Explicitly-correlated Gaussian geminals in electronic structure calculations

Krzysztof Szalewicz & Bogumił Jeziorski

Taylor & Francis
Taylor & Francis Group

INVITED ARTICLE

Explicitly-correlated Gaussian geminals in electronic structure calculations

Krzysztof Szalewicz[ab]* and Bogumił Jeziorski[c]

[a]Department of Physics and Astronomy, University of Delaware, Newark, DE, 19716, USA;
[b]Laboratoire d'Astrophysique de Grenoble, Universite Joseph Fourier, Grenoble, 38041, France;
[c]Faculty of Chemistry, University of Warsaw, Pasteura 1, Warsaw, 02-093, Poland

Explicitly correlated functions have been used since 1929, but initially only for two-electron systems. In 1960, Boys and Singer showed that if the correlating factor is of Gaussian form, many-electron integrals can be computed for general molecules. The capability of explicitly correlated Gaussian (ECG) functions to accurately describe many-electron atoms and molecules was demonstrated only in the early 1980s when Monkhorst, Zabolitzky and the present authors cast the many-body perturbation theory (MBPT) and coupled cluster (CC) equations as a system of integro-differential equations and developed techniques of solving these equations with two-electron ECG functions (Gaussian-type geminals, GTG). This work brought a new accuracy standard to MBPT/CC calculations. In 1985, Kutzelnigg suggested that the linear r_{12} correlating factor can also be employed if n-electron integrals, $n > 2$, are factorised with the resolution of identity. Later, this factor was replaced by more general functions $f(r_{12})$, most often by $e^{-\gamma r_{12}}$, usually represented as linear combinations of Gaussian functions which makes the resulting approach (called F12) a special case of the original GTG expansion. The current state-of-art is that, for few-electron molecules, ECGs provide more accurate results than any other basis available, but for larger systems the F12 approach is the method of choice, giving significant improvements over orbital calculations.

Keywords: correlation energy; explicitly correlated functions; Gaussian geminals; coupled-cluster method; strong orthogonality

1. Introduction

The N-electron wave functions Ψ, which are solutions of the Schrödinger equation, are usually approximated by finite sums of orbital products. Since the resulting equations can be formulated in terms of matrix operations, one sometimes uses the name *algebraic approach* for the whole family of methods using such an approximation. For example, in the configuration interaction method, the wave functions are sums of determinants built from a chosen set of spinorbitals. Although such expansions become complete when the size of orbital basis set becomes infinite [1], the algebraic approach has difficulties with recovering one particular feature of Ψ, called the electron-electron cusp, i.e. the cusp in the wave function appearing when the distance r_{ij} between two electrons goes to zero. This problem is well illustrated on the example of a two-electron atom or ion in an ^1S state. In view of spherical symmetry, the exact wave function Ψ for this state depends only on interparticle distances, including the interelectronic distance r_{12}. If one tries to

approximate Ψ as a *finite sum* $\tilde{\Psi}$ of orbital products $\phi_i(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2)$, then

$$\lim_{r_{12}\to 0} \frac{\partial \tilde{\Psi}}{\partial r_{12}} = 0, \tag{1}$$

while the exact function Ψ satisfies [2]

$$\lim_{r_{12}\to 0} \frac{\partial \Psi}{\partial r_{12}} = \frac{1}{2} \lim_{r_{12}\to 0} \Psi \tag{2}$$

with the right-hand side (r.h.s.) not vanishing for singlet states. The cusp condition, given by Equation (2), is a consequence of the Coulomb-type singularity of the electronic Hamiltonian when $\boldsymbol{r}_1 = \boldsymbol{r}_2$. Equation (1) can be proved by expressing $\tilde{\Psi}$ as the finite partial-wave expansion

$$\tilde{\Psi} = \sum_{l=1}^{n} R_l(r_1, r_2) P_l(\cos\gamma), \tag{3}$$

where $r_i = |\boldsymbol{r}_i|$, γ is the angle between the vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, P_l is the Legendre polynomial and $R_l(r_1, r_2)$ is a coordinate-dependent expansion coefficient.

*Corresponding author. Email: szalewic@udel.edu

Since $\cos \gamma$ is a quadratic function of r_{12} (for fixed r_1 and r_2), the derivative in Equation (1) must vanish in the limit of $r_{12} \to 0$. One can say equivalently that if $\phi(r) = \Psi(a, r)$, where $\Psi(r_1, r_2)$ is the exact wave function and a an arbitrary point in space not coinciding with a nuclear position, then $\phi(r)$ has a cusp-type singularity at $r = a$, while for any finite expansion of $\Psi(r_1, r_2)$ in terms of orbital products, the function $\phi(r)$ will obviously be analytic at any r (except at the nuclear positions).

A natural way to deal with this problem is to introduce wave functions depending explicitly on the r_{ij} distances. This approach was applied for the first time by Hylleraas [3] in 1929, who used a linear r_{12} factor multiplying products of Slater orbitals. Various extended forms of the Hylleraas functions are still used in very accurate calculations for three-body systems, in particular for the helium atom. The Hylleraas basis set was generalised in 1933 to the case of two-electron diatomic molecules by James and Coolidge (JC) [4]. In 1964, Kolos and Wolniewicz [5] extended the JC basis to allow for the correct description of molecular dissociation (the extended basis will be referred to as KW basis).

Applications of bases containing linear r_{12} factors and Slater orbitals have turned out to be nearly impossible so far for molecules with more than two electrons (an exception is the work of Clary and Handy [6] published in 1977). It took about 30 years since the seminal work of Hylleraas to find an explicitly correlated basis set that could be applied to many-electron molecules. This breakthrough was achieved in 1960 when Boys [7] and Singer [8] proposed to change the r_{12} dependence from a linear factor to a Gaussian exponential. The most general form of such an explicitly correlated Gaussian (ECG) function contains all distances r_{ij} between electrons in an atom or molecule, but most often only the two-electron functions are used, which are then called Gaussian-type geminals (GTG). Early applications of GTGs in variational calculations [9–12] proved the viability of the method, but the first physically relevant molecular applications of this basis were carried out only in the late 1970s [13–17]. In particular, GTG calculations on H_2 published by the present authors in 1979 [15] recovered the energy of this molecule to within 0.05 mH, whereas the previous most accurate GTG work had a 4 mH error [18] and the most accurate H_2 energy at that time had a 0.01 mH error [19]. Thus, it has been shown that GTGs are capable of achieving as high accuracies as linear-r_{12} methods. This calculation required an optimisation of nearly 300 nonlinear parameters which was performed using conjugated

gradient algorithms. Current state-of-art calculations for H_2 will be discussed below.

Motivated by the success of these applications, especially that of [15,17], and by the emerging prominence of the many-body perturbation theory (MBPT) and the coupled-cluster (CC) methods [20–23], the present authors started a collaborative effort with Monkhorst and Zabolitzky in 1981 to introduce explicitly correlated functions to MBPT/CC methods [24–28]. To achieve this goal, the coupled cluster equations at the pair level were reformulated as a system of integro-differential equations for spin-free pair functions [27] and variational techniques were developed [24,28] to solve these equations using the basis of GTGs. This work, performed mostly in the Quantum Theory Project (QTP) at the University of Florida, brought a new accuracy standard to the MBPT/CC calculations and resulted in a series of benchmark studies for small systems. The GTG method was also combined with symmetry-adapted perturbation theory (SAPT) [29,30] and used to compute very accurate helium–helium interaction potential [31–33] which correctly predicted low-temperature bulk properties of helium and the properties of the helium dimer. In a more recent work, performed with Bukowski, the present authors proved the completeness of the GTG basis [34,35] (see also [36]), and showed how single excitations can be included [37] or how GTGs can be used to calculate analytical gradients and properties within the framework of MBPT [38]. These developments are extensively reviewed in [39].

