040207	-0.079914	-0.020312	-1.140433
0.55,1.0	-1.040207	-0.079914	-0.020612	-1.140732
0.55,1.0,1.9	-1.108529	-0.079914	-0.020612	-1.209055
cc-pVTZ-F12:				
none	-1.020649	-0.077546	-0.019367	-1.117562
1.0	-1.104856	-0.083657	-0.020562	-1.209076
0.55,1.0	-1.104856	-0.083657	-0.020753	-1.209266
0.55,1.0,2.0	-1.127407	-0.083657	-0.020753	-1.231817
cc-pVQZ-F12:				
none	-1.081396	-0.081754	-0.019867	-1.183016
1.0	-1.127094	-0.085079	-0.020692	-1.232865
0.55,1.0	-1.127094	-0.085079	-0.020811	-1.232983
0.55,1.0,2.2	-1.136112	-0.085079	-0.020811	-1.242001

^aThe first, second, and third values are used for vv , cv , cc pairs, respectively. If less than 3 values are given, the last value is also used for the missing ones.

Table 5. Computed CCSD(T)-F12b spectroscopic constants for Br_2 with different numbers of geminals. The geminal exponents are the same as in Table 1. r_e in Å, ω_e and $\omega_e x_e$ in cm^{-1} , D_e in eV.

Basis	Geminals	r_e	ω_e	$\omega_e x_e$	D_e
VDZ-F12	0	2.3211	305.6	1.02	1.88
VTZ-F12	0	2.2994	320.6	1.04	2.09
VQZ-F12	0	2.2884	325.8	1.00	2.19
VDZ-F12	1	2.2815	326.8	1.02	2.19
VTZ-F12	1	2.2806	328.0	1.03	2.22
VQZ-F12	1	2.2775	330.1	1.01	2.26
VDZ-F12	2	2.2756	331.0	1.02	2.26
VTZ-F12	2	2.2790	328.7	1.02	2.24
VQZ-F12	2	2.2767	330.4	1.01	2.26
VDZ-F12	3	2.2758	330.9	1.02	2.26
VTZ-F12	3	2.2789	328.7	1.02	2.24
VQZ-F12	3	2.2767	330.4	1.01	2.26
aug-wCV[Q5]Z-PP	0	2.2740	331.2	0.99	2.23
Experiment ^a		2.2811	325.3	1.08	2.14

^a D_e value corrected for spin-orbit effect

explicit correlation (denoted 0 geminals in the tables), and very much improved by the F12 treatment. Taking Br_2 as an example, the standard CCSD(T) calculation with VDZ-F12 basis yields a distance that is 0.047 Å too long. This error is reduced by the F12-treatment to 0.008 and 0.002 Å with 1 or 2 geminal exponents, respectively. Using a separate exponent for the cc correlation has only a very minor effect. Already with a single geminal exponent the F12 values with VDZ-F12 are better than the conventional ones with VQZ-F12 basis. Further increase of the basis set to VQZ-F12 leads only to a shortening by 0.001 Å. The effects are qualitatively similar for the other molecules. For Cu_2 , where the OBS is designed to include d -correlation effects, the improvements by the F12 terms are somewhat smaller, but there is still a significant effect, in particular for the smaller basis sets. Overall, the results clearly show that using an optimized geminal exponent for cv correlation leads to an improvement, while the third exponent for cc correlation has only a minor effect.

A significant improvement by the F12 treatment is also found for the vibrational

Table 6. Computed CCSD(T)-F12b spectroscopic constants for As_2 with different numbers of geminals. The geminal exponents are the same as in Table 2. r_e in Å, ω_e and $\omega_e x_e$ in cm^{-1} , D_e in eV.

Basis	Geminals	r_e	ω_e	$\omega_e x_e$	D_e
VDZ-F12	0	2.1129	420.4	1.04	3.33
VTZ-F12	0	2.1089	425.8	0.97	3.64
VQZ-F12	0	2.0987	432.3	0.96	3.84
VDZ-F12	1	2.0943	435.7	1.03	3.81
VTZ-F12	1	2.0963	434.9	0.99	3.91
VQZ-F12	1	2.0921	438.3	0.98	3.98
VDZ-F12	2	2.0937	437.2	1.02	3.86
VTZ-F12	2	2.0945	436.2	0.99	3.92
VQZ-F12	2	2.0917	438.7	0.98	3.98
VDZ-F12	3	2.0944	436.7	1.01	3.86
VTZ-F12	3	2.0951	435.9	0.99	3.92
VQZ-F12	3	2.0918	438.6	0.98	3.98
aug-wCV[Q5]Z-PP	0	2.0902	440.5	0.99	4.03
Experiment		2.1026	429.6	1.12	3.99

Table 7. Computed CCSD(T)-F12b spectroscopic constants for Ga_2 with different numbers of geminals. The geminal exponents are the same as in Table 3. r_e in Å, ω_e and $\omega_e x_e$ in cm^{-1} , D_e in eV.

