Explicitly correlated electronic structure theory from R12/F12 ansätze

Seiichiro Ten-no[1,2*] and Jozef Noga[3,4*]

Fundamental aspects of the explicitly correlated R12 and F12 theories are summarized in the perspective of recent advances related to our contribution in this field. Starting from the basics of pair functions and second quantized formulations, the R12/F12 *ansätze* have been applied to MP2, coupled-cluster, and equation of motion coupled-cluster theories. Emphasis is given to approaches that use the rational generator to create the exact cusp conditions (SP *ansatz*). Computational aspects of the evaluation of many-electron integrals are also discussed in conjunction with the use of the Slater-type geminal, which is the predominant choice for the correlation factor in modern R12/F12 theories. © 2011 John Wiley & Sons Ltd.

INTRODUCTION

It has been known for more than 80 years that introduction of the interelectronic distance coordinate

$$r_{12} = |\vec{r}_2 - \vec{r}_1| \qquad (1)$$

directly into the wavefunction expansion is an efficient tool to treat the dynamical electron correlation effects.[1] In todays' terminology, approaches possessing this feature are denoted as explicitly correlated electronic structure theory.[2] This feature makes them different from the traditional *ab initio* correlated methods, when—in algebraic approximation—the electron correlation is treated via wavefunction expansions merely in terms of the configuration state functions (or Slater determinants). In quantum chemical calculations, these traditional configuration interaction (CI) type expansions suffer from a well-recognized drawback, namely, a frustratingly slow convergence of the calculated energies toward the one-particle basis set limit values. This hindrance is related to the improper description of the electron–electron cusp,[3] unlike in explicitly correlated approaches. On the other hand, for many-electron systems, an explicit introduction of the interelectronic distance coordinate directly into the wavefunction is by far not a trivially solvable computational problem. From the variety of approaches,[2] methodologies based on the idea of Kutzelnigg[5]—nowadays known as R12 theories—most effectively combine the advantages of the traditional CI-type expansions with the explicit treatment of the electron–electron cusp. As a result, the error of the energy with respect to the basis set limit changes from $\propto (L + 1)^{-3}$ for the traditional expansion to $\propto (L + 1)^{-7}$ in R12 theories,[6] in which L is the highest angular momentum involved in the basis set (in a close to saturated manner).

The original R12 methods considered only terms linear in r_{12} sufficient to describe the electronic cusps at the small vicinity of the coalescence of two electrons. For larger interelectronic distances the linear r_{12} leads to an unphysical description of the cusp profile, which implies that this defect has to be treated by the use of fairly extended basis sets. With less flexible sets, the aforementioned drawback leads to numerical problems and a loss of accuracy. Consequently, the short-range correlation factors are getting used in the so-called explicitly correlated F12 methods. The predominant choice of such correlation factors is the use of Slater-type geminals (STG),[7]

---

*Correspondence to: tenno@cs.kobe-u.ac.jp; noga@fns.uniba.sk

[1]Graduate School of System Informatics, Kobe University, Nada-ku, Kobe, Japan

[2]CREST, Japan Science and Technology Agency (JST), Saitama, Japan

[3]Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava, Slovakia

[4]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

TABLE 1 | Definition of Spin-Orbital Indices

Indices	Type of Spin-Orbitals	Dimension
$i, j, \ldots$	Occupied spin-orbitals	O
$a, b, \ldots$	Virtual spin-orbitals in the given basis	V
$p, q, \ldots$	Any spin-orbitals in the given basis	N
$p'', q'', \ldots$	Complementary auxiliary basis (CABS)	C
$p', q', \ldots$	Spin-orbitals in CABS + given basis	$C + N$
$\alpha, \beta, \ldots$	Virtual spin-orbitals in the complete basis	
$\kappa, \lambda, \ldots$	Any spin-orbitals in the complete basis	

which gives rise to a dramatic improvement of the accuracy with wider applicability. It has been shown that F12 methods with triple-zeta bases yield results equivalent to those from the standard orbital expansions with quintuple-zeta basis sets.

Several excellent reviews dealing with the R12/F12-based theories have appeared during the last five years,[8] fully covering the recent progress made in this field. The main aim of this overview is to provide an insight into the explicitly correlated theory from the perspective of the contribution of the authors. We shall focus on an alternative understanding of the R12/F12-concept. As well, some technical aspects related to the practical implementation of this theory will be outlined.

BASICS OF THE R12/F12 METHODS

In order to introduce the reader into the background of R12/F12 theories, in our formulations we shall employ notations of spin-orbital indices as listed in Table 1. If needed, the corresponding capital letters are used for the spatial part of the orbitals. We use a given basis set (GBS) for practical calculations and its orthogonal complement (OC) in the complete basis set (CBS). The dimensions of the occupied, virtual, and general orbitals in GBS are O, V, and $N = O + V$, respectively. In some considerations and practical implementations the OC space will be replaced by a finite complementary auxiliary basis (CABS)[12, 13] whose dimension is denoted by C.

Second-order many-body perturbation theory (MBPT2) with the Møller–Plesset partitioning of the Hamiltonian (MP2) is the simplest post Hartree–Fock model for the electron correlation. MP2 was the first model that was combined with the R12 *ansatz*[5] for many electron systems by Klopper and Kutzelnigg.[14] This initial implementation used linear r_{12} in the wavefunction expansion. The theory was formulated within what is nowadays known as the 'standard approximation' (SA)[6] and it was not invariant with respect to rotations among the orbitals in the occupied

orbital subspace. Even though the R12 theory has evolved both toward large (or much larger) molecular systems and toward highly accurate methods, the MP2–R12 (or, more generally, the MBPT2–R12) has reattracted the attention in the last decade. Development along this line has been related to alternative techniques in evaluation of the matrix elements, using alternative wavefunction ansätze and/or introducing correlation factors alternative to linear r_{12}. In the following, we shall recapitulate some ideas related mainly to our work.

Hylleraas Energy Functional

As in MP2 the unperturbed Hamiltonian is represented by the (true) Fock operator, the energy can be expressed as a sum of contributions ($\epsilon_{ij}^{(2)}$) from strictly decoupled pair functions u_{ij}. The Hylleraas energy functional for each ij pair,

$$h(u_{ij}) = \langle u_{ij}|\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j|u_{ij}\rangle$$
$$+ 2\mathrm{Re}\langle u_{ij}|r_{12}^{-1}|\{ij\}\rangle \geq \epsilon_{ij}^{(2)}, \qquad (2)$$

is minimized to determine u_{ij} under the orthogonalization constraints

$$\langle u_{ij}|\{kl\}\rangle = 0, \quad \forall k, l. \qquad (3)$$

The curly bracket denotes an antisymmetric product,

$$\{pq\} = \frac{1}{\sqrt{2}}[\phi_p(1)\phi_q(2) - \phi_q(1)\phi_p(2)], \qquad (4)$$

and ε_p is the orbital energy related to the orbital ϕ_p. Explicitly correlated electronic structure methods overcome the slow convergence of orbital expansions by employing geminal basis functions that resemble the cusp behavior of the exact wavefunction. Each pair function u_{ij} is expressed as a sum of the standard products of virtual orbitals and a term explicitly dependent on the interelectronic distance in the unitary invariant manner,[15]

$$|u_{ij}\rangle = \frac{1}{2}\sum_{ab} c_{ab}^{ij}|\{ab\}\rangle + \frac{1}{2}\sum_{kl} c_{kl}^{'ij} \hat{Q}_{12} f_{12}|\{kl\}\rangle, \qquad (5)$$

in which $f_{12} = f(r_{12})$ is a spherically symmetric geminal correlation factor which models the correlation holes appropriately, and $\hat{Q}_{12}$ is the strong orthogonality projection operator with respect to the reference functions,

$$\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) - \hat{V}_1\hat{V}_2. \qquad (6)$$