In 1985, in independent development, Kutzelnigg [40] suggested that the linear r_{ij} correlating factors can also be used in MBPT/CC calculations for general molecules provided that these factors are multiplied by Gaussian orbitals and that the resolution of identity is used to compute more-than-two-electron integrals. The first calculation utilising these ideas was published two years later [41] and their broader realisation, referred to as the R12 approach, was achieved in the early 1990s [42,43]. Since the 1990s, the developments in applications of explicitly correlated functions have accelerated significantly and in the last decade the explicitly correlated approach certainly entered the mainstream of computational chemistry. The most recent important development is the emergence of the so-called F12 methods replacing the linear r_{ij} correlating factor by more general functions $f(r_{12})$, most often the Slater factor $e^{-\gamma r_{12}}$. When $f(r_{12})$ is expanded in Gaussian functions, which is often done, this approach reduces to the application of the conventional GTG expansion. Excellent discussions of explicitly correlated

methods can be found in Section 4 of the review by Helgaker *et al.* [44] and in the review by Tew *et al.* [45].

In addition to reviewing the development of ECG methods, we will also survey the most recent applications of ECG basis sets and in particular of GTGs. Presently, some applications of ECG functions to small molecules reach accuracies much better than 1 mH that is typically considered a high quality in large-scale electronic structure calculations. For example, it has been possible to reduce uncertainties to nanoH level for the helium dimer and below picoH level for the hydrogen molecule [46] using ECG/GTG bases. At this level of accuracy, relevant, e.g., for creating new metrology standards, one has to include several physical interactions beyond the nonrelativistic Born–Oppenheimer (BO) level: the adiabatic, relativistic and quantum electrodynamics (QED) corrections [47]. The contribution of these subtle effects can also be computed with ECG bases.

2. Explicitly correlated geminals in many-body perturbation theory and coupled-cluster methods

Consider a two-electron atom or molecule in a spin-free approach. The wave function of such a system is most often expanded in terms of products of orbitals:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{i,j} c_{ij}\, \phi_i(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2). \qquad (4)$$

As discussed in Section 1, such expansions converge slowly since it is difficult to describe the electron-electron cusp using orbital products. A general explicitly correlated expansion of the same wave function can be written as

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{i,j,k} c_{ijk}\, \phi_i(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_2)f_k(r_{12}). \qquad (5)$$

The components of this expansion are called geminals and come in several variations depending on the form of the factor $f_k(r_{12})$. The popular factors have been:

(a) linear-R12

$$f_k(r_{12}) = r_{12}, \qquad (6)$$

(b) Slater-type

$$f_k(r_{12}) = \mathrm{e}^{-\alpha_k r_{12}}, \qquad (7)$$

(c) Gaussian-type

$$f_k(r_{12}) = \mathrm{e}^{-\alpha_k r_{12}^2}. \qquad (8)$$

When the orbital factors multiplying $\exp(-\alpha r_{12}^2)$ are also of the Gaussian form, one obtains the GTG basis of Boys and Singer. This is presently the only explicitly correlated basis for which molecular integrals can be analytically computed for many-electron molecules. The Slater-type correlating factors have been initially used only for three-body systems, like the helium atom, exhibiting extraordinary effectiveness [48]. Such factors were introduced in the many-electron context by Tenno [49] in 2004 and have been often used since then.

Although the orbital product basis sets are complete if the one-electron bases are complete, the advantage of applying the explicit correlation factor is that one can significantly reduce the number of orbital products used. The appropriate theorems concerning the completeness of GTG bases have been proved in [34–36,50]. It should be emphasised, however, that only the Slater and the linear correlation factors can guarantee the exact fulfillment of the cusp condition of Equation (2). When the Gaussian correlation factors $\exp(-\alpha r_{12}^2)$ are used, Equation (1) still holds. This sounds paradoxical in view of the mathematical completeness of the Gaussian geminal basis and, especially, its excellent performance in practical applications. This paradox can be explained by the fact that a single Gaussian geminal function $\exp(-\alpha r_{12}^2)$ can approximate a cusp arbitrarily well (can have arbitrarily large second derivative) by increasing the nonlinear parameter α. Achieving a similar approximation of the cusp with Equation (4) would require using many very high angular momentum terms in the expansion of the wave function. Also, what really matters is the correct description of the correlation hole for small but nonzero values of r_{12} (rather than the exact fulfilment of Equation (2)) and this hole is much easier to describe with explicit r_{12} dependence of the wave function.

Results of initial applications of the ECG basis to the helium atom and hydrogen molecule [9–12] were not competitive to those obtainable by other approaches. In 1972, Pan and King [51] reported, however, an application of GTGs to the neon atom using the second-order MBPT approach based on the Møller–Plesset partition of electronic Hamiltonian – the method now known as MP2. This application resulted in the best MP2 energy for neon available at that time (and until the late 1970s). The success of the work of Pan and King inspired the present authors as well as Adamowicz and Sadlej to extend their approach to molecules. This resulted in a series of applications [14–17] that led to predictions accurate enough to be confronted with experiment.

Another reason that the work of Pan and King was followed by the quantum chemists in Warsaw was undoubtedly the influence of Kolos, whose benchmark calculations for H_2 in explicitly correlated basis sets have been among the most important results achieved in this field. There was therefore a natural quest for extending such an approach to larger molecules. We also realised that GTGs could be used to perform calculations not possible with the JC or KW bases. For instance, it is very easy to analytically compute the Fourier transformation of the ECG basis [15]. Kolos appreciated this merit of the GTG basis and later participated in the GTG studies of electron scattering on H_2 [52–55] performed in 1982 at the QTP.

In applications of GTGs performed within the MBPT/CC framework, one has to repeatedly solve the pair equation of the following general form [27,28,39]:

$$\left[\hat{f}(1) + \hat{f}(2) - \varepsilon_\alpha - \varepsilon_\beta\right]\tau^s_{\alpha\beta}(1,2) = R^s_{\alpha\beta}(1,2), \quad (9)$$

where the arguments $i = 1$ or 2 are short-hand notation for the electron coordinates r_i, $\hat{f}(i)$ is the one-electron Fock Hamiltonian, ε_α is the orbital energy of the Hartree–Fock orbital ϕ_α, $s = 1$ or 3 denotes the singlet or triplet spin symmetry, respectively, and the function appearing on the r.h.s. depends on the level of theory. In the simplest MP2 case, this function is given by

$$R^s_{\alpha\beta} = -\hat{q}_2\frac{1}{r_{12}}\phi^s_{\alpha\beta}, \quad (10)$$

where $\phi^s_{\alpha\beta}(1,2) = [\phi_\alpha(1)\phi_\beta(2) + (2-s)\phi_\alpha(2)\phi_\beta(1)]$ and $\hat{q}_2$ is the so-called strong orthogonality (SO) projector

$$\hat{q}_2(1,2) = \hat{q}_1(1)\hat{q}_1(2) \quad (11)$$

defined in terms of the standard one-electron operator

$$\hat{q}_1 = 1 - \hat{p}, \qquad \hat{p} = \sum_{\alpha=1}^{N/2} \hat{p}_\alpha, \qquad \hat{p}_\alpha = |\phi_\alpha\rangle\langle\phi_\alpha| \quad (12)$$

projecting outside the space spanned by $N/2$ doubly occupied orbitals ϕ_α. In higher orders of MBPT and in the CC method, the function $R^s_{\alpha\beta}$ on the r.h.s. of Equation (9) depends on all pair functions obtained in lower orders of MBPT or in the previous iteration of CC equations. Similarly, as in the first-order, the r.h.s. of Equation (9) satisfies the strong orthogonality condition, $R^s_{\alpha\beta} = \hat{q}_2 R^s_{\alpha\beta}$.