Basis	Geminals	r_e	ω_e	$\omega_e x_e$	D_e
aug-cc-pVDZ-PP	0	2.6798	164.5	0.58	1.22
aug-cc-pVTZ-PP	0	2.6751	169.6	0.57	1.30
aug-cc-pVQZ-PP	0	2.6561	172.7	0.59	1.34
aug-cc-pVDZ-PP	1	2.6556	172.2	0.66	1.27
aug-cc-pVTZ-PP	1	2.6533	173.4	0.59	1.33
aug-cc-pVQZ-PP	1	2.6480	174.2	0.59	1.35
aug-cc-pVDZ-PP	2	2.6499	172.9	0.63	1.30
aug-cc-pVTZ-PP	2	2.6521	173.2	0.59	1.33
aug-cc-pVQZ-PP	2	2.6483	174.0	0.59	1.35
aug-cc-pVDZ-PP	3	2.6521	172.5	0.63	1.30
aug-cc-pVTZ-PP	3	2.6543	173.0	0.59	1.33
aug-cc-pVQZ-PP	3	2.6492	173.9	0.59	1.35
aug-wCV[Q5]Z-PP	0	2.6464	174.4	0.57	1.36

Table 8. Computed CCSD(T)-F12b spectroscopic constants for Cu_2 with different numbers of geminals. The geminal exponents are the same as in Table 4. r_e in Å, ω_e and $\omega_e x_e$ in cm^{-1} , D_e in eV.

Basis	Geminals	r_e	ω_e	$\omega_e x_e$	D_e
aug-cc-pVDZ-PP	0	2.2357	258.1	0.94	1.93
aug-cc-pVTZ-PP	0	2.2213	266.1	1.04	1.97
aug-cc-pVQZ-PP	0	2.2166	266.7	1.03	2.00
aug-cc-pVDZ-PP	1	2.2222	264.5	1.00	2.01
aug-cc-pVTZ-PP	1	2.2162	267.9	1.03	2.01
aug-cc-pVQZ-PP	1	2.2146	267.8	1.02	2.02
aug-cc-pVDZ-PP	2	2.2227	264.4	1.00	2.00
aug-cc-pVTZ-PP	2	2.2162	267.9	1.03	2.01
aug-cc-pVQZ-PP	2	2.2145	267.9	1.02	2.02
aug-cc-pVDZ-PP	3	2.2203	263.0	1.00	1.99
aug-cc-pVTZ-PP	3	2.2159	267.1	1.03	2.00
aug-cc-pVQZ-PP	3	2.2143	267.4	1.03	2.01
aug-cc-pV[Q5]Z-PP	0	2.2146	268.6	1.01	2.03
Experiment		2.2197	264.6	1.02	

Table 9. Computed spectroscopic constants of homonuclear diatomics using different CCSD(T)-F12x approximations with 3 geminals (see text) ω_e and $\omega_e x_e$ in cm^{-1} .

Basis	Method	$R_e/\text{\AA}$	ω_e	$\omega_e x_e$
Br ₂ :				
cc-pVDZ-F12	F12a	2.2764	330.7	1.02
cc-pVTZ-F12	F12a	2.2793	328.8	1.02
cc-pVQZ-F12	F12a	2.2767	330.5	1.01
cc-pVDZ-F12	F12b	2.2758	330.9	1.02
cc-pVTZ-F12	F12b	2.2794	328.5	1.02
cc-pVQZ-F12	F12b	2.2769	330.3	1.01
cc-pVDZ-F12	(F12*)	2.2759	333.2	0.98
cc-pVTZ-F12	(F12*)	2.2766	331.7	1.00
cc-pVQZ-F12	(F12*)	2.2752	332.0	1.00
aug-wCV[Q5]Z-PP		2.2740	331.2	0.99
As ₂ :				
cc-pVDZ-F12	F12a	2.0935	437.5	1.01
cc-pVTZ-F12	F12a	2.0941	436.9	0.98
cc-pVQZ-F12	F12a	2.0915	439.0	0.98
cc-pVDZ-F12	F12b	2.0939	436.9	1.02
cc-pVTZ-F12	F12b	2.0949	436.0	0.99
cc-pVQZ-F12	F12b	2.0920	438.6	0.98
cc-pVDZ-F12	(F12*)	2.0909	442.6	0.97
cc-pVTZ-F12	(F12*)	2.0921	440.4	0.96
cc-pVQZ-F12	(F12*)	2.0905	440.6	0.96
aug-wCV[Q5]Z-PP		2.0902	440.5	0.99
Cu ₂ :				
aug-cc-pVDZ-PP	F12a	2.2159	264.0	1.00
aug-cc-pVTZ-PP	F12a	2.2142	267.1	1.03
aug-cc-pVQZ-PP	F12a	2.2135	266.6	1.02
aug-cc-pVDZ-PP	F12b	2.2181	262.7	1.01
aug-cc-pVTZ-PP	F12b	2.2149	266.5	1.03
aug-cc-pVQZ-PP	F12b	2.2138	266.4	1.02
aug-cc-pVDZ-PP	(F12*)	2.2201	261.5	1.00
aug-cc-pVTZ-PP	(F12*)	2.2159	266.0	1.02
aug-cc-pVQZ-PP	(F12*)	2.2143	266.1	1.02
aug-cc-pV[Q5]Z-PP		2.2146	268.6	1.02

