Explicitly correlated wave functions: summary and perspective

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Abstract We summarize explicitly correlated electronic structure theory in perspective of future work in the field. Earlier stages of approaches with different *Ansätze* in physics and chemistry are described. We then discuss recent advances focusing on explicitly correlated wave functions using cusp conditions. Removal of Coulomb singularities in terms of the rational generator is brought out from the viewpoint of many-body perturbation theory. On the basis of decomposition schemes for many-electron integrals in R12 and F12 methods, we further discuss the possibility of increasing the accuracy of molecular numerical integration and massively parallel calculations of explicitly correlated methods.

Keywords Cusp conditions · R12 theory · F12 theory · SP *Ansatz* · Slater-type geminals · Many-electron integrals · Resolution of the identity · Auxiliary basis set · Numerical quadratures · Pseudospectral reweighting · Hybrid parallelization

1 Introduction

Explicitly correlated wave function treatment is the most strengthened strategy for accurate electronic structure calculations in modern quantum chemistry. The success of ab initio theory is certainly due to the popularity of

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Gaussian-type basis functions, in which efficient algorithms for molecular integrals are readily available. Nevertheless, all standard post Hartree–Fock (HF) calculations in many-body perturbation theory (MBPT), configuration interaction (CI), and coupled–cluster (CC) theory suffer from a slow convergence of electron correlation even with one-electronic basis sets specifically designed for electron correlation [1–7] to minimize the basis set error with respect to the limiting energy for the same wave function model.

The use of extrapolation schemes has successfully filled up the deficiency of basis set convergence. The two-point extrapolation formula of Helgaker et al. [8, 9],

$$E_X = E_\infty + AX^{-3}, \tag{1}$$

for the correlation consistent polarized hierarchy of Dunning, cc-pVXZ with the cardinal number X, has been applied for accurate molecular equilibrium structures, atomization energies, and reaction enthalpies [10, 11], yet the information about wave function in near basis set limit is missing. Before long, a wide interest in the direct treatment of Coulomb holes arose in the community, and several research groups have been engaged in explicitly correlated electronic structure theory extensively for the last decade. The recent advances with novel ideas crucial for practical applications are largely indebted to the signpost paper of Kutzelnigg [12] published at the halfway point of the 50 year history of the present journal. Many review articles have appeared recently [13–18], and the readers should refer to them for theoretical details.

In the present perspective, we first outline earlier stages of explicitly correlated wave functions in the following section. We shall start from the Hylleraas expansion for the ground state He atom, the uses of possible wave functions forms for explicit electron correlation in transcorrelated,

quantum Monte Carlo, Gaussian-type geminal (GTG), and R12 methods are described. In Sect. 3, we outline explicitly correlated theory using cusp conditions. In terms of the rational generator with a short-range correlation factor as the Slater-type geminal function, we investigate the expansion of explicitly correlated wave functions perturbationally. In Sect. 4, summary and perspective on computational methods for many-electron integrals are presented.

2 Earlier stages of explicitly correlated methods

The Hylleraas expansion for the ground state of He [19],

$$\psi = e^{-\zeta s} \sum_{nlm} c_{nlm} s^n t^l u^m, \tag{2}$$

with the coordinates, $s = r_1 + r_2$, $t = -r_1 + r_2$, and $u = r_{12}$, has exhibited that the inclusion of the inter-electronic distance u is significantly important. The use of only three terms 1, u, and t^2 in $s^n t^l u^m$, is accurate to 0.035 eV [20]. More general expansion of Kinoshita with negative powers of variables s and u, which suffices for a formal solution of the wave function, has given extremely accurate energies [21]. Calculations with analogous expansions were performed for the H_2 molecule [22, 23].