Equation (9) has to be solved with the condition that the pair functions are strongly orthogonal to the occupied space:

$$\tau^s_{\alpha\beta} = \hat{q}_2\tau^s_{\alpha\beta}. \quad (13)$$

The SO condition is trivially fulfilled in algebraic MBPT/CC approaches since the pair functions are expanded in terms of virtual Hartree–Fock orbitals. In explicitly correlated approaches, this condition leads to very significant complications and additional costs of calculations. To see this, let us consider the Hylleraas functional used to solve Equation (9)

$$\mathcal{J}^s_{\alpha\beta}[\tilde{\tau}] = \langle\tilde{\tau}|\,\hat{f}(1) + \hat{f}(2) - \varepsilon_\alpha - \varepsilon_\beta|\hat{q}_2\tilde{\tau}\rangle - 2\mathrm{Re}\langle\tilde{\tau}|R^s_{\alpha\beta}\rangle. \quad (14)$$

We assumed here that the Hartree–Fock problem has been solved exactly so that $\hat{f}(1)$ commutes with $\hat{q}_2$ and, consequently, the SO projection has to be carried out only in the ket. Since the action of the projector $\hat{q}_2$ leads to an additional integration

$$\hat{p}_\alpha(2)\,\tilde{\tau} = \phi_\alpha(2)\int\phi_\alpha(2')\tilde{\tau}(1,2')\mathrm{d}2', \quad (15)$$

the 'overlap' component of $\mathcal{J}^s_{\alpha\beta}[\tilde{\tau}]$ quadratic in pair functions contains the following integral

$$\langle\tilde{\tau}|\hat{p}_\alpha(2)\,\tilde{\tau}\rangle = \int\tilde{\tau}(1,2)\phi_\alpha(2)\phi_\alpha(2')\tilde{\tau}(1,2')\mathrm{d}1\mathrm{d}2\mathrm{d}2'. \quad (16)$$

This integral is a nonseparable three-electron one instead of a two-electron one which would appear if the SO condition was not imposed. Since the operators $\hat{f}(i)$ contain an implicit integration over the third electron coming from their Coulomb and exchange parts, the quadratic term leads to four-electron integrals. Whereas these integrals can be reduced to two-electron ones in a fairly straightforward way, the resulting expressions are time consuming to compute.

In the early GTG calculations, all the needed four-electron integrals were computed [14,17,51]. A method of avoiding such calculations, called the weak-orthogonality (WO) approach, was proposed in [24,25]. In this method, the operator $\hat{q}_2$ is removed from the quadratic term in Equation (14) and a 'penalty' term

$$(\varepsilon_\alpha/2 + \varepsilon_\beta/2 - \varepsilon_1 + \eta)\,\langle\tilde{\tau}|\hat{p}(1) + \hat{p}(2)|\tilde{\tau}\rangle \quad (17)$$

is added to the functional, where η is the so-called SO-enforcing parameter. The penalty term was chosen such that for $\eta > 0$ the minimum of the WO functional is attained when $\tilde{\tau}$ becomes identical with the strongly orthogonal pair function $\tau^s_{\alpha\beta}(1,2)$ satisfying Equation (9). The penalty term obviously vanishes for a strongly-orthogonal $\tilde{\tau}$. An improved form of the WO functional (with a somewhat more complicated penalty term) was proposed in [56] and this improved form is now used in practical calculations [39]. Appropriately large values of η will result in pair functions being strongly orthogonal to an arbitrary accuracy. In practice, one sets this parameter to values which give a balanced treatment of the description of pair correlation and of strong orthogonality.

It turned out that it is much easier to fulfil the latter condition than the former and the results in larger basis sets were practically independent of η.

Tew *et al.* [57] made an important observation that the results obtained with the WO functional can be dramatically improved when the trial function $\hat{\tau}$ is first projected with the orbital approximation to $\hat{q}_2$ defined by

$$\hat{q}_{2,\text{orb}} = 1 - \hat{p}(1)\hat{p}(2) - \hat{p}(1)\hat{q}_{1,\text{orb}}(2) - \hat{q}_{1,\text{orb}}(1)\hat{p}(2), \tag{18}$$

where

$$\hat{q}_{1,\text{orb}} = \sum_{\rho}^{n_v} |\phi_\rho\rangle\langle\phi_\rho|, \tag{19}$$

the sum ranging over the finite set of n_v virtual orbitals ϕ_ρ available in a given calculation. When $n_v = \infty$ and the set of orbitals is complete then $\hat{q}_{1,\text{orb}} = \hat{q}_1$ and $\hat{q}_{2,\text{orb}} = \hat{q}_2$. If the products of virtual orbitals are included in the basis used to represent $\hat{\tau}$, as it is done in the so-called F12 methods which will be discussed later on, then this approximate projection does not lead to new integrals, as compared to the application of the WO functional. Tew *et al.* [57] refer to this specific realisation of the WO functional (with trial function $\tilde{\tau}$ replaced by $\hat{q}_{2,\text{orb}} \tilde{\tau}$) as the intermediate orthogonality functional (IO).

At the MP2 level, the approach described above is completely sufficient, but at the CCD or CCSD levels (CC method with double or single and double excitations, respectively) the presence of $\hat{q}_2$ in the terms on the r.h.s. of Equation (9) still results in four-electron integrals and the calculation of these integrals is the time-limiting step of these methods. In order to speed up such calculations, an additional approximation was proposed in [28]. First, one defines an *approximate* SO 'projector' (neither idempotent nor Hermitian)

$$\hat{q}_B = \hat{P}_B \hat{q}_2, \tag{20}$$

where $\hat{P}_B$ is the orthogonal projector on the geminal basis set used. The operator $\hat{q}_B$ is an approximation to $\hat{q}_2$ and it becomes exact when the geminal basis set becomes complete. One may view the function $\hat{q}_B \tau$ as the least-square approximation of the strongly projected pair function $\hat{q}_2 \tau$ by a linear combination of the geminal basis functions used in the calculation. The approximate projector $\hat{q}_B$ can be applied to pair functions between CCD or CCSD iterations at virtually no additional costs, resulting in a significant reduction of the SO-violating components. Such a method of solving CC equations is referred to as the weak-orthogonality plus projection (WOP) approach

[28,39]. The application of the WOP method does not eliminate, however, the four-electron integrals already appearing at the level of linear CCD (LCCD) method. Such elimination can be achieved using the so-called superweak orthogonality functional combined with the $\hat{q}_B$ approximate projection, i.e. the SWOP method [28,39]. In this method, the $\hat{q}_2$ operator in Equation (10) or on the r.h.s. of Equation (9) is replaced by the much simpler projection $1 - \hat{p}(1)\hat{p}(2)$. The pair functions obtained by solving Equation (9) or by minimising the corresponding functional (now referred to as the superweak orthogonality functional) are not strongly orthogonal, but their strong-orthogonality violating components can be eliminated *a posteriori* by the $\hat{q}_2$ projection and, in practice, by using the $\hat{q}_B$ operator [28]. When the geminal basis is sufficiently large, the SWOP method gives practically the same results as the reference calculation with the exact $\hat{q}_B$ projection and the consequent four-electron integrals [28,37].

With the SWOP approach, only three-electron integrals remain at the FCCD (factorisable CCD) level [27]. This result is very important in practice since the difference between the CCD and FCCD energies is very small and can be accurately computed using orbital basis sets only [58]. Furthermore, the single excitation contribution to the CCSD energy is also converging fast in the algebraic approach. As a matter of fact, the explicitly correlated basis appears to be essential only in computations at the FCCD level of theory. The remaining contributions to the CCSD energy (non-factorisable part of the CCD energy and the single excitation contribution) are not sensitive to the wave function cusps and can be accurately obtained with orbital bases. Therefore, the most efficient computational strategy is to combine results from the geminal and orbital calculations and to compute only FCCD energies in GTG basis sets and the remaining CCSD components in orbital-only basis sets [58,59]. Note that the FCCD method is equivalent to the ACP-D45 method of Jankowski and Paldus [60] or the ACCD method of Chiles and Dykstra [61], both methods [60,61] originally formulated in the algebraic approach. The smallness of the CCD contributions beyond the FCCD level is also consistent with the good performance of coupled electron pair approximation (CEPA)-type methods [62–64]. These methods take account of the large, exclusion principle violating (EPV) terms included in the FCCD energy and neglect the non-EPV terms responsible for the difference between CCD and FCCD energies. One may add that when SWOP is used, the four-electron integrals do not appear at the theory levels up to FCCSD (factorisable CCSD) [37,39] and in particular are not

present in the FQCCSD method [37] which additionally neglects terms beyond those quadratic in the cluster operators and provides results very close to those obtained at the CCSD level [37].