frequencies. However, for these properties the use of different geminal exponents seems to be less important. It appears that the largest part of the improvement comes from the valence shell. One may note that both for equilibrium distances and for harmonic frequencies the VDZ-F12 results for Br₂, As₂ and Ga₂ seem slightly better than the VTZ-F12 ones. This has also been observed by Peterson and Hill[39] and is probably due to some fortuitous error cancellation due to intramolecular BSSE effects. If the much larger aug-cc-pwCVnZ-PP basis sets are used, a smooth convergence pattern is found.

A drawback of the calculations shown so far is the dependence of the optimum geminal exponents on the atom or molecule. In calculations for molecules containing different heavy atoms one will have to use compromise values. In Tables 9 and 10 we compare results for the dimers and some halides obtained the same set of three exponents for all molecules. These were chosen to be (0.8,1.5,1.9), (0.9,1.6,2.2), and (1.0,1.7,2.3) for double- ζ , triple- ζ , and quadruple- ζ , respectively. Using these values the equilibrium distances and harmonic wave numbers change at most by 0.001 Å and 1.2 cm^{-1} , respectively, even for the double- ζ basis sets.

Table 10. Computed spectroscopic constants of gallium and copper halides using different CCSD(T)-F12x approximations with 3 geminals (see text). ω_e and $\omega_e x_e$ in cm^{-1} .

Basis	Method	$R_e/\text{\AA}$	ω_e	$\omega_e x_e$
GaCl:				
cc-pVDZ-F12	F12a	2.2017	366.9	1.26
cc-pVTZ-F12	F12a	2.2041	364.6	1.25
cc-pVQZ-F12	F12a	2.2026	365.7	1.25
cc-pVDZ-F12	F12b	2.2008	367.8	1.27
cc-pVTZ-F12	F12b	2.2038	364.9	1.25
cc-pVQZ-F12	F12b	2.2026	365.8	1.25
cc-pVDZ-F12	(F12*)	2.2025	367.3	1.27
cc-pVTZ-F12	(F12*)	2.2042	365.3	1.25
cc-pVQZ-F12	(F12*)	2.2024	366.1	1.25
aug-wCV[Q5]Z-PP		2.2000	367.4	1.27
Experiment		2.2017	365.3	1.2
CuCl ^a :				
cc-pVDZ-F12	F12a	2.0521	415.8	1.60
cc-pVTZ-F12	F12a	2.0486	417.7	1.61
cc-pVQZ-F12	F12a	2.0470	418.2	1.62
cc-pVDZ-F12	F12b	2.0531	414.4	1.58
cc-pVTZ-F12	F12b	2.0489	417.2	1.61
cc-pVQZ-F12	F12b	2.0470	418.0	1.61
cc-pVDZ-F12	(F12*)	2.0559	413.0	1.56
cc-pVTZ-F12	(F12*)	2.0497	416.8	1.59
cc-pVQZ-F12	(F12*)	2.0471	418.0	1.61
aug-wCV[Q5]Z-PP		2.0471	418.8	1.59
Experiment		2.0512	415.3	1.58
CuBr ^a :				
cc-pVDZ-F12	F12a	2.1716	313.8	0.93
cc-pVTZ-F12	F12a	2.1684	315.8	0.96
cc-pVQZ-F12	F12a	2.1669	316.0	0.94
cc-pVDZ-F12	F12b	2.1732	312.4	0.92
cc-pVTZ-F12	F12b	2.1688	315.2	0.95
cc-pVQZ-F12	F12b	2.1669	315.8	0.94
cc-pVDZ-F12	(F12*)	2.1757	311.7	0.91
cc-pVTZ-F12	(F12*)	2.1696	315.2	0.94
cc-pVQZ-F12	(F12*)	2.1670	315.9	0.94
aug-cc-p[Q5]Z-PP		2.1663	316.4	0.94
Experiment		2.1734	314.8	0.96

^aFor Cu the same basis sets as in Table 4 have been used

In most cases the changes are even smaller. An exception is Cu_2 with the aug-cc-pVDZ-PP basis set; in this case the distance shortens by 0.003 Å, but the values in Table 9 with the compromise exponents are more accurate than those in Table 8. As already noted earlier, the larger exponents yield better results for Cu_2 .