The exact wave function must obey cusp conditions that prescribe the proper discontinuity behavior at the coalescence point. We shall focus on the solution of the Schrödinger equation of two-electrons letting r, θ, and φ spherical polar coordinates of the inter-electronic distance vector $\mathbf{r}_{12}$. The wave function around the coalescence point written as

$$\psi = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} r^l f_{lm}(r) Y_l^m(\theta, \varphi), \tag{3}$$

satisfies the cusp conditions [24, 25],

$$f_{lm} = \left[1 + \frac{\lambda r}{2(l+1)} + O(r^2) \right] f_{lm}^{(0)}, \tag{4}$$

where f_{lm} is a function of the center of mass coordinate, $\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}$, λ is a strength parameter of the Coulomb interaction in the electron repulsion part, and $f_{lm}^{(0)}$ is the first term of the expansion, $f_{lm} = \sum_{k=0}^{\infty} r^k f_{lm}^{(k)}$. For solutions of a spin-free Hamiltonian, the spatial wave function is either symmetric (singlet) or antisymmetric (triplet) to interchange of the particles, and thus the expansion contains only terms either with even or odd l as [25]

$$\psi^{(S)} = \hat{\psi}_0^{(S)} \left(1 + \frac{\lambda}{2} r \right) + O(r^2), \tag{5}$$

$$\psi^{(T)} = \mathbf{r}_{12} \cdot \mathbf{w}_{12} \left(1 + \frac{\lambda}{4} r \right) + O(r^3), \tag{6}$$

where $\hat{\psi}_0^{(S)} = f_{00}^{(0)} Y_0^0$ and $\mathbf{r}_{12} \cdot \mathbf{w}_{12} = \sum_{l=-1}^{1} f_{1m}^{(0)} Y_1^m r$. (5) is rewritten as

$$\lim_{r \to 0} \frac{\partial \psi^{(S)}}{\partial r} = \frac{\lambda}{2} \hat{\psi}_0^{(S)}(r = 0), \tag{7}$$

whose spherical average is equivalent to the cusp condition of Kato [24]. In either case, it is essential that the cusp behavior assures the regularity of the entire Schrödinger equation at the coalescence point with Coulomb singularity.

Kutzelnigg and Morgan suggested that a further expansion of $\mathbf{R}$ in spherical harmonics leads to unnatural parity states [26], and the alternation rules that account for most of violations of Hund's first rule are associated with the parity cases [27]. The leading term of $f_{00}^{(0)}$ is absent in unnatural parity singlet states, which follow a cusp condition different from (5) and (6). It is also noted that the exact solution at the triple coalescence point is more complicated with logarithmic terms as $\rho^2 ln \rho$ for $\rho = (r_1^2 + r_2^2)^{1/2}$ [28–30], and the importance of such a term for a improved convergence was shown numerically [31].

For correlated N-electronic wave functions, the most popular expansion is in the form,

$$\psi = C \sum_k d_k D_k, \tag{8}$$

where D_k are Slater determinants of spin-orbitals, and C is a product of n-electron correlation factors J_n,

$$C = \prod_{n=2}^{N} J_n. \tag{9}$$

The simplest choice of this type is the Jastrow–Slater wave function consisting of two-body correlation factors [32] and a single Slater-determinant,

$$\psi = \prod_{i > j} J_2(\mathbf{r}_i, \mathbf{r}_j) D(\phi_1, \phi_2, \ldots, \phi_N). \tag{10}$$

Various function forms have been proposed for J_n using power series of electron–nucleus and electron–electron distances and their scaled variables as $r_{ij}/(a + r_{ij})$. However, the difficulty of calculating the multidimensional integrals arising from $C\hat{H}C$ in a variational treatment has hindered the use of the wave function *Ansatz* in ordinary electronic structure calculations of molecules. The variational Monte Carlo (VMC) techniques permit the use of the correlated wave function (8) by minimizing the energy variance [33].

Boys and Handy [34] introduced a method to determine the variables C and D with the transcorrelated Hamiltonian,

$$\hat{H}_T = C^{-1} \hat{H} C. \tag{11}$$

As C is commutable with any operators in $\hat{H}$ except for the kinetic energy one, only a few additional terms arise from the similarity transformation. For C of only two-body correlation factor $J_2(\mathbf{r}_i, \mathbf{r}_j) = \exp(f_{ij})$, the transcorrelated Hamiltonian $C^{-1}\hat{H}C$ contains extra two-electron operators from the commutators, $[\nabla_