The GTG method with the approximations discussed above has become a reasonably effective computational approach which led to benchmark correlation energies for several atoms and molecules, for a summary of these results see [39]. The most time-consuming step in such calculations are optimisations of nonlinear parameters appearing in GTGs. The explicit form of a geminal expansion is

$$\tau(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^{K} c_i \, x_1^{l_{1i}} y_1^{m_{1i}} z_1^{n_{1i}} \mathrm{e}^{-\gamma_{1i}|\mathbf{r}_1 - \mathbf{A}_i|^2}$$
$$\times x_2^{l_{2i}} y_2^{m_{2i}} z_2^{n_{2i}} \mathrm{e}^{-\gamma_{2i}|\mathbf{r}_2 - \mathbf{B}_i|^2} \times \mathrm{e}^{-\gamma_{12i}|\mathbf{r}_1 - \mathbf{r}_2|^2}. \quad (21)$$

The nonlinear parameters are γ_{1i}, γ_{2i}, γ_{12i}, $\mathbf{A}_i$ and $\mathbf{B}_i$, the total of nine parameters per geminal. In the most often used approach, the geminals are optimised separately for each pair function. Since the number of pair functions is N^2, the cost of optimisations becomes more significant for larger molecules and in fact the GTG calculations have been restricted to systems with up to 10 electrons (using approximate CCD methods for Ne [56] and only the MP2 level for water [34]). On the other hand, if the nonlinear parameters are carefully optimised, the GTG bases allow one to reach nanoH accuracies (sub-picoH for the hydrogen molecule). To reach such an accuracy, one has to use several hundreds basis functions per pair, i.e. optimise several thousands of nonlinear parameters.

A number of methods have been devised to speed up the optimisation. The random-tempering approach uses random generation of exponents and positions of geminals that is controlled by a few optimised parameters [65–68]. Later, various inexpensive methods of producing initial sets of exponents and positions were proposed [69], so that only short optimisations were needed to arrive at very accurate energies. One other issue was that the nonlinear parameters optimised at the MP2 level are not fully optimal at the CC levels for systems where the post-MP2 contributions are large. This problem has recently been solved by using an independent electron pair functional for the nonlinear optimisations [70].

3. ECG functions in variational calculations

The GTG bases can also be applied in standard variational calculations for two-electron systems and offer some advantages even in applications to the He atom [71]. A number of investigations of H_2 used this basis [15,52,53,68,72]. Although the accuracy of the H_2 energy was not as high as obtainable at that time with KW basis set, it was higher than obtainable with conventional orbital methods. Therefore, benchmark results could be obtained for properties which would be very difficult to compute using the KW bases, such as the Compton profile [15], electron scattering cross sections [52,53] and electron densities [72]. A microH accuracy of H_2 energy was achieved in [68] and in 1994 Rychlewski *et al.* [73] published a GTG result with only a nanoH error, more accurate than the best value obtained in KW bases at that time. This accuracy has been further improved over the years by increasing the basis set size, to reach recently 60 fH [46] (Table 1).

Table 1. Electronic energies of H_2 (in Hartree) at $R = 1.4011$ bohr as a function of the number of expansion terms.

Basis size	Energy	Reference
	Gaussian geminals	
300	−1.174 475 929 976	
600	−1.174 475 931 326	
1200	−1.174 475 931 395	
2400	−1.174 475 931 399 860	
4800	−1.174 475 931 400 135	
extrap.	−1.174 475 931 400 21(6)	
	Generalised James–Coolidge (R12)	
883	−1.174 475 930 742	Wolniewicz 1995 [74]
3246	−1.174 475 931 397 74	Kurokawa *et al.* 2005 [75]
7034	−1.174 475 931 399 84	Sims and Hagstrom 2006 [76]
extrap.	−1.174 475 931 399(1)	Sims and Hagstrom 2006 [76]
6776	−1.174 475 931 400 03	Nakatsuji *et al.* 2007 [77]
22363	−1.174 475 931 400 215 99	Pachucki 2010 [78]
extrap.	−1.174 475 931 400 216 7(3)	Pachucki 2010 [78]

Note: Gaussian geminal results are from [46].

At the moment of writing this review, this value constitutes the most accurate electronic binding energy of H_2 reported in the literature. However, the recent yet unpublished result of Pachucki [78] is significantly more accurate and also shows that the error estimate of 60 fH was very conservative as the difference between the two results is smaller than 12 fH. The ECG value is more accurate than the best previous values obtained in JC-type basis sets [74,76]. The closest published result is that obtained using the iterative solution of the Schrödinger equation starting from a simple JC-type function [75,77].

In the variational approach for systems with more than two electrons, ECG expansions can be written

$$\Psi = \mathcal{A}_N \left\{ \Xi^{N,S,M_S} \hat{P} \sum_{k=1}^{K} c_k \phi_k(1,2,\ldots,N) \right\}, \quad (22)$$

where $\mathcal{A}_N$ is the N-electron antisymmetriser, Ξ^{N,S,M_S} is one of the N-electron spin functions corresponding to spin quantum numbers S and M_S, $\hat{P}$ is the point-group symmetry projector, c_k are variational parameters and $\phi_k(1,2,\ldots,N)$ are ECG basis functions. The explicit form of the latter functions is

$$\phi_k(1,2,\ldots,N) = \prod_{i=1}^{N} e^{-\alpha_{ki}|\mathbf{r}_i - A_{ki}|^2} \prod_{i>j=1}^{N} e^{-\beta_{kij}|\mathbf{r}_i - \mathbf{r}_j|^2}, \quad (23)$$

where α_{ki}, β_{kij} and $A_{ki} = (X_{ki}, Y_{ki}, Z_{ki})$ are nonlinear variational parameters.

The ECG functions correlating more than two electrons were applied for the first time in 1975 by Karunakaran and Christoffersen [79,80], but using only a few such functions in the expansion. The first physically meaningful applications were published in the early 1990s by Cencek and Rychlewski [81] (the H_3 and LiH molecules) and by Schwegler *et al.* [82] (the beryllium atom). One should also mention that at about the same time the ECG functions have been applied in fully nonadiabatic calculations (without using the BO approximation) by Kozlowski and Adamowicz [83]. Numerous ECG applications to three-, four- and five-electron systems have been published since then – some of this work has been reviewed in [84,85] and a few recent examples are [86–88]. Very accurate ECG calculations for the helium dimer will be described in Section 5. Within the past year, the ECG method has been applied to six-electron systems, the BH molecule [88] and the carbon atom [89]. An application to a four-atom nonlinear molecule was also reported (for the dimer of H_2 [90]).

4. Gaussian approximations of the correlation factors for many-electron systems

As already discussed in Section 1, the linear-r_{12} functions, although introduced in the early days of quantum mechanics [3,4], have been for a long time used only for two-electron systems. The benchmark calculations performed for the helium atom by Pekeris [91] and Drake [92] and for the H_2 molecule by Kolos and Wolniewicz [19,93] competed with experimental measurements for these systems and such competition continues until today [94]. Such functions have also been used in several exotic applications such as muon-catalysed fusion [95,96] including a treatment of nuclear forces [97,98] and the study of the β-decay spectrum of molecular tritium, relevant for the determination of neutrino mass [99–104].