In Tables 9 and 10 we also compare the CCSD(T)-F12a, -F12b, and (F12*) approximations. Since currently we have only a closed-shell implementation of CCSD(F12*), there are no dissociation energies and open-shell molecules in this comparison. The F12a and F12b approximations yield very similar results in all cases. The differences to (F12*) are somewhat larger; naturally, they decrease with increasing basis set. No clear conclusion is possible about which is the most accurate method; for Br_2 , As_2 the (F12*) results for the DZ and TZ basis sets look slightly better, but the opposite appears to be the case for Cu_2 and the halides. We also found in other cases that the relative accuracy of the various

F12 approximations depends on the molecule and considered property, but the differences between these methods are usually smaller than the intrinsic error of the CCSD(T) method at its CBS limit. One may therefore safely use the F12b approximation, which is computationally significantly cheaper than (F12*).

In the Tables we also reported results obtained by extrapolating the correlation energies obtained with the large aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets (aug-cc-pVQZ-PP and aug-cc-pV5Z-PP in case of Cu₂) using $E_n = E_{\text{CBS}} + A/n^3$, where n is the cardinal number of the basis set. The best F12 results are quite close to the extrapolated values, but it is not clear which results are more accurate. According to previous experience, it may well be that the quadruple- ζ F12 results are closer to the true basis set limits than the extrapolated ones. It should be noted, however, that the triples contributions are not explicitly correlated, and therefore introduce some remaining basis set truncation errors.

A final note concerns the comparison of the CCSD(T)-F12b values with the experimental values. Despite the fact that the VQZ-F12 results should be very close to the basis set limits, the deviations from the experimental values are quite large. This is due to surprisingly large contributions of higher excitations; for example, the CCSDTQ – CCSD(T) correction for the equilibrium distances of Br₂ and As₂ amounts to about 0.0024 Å and 0.0043 Å, respectively, and even this does not cover the full contribution of higher excitations. The effect comes mainly from the valence electrons, and is probably due to the rather small HOMO-LUMO gap in these molecules. In contrast to CCSD(T), internally contracted MRCI calculations[54] with full valence CASSCF reference functions yields excellent agreement with experimental values, if the $cc+cv$ corrections are added. A more detailed investigation of these effects will be published elsewhere[52].

4. Conclusions

A modification of the MP2-F12 and CCSD-F12x methods has been proposed and tested, in which different geminal exponents are used for the correlation of core-core, core-valence and pure valence orbital pairs. It has been demonstrated for a number of diatomic molecules involving d -shell correlation that this leads to much improved correlation energies and molecular properties. Most important is an additional exponent for core-valence correlation, while the pure core-core correlation has—despite its huge contribution to the correlation energy—hardly any effect on the equilibrium distances and vibrational frequencies. The additional computational cost for using two or three exponents is rather small, since only terms that scale with $\mathcal{O}(N^3)$ and $\mathcal{O}(N^4)$ are affected. The dominating $\mathcal{O}(N^5)$ terms in MP2-F12 and $\mathcal{O}(N^6)$ ones in CCSD-F12 are entirely unchanged.

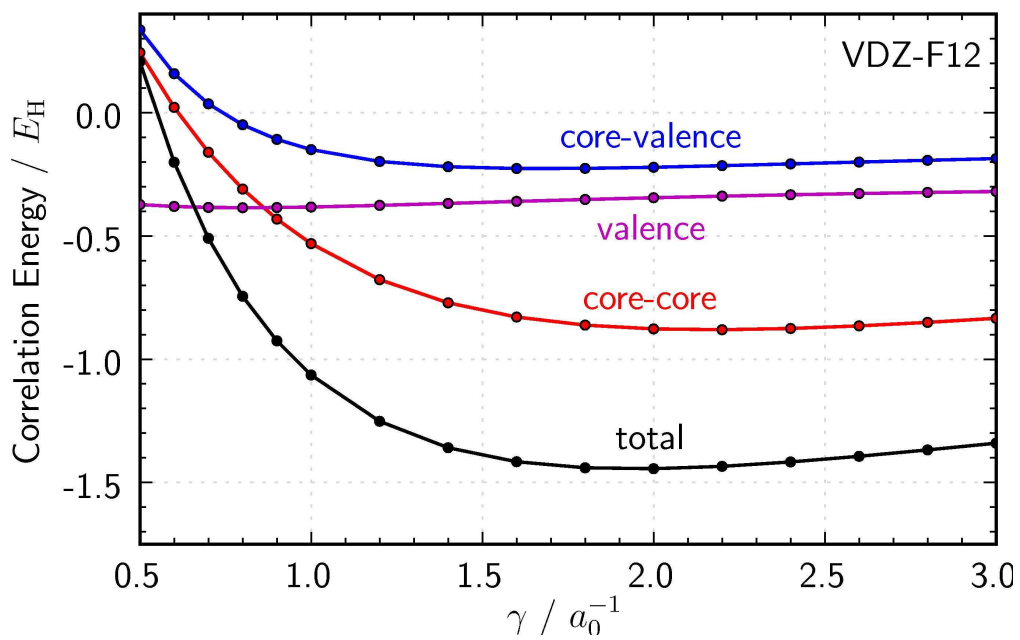
The results demonstrate that F12 methods are extremely well suited to treat inner-shell correlation effects and eliminate the frustratingly slow convergence of core-valence effects with basis set size. This makes it possible to use much smaller orbital basis sets than in standard CCSD(T) calculations. The new cc-pVnZ-F12-PP basis sets of Peterson and Hill, which have been used here for Br, As, and Ga, are only marginally larger than pure valence basis sets; they just include one additional steep d and one f function. Our results show that with appropriately chosen geminal exponents near basis set limit results are obtained at the triple- ζ level. Even with just double- ζ basis sets very good accuracy is achieved. Thus, it can be expected that the current method will be very useful, e.g. for transition metal complexes, as long as there is a clear distinction between core and valence orbitals. Further systematic studies for transition metal compounds are under way.