$\hat{O}_n$ and $\hat{V}_n$ are projection operators onto the occupied and virtual orbitals, respectively,

$$\hat{O}_n = \sum_i |\phi_i(n)\rangle\langle\phi_i(n)|, \qquad (7)$$

$$\hat{V}_n = \sum_a |\phi_a(n)\rangle\langle\phi_a(n)|. \qquad (8)$$

The amplitudes c_{ab}^{ij} and $c_{kl}^{\prime ij}$ are antisymmetric with respect to the interchanges of the lower or upper indices. The use of projector (6) guarantees that there is no overlap between the first (conventional) and the second (geminal) part of the pair function $|u_{ij}\rangle$. On the other hand, this projector also assures that in the second term of the right-hand side of Eq. (5) just f_{12} parts describable by the GBS are out-projected. Although this projector has been implicitly used in early R12 considerations related to the evaluation of matrix elements,[6] due to SA its practical application turned out to be equivalent to $(1 - \hat{P}_1)(1 - \hat{P}_2)$ with the projector onto GBS, $\hat{P}_n = \hat{O}_n + \hat{V}_n$. An *a priori* use of the latter projector is equivalent to the *ansatz* 1 of Klopper and Samson[12] to distinguish it from the *ansatz* 2 that relates to Eq. (6) without the last term and that is equivalent to the use of the strong orthogonality projection operator of Pan and King.[16] It has to be noted that while in *ansatz* 1 a significant part of the description of f_{12} is missing; in the definition of the *ansatz* 2 of Klopper and Samson, there is a partial overlap between the conventional and the geminal part of the pair function (5) (see also section *Second Quantized Formulation*). The use of the full projector (6) is sometimes referred to as *ansatz* 3.[17]

Modern explicitly correlated R12-based electronic structure methods almost exclusively employ the STG[7] in the form

$$f_{12} = -\gamma^{-1}\exp(-\gamma r_{12}) \qquad (9)$$

with the length-scale parameter γ. Its main advantage is related to the fact that STG covers a wider range of the correlation hole better than other correlation factors prevalent in the literature such as Gaussian-type geminals (GTG) and linear r_{12} functions. In practical evaluations of the necessary integrals, representation of STG by a linear combination of GTGs is an alternative approach beside the analytical evaluation outlined in section *Integrals over Slater-Type Geminals*.

We shall briefly address the terminologies of R12 and F12. The original R12 method features the use of the linear r_{12} correlation factor and the systematic approximation for many-electron integrals with the resolution of the identity (RI).[6] The terminology of F12 was first used by May and Manby[18] to distinguish the use of nonlinear correlation factors. They used the density fitting version of the RI approximation, and the linear r_{12} behavior is fitted by a linear combination of GTGs as shown in the work of Persson and Taylor.[19] Almost at the same time, one of us (Seiichiro Ten-no) proposed the use of STG for R12-type calculations.[7] Since then, various authors have shown the drastically improved accuracy of STG.[20] Nowadays, STG is the predominant choice of correlation factor, and explicitly correlated methods with STG are mostly called F12. (There remain some researchers who intend to keep the original terminology of R12 for the nonlinear correlation factor.) It should be noted that SP *ansatz*[23] with fixed geminal amplitudes to cusp conditions (see section *SP Ansatz with the Rational Generator*) is granted only for nonlinear correlation factors. The long-range behavior of linear r_{12} is unphysical, and the unitary invariant *ansatz* of Klopper[15] is crucial for R12 to eliminate the error.

SP *Ansatz* with the Rational Generator

The exact wavefunction obeys the cusp conditions,[3] which indicate the presence of a discontinuity at the coalescence of two electrons,

$$\Psi^{(s)} = \left[1 + \frac{r_{12}}{2(1+s)} + O(r_{12}^2)\right]\Phi^{(s)}, \qquad (10)$$

in which $\Phi^{(s)}$ is a noninteracting component of the wavefunction and s takes 0 (s-wave) and 1 (p-wave) for singlet and triplet pairs, respectively. Equation (10) can be hardly represented by orbital products. We can modify the form of (5) so that the s- and p-wave cusp conditions are plugged into the pair function directly, which gives rise to the SP *ansatz*[23, 56]

$$|u_{ij}\rangle = \frac{1}{2}\sum_{ab} c_{ij}^{ab}|\{ab\}\rangle + \hat{\mathcal{R}}_{12}|\{ij\}\rangle. \qquad (11)$$

Here $\hat{\mathcal{R}}_{12}$ is the rational generator for the cusp conditions,[23]

$$\hat{\mathcal{R}}_{12} = \hat{Q}_{12}f_{12}\left(\frac{3}{8} + \frac{1}{8}\hat{p}_{12}\right). \qquad (12)$$

and $\hat{p}_{12}$ is the permutation operator over the position vectors $\vec{r}_1$ and $\vec{r}_2$:

$$\hat{p}_{12}\Phi^{(s)} = (-1)^s\Phi^{(s)} \qquad (13)$$

because the singlet and triplet pairs are symmetric and antisymmetric with respect to the permutation of spatial coordinates (or equivalently of orbital indices). Using the commutability between the Fock and strong orthogonality projection operators, it is confirmed that the above form eliminates the Coulomb singularity of the perturbation in the first-order equation. Comparison between (5) and (11) immediately leads to the amplitudes,

$$c_{kl}^{\prime ij} = \frac{3}{8}\delta_{ik}\delta_{jl} + \frac{1}{8}\langle kl|\hat{p}_{12}|ij\rangle. \tag{14}$$

The SP *ansatz* is referred to as 'the diagonal orbital invariant' and the amplitudes are particularly simple in the spin-free formulation as shown in the forthcoming sections. The SP *ansatz* is computationally effective especially for coupled cluster (CC) calculations (*vide infra*).

Second Quantized Formulation

Exact reformulation of an n-particle operator in the second quantized form means that the operator should be expanded in the CBS. Hence, within the frame of the second quantization formalism with normal ordering related to the Hartree–Fock reference ($|0\rangle$) any two-particle operator ($\hat{X}$) is rewritten as

$$\hat{X}_N = \frac{1}{4}\sum_{\kappa,\lambda,\mu,\nu} \bar{X}_{\kappa\lambda}^{\mu\nu}\{\hat{a}_\kappa^\dagger \hat{a}_\lambda^\dagger \hat{a}_\nu \hat{a}_\mu\}$$
$$+ \sum_{\kappa,\mu}\sum_i \bar{X}_{\kappa i}^{\mu i}\{\hat{a}_\kappa^\dagger \hat{a}_\mu\}. \tag{15}$$

Where appropriate, we shall use the tensor notation for integrals over an arbitrary n-particle operator ($\hat{X}_{12\ldots}$), i.e.,

$$X_{\kappa_1\kappa_2\ldots}^{\lambda_1\lambda_2\ldots} = \langle \kappa_1\kappa_2\ldots|\hat{X}_{12\ldots}|\lambda_1\lambda_2\ldots\rangle \tag{16}$$

and the overbars denote antisymmetrized integrals, $\bar{X}_{\kappa_1\kappa_2}^{\lambda_1\lambda_2} = X_{\kappa_1\kappa_2}^{\lambda_1\lambda_2} - X_{\kappa_1\kappa_2}^{\lambda_2\lambda_1}$.