An extension of the bases with the linear-r_{12} factor to many-electron atoms, called Hylleraas configuration interaction (CI) method, was developed by Sims and Hagstrom [105] and by Woznicki *et al.* [106–108]. An extension to the general molecular systems was proposed by Kutzelnigg in 1985 [40]. Although the calculations of [40] were performed only for the helium atom, an important finding was that very accurate energies can be obtained by multiplying only the leading CI configuration by the factor r_{12} and using the rest of the CI expansion in the orbital form. This results in significant simplifications of the method compared to the Hylleraas CI. Still, an application of this approach to molecules would have produced very difficult many-electron integrals. Kutzelnigg proposed to reduce such integrals to two-electron ones by inserting an approximate resolution of identity. This idea was applied by Kutzelnigg, Klopper and Noga at various levels of MBPT/CC theory [41–43]. For a review of the R12-MBPT/CC approach see [44,109,110]. One main advantage of this approach is that costly optimisations of nonlinear parameters are avoided and standard orbital basis sets can be employed. Even if some specific basis sets have been optimised for this method, such optimisations can be done once for each atom and later used for an arbitrary molecule. Another main advantage is that the use of the resolution of identity allows much faster calculations of the integrals than in the traditional GTG method. The R12-MBPT/CC approaches also involve a variety of additional approximations made to speed up calculations. As one of the consequences, the R12-MP2 energies are no longer upper bounds to exact values. The errors due to these approximations were analysed in [111]. Although for small systems the R12-MBPT/CC results were less accurate than the GTG ones, the former method could be applied to any medium-size molecule.

The weakness of the linear-r_{12} factor is that at large interelectronic separations it is difficult to damp it by exponential terms. This obvious observation led to a family of the so-called F12 methods, where r_{12} is replaced by $f(r_{12})$ which behaves similar to r_{12} at small separations but does not diverge at large ones. The first step in these directions was made in 1994 by Bukowski and the present authors in [69], where r_{12} was expanded in terms of GTGs

$$ r_{12} = \sum c_i e^{-\alpha_i r_{12}^2}. \tag{24} $$

An alternative would be to expand the products $r_{12}\,\phi_{\alpha\beta}^s$ in terms of a geminal basis by minimising the following, easily computable functional [69]

$$ G[\tilde{\tau}] = \left\| \frac{1}{\sqrt{r_{12}}}\,\tilde{\tau} - \sqrt{r_{12}}\,\phi_{\alpha\beta}^s \right\|^2. \tag{25} $$

Persson and Taylor [112,113] also used expansion (24) and products of orbitals from standard basis sets to avoid optimisations of nonlinear parameters. This approach has been further developed by Dahle *et al.* [114,115]. A significant achievement was a calculation of the most accurate MP2 energies for water [115]. The GTG method without nonlinear optimisations always gave significant improvements over the corresponding orbital level, but calculations were still time consuming due to explicit calculations of many-electron integrals and large size of geminal expansions. A logical next step was to use the resolution of identity in such an approach and this possibility was investigated by May and Manby [116] in 2004. The method with the resolution of identity worked very well and it was implemented in standard quantum chemistry packages up to CCSD(T) [117] (CCSD plus noniterated triple excitations) level and even CCSDTQ [118] (complete excitations up to quadruple ones) level. Several variants of F12 approaches have been proposed in recent years, also including a variant which uses the Slater-type correlating factor [49,119,120]. Note that all these methods use the explicitly-correlated factors only in the pair functions. A way of including such factors in the triple-excitation functions at the CCSD(T) level has recently been proposed by Köhn [121].

Whereas the most effective implementations of F12-MBPT/CC methods use only modestly larger computer resources than calculations in the same orbital-only basis and at the same level of theory, this effectiveness has been achieved applying a series of approximations. In addition to the standard approximations in calculating the matrix elements of the Fock operator, these methods retain explicitly correlated functions only in linear terms [117] of CC equations.

The result is that if one aims at benchmark accuracies, such F12-MBPT/CC implementations may not be competitive with orbital calculations in very large basis sets followed by extrapolations to the complete basis set (CBS) limit. The performance of the F12-CCSD(T) has been recently investigated in [122]. Application of singly and doubly augmented orbital basis sets with cardinal number up to $X = 7$ followed by CBS extrapolations gave the frozen-core (FC) CCSD(T) interaction energy of Ar_2 at $R = 3.75$ Å equal to -97.445 ± 0.063 cm^{-1}. The F12-CCSD(T)/FC calculations in the largest available basis set with $X = 5$ gave -97.720, and -97.592 cm^{-1} after an extrapolation from the $X = Q$ and 5 results. While the later value is close to the benchmark, it is outside its error bars. In the case of the CCSD(T) method, the additional reason for the relatively slow convergence could be that the F12-CCSD(T)/FC implementation used [117] does not include explicit correlations in the triples components of wave function.

5. Applications of ECG functions to calculations of helium dimer potential

GTGs were first applied to intermolecular interactions to calculate the dispersion energy of He_2 [13], which requires a similar effort as an MP2 calculation. Later, GTGs were used to compute several further interaction energy components for the same system [17]. This work represents the first application of GTGs beyond the MP2 level. The computed interaction energy components are defined by SAPT whose initial version accounting for intramonomer correlation effects was also developed in [17]. A comprehensive theory of these effects was presented later in [123–126].

The complete He_2 SAPT potential based on GTG calculations was published in 1996 [31,32] and has since become one of the most often-used *ab initio* potentials for this system (henceforth it will be called SAPT96). These calculations were performed at the nonrelativistic BO level and we will denote this type of potential as $V_{BO}(R)$. In the development of SAPT96, the GTG bases were used to describe the bulk of the He_2 interaction energy, whereas a small remaining contribution was computed using orbital basis sets. The orbital calculations for some terms of the second order in the intermolecular perturbation operator $\hat{V}$, which were not programmed using GTGs, were performed using the standard SAPT approach [29,30]. Some very small terms in the second order as well as terms of higher orders in $\hat{V}$ were computed using a special version of the SAPT program applicable only to He_2 but including all intramonomer

correlation effects. Since, in practice, SAPT converges to the full CI (FCI) interaction energies computed in these same basis set [15,127–131], the small high-order contributions could alternatively be computed using the FCI method.

Recently, the calculations of [31,32] have been repeated with increased accuracy [33,58,59,132]. In particular, basis sets much larger than those in 1996 could be used. The orbital components were extrapolated to the CBS limits. Both the SAPT approach as well as the supermolecular approach were used. The latter one was earlier applied to He_2 in [133]. The use of two independent approaches which agree with each other to within the estimated uncertainties is a strong conformation of the soundness of final results. Furthermore, one can use (for a given interatomic separation R) the approach which has smaller error bars [33]. The GTG results were also used to test the performance of various types of CBS extrapolations [58,132,134]. In 2007 SAPT calculations [33], the first-order and most of the second-order contributions to the interaction energy were obtained using GTG basis sets and are converged to about 0.1 mK, or 0.3 nH, near the minimum and for larger R. Thus, the main uncertainty in the potential originates from the relatively small contributions computed using orbital basis sets, in particular the FCI contribution. Compared to the SAPT96 potential, the uncertainties have been decreased by more than an order of magnitude. We will refer to the potential of [33,59] as to CCSAPT07.

A summary of the most accurate calculations for the near-equilibrium distance of 5.6 bohr is given in Table 2. The ECG value has the smallest uncertainty and both the CCSAPT07 and quantum Monte Carlo (QMC) value of Anderson [135] are consistent with it. The uncertainty of the ECG value is only 0.2 mK or 0.6 nH.

The estimated uncertainty of the CCSAPT07 potential at the minimum distance is 300 ppm relative to the total well depth. However, since the total electronic energy of the dimer is about 6 atomic units, this translates to 2 ppb accuracy relative to this energy. The estimates of uncertainties given above are not

rigorous and have been obtained by analysing the rate of convergence of the results with basis set size and performing extrapolations to the CBS limits in several different ways. One way of judging the reliability of such estimates is to analyse the estimates from past publications since these are tested as newer and more accurate calculations become available. In the recent series of calculations from our group [33,58,59,132,134], the uncertainties are fully compatible. In the case of the SAPT96 potential [31,32], the uncertainties are for most points consistent with those of the CCSAPT07 potential, but for a few points, including the minimum separation, these uncertainties were underestimated by up to about a factor of two (mainly due to the slower than expected convergence of the contribution obtained from high-order SAPT or from FCI calculations). The reliability of the estimates can also be evaluated by comparisons with calculations using completely different methods such as the QMC method [135] or the four-electron ECG method [46] discussed above. Both comparisons show consistency with error estimates of [33,59].