Acknowledgments

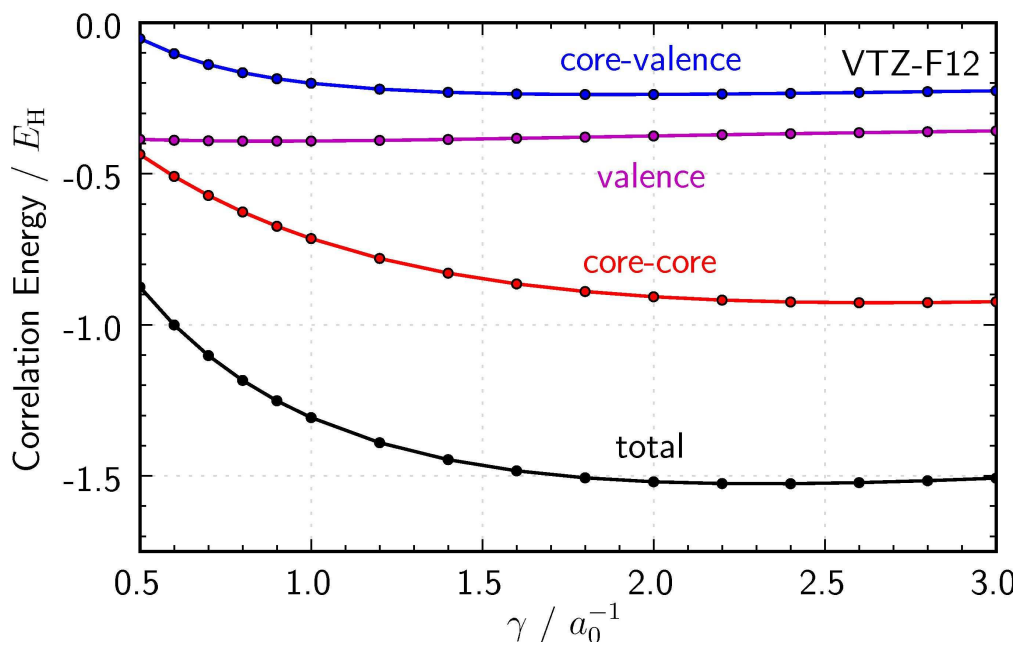
This work was funded by the DFG as part of a NSF-DFG grant and by the Stuttgart SimTech Cluster of Excellence. HJW also acknowledges generous support from the Fonds der Chemischen Industrie. We are grateful to Kirk Peterson and Grant Hill for providing their new basis sets prior to publication and for many helpful discussions. HJW thanks C. Hättig and D. Tew for providing test results for their (F12*) method, which were very useful for debugging our implementation.