It is useful to partition the operator (15) into the part describable by the GBS

$$\hat{X}_N^{\text{GBS}} = \frac{1}{4}\sum_{p,q,r,s} \bar{X}_{pq}^{rs}\{\hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r\}$$
$$+ \sum_{p,r}\sum_i \bar{X}_{pi}^{ri}\{\hat{a}_p^\dagger \hat{a}_r\} \tag{17}$$

and a complementary part that can only be described with the aid of the OC of the CBS.[24] To facilitate the text, we shall use calligraphic letters to distinguish these operators, i.e.,

$$\hat{\mathcal{X}} = \hat{X}_N - \hat{X}_N^{\text{GBS}}. \tag{18}$$

With n electrons in the considered system, $\hat{f} = \sum_{k>l}^n f_{kl}$ represents the global operator of the correlation factor whose normal order form ($\hat{f}_N$) can be expressed as (15) with $\hat{X} = \hat{f}$. In this case, we shall use $\hat{\mathcal{F}}$ to denote the complementary part of $\hat{f}_N$ corresponding to Eq. (18). Acting of $\hat{\mathcal{F}}$ on $|0\rangle$, which denotes the Hartree–Fock wavefunction in GBS, gives rise to

$$\hat{\mathcal{F}}|0\rangle = \frac{1}{4}\sum_{i,j,\alpha,\beta} \bar{\mathcal{F}}_{\alpha\beta}^{ij}\{\hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_j \hat{a}_i\}|0\rangle$$
$$+ \sum_{i,\alpha}\sum_j \bar{\mathcal{F}}_{\alpha j}^{ij}\{\hat{a}_\alpha^\dagger \hat{a}_i\}|0\rangle. \tag{19}$$

On the right-hand side, the surviving parts of $\mathcal{F}$ represent excitation operators from the reference determinant to hypothetical excited configurations involving orbitals from the OC basis. The first term of the right-hand side stands behind the established R12/F12 approaches. The second term disappears faster than the first term for a basis set which gives the exact HF solution. In this case, the GBS should correspond to the Hartree–Fock limit basis and the matrix elements $\bar{\mathcal{F}}_{\alpha j}^{ij}$ become zero by definition. The importance of this term in practical calculations with smaller basis sets is by far not negligible, as it was stressed in Ref 24. In the same work diverse possibilities for the Hamiltonian partitioning were discussed when the GBS is not a Hartree–Fock limit one, which at same time means that the Fockian in Eq. (2) would not be the exact one. Hence, the generalized Brillouin theorem

$$\langle\alpha|\hat{F}|i\rangle = 0 \tag{20}$$

does not hold.

Using Eqs (15)–(19) and the latter relation, the *ansatz* of Eq. (5) can be rewritten employing the first-order excitation operators,[24, 25]

$$\hat{T}_2 = \frac{1}{4}\sum_{ijab} c_{ab}^{ij}\{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i\}, \tag{21}$$

$$\hat{T}_{2'} = \frac{1}{4}\sum_{ijkl} c_{kl}^{\prime ij}\sum_{\alpha>\beta} \bar{\mathcal{F}}_{\alpha\beta}^{kl}\{\hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_j \hat{a}_i\}. \tag{22}$$

Similarly, one can express the rational generator operator of Eq. (12) in the SP *ansatz* as

$$\hat{T}_{2'}^{(\text{SP})} = \frac{1}{4}\sum_{ij}\sum_{\alpha\beta} \bar{\mathcal{R}}_{\alpha\beta}^{ij}\{\hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_j \hat{a}_i\}. \tag{23}$$

The rational generator is fixed irrespective of the wavefunction order.

Geminal Basis for the Open-Shell Molecules

The operator (23) can be generally rewritten using spatial parts of the orbitals as

$$\hat{T}_{2'}^{(SP)} = \frac{1}{2} \sum_{IJ} \sum_{\alpha\beta} \langle \alpha_\uparrow \beta_\uparrow | \hat{\mathcal{R}}_{12} | I_\uparrow J_\uparrow \rangle \{ \hat{a}_{\alpha_\uparrow}^\dagger \hat{a}_{\beta_\uparrow}^\dagger \hat{a}_{J_\uparrow} \hat{a}_{I_\uparrow} \}$$

$$+ \frac{1}{2} \sum_{I'J'} \sum_{\alpha'\beta'} \langle \alpha'_\downarrow \beta'_\downarrow | \hat{\mathcal{R}}_{12} | I'_\downarrow J'_\downarrow \rangle \{ \hat{a}_{\alpha_\downarrow}^\dagger \hat{a}_{\beta_\downarrow}^\dagger \hat{a}_{J'_\downarrow} \hat{a}_{I'_\downarrow} \}$$

$$+ \sum_{IJ'} \sum_{\alpha\beta'} \langle \alpha_\uparrow \beta'_\downarrow | \hat{\mathcal{R}}_{12} | I_\uparrow J'_\downarrow \rangle \{ \hat{a}_{\alpha_\uparrow}^\dagger \hat{a}_{\beta'_\downarrow}^\dagger \hat{a}_{J'_\downarrow} \hat{a}_{I_\uparrow} \}, \tag{24}$$

where we have distinguished the spatial parts of the up and down spin orbitals by a prime. Spin flipped geminals appear in the last term of Eq. (24) as a result of the multiplication of the permutation operator in the rational generator as $\hat{p}_{12} |I_\uparrow J'_\downarrow\rangle = |J'_\uparrow I_\downarrow\rangle$. In the spin-free formulation for a closed shell reference, Eq. (23) can be re-expressed in terms of the unitary group generator, $\hat{E}_{PQ} = \hat{a}_{P_\uparrow}^\dagger \hat{a}_{Q_\uparrow} + \hat{a}_{P_\downarrow}^\dagger \hat{a}_{Q_\downarrow}$ and the spatial parts of the occupied orbitals are identical for up and down spins. For restricted Hartree-Fock (RHF) (or complete active space self-consistent field (CASSCF) more generally), the α and β orbitals are identical, and the corresponding geminal amplitudes over spatial orbitals become particularly simple as[26]

$$c'^{IJ}_{KL} = \frac{3}{8} \delta_{IK} \delta_{JL} + \frac{1}{8} \delta_{IL} \delta_{JK}. \tag{25}$$

The use of the operator (22) without spin-flipped pair functions is more complicated for wave functions with different orbitals for different spins (e.g. unrestricted Hartree-Fock). Consequently, in this *ansatz* the exact cusp conditions are not fully satisfied, and the geminal space should be augmented with such spin flipped functions.[27]

COUPLED CLUSTER F12 METHODS

Generalization of the R12 theory to the CC type of wavefunction expansion was introduced twenty years ago.[25, 32] Since then, there has been an enormous development in this field, eventually leading to approaches whose computational demands with the GBS do not significantly exceed the requirements for the calculations using traditional CC *ansatz*, at the same time providing results with substantially improved accuracy. A general CC approach with singles and doubles based on R12/F12 theory using both one- and two-particle part of $\hat{\mathcal{F}}$ has been formulated more recently.[33] In this formulation, the ground state CCSD-R12/F12 wavefunction Ψ_0 is expressed as

$$|\Psi_0\rangle = e^{\hat{T}}|0\rangle, \tag{26}$$

where the cluster operator $\hat{T}$ has the form

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{1'} + \hat{T}_{2'}. \tag{27}$$