The availability of accurate potentials for the helium dimer has become very important for thermophysical measurements of bulk helium. It was realised in the 1990s [31,32,136–138] that thermophysical properties of helium computed *ab initio* have smaller uncertainties than the corresponding measured values. Thus, theoretical results could be used to calibrate thermophysical measurements [139] and create new metrology standards [139–146]. However, with the accuracy level achieved for the nonrelativistic BO potential, various post-$V_{BO}(R)$ effects become comparable or even larger than the BO-level uncertainties and therefore their knowledge becomes of importance. The largest in magnitude post-$V_{BO}(R)$ contributions are the adiabatic (diagonal), relativistic and quantum electrodynamics corrections. The adiabatic correction was computed for a large number of values of R by Komasa *et al.* [147] using the ECG basis and by Hellmann *et al.* [148] using orbitals, but the results were not consistent. The relativistic [149] and quantum electrodynamic contributions [150] were initially known only at the van der Waals minimum distance. All these corrections have recently been computed for a large number of R's and the results have been fitted to an analytic function and smoothly connected with the asymptotic dependence [47], including retardation effects. The resulting total potential has 50 ppm uncertainty at the minimum. For most contributions, both the four-electron ECG and orbital bases were used for each R. For larger R, the latter results had smaller error bars and were used in the fitting of analytic potential. The reason that the quality of ECG

Table 2. Nonrelativistic BO interaction energies (in K) for the helium dimer at the near-equilibrium distance of 5.6 bohr.

SAPT96 [31,32]	-11.059 ± 0.03
CCSAPT07 [33]	-11.0037 ± 0.0031
ECG [46]	-11.0006 ± 0.0002
QMC [135]	-10.998 ± 0.005

results decreases at larger R is that it is not possible to define a monomer basis set corresponding to a given dimer basis set. Two techniques have been developed to go around this problem: the monomer-contraction method [46,90,149] and the direct computation method [151]. Note that the same problem does not appear in MBPT/CC calculations employing GTG bases and in fact one can make counterpoise correction for the basis set superposition error in such calculations [133].

The uncertainties of the bulk helium properties, such as, for example, the second virial coefficient, computed from the current *ab initio* potentials are a few times smaller than the uncertainties of the best measurements [146]. The *ab initio* predictions [47] can also be compared to experimental values for the bound state of $^4He_2$. This very unusual, extremely long molecule has been studied experimentally since the mid-1990s [152–154]. The computed value of $\langle R \rangle = 47.1 \pm 0.5$ Å (using atomic masses in nuclear dynamics calculations) can be compared with the best measurement of this quantity from [154] which gave $\langle R \rangle = 52 \pm 4$ Å, i.e. the error bars of the two values nearly touch. The *ab initio* dissociation energy D_0 of 1.62 ± 0.03 mK is 16% above the upper limit of the value of $1.1 \, ^{+0.3}_{-0.2}$ mK obtained in [154]. Thus, the agreement is not perfect but reasonable. Currently, the theoretical uncertainties of $\langle R \rangle$ are eight times smaller than experimental ones, however, future experiments may achieve a higher precision [155,156].

6. Conclusions

The use of explicitly correlated functions, originated in the early days of quantum mechanics and applicable for a long time only to two-electron systems, has recently become a mainstream method applicable to arbitrary medium-size molecules. The first explicitly correlated calculations for many-electron molecules performed in the late 1970s used ECG functions and such functions currently provide more accurate results than any other method for small molecules. With increase of computer power, ECG calculations are performed for larger and larger molecules since such calculations are conceptually simple and can, in principle, provide an almost arbitrary accuracy. However, variational many-electron ECG calculations with fully optimised basis functions will always be limited to relatively small systems because of the $N!$ increase of costs of such calculations. On the other hand, the application of fully optimised GTG bases in MBPT/CC calculations appears to be feasible for systems with few dozens of electrons. For larger

systems, linear-r_{12} methods with the resolution of identity, originated in early 1990s, although still continue to be a popular computational tool, are being replaced by the F12 methods. The latter methods, developed in the last decade, represent an essential improvement over the linear-r_{12} approaches and extend the applicability of GTG bases to large polyatomic molecules.

ECG functions allowed one to reach unprecedented accuracy for the helium dimer. Properties of this dimer as well as of bulk helium predicted entirely from first principles have uncertainties several times smaller than the best measurements. The theoretical results will be used to establish new standards for the Boltzmann constant, temperature and pressure.

References

[1] B. Klahn and W.A. Bingel, Theor. Chim. Acta **44**, 9, 27 (1977).
[2] T. Kato, Commun. Pure Appl. Math. **10**, 151 (1957).
[3] E.A. Hylleraas, Z. Phys. **54**, 347 (1929).
[4] H.M. James and A.S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[5] W. Kolos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).
[6] D.C. Clary and N.C. Handy, Chem. Phys. Lett. **51**, 483 (1977).
[7] S.F. Boys, Proc. R. Soc. London, Ser. A **258**, 402 (1960).
[8] K. Singer, Proc. R. Soc. London, Ser. A **258**, 412 (1960).
[9] J.V.L. Longstaff and K. Singer, Proc. R. Soc. London, Ser. A **258**, 421 (1960).
[10] J.V.L. Longstaff and K. Singer, Theor. Chim. Acta **2**, 265 (1964).
[11] W.A. Lester Jr and M. Krauss, J. Chem. Phys. **41**, 1407 (1964).
[12] J.V.L. Longstaff and K. Singer, J. Chem. Phys. **42**, 801 (1965).
[13] G. Chalasinski, B. Jeziorski, J. Andzelm and K. Szalewicz, Mol. Phys. **33**, 971 (1977).
[14] L. Adamowicz and A.J. Sadlej, J. Chem. Phys. **69**, 3992 (1978).
[15] B. Jeziorski and K. Szalewicz, Phys. Rev. A **19**, 2360 (1979).
[16] K. Szalewicz, L. Adamowicz and A.J. Sadlej, Chem. Phys. Lett. **61**, 548 (1979).