References

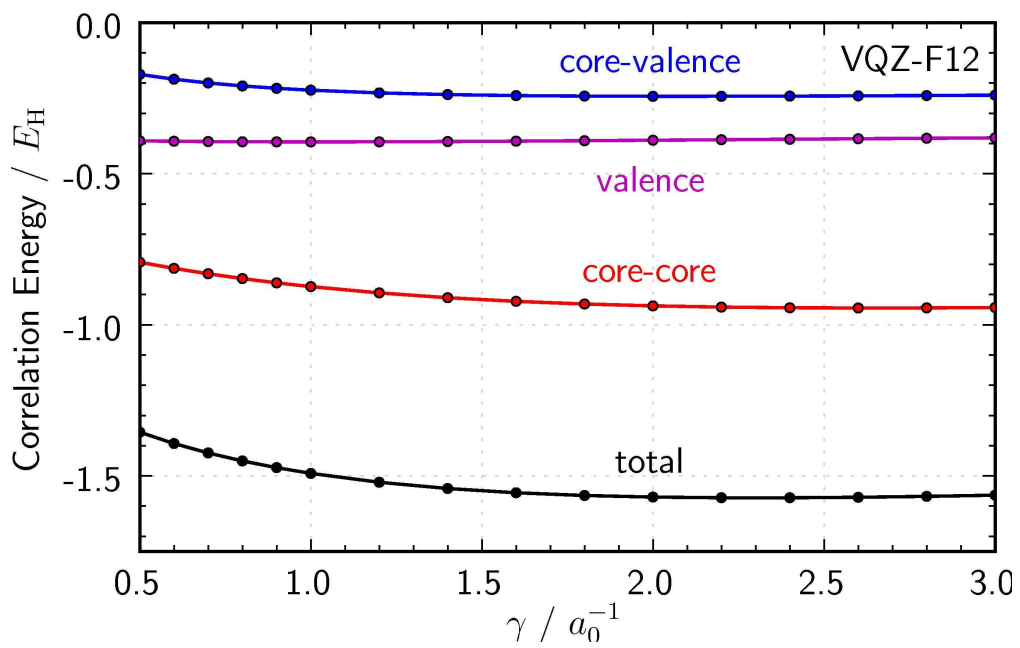
- [1] W. Klopper, F.R. Manby, S. Ten-no and E.F. Valeev, *Int. Rev. Phys. Chem.* **25**, 427 (2006).
- [2] D. Tew, C. Hättig, R. Bachorz and W. Kopper, in *Recent Progress in Coupled Cluster Methods*, ed. P. Čársky, J. Paldus, J. Pittner, pp. 535–572 (Springer, 2010).
- [3] H.-J. Werner, T.B. Adler, G. Knizia and F.R. Manby, in *Recent Progress in Coupled Cluster Methods*, ed. P. Čársky, J. Paldus, J. Pittner, pp. 573–619 (Springer, 2010).
- [4] T. Kato, *Comm. Pure Appl. Math.* **10**, 151–177 (1957).
- [5] R.T. Pack and W. Byers Brown, *J. Chem. Phys.* **45**, 556–559 (1966).
- [6] S. Ten-no, *J. Chem. Phys.* **121**, 117–129 (2004).
- [7] S. Ten-no, *Chem. Phys. Lett.* **398**, 56–61 (2004).
- [8] G. Knizia, T.B. Adler and H.-J. Werner, *J. Chem. Phys.* **130**, 054104 (2009).
- [9] G. Rauhut, G. Knizia and H.-J. Werner, *J. Chem. Phys.* **130**, 054105 (2009).
- [10] O. Marchetti and H.-J. Werner, *J. Phys. Chem. A* **113**, 11580–11585 (2009).
- [11] T.B. Adler, H.-J. Werner and F.R. Manby, *J. Chem. Phys.* **130**, 054106 (2009).
- [12] E.F. Valeev, *J. Chem. Phys.* **125**, 244106 (2006).
- [13] T. Shiozaki, M. Kamiya, S. Hirata and E.F. Valeev, *Phys. Chem. Chem. Phys.* **10**, 3358 (2008).
- [14] A. Köhn, G.W. Richings and D.P. Tew, *J. Chem. Phys.* **129**, 201103 (2008).
- [15] T. Shiozaki, M. Kamiya, S. Hirata and E.F. Valeev, *J. Chem. Phys.* **130**, 054101 (2009).
- [16] A. Köhn, *J. Chem. Phys.* **130**, 131101 (2009).
- [17] H. Fliegl, W. Klopper and C. Hättig, *J. Chem. Phys.* **122**, 084107 (2005).
- [18] H. Fliegl, C. Hättig and W. Klopper, *Int. J. Quantum Chem.* **106**, 2306 (2006).
- [19] D.P. Tew, W. Klopper, C. Neiss and C. Hättig, *Phys. Chem. Chem. Phys.* **9**, 1921–1930 (2007).
- [20] D.P. Tew, W. Klopper and C. Hättig, *Chem. Phys. Lett.* **452**, 326–332 (2008).
- [21] T.B. Adler, G. Knizia and H.-J. Werner, *J. Chem. Phys.* **127**, 221106 (2007).
- [22] M. Torheyden and E.F. Valeev, *Phys. Chem. Chem. Phys.* **10**, 3410–3420 (2008).
- [23] E.F. Valeev and T.D. Crawford, *J. Chem. Phys.* **128**, 244113 (2008).
- [24] T. Shiozaki, E.F. Valeev and S. Hirata, *J. Chem. Phys.* **131**, 044118 (2009).
- [25] C. Hättig, D.P. Tew and A. Köhn, *J. Chem. Phys.* **132**, 231102 (2010).
- [26] H.-J. Werner, T.B. Adler and F.R. Manby, *J. Chem. Phys.* **126**, 164102 (2007).
- [27] G. Knizia and H.-J. Werner, *J. Chem. Phys.* **128**, 154103 (2008).
- [28] W. Klopper, *Chem. Phys. Lett.* **186**, 583–585 (1991).
- [29] E.F. Valeev, *Chem. Phys. Lett.* **395**, 190–195 (2004).
- [30] H.-J. Werner, P.J. Knowles, R. Lindh, F.R. Manby and M. Schütz et al., *MOLPRO*, version 2009.1, a package of ab initio programs Cardiff, UK, 2009, see <http://www.molpro.net>.
- [31] F.R. Manby, *J. Chem. Phys.* **119**, 4607–4613 (2003).
- [32] A.J. May and F.R. Manby, *J. Chem. Phys.* **121**, 4479–4485 (2004).
- [33] S. Obara and A. Saika, *J. Chem. Phys.* **84** (7), 3963–3974 (1986).
- [34] S. Obara and A. Saika, *J. Chem. Phys.* **89** (3), 1540–1559 (1988).
- [35] R. Ahlrichs, *Phys. Chem. Chem. Phys.* **8**, 3072–3077 (2006).
- [36] R. Ahlrichs, *Phys. Chem. Chem. Phys.* **6**, 5119–5121 (2004).
- [37] S. Höfener, F.A. Bischoff, A. Glöß and W. Klopper, *Phys. Chem. Chem. Phys.* **10**, 3390–3399 (2008).
- [38] F.R. Manby, H.-J. Werner, T.B. Adler and A.J. May, *J. Chem. Phys.* **124**, 094103 (2006).
- [39] K.A. Peterson and J.G. Hill (2010), private communication.
- [40] J.G. Hill, S. Mazumder and K.A. Peterson, *J. Chem. Phys.* **132**, 054108 (2010).
- [41] K.A. Peterson and C. Puzzarini, *Theor. Chem. Acc.* **114**, 283–296 (2005).
- [42] J.G. Hill (2010), private communication.
- [43] A. Hellweg, C. Haettig, S. Hoefener and W. Klopper, *Theor. Chem. Acc.* **117**, 587–597 (2007).
- [44] T.H. Dunning, Jr., K.A. Peterson and A.K. Wilson, *J. Chem. Phys.* **114**, 9244–9253 (2001).
- [45] K.E. Yousaf and K.A. Peterson, *Chem. Phys. Lett.* **476**, 303–307 (2009).
- [46] F. Weigend, *J. Comput. Chem.* **29**, 167–175 (2007).
- [47] K.A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.* **119**, 11113 (2003).
- [48] B. Metz, H. Stoll and M. Dolg, *J. Chem. Phys.* **113**, 2563 (2000).
- [49] D. Figgen, G. Rauhut, M. Dolg and H. Stoll, *Chem. Phys.* **311**, 227 (2005).
- [50] F.A. Bischoff, S. Höfener, A. Glöß and W. Klopper, *Theor. Chem. Acc.* **121**, 11–19 (2008).
- [51] P.J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.* **99** (7), 5219–5227 (1993).
- [52] C. Krause, H. Stoll, K.A. Peterson and H.-J. Werner (2010), to be published.
- [53] K. Peterson and K. Yousaf (2010), private communication.
- [54] H.-J. Werner and P.J. Knowles, *J. Chem. Phys.* **89**, 5803–5814 (1988).