$\hat{T}_1$ and $\hat{T}_2$ are regular single and double excitation operators, and $\hat{T}_{2'}$ is a CC generalization of the excitation operator (22):

$$\hat{T}_{2'} = \frac{1}{4} \sum_{ijkl} t''^{ij}_{kl} \sum_{\alpha > \beta} \bar{\mathcal{F}}^{kl}_{\alpha\beta} \{ \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_j \hat{a}_i \}, \tag{28}$$

and

$$\hat{T}_{1'} = \sum_{ik} t'^i_k \sum_\alpha \sum_l \bar{\mathcal{F}}^{kl}_{\alpha l} \{ \hat{a}_\alpha^\dagger \hat{a}_i \}. \tag{29}$$

Intermediate normalization is assumed, i.e.,

$$\langle 0 | \Psi_0 \rangle = 1. \tag{30}$$

With the *ansatz* (26) the amplitudes are optimized in the orbital invariant manner.[15] Essentially, one minimizes the Arponen-like energy functional[35]

$$E(\hat{\Lambda}, \hat{T}) = \langle 0 | (1 + \hat{\Lambda}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle \tag{31}$$

with respect to the amplitudes of $\hat{\Lambda}$, which implies that

$$E = \langle 0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle. \tag{32}$$

Due to the asymmetric nature of the latter functional, $\hat{\Lambda}$ is not equal to $\hat{T}^\dagger$. Explicit equations for this *ansatz* have been given in Refs 33, 34. As we have shown on a model study limited to single excitations $\hat{T}_1$ and $\hat{T}_{1'}$, an infinite-order treatment of the orbital relaxation within the CC *ansatz* is quite important.[36] The main message was that whereas the approach using $\hat{T}_{1'}$ somewhat underestimates this effect, an alternative treatment with extending the true single excitations space using CABS gives rise to overestimation of the energies. This uncertainty remains also with a pragmatic correction for the orbital relaxation stemming from the second-order perturbation theory which is often used in the explicitly correlated CC approaches.[37]

In the SP *ansatz*, the one-particle part (29) disappears by definition and the $\hat{T}_{2'}^{(SP)}$ remains as in (23). Evidently, the final CCSD-F12(SP) equations are drastically simplified. In that case, however, the energy expression (32) is not valid, since the functional (31) was not minimized with respect to the amplitudes of $\hat{\Lambda}_{2'}$. Instead, the energy is calculated as

$$E = \langle 0 | (1 + \hat{\Lambda}_{2'}^{(SP)}) e^{-\hat{T}} \hat{H} e^{\hat{T}} | 0 \rangle, \tag{33}$$

where the amplitudes of $\hat{\Lambda}_{2'}^{(SP)}$ are fixed to cusp conditions and hence the same as for $\hat{T}_{2'}^{(SP)}$.

Restriction of the functional (31) to second-order terms in the fluctuation potential (in our case, the two particle part of $\hat{H}_N$) and the amplitudes of $\hat{T}_{2'}$, $\hat{T}_{2'}^\dagger$ leads to fairly successful approximation denoted as CCSD(F12).[38] More detailed description of various other approximations can be found in Ref 8.

Toward More General CC-F12 Ansatz

A great (theoretical and computational) advantage of the CC *ansatz* using excitation operators $\hat{T}_{n'}$ of Eqs (28) and/or (29) together with the 'conventional' excitation operators $\hat{T}_n$ is hidden in the fact that all operators in the exponential mutually commute. This enables a straightforward using of the algebraic and/or diagrammatic techniques that are known from the conventional single reference CC theory, albeit with some modifications.[25,40] From the physical point of view the operator (28) means that in the reference determinant one replaces a pair of occupied orbitals $|ij\rangle$ with a pair $|kl\rangle$ multiplied by the correlation factor from which the 'content' describable by the GBS has been outprojected. Via disconnected clusters ($\frac{1}{m!}\hat{T}^m$) that arise from the Taylor expansion of the exponential operator in CC-R12/F12 the aforementioned substitution is extended to excited determinants, too, but still restricted to the action of the correlation factor on the pair of orbitals from the space of occupied orbitals. This is fully justified when the reference determinant is prevailing and we are predominantly concerned about the ground state energies. In the description of excited states, such an approach is unbalanced and at least pairs with selected virtual orbitals have to be treated in the same manner.[41]

In principle, in the exponential of (26) one can consider the full operator $\hat{\mathcal{F}}$. If the correlation factor was r_{12} and without parameters related to individual replacement operators in $\hat{\mathcal{F}}$, such an approach would eventually resemble the CC analog of the Hylleraas configuration interaction.[42] At the same time, however, this approach would become practically unfeasible even for small systems. One way to overcome this difficulty is to use the similarity transformed Hamiltonian, the so-called transcorrelated Hamiltonian of Boys and Handy, which terminates at the three-electron interactions.[43] The special form of the transcorrelated Hamiltonian,

$$\hat{H}_{TC} = \exp\left(-\frac{1}{2}\hat{\mathcal{F}}\right)\hat{H}\exp\left(\frac{1}{2}\hat{\mathcal{F}}\right), \qquad (34)$$

which cancels the Coulomb singularity, has been applied to MBPT2 and coupled electron pair approximations[44] with the RI approximation for three-electron integrals.

More general is an extension of the replacement operators of (28) and (29) to

$$\hat{T}_{2'} = \frac{1}{4}\sum_{pqrs} t'^{pq}_{rs}\sum_{\kappa>\lambda}\bar{\mathcal{F}}^{rs}_{\kappa\lambda}\{\hat{a}^\dagger_\kappa\hat{a}^\dagger_\lambda\hat{a}_q\hat{a}_p\}. \qquad (35)$$

and

$$\hat{T}_{1'} = \sum_{pr} t'^p_r\sum_\kappa\sum_l\bar{\mathcal{F}}^{rl}_{\kappa l}\{\hat{a}^\dagger_\kappa\hat{a}_p\}. \qquad (36)$$

Here, one should keep in mind that $\mathcal{F}$ inherently excludes matrix elements describable in the GBS, hence at least one of the indices κ, λ must belong to the OC basis. Several extended *ansätze* have been examined in GTG calculations at the MP2 level by Dahle et al.[47]

$\hat{T}_1$ would now disappear only if the GBS were saturated for all angular momenta involved in it. In this generalization, the SP *ansatz* corresponds to

$$\hat{T}^{(SP)}_{2'} = \frac{1}{4}\sum_{pq}\sum_{\kappa\lambda}\bar{\mathcal{R}}^{pq}_{\kappa\lambda}\{\hat{a}^\dagger_\kappa\hat{a}^\dagger_\lambda\hat{a}_q\hat{a}_p\}. \qquad (37)$$

Further constraints on $\hat{T}$ were applied in the recently proposed extended SP (XSP) *ansatz* of Köhn,[48] where the summation over pq in (37) takes over all *ai* pairs, and the geminal operator is contracted with the response singles (*vide infra*). Moreover, summation over $\kappa\lambda$ remained as in (37), i.e., over $\alpha\beta$, which is different as soon as $\hat{T}$ acts on an excited determinant. Obviously, acting on $|0\rangle$, both $\hat{T}_{2'}$ and $\hat{T}_{2'}$ provide the same result.