[17] K. Szalewicz and B. Jeziorski, Mol. Phys. **38**, 191 (1979).
[18] N.C. Handy, Mol. Phys. **26**, 169 (1973).
[19] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
[20] R.J. Bartlett and G.D. Purvis III, Int. J. Quantum Chem. **14**, 651 (1978).
[21] R.J. Bartlett and G.D. Purvis III, Phys. Scr. **21**, 225 (1980).
[22] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. **75**, 1284 (1981).
[23] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[24] K. Szalewicz, B. Jeziorski, H.J. Monkhorst and J.G. Zabolitzky, Chem. Phys. Lett. **91**, 169 (1982).
[25] K. Szalewicz, B. Jeziorski, H.J. Monkhorst and J.G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).
[26] K. Szalewicz, B. Jeziorski, H.J. Monkhorst and J.G. Zabolitzky, J. Chem. Phys. **79**, 5543 (1983).
[27] B. Jeziorski, H.J. Monkhorst, K. Szalewicz and J.G. Zabolitzky, J. Chem. Phys. **81**, 368 (1984).
[28] K. Szalewicz, B. Jeziorski, H.J. Monkhorst and J.G. Zabolitzky, J. Chem. Phys. **81**, 2723 (1984).
[29] B. Jeziorski, R. Moszynski and K. Szalewicz, Chem. Rev. **94**, 1887 (1994).
[30] K. Szalewicz, K. Patkowski and B. Jeziorski, Structure Bonding **116**, 43 (2005).
[31] H.L. Williams, T. Korona, R. Bukowski, B. Jeziorski and K. Szalewicz, Chem. Phys. Lett. **262**, 431 (1996).
[32] T. Korona, H.L. Williams, R. Bukowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **106**, 5109 (1997).
[33] M. Jeziorska, W. Cencek, K. Patkowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **127**, 124303 (2007).
[34] R. Bukowski, B. Jeziorski, S. Rybak and K. Szalewicz, J. Chem. Phys. **102**, 888 (1995).
[35] B. Jeziorski, R. Bukowski and K. Szalewicz, Int. J. Quantum Chem. **61**, 769 (1997).
[36] R.N. Hill, Int. J. Quantum Chem. **68**, 357 (1998).
[37] R. Bukowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **110**, 4165 (1999).
[38] R. Bukowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **108**, 7946 (1998).
[39] R. Bukowski, B. Jeziorski and K. Szalewicz, in *Explicitly Correlated Functions in Chemistry and Physics*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 185.
[40] W. Kutzelnigg, Theor. Chim. Acta **68**, 445 (1985).
[41] W. Klopper and W. Kutzelnigg, Chem. Phys. Lett. **134**, 17 (1987).
[42] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).
[43] J. Noga, W. Kutzelnigg and W. Klopper, Chem. Phys. Lett. **199**, 497 (1992).
[44] T. Helgaker, W. Klopper and D.P. Tew, Mol. Phys. **106**, 2107 (2008).
[45] D.P. Tew, C. Hattig, R.A. Bachorz and W. Klopper, in *Recent Progress in Coupled-Cluster Methods: Theory and Applications*, edited by P. Carsky, J. Paldus and J. Pittner (Springer, Berlin, 2010), p. 535.
[46] W. Cencek and K. Szalewicz, Int. J. Quantum Chem. **108**, 2191 (2008).
[47] M. Przybytek, W. Cencek, J. Komasa, G. Lach, B. Jeziorski and K. Szalewicz, Phys. Rev. Lett. **104**, 183003 (2010).
[48] G. Lach, B. Jeziorski and K. Szalewicz, Phys. Rev. Lett. **92**, 233001 (2004).
[49] S. Ten-no, Chem. Phys. Lett. **398**, 56 (2004).
[50] H.F. King, J. Chem. Phys. **46**, 705 (1967).
[51] K.C. Pan and H.F. King, J. Chem. Phys. **56**, 4667 (1972).
[52] W. Kolos, H.J. Monkhorst and K. Szalewicz, J. Chem. Phys. **77**, 1323 (1982).
[53] W. Kolos, H.J. Monkhorst and K. Szalewicz, J. Chem. Phys. **77**, 1335 (1982).
[54] W. Kolos, H.J. Monkhorst and K. Szalewicz, At. Data Nucl. Data Tables **28**, 239 (1983).
[55] K. Szalewicz, W. Kolos, H.J. Monkhorst and C. Jackson, J. Chem. Phys. **80**, 1435 (1984).
[56] K.B. Wenzel, J.G. Zabolitzky, K. Szalewicz, B. Jeziorski and H.J. Monkhorst, J. Chem. Phys. **85**, 3964 (1986).
[57] D.P. Tew, W. Klopper and F.R. Manby, J. Chem. Phys. **127**, 174105 (2007).
[58] W. Cencek, M. Jeziorska, R. Bukowski, M. Jaszunski, B. Jeziorski and K. Szalewicz, J. Phys. Chem. A **108**, 3211 (2004).
[59] K. Patkowski, W. Cencek, M. Jeziorska, B. Jeziorski and K. Szalewicz, J. Phys. Chem. A **111**, 7611 (2007).
[60] K. Jankowski and J. Paldus, Int. J. Quantum Chem. **18**, 1243 (1980).
[61] R.A. Chiles and C.E. Dykstra, Chem. Phys. Lett. **80**, 69 (1981).
[62] R. Ahlrichs, H. Lischka, V. Staemmler and W. Kutzelnigg, J. Chem. Phys. **62**, 1225 (1975).
[63] S. Koch and W. Kutzelnigg, Theor. Chim. Acta **59**, 387 (1981).
[64] W. Kutzelnigg, in *Recent Progress in Coupled-Cluster Methods: Theory and Applications*, edited by P. Čársky, J. Paldus and J. Pittner (Springer, Berlin, 2010), p. 299.
[65] S.A. Alexander, H.J. Monkhorst and K. Szalewicz, J. Chem. Phys. **85**, 5821 (1986).
[66] S.A. Alexander, H.J. Monkhorst and K. Szalewicz, J. Chem. Phys. **87**, 3976 (1987).
[67] S.A. Alexander, H.J. Monkhorst and K. Szalewicz, J. Chem. Phys. **89**, 355 (1988).
[68] S.A. Alexander, H.J. Monkhorst, R.D. Roeland and K. Szalewicz, J. Chem. Phys. **93**, 4230 (1990).
[69] R. Bukowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **100**, 1366 (1994).
[70] M. Przybytek, B. Jeziorski and K. Szalewicz, Int. J. Quantum Chem. **109**, 2872 (2009).
[71] W. Cencek, K. Szalewicz and B. Jeziorski, Phys. Rev. Lett. **86**, 5675 (2001).

[72] R. Moszynski and K. Szalewicz, J. Phys. B **20**, 4347 (1987).

[73] J. Rychlewski, W. Cencek and J. Komasa, Chem. Phys. Lett. **229**, 657 (1994).

[74] L. Wolniewicz, J. Chem. Phys. **103**, 1792 (1995).

[75] J.S. Sims and S.A. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).

[76] Y. Kurokawa, H. Nakashima and H. Nakatsuji, Phys. Rev. A **72**, 062502 (2005).

[77] H. Nakatsuji, H. Nakashima, Y. Kurokawa and A. Ishikawa, Phys. Rev. Lett. **99**, 240402 (2007).

[78] K. Pachucki, Phys. Rev. **A82**, 032509 (2010).

[79] K.M. Karunakaran and R.E. Christoffersen, J. Chem. Phys. **62**, 1992 (1977).

[80] K.M. Karunakaran and R.E. Christoffersen, Int. J. Quantum Chem. **22**, 11 (1982).

[81] W. Cencek and J. Rychlewski, J. Chem. Phys. **98**, 1252 (1993).

[82] E. Schwegler, P.M. Kozlowski and L. Adamowicz, J. Comp. Chem. **14**, 566 (1993).

[83] P.M. Kozlowski and L. Adamowicz, J. Chem. Phys. **96**, 9013 (1992).

[84] J. Rychlewski and J. Komasa, in *Explicitly Correlated Functions in Chemistry and Physics*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 91.

[85] S. Bubin, M. Cafiero and L. Adamowicz, Adv. Chem. Phys. **131**, 377 (2005).

[86] M. Pavanello, W.C. Tung and L. Adamowicz, J. Chem. Phys. **131**, 184106 (2009).

[87] M. Stanke, J. Komasa, S. Bubin and L. Adamowicz, Phys. Rev. A **80**, 022514 (2009).

[88] S. Bubin, M. Stanke and L. Adamowicz, J. Chem. Phys. **131**, 044128 (2009).

[89] K.L. Sharkey, S. Bubin and L. Adamowicz, J. Chem. Phys. **132**, 184106 (2010).

[90] K. Patkowski, W. Cencek, P. Jankowski, K. Szalewicz, J.B. Mehl, G. Garberoglio and A.H. Harvey, J. Chem. Phys. **129**, 094304 (2008).

[91] C.L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[92] G.W.F. Drake, Nucl. Instr. Meth. Phys. Res. B **31**, 7 (1988).

[93] W. Kolos and L. Wolniewicz, J. Chem. Phys. **49**, 404 (1968).

[94] K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki and B. Jeziorski, J. Chem. Theory Comput. **5**, 3039 (2009).

[95] K. Szalewicz, H.J. Monkhorst, W. Kolos and A. Scrinzi, Phys. Rev. A **37**, 5494 (1987).

[96] S.E. Haywood, H.J. Monkhorst and K. Szalewicz, Phys. Rev. A **37**, 3393 (1988).

[97] K. Szalewicz, B. Jeziorski, A. Scrinzi, X. Zhao, R. Moszynski, W. Kolos, P. Froelich, H.J. Monkhorst and A. Velenik, Phys. Rev. A **42**, 3768 (1990).

[98] B. Jeziorski, K. Szalewicz, A. Scrinzi, X. Zhao, R. Moszynski, W. Kolos and A. Velenik, Phys. Rev. A **43**, 1640 (1991).

[99] W. Kolos, B. Jeziorski, K. Szalewicz and H.J. Monkhorst, Phys. Rev. A **31**, 551 (1985).