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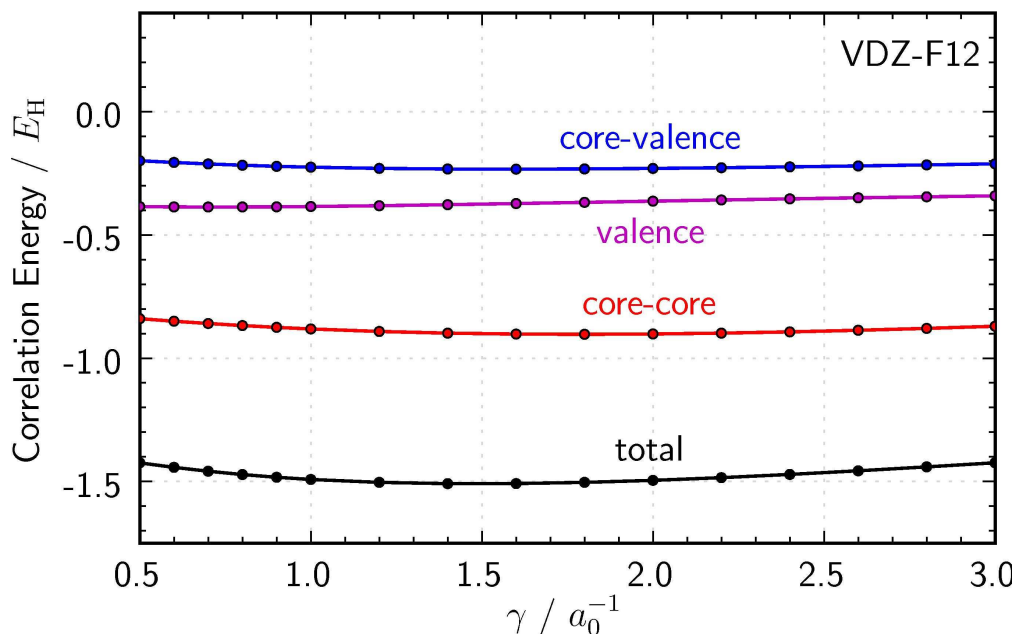