EOM-CC-F12 Methods

In the EOM-CCSD-F12 method, the κth excited state ($|\Psi_\kappa\rangle$) satisfies the Schrödinger equation,

$$\hat{H}|\Psi_\kappa\rangle = E_\kappa|\Psi_\kappa\rangle, \qquad (38)$$

$$|\Psi_\kappa\rangle = \hat{R}_\kappa|\Psi_0\rangle, \qquad (39)$$

where the total replacement operator

$$\hat{R}_\kappa = \hat{R}_{\kappa 1} + \hat{R}_{\kappa 2} + \hat{R}_{\kappa 2'}, \qquad (40)$$

with the usual single- and double- excitation operators

$$\hat{R}_{\kappa 1} = \sum_{ia}(r_\kappa)^a_i\{\hat{a}^\dagger_a\hat{a}_i\}, \qquad (41)$$

$$\hat{R}_{\kappa 2} = \frac{1}{4}\sum_{ijab}(r_\kappa)^{ab}_{ij}\{\hat{a}^\dagger_a\hat{a}^\dagger_b\hat{a}_j\hat{a}_i\}, \qquad (42)$$

and the geminal doubles operator,

$$\hat{R}_{\kappa 2'} = \frac{1}{4}\sum_{ijkl}(r'_\kappa)^{ij}_{kl}\hat{\Omega}^{kl}_{ij} + \frac{1}{2}\sum_{ijka}(r'_\kappa)^{ij}_{ka}\hat{\Omega}^{ka}_{ij}, \qquad (43)$$

$$\hat{\Omega}^{pq}_{ij} = \frac{1}{2}\sum_{\alpha\beta}\bar{\mathcal{F}}^{pq}_{\alpha\beta}\{\hat{a}^\dagger_\alpha\hat{a}^\dagger_\beta\hat{a}_j\hat{a}_i\}. \qquad (44)$$

The geminal operator $\hat{\Omega}_{ij}^{ka}$ in the second term of Eq. (43) represents the cusp treatment between the excited electron in the virtual space and those in the occupied orbitals. Importance of the inclusion of such an operator for the description of excited states was pointed out by Neiss et al.[41] Substituting Ψ_κ into (38) and subtracting the ground-state conditions with suitable projections, we obtain the commonly known commutator form of the equation of motion (EOM) expressions,

$$\langle 0 | (\hat{a}_a \hat{a}_i^\dagger)[\hat{\bar{H}}, \hat{R}_\kappa]|0\rangle = \omega_\kappa (r_\kappa)_i^a, \quad \forall a, i, \quad (45)$$

$$\langle 0 | (\{\hat{a}_a \hat{a}_b \hat{a}_j^\dagger \hat{a}_i^\dagger\})[\hat{\bar{H}}, \hat{R}_\kappa]|0\rangle = \omega_\kappa (r_\kappa)_{ij}^{ab}, \quad \forall a, b, i, j, \quad (46)$$

$$\langle 0 | (\hat{\Omega}_{ij}^{kp})^\dagger [\hat{\bar{H}}, \hat{R}_\kappa]|0\rangle = \omega_\kappa \langle 0 | (\hat{\Omega}_{ij}^{kp})^\dagger \hat{R}_{\kappa 2'}|0\rangle,$$
$$\forall i, j, k, p, \quad (47)$$

where we have introduced the similarity transformed Hamiltonian $\hat{\bar{H}} = e^{-\hat{T}} \hat{H} e^{\hat{T}}$, and ω_κ are excitation energies. Although the solutions of Eqs (45), (46), and (47) yield desirable excitation energies and amplitudes of $\hat{R}_\kappa$, numerically stable solutions can be obtained for the ground state by the use of SP *ansatz* in which the geminal amplitudes are fixed to the cusp conditions. More recently, Köhn extended the use of the SP *ansatz* for excited states [48] using the geminal operator,

$$\hat{R}_{\kappa 2'}^{(SP)} = \frac{1}{2} \sum_{ijc} \sum_{\alpha\beta} \bar{\mathcal{R}}_{\alpha\beta}^{ic}(r_\kappa)_j^c \{\hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_j \hat{a}_i\}. \quad (48)$$

In this case, Eq. (47) is not used, but extra terms are added in $\hat{\bar{H}}$ due to the contribution from the geminal operator. The details are discussed for CC linear response theory [48] and for EOM-CCSD.[49]

Multireference CC-F12

Quite recently, we have extended the CC-R12/F12 ansatz to a multireference treatment within the Brillouin–Wigner theory.[50, 51] Our work is based on the Jeziorski–Monkhorst *ansatz*[52] using a cluster operator augmented by the R12/F12 excitations to the complementary orbital basis. The model space is assumed to be spanned by M orthogonal reference configurations $|\Phi_\mu\rangle$, whereas the projection of the exact wavefunction (for the state ω) on the model space $|\Psi_\omega^P\rangle$ is expanded as a linear combination of reference configurations

$$|\Psi_\omega^P\rangle = \sum_{\mu=1}^M C_\mu^\omega |\Phi_\mu\rangle. \quad (49)$$

P stands for the projection operator onto the model space

$$\hat{P} = \sum_{\mu=1}^M |\Phi_\mu\rangle\langle\Phi_\mu|. \quad (50)$$

The exact wavefunction of the ωth electronic state is then obtained as

$$|\Psi_\omega\rangle = \sum_{\mu=1}^M C_\mu^\omega e^{\hat{T}(\mu)} |\Phi_\mu\rangle, \quad (51)$$

where $\hat{T}(\mu)$ is, in general, an excitation operator of the same form as (27) but related (normal ordered) to the specific reference $|\Phi_\mu\rangle$. The amplitudes of $\hat{T}(\mu)$ and the expansion coefficients C_μ^ω are determined using the generalized Bloch equation (for details, see Ref 50). Using of the SP *ansatz* is straightforward with the rational generators (23) related to individual references, i.e., $\hat{T}_{2'}^{(SP)}(\mu)$.

The use of internally contracted geminal basis[26] is an attractive alternative to provide efficient MR R12/F12 methods reducing the number of geminal amplitudes. The SP *ansatz* leads to such expansion naturally and has been employed in MR second-order perturbation theory.[26, 53, 54] Extension of these methods to other MR methods is one of the important challenges in the field of R12/F12.

MATRIX ELEMENTS IN R12/F12 METHODS

The matrix elements involving the correlation factor in the exact (first quantized) formulation may lead to many-particle integrals (*vide infra*). The second quantized formulation by its nature automatically factorizes these integrals to products of one- and/or two- particle integrals summed up over the indices belonging to the virtual orbitals in the CBS basis, which in turn can be expressed through the resolution of identity employing

$$\sum_\alpha = \sum_\kappa - \sum_o. \quad (52)$$

Hence, typically

$$\sum_{\alpha>\beta} \bar{A}_{pq}^{\alpha\beta} \bar{f}_{\alpha\beta}^{rs} = \sum_{\kappa>\lambda} \bar{A}_{pq}^{\kappa\lambda} \bar{f}_{\kappa\lambda}^{rs} - \sum_{\kappa>m} \bar{A}_{pq}^{\kappa m} \bar{f}_{\kappa m}^{rs}, \quad (53)$$

where $\hat{A}$ is either $\hat{g} = r_{12}^{-1}$ or $\hat{f}_{12}$. Recognizing the two-particle resolution of identity in the first term, one arrives at a new type of two-particle integrals over $\hat{A}\hat{f}$. Operators that appear in the R12/F12 theories in this manner are listed in Table 2 together with f_{12}. Two-electron integrals over these operators have to be