[100] O. Fackler, B. Jeziorski, W. Kolos, H.J. Monkhorst and K. Szalewicz, Phys. Rev. Lett. **55**, 1388 (1985).

[101] W. Kolos, B. Jeziorski, H.J. Monkhorst and K. Szalewicz, Int. J. Quantum Chem. **S19**, 421 (1986).

[102] K. Szalewicz, O. Fackler, B. Jeziorski, W. Kolos and H.J. Monkhorst, Phys. Rev. A **35**, 965 (1987).

[103] W. Kolos, B. Jeziorski, J. Rychlewski, K. Szalewicz, H.J. Monkhorst and O. Fackler, Phys. Rev. A **37**, 2297 (1988).

[104] P. Froelich, B. Jeziorski, W. Kolos, H.J. Monkhorst, A. Saenz and K. Szalewicz, Phys. Rev. Lett. **71**, 2871 (1993).

[105] J.S. Sims and S. Hagstrom, Phys. Rev. A **4**, 908 (1971).

[106] W. Woznicki, in *Theory of Electronic Shells in Atoms and Molecules*, edited by A. Jucys (Minits, Vilnus, 1971), p. 103.

[107] J. Muszynska, D. Papierowska and W. Woznicki, Chem. Phys. Lett. **76**, 136 (1980).

[108] J. Pipin and W. Woznicki, Chem. Phys. Lett. **95**, 392 (1983).

[109] W. Klopper and J. Noga, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, edited by J. Rychlewski (Kluwer, Dordrecht, 2003), p. 149.

[110] W. Klopper, F.R. Manby, S. Ten-no and E.F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).

[111] A. May, E. Valeev, R. Polly and F.R. Manby, Phys. Chem. Chem. Phys. **7**, 2710 (2005).

[112] B.J. Persson and P.R. Taylor, J. Chem. Phys. **105**, 5915 (1996).

[113] B.J. Persson and P.R. Taylor, Theor. Chim. Acta **97**, 240 (1997).

[114] P. Dahle, T. Helgaker, D. Jonsson and P.R. Taylor, Phys. Chem. Chem. Phys. **9**, 3112 (2007).

[115] P. Dahle, T. Helgaker, D. Jonsson and P.R. Taylor, Phys. Chem. Chem. Phys. **10**, 3377 (2008).

[116] A.J. May and F.R. Manby, J. Chem. Phys. **121**, 4479 (2004).

[117] T.B. Adler, G. Knizia and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007).

[118] T. Shiozaki, M. Kamiya, S. Hirata and E.F. Valeev, J. Chem. Phys. **130**, 054101 (2009).

[119] D.P. Tew and W. Klopper, J. Chem. Phys. **123**, 074101 (2005).

[120] J. Noga, S. Kedzuch, J. Simunek and S. Ten-no, J. Chem. Phys. **128**, 174103 (2008).

[121] A. Kohn, J. Chem. Phys. **130**, 131101 (2009).

[122] K. Patkowski and K. Szalewicz, J. Chem. Phys. **133**, 094304 (2010).

[123] S. Rybak, K. Szalewicz, B. Jeziorski and M. Jaszunski, J. Chem. Phys. **86**, 5652 (1987).

[124] S. Rybak, K. Szalewicz and B. Jeziorski, J. Chem. Phys. **91**, 4779 (1989).

[125] P. Jankowski, B. Jeziorski, S. Rybak and K. Szalewicz, J. Chem. Phys. **92**, 7441 (1990).

[126] S. Rybak, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **95**, 6579 (1991).

[127] G. Chałasiński, B. Jeziorski and K. Szalewicz, Int. J. Quantum Chem. **11**, 247 (1977).

[128] B. Jeziorski, G. Chałasiński and K. Szalewicz, Int. J. Quantum Chem. **14**, 271 (1978).

[129] B. Jeziorski, W.A. Schwalm and K. Szalewicz, J. Chem. Phys. **73**, 6215 (1980).

[130] T. Ćwiok, B. Jeziorski, W. Kolos, R. Moszyński and K. Szalewicz, J. Chem. Phys. **97**, 7555 (1992).

[131] K. Patkowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **120**, 6849 (2004).

[132] M. Jeziorska, R. Bukowski, W. Cencek, M. Jaszuński, B. Jeziorski and K. Szalewicz, Coll. Czech. Chem. Commun. **68**, 463 (2003).

[133] R. Bukowski, B. Jeziorski and K. Szalewicz, J. Chem. Phys. **104**, 3306 (1996).

[134] M. Jeziorska, W. Cencek, K. Patkowski, B. Jeziorski and K. Szalewicz, Int. J. Quantum Chem. **108**, 2053 (2008).

[135] J.B. Anderson, J. Chem. Phys. **120**, 9886 (2004).

[136] T. van Mourik and J.H. van Lenthe, J. Chem. Phys. **102**, 7479 (1995).

[137] R.A. Aziz, A.R. Janzen and M.R. Moldover, Phys. Rev. Lett. **74**, 1586 (1995).

[138] A.R. Janzen and R.A. Aziz, J. Chem. Phys. **107**, 914 (1997).

[139] J.J. Hurly and M.R. Moldover, J. Res. Natl. Inst. Stand. Technol. **105**, 667 (2000).

[140] M.R. Moldover, J. Res. Natl. Inst. Stand. Technol. **103**, 167 (1998).

[141] E.F. May, L. Pitre, J.B. Mehl, M.R. Moldover and J.W. Schmidt, Rev. Sci. Instr. **75**, 3307 (2004).

[142] J. Fischer and B. Fellmuth, Rep. Prog. Phys. **68**, 1043 (2005).

[143] E.F. May, M.R. Moldover, R.F. Berg and J.J. Hurly, Metrologia **43**, 247 (2006).

[144] B. Fellmuth, C. Gaiser and J. Fischer, Meas. Sci. Technol. **17**, R145 (2006).

[145] L. Pitre, M.R. Moldover and W.L. Tew, Metrologia **43**, 142 (2006).

[146] J.B. Mehl, C. R. Physique **10**, 859 (2009).

[147] J. Komasa, W. Cencek and J. Rychlewski, Chem. Phys. Lett. **304**, 293 (1999).

[148] R. Hellmann, E. Bich and E. Vogel, Mol. Phys. **105**, 3013 (2007).

[149] W. Cencek, J. Komasa, K. Pachucki and K. Szalewicz, Phys. Rev. Lett. **95**, 233004 (2005).

[150] K. Pachucki and J. Komasa, J. Chem. Phys. **124**, 064308 (2006).

[151] K. Piszczatowski, G. Lach and B. Jeziorski, Phys. Rev. A **77**, 062514 (2008).

[152] F. Luo, C.F. Giese and W.R. Gentry, J. Chem. Phys. **104**, 1151 (1996).

[153] W. Schollkopf and J.P. Toennies, J. Chem. Phys. **104**, 1155 (1996).

[154] R.E. Grisenti, W. Schollkopf, J.P. Toennies, G.C. Hegerfeldt, T. Kohler and M. Stoll, Phys. Rev. Lett. **85**, 2284 (2000).

[155] T. Havermeier, T. Jahnke, K. Kreidi, R. Wallauer, S. Voss, M. Schoeffler, S. Schoessler, L. Foucar, N. Neumann, J. Titze, H. Sann, M. Kuehnel, J. Voigtsberger, A. Malakzadeh, N. Sisourat, W. Schoellkopf, H. Schmidt-Boecking, R.E. Grisenti and R. Doerner, Phys. Rev. Lett. **104**, 153401 (2010).

[156] T. Havermeier, T. Jahnke, K. Kreidi, R. Wallauer, S. Voss, M. Schoeffler, S. Schoessler, L. Foucar, N. Neumann, J. Titze, H. Sann, M. Kuehnel, J. Voigtsberger, A. Malakzadeh, N. Sisourat, W. Schoellkopf, H. Schmidt-Boecking, R.E. Grisenti and R. Doerner, Phys. Rev. Lett. **104**, 133401 (2010).