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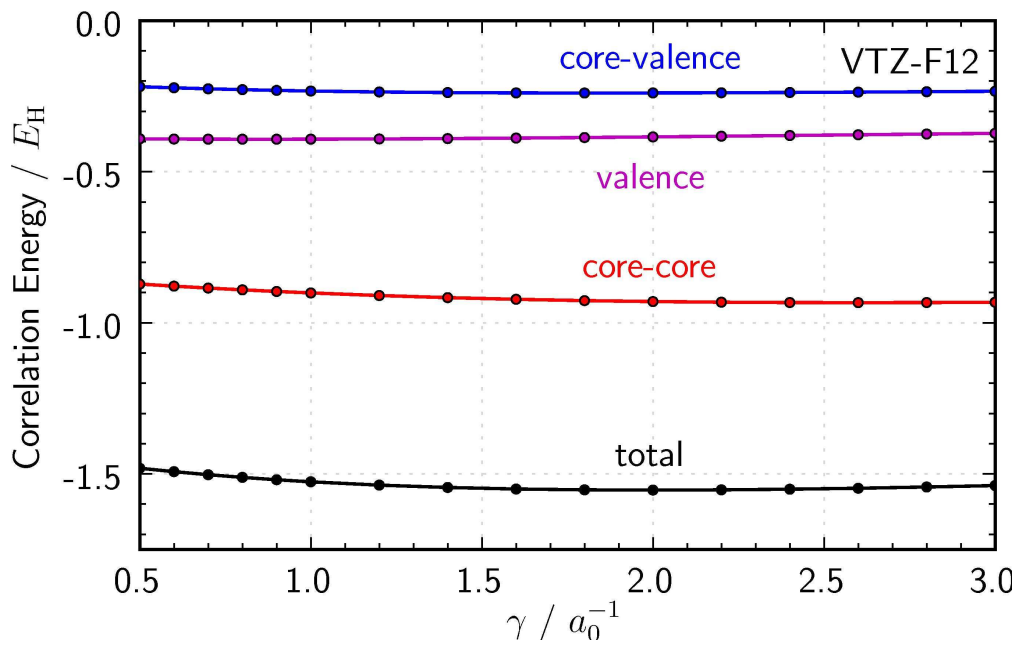


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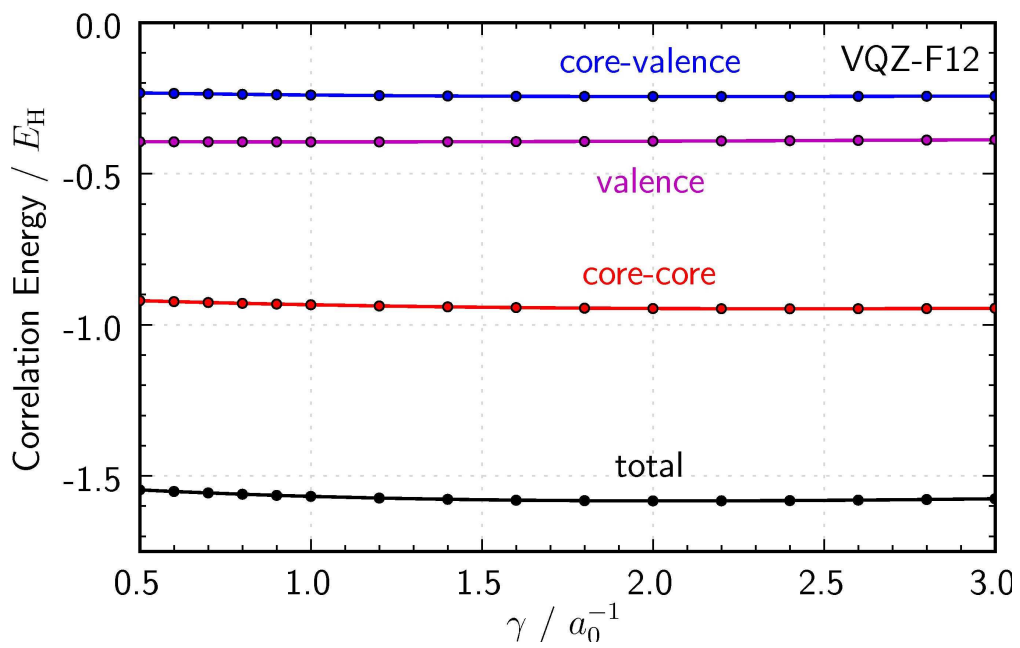


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