TABLE 2 | Operators of Two-Electron Integrals in R12/F12 Methods

Operator	Omissible Case
f_{12}	–
f_{12}/r_{12}	R12
$-(\nabla_1^2 f_{12}) - (\nabla_1 f_{12}) \cdot (\nabla_1 - \nabla_2)$	Approximation C
f_{12}^2	–
f_{12}^2/r_{12}	–
$-(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12})$	R12, STG (Proportional to f_{12}^2)

evaluated in addition to the usual two-electron repulsion ones. Operators f_{12}/r_{12} and $-(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12})$ are simple constants in the R12 case ($f_{12} = r_{12}$). Moreover, $-(\nabla_1 f_{12}) \cdot (\nabla_1 f_{12})$ can be skipped in the STG case as it is proportional to f_{12}^2.[7] Operator in the third entry of the Table 2 follows from the terms like the first term of Eq. (2), or formally a similar term in the CC-R12/F12. In these terms, the product

$$\sum_{\alpha, \beta} \bar{\mathcal{F}}_{ij}^{\alpha\beta} F_\alpha^\gamma \bar{\mathcal{F}}_{\gamma\beta}^{kl} \tag{54}$$

has to be evaluated, which is not as straightforward task as for the products of the (53) type. In the essential early work on the evaluation of matrix elements in the R12 theory, assumptions like the generalized Brillouin theorem or even the extended Brillouin theorem ($F_p^{\alpha'} = 0, \alpha' \in \mathrm{OC}$) have been applied *a priori* in the spirit of the SA.[6] Subsequent derivation leads to integrals over the commutator of the kinetic energy operator with f_{12} that is hidden in the pertinent third entry of the Table 2. Not so long ago, we showed that if no *a priori* assumptions are applied in the evaluation of (54), integrals over the aforementioned commutator are not needed.[55] This has been denoted as approximation 'C' to distinguish this approach from the formerly introduced approximations 'A' and 'B'.[6] Consequently, using STG along with the C approximation in F12 implies the requirement of two-electron integrals over $\exp(-\alpha r_{12})$ and $\exp(-\alpha r_{12})/r_{12}$ with $\alpha = \gamma$ and $\alpha = 2\gamma$. With STG correlation factor, the integrals over the commutator are in fact reduced to the ones over $\exp(-\alpha r_{12})$ in the approximations A and B, as well.

Many-Electron Integrals

The second term of Eq. (53) would give rise to three-particle integrals. The simplest of such integrals are

in $\langle u_{ij} | r_{12}^{-1} | \{ij\} \rangle$ of Eq. (2) in the form,

$$\langle ij | r_{12}^{-1} \hat{O}_2 f_{12} | kl \rangle = \sum_m \langle ijm | r_{12}^{-1} f_{13} | kml \rangle$$

$$= \sum_{\kappa m} g_{ij}^{\kappa m} f_{\kappa m}^{kl}. \tag{55}$$

R12 and F12 methods replace the summation over the complete basis by a finite one using the unification of GBS and CABS to decompose the required many-electron integrals into products of two-electron integrals,

$$\sum_\kappa g_{ij}^{\kappa m} f_{\kappa m}^{kl} \overset{\mathrm{CABS}}{\simeq} \sum_{p'} g_{ij}^{p'm} f_{p'm}^{kl}. \tag{56}$$

From considerations at an atomic level follows that such an expansion is justified as soon as the basis of p' functions is saturated at the level of $3L_{\mathrm{occ}}$.[6] To treat such a CABS is relatively inexpensive for smaller molecular systems involving atoms of the first two periods, but alternatives for larger systems are more than welcome. Such an alternative is provided by the use of numerical quadratures (QD)[23] when the three-electron integrals are evaluated as

$$\langle ijm | r_{12}^{-1} f_{13} | kml \rangle \overset{\mathrm{QD}}{\simeq} \sum_g \bar{\phi}_i(\mathbf{r}_g) \phi_k(\mathbf{r}_g) g_{jm}^g f_{ml}^g, \tag{57}$$

$$g_{pq}^g = \int d\mathbf{r} \phi_p(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}_g|} \phi_q(\mathbf{r}), \tag{58}$$

$$f_{pq}^g = \int d\mathbf{r} \phi_p(\mathbf{r}) f(|\mathbf{r} - \mathbf{r}_g|) \phi_q(\mathbf{r}), \tag{59}$$

$\bar{\phi}_i(\mathbf{r}_g) = \phi_i(\mathbf{r}_g) w_g$ with the quadrature weights w_g, and we have suppressed the integration over the spin coordinate. The formal computational costs for the elementary objects scales as $N^3(N + C)$ for CABS (56) and $N^2 G$ for QD (57) where G is the number of the quadrature points. The number of grid points is usually of the order of 10,000 per atom for good accuracy of integrals.[23, 56] Hence, QD is more advantageous for large molecules. For cyclic three-electron integrals with $r_{12}^{-1} f_{13} f_{23}$, QD cannot be applied for both of the 1 and 2 electronic coordinates due to the divergence of r_{12}^{-1} at coincident quadrature points. A hybrid QD/CABS technique should be introduced for these classes of integrals, similarly as in the hybrid QD/RI method used for four-electron integrals in MP2-F12.[56] It is noted that the density fitting technique can increase the efficiency and accuracy of the RI approximation.[57, 58] The robust expansion of density fitting leads to an energy error only quadratic to the density error.[57]

Integrals over Slater-Type Geminals

All integral expressions needed in F12 methods of the analytic STG can be obtained from integrals over the Yukawa potential,

$$\left(\mathbf{ab} \left| \frac{e^{-\gamma r_{12}}}{r_{12}} \right| \mathbf{cd} \right)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_\mathbf{a}(\mathbf{r}_1) \varphi_\mathbf{b}(\mathbf{r}_1) \frac{e^{-\gamma r_{12}}}{r_{12}} \varphi_\mathbf{c}(\mathbf{r}_2) \varphi_\mathbf{d}(\mathbf{r}_2), \qquad (60)$$

which can be calculated using standard algorithms for electron repulsion integrals,[59–61, 63] where φ stands for the standard Cartesian Gaussian-type functions (GTFs),

$$\varphi_\mathbf{a}(\mathbf{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{a_z} e^{-\zeta_a |\mathbf{r} - \mathbf{A}|^2}, \qquad (61)$$

and the functions $\varphi_\mathbf{b}$, $\varphi_\mathbf{c}$, $\varphi_\mathbf{d}$ are defined in the same way with the exponents, ζ_b, ζ_c, and ζ_d at the centers $\mathbf{B}$, $\mathbf{C}$, and $\mathbf{D}$. The Yukawa potential can be expressed in terms of Gaussian functions in the integral transformation,[7]

$$\frac{e^{-\gamma r}}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty du \exp\left(-\frac{\gamma^2}{4u^2} \right) \exp(-u^2 r^2). \qquad (62)$$

The Obara–Saika recurrence relation[61] to increase the angular momentum indices holds for the auxiliary integrals over the Yukawa potential,

$$\left(\mathbf{ab} \left| \frac{e^{-\gamma r_{12}}}{r_{12}} \right| \mathbf{cd} \right)^{(m)} = \frac{2}{\sqrt{\pi}} \int_0^\infty du \left(\frac{u^2}{\rho + u^2} \right)^m$$

$$\times \exp\left(-\frac{\gamma^2}{4u^2} \right) (\mathbf{ab}|e^{-u^2 r_{12}^2}|\mathbf{cd}), \qquad (63)$$

where $\rho = \frac{\zeta \eta}{\zeta + \eta}$ is of only orbital exponents, $\zeta = \zeta_a + \zeta_b$ and $\eta = \zeta_c + \zeta_d$. The auxiliary integrals with $m = 0$ are identical to $(\mathbf{ab}|\frac{e^{-\gamma r_{12}}}{r_{12}}|\mathbf{cd})$, which can be obtained from the integrals over s-type functions,

$$\left(00 \left| \frac{e^{-\gamma r_{12}}}{r_{12}} \right| 00 \right)^{(m)} = 2\sqrt{\frac{\rho}{\pi}} S_{ab} S_{cd} G_m(T, U), \quad (64)$$

for all m from 0 to the total angular momentum of the orbitals, where S_{ab} and S_{cd} are overlap functions of the corresponding s-type functions,

$$S_{ab} = \left(\frac{\pi}{\zeta} \right)^{\frac{3}{2}} e^{-\frac{\zeta_a \zeta_b}{\zeta}(\mathbf{A} - \mathbf{B})^2}, \qquad (65)$$

$$S_{cd} = \left(\frac{\pi}{\eta} \right)^{\frac{3}{2}} e^{-\frac{\zeta_c \zeta_d}{\eta}(\mathbf{C} - \mathbf{D})|^2}, \qquad (66)$$

and $G_m(T, U)$ is the generalized Boys function,[7, 56]

$$G_m(T, U) = \int_0^1 dt t^{2m} \exp[-Tt^2 + U(1 - t^{-2})], \qquad (67)$$

with

$$T = \rho(\mathbf{P} - \mathbf{Q})^2, \qquad (68)$$

$$U = \frac{\alpha^2}{4\rho}, \qquad (69)$$

$$\mathbf{P} = \frac{\zeta_a \mathbf{A} + \zeta_b \mathbf{B}}{\zeta}, \quad \mathbf{Q} = \frac{\zeta_c \mathbf{C} + \zeta_d \mathbf{D}}{\eta}. \qquad (70)$$

The expression for integrals over STG can be obtained by differentiating the Yukawa one with respect to the exponent. It should be noted that $G_{-1}(T, U)$ arises from the differentiation. All other integrals needed for the Approximations A and B can be obtained from the standard algorithms as variants of the Yukawa integrals.[7]

In the Coulomb potential limit ($\gamma = 0$), all integral evaluation is not changed except that $G_m(T, U)$ is reduced to the usual Boys function,

$$F_m(T) = \int_0^1 dt t^{2m} \exp(-Tt^2). \qquad (71)$$

In other words, any $F_m(T)$-based algorithms for electron repulsion integrals can be used for Yukawa integrals by replacing $F_m(T)$ by $G_m(T, U)$. F12 integrals in our modified DIRCCR12-OS program[33] are actually implemented in such a way using the McMurchie–Davidson algorithm. More recently, Shiozaki introduced a method using orthogonal quadratures which is a generalization of the Dupuis–Rys–King algorithm.[64]

CONCLUSIONS

Nowadays, the explicitly correlated *ab initio* methods based or being inspired by the original idea of R12 treatment represent practical alternatives in order to achieve the CBS accuracy. Their greatest methodological advantage is that these methods essentially preserve the orbital product expansion, but at the same time the electron correlation cusp is effectively described by introducing orbital pair products multiplied by a correlation factor. For the last decade, it has been revealed that Slater-type geminal is the most advantageous choice for the explicitly

correlated part. Moreover, the employment of theoretical cusp conditions for the orbital pair products with STG (the SP *ansatz*) has provided a much cheaper yet efficient alternative to the full optimization of the

weight coefficients for the individual pair function. In this overview, we have summarized the basic aspects of these theories in the context of our contribution to the field.

ACKNOWLEDGMENTS

REFERENCES

1. Hylleraas EA. New calculation of the energy of helium in the ground-state, and the deepest terms of ortho-helium. *Z Phys* 1929, 54:347–366.

2. Rychlewski J, ed. *Progress in Theoretical Chemistry and Physics: Explicitly Correlated Wave Functions in Chemistry and Physics*. Dordrecht: Kluwer Academic Publisher; 2003.

3. Kato T. On the eigenfunctions of many-particle systems in quantum mechanics. *Commun Pure Appl Math* 1957, 10:151–177.

4. Pack RT, Brown WB. Cusp conditions for molecular wavefunctions. *J Chem Phys* 1966, 45:556–559.

5. Kutzelnigg W. r_{12}-Dependent terms in the wave function as closed sums of partial wave amplitudes for large l. *Theor Chim Acta* 1985, 68:445–469.

6. Kutzelnigg W, Klopper W. Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. I. General theory. *J Chem Phys* 1991, 94:1985–2001.

7. Ten-no S. Initiation of explicitly correlated Slater-type geminal theory. *Chem Phys Lett* 2004, 398:56–61.

8. Klopper W, Manby FR, Ten-no S, Valeev EF. R12 methods in explicitly correlated molecular electronic structure theory. *Int Rev Phys Chem* 2006, 25:427–468.

9. Helgaker T, Klopper W, Tew DP. Quantitative quantum chemistry. *Mol Phys* 2008, 106:2107–2143.

10. Werner H-J, Adler TB, Knizia G, Manby FR. Efficient explicitly correlated coupled-cluster approximations. In: Čársky P, Paldus J, Pittner J, eds. *Recent Progress in Coupled Cluster Methods*. Dordrecht, Heidelberg, London, New York: Springer; 2010, 573–620.

11. Tew DP, Hättig C, Bachorz RA, Klopper W. Explicitly correlated coupled-cluster theory. In: Čársky P, Paldus J, Pittner J, eds. *Recent Progress in Coupled Cluster Methods*. Dordrecht, Heidelberg, London, New York: Springer; 2010, 535–572.

12. Klopper W, Samson CCM. Explicitly correlated second-order Møller–Plesset methods with auxiliary basis sets. *J Chem Phys* 2002, 116:6397–6410.

13. Valeev EF. Improving on the resolution of the identity in linear R12 ab initio theories. *Chem Phys Lett* 2004, 395:190–195.

14. Klopper W, Kutzelnigg W. Møller–Plesset calculations taking care of the correlation CUSP. *Chem Phys Lett* 1987, 134:17–22.

15. Klopper W. Orbital-invariant formulation of the MP2-R12 method. *Chem Phys Lett* 1991, 186:583–585.

16. Pan K-C, King HF. Gaussian geminals for electron pair correlation. *J Chem Phys* 1970, 53:4397–4399.

17. Werner H-J, Adler TB, Manby FR. General orbital invariant MP2-F12 theory. *J Chem Phys* 2007, 126:164102(18).

18. May AJ, Manby FR. An explicitly correlated second order Moller–Plesset theory using a frozen Gaussian geminal. *J Chem Phys* 2004, 121:4479–4485.

19. Persson BJ, Taylor PR. Accurate quantum–chemical calculations: the use of Gaussian-type geminal functions in the treatment of electron correlation. *J Chem Phys* 1996, 105:5915–5926.

20. May AJ, Valeev E, Polly R, Manby FR. Analysis of the errors in explicitly correlated electronic structure theory. *Phys Chem Chem Phys* 2005, 7:2710–2713.

21. Tew DP, Klopper W. New correlation factors for explicitly correlated electronic wave functions. *J Chem Phys* 2005, 123:074101(13).

22. Valeev EF. Combining explicitly correlated R12 and Gaussian geminal electronic structure theories. *J Chem Phys* 2006, 125:244106(10).

23. Ten-no S. Explicitly correlated second order perturbation theory: introduction of a rational generator and numerical quadratures. *J Chem Phys* 2004, 121:117–129.

24. Noga J, Kedžuch S, Šimunek J. Second order explicitly correlated R12 theory revisited: a second quantization framework for treatment of the operators' partitionings. *J Chem Phys* 2007, 127:034106(11).

25. Noga J, Kutzelnigg W. Coupled cluster theory that takes care of the correlation cusp by inclusion of linear terms in the interelectronic coordinates. *J Chem Phys* 1994, 101:7738–7762.

26. Ten-no S. A simple F12 geminal correction in multireference perturbation theory. *Chem Phys Lett* 2007, 447:175–179.

27. Bokhan D, Ten-no S, Noga J. Implementation of the CCSD(T)-F12 method using cusp conditions. *Phys Chem Chem Phys* 2008, 10:3320–3326.

28. Bokhan D, Bernadotte S, Ten-no S. Explicitly correlated second-order Moller–Plesset perturbation theory for unrestricted Hartree–Fock reference functions with exact satisfaction of cusp conditions. *J Chem Phys* 2009, 131:084105(7).

29. Knizia G, Adler TB, Werner H-J. Simplified CCSD(T)-F12 methods: theory and benchmarks. *J Chem Phys* 2009, 130:054104(20).

30. Wilke JJ, Schaefer HF. The subtleties of explicitly correlated Z-averaged perturbation theory: choosing an R12 method for high-spin open-shell molecules. *J Chem Phys* 2009, 131:244116(10).

31. Tew DP, Klopper W. Open-shell explicitly correlated F12 methods. *Mol Phys* 2010, 108:315–325.

32. Noga J, Kutzelnigg W, Klopper W. CC-R12, a correlation cusp corrected coupled-cluster method with a pilot application to the Be_2 potential curve. *Chem Phys Lett* 1992, 199:497–504.

33. Noga J, Kedžuch S, Šimunek J, Ten-no S. Explicitly correlated coupled cluster F12 theory with single and double excitations. *J Chem Phys* 2008, 128:174103(10).

34. Explicitly correlated coupled cluster F12 theory with single and double excitations. *J Chem Phys* 128, 174103 (2008) Erratum: *J Chem Phys* 2009, 130:029901(1).

35. Arponen J, Bishop RF, Pajanne E. Extended coupled-cluster method. I. Generalized coherent bosonization as a mapping of quantum theory into classical Hamiltonian mechanics. *Phys Rev A* 1987, 36:2519–2538.

36. Noga J, Šimunek J. On the one-particle basis set relaxation in R12 based theories. *Chem Phys* 2009, 356:1–6.

37. Alder TB, Knizia G, Werner H-J. A simple and efficient CCSD(T)-F12 approximation. *J Chem Phys* 2007, 127:221106(4).

38. Fliegl H, Klopper W, Hättig C. Coupled-cluster theory with simplified linear-r_{12} corrections: the CCSD(R12) model. *J Chem Phys* 2005, 122:084107(10).

39. Tew DP, Klopper W, Neiss C, Hättig C. Quintuple-zeta quality coupled-cluster correlation energies with triple-zeta basis sets. *Phys Chem Chem Phys* 2007, 9:1921–1930.

40. Noga J, Kutzelnigg W, Klopper W. CC-R12: an explicitly correlated coupled-cluster theory. In: Bartlett RJ, ed. *Recent Advances in Computational Chemistry*. Vol 3. Singapore: World Scientific; 1997, 1–48.

41. Neiss C, Hättig C, Klopper W. Extensions of r_{12} corrections to CC2-R12 for excited states. *J Chem Phys* 2006, 125:064111(7).

42. Hylleraas EA. Schrödinger two-electron atomic problem. *Advan Quantum Chem* 1964, 1:1–33.

43. Boys SF, Handy NC. The determination of energies and wavefunctions with full electronic correlation. *Proc R Soc A* 1969, 310:43–61.

44. Ten-no S. A feasible transcorrelated method for treating electronic cusps using a frozen Gaussian geminal. *Chem Phys Lett* 2000, 330:169–174.

45. Hino O, Tanimura Y, Ten-no S. Biorthogonal approach for explicitly correlated calculations using the transcorrelated Hamiltonian. *J Chem Phys* 2001, 115:7865–7871.

46. Hino O, Tanimura Y, Ten-no S. Application of the transcorrelated Hamiltonian to the linearized coupled cluster singles and doubles model. *Chem Phys Lett* 2002, 353:317–323.

47. Dahle P, Helgaker T, Jonsson D, Taylor PR. Accurate quantum–chemical calculations using Gaussian-type geminal and Gaussian-type orbital basis sets: applications to atoms and diatomics. *Phys Chem Chem Phys* 2007, 9:3112–3126.

48. Köhn A. A modified ansatz for explicitly correlated coupled-cluster wave functions that is suitable for response theory. *J Chem Phys* 2009, 130:104104(14).

49. Bokhan D, Ten-no S, unpublished work (2010).

50. Kedžuch S, Demel O, Pittner J, Noga J. Multireference R12 coupled cluster theory. In: Čársky P, Paldus J, Pittner J, eds. *Recent Progress in Coupled Cluster Methods*. Dordrecht, Heidelberg, London, New York: Springer; 2010, 251–266.

51. Kedžuch S, Demel O, Pittner J, Ten-no S, Noga J. Multireference F12 coupled cluster theory. *Chem Phys Lett* In press.

52. Jeziorski B, Monkhorst HJ. Coupled-cluster method for multideterminantal reference states. *Phys Rev A*, 1981, 24:1668–1681.

53. Torheyden M, Valeev EF. Universal perturbative explicitly correlated basis set incompleteness correction. *J Chem Phys* 2009, 131:171103(4).

54. Shiozaki T, Werner H-J. Communication: second-order multireference perturbation theory with explicit correlation: CASPT2-F12. *J Chem Phys* 2010, 133:141103(4).

55. Kedžuch S, Milko M, Noga J. Alternative formulation of the matrix elements in MP2-R12 theory. *Int J Quantum Chem* 2005, 105:929–936.

56. Ten-no S. New implementation of second-order Møller–Plesset perturbation theory with an analytic Slater-type geminal. *J Chem Phys* 2007, 126:014108(12).

57. Manby FR. Density fitting in second-order linear-r_{12} Møller–Plesset perturbation theory. *J Chem Phys* 2003, 119:4607–4613.

58. Ten-no S, Manby FR. Density fitting for the decomposition of three-electron integrals in explicitly correlated electronic structure theory. *J Chem Phys* 2003, 119:5358–5363.

59. Dupuis M, Rys J, King HF. Evaluation of molecular integrals over Gaussian basis functions. *J Chem Phys* 1976, 65:111–116.

60. McMurchie LE, Davidson ER. One- and two-electron integrals over Cartesian Gaussian functions. *J Comput Phys* 1978, 26:218–231.

61. Obara S, Saika A. Efficient recursive computation of molecular integrals over Cartesian Gaussian functions. *J Chem Phys* 1986, 84:3963–3974.

62. Obara S, Saika A. General recurrence formulas for molecular integrals over Cartesian Gaussian functions. *J Chem Phys* 1988, 89:1540–1559.

63. Ahlrichs R. A simple algebraic derivation of the Obara–Saika scheme for general two-electron interaction potentials. *Phys Chem Chem Phys* 2006, 8:3072–3077.

64. Shiozaki T. Evaluation of Slater-type geminal integrals using tailored Gaussian quadrature. *Chem Phys Lett* 2009, 479:160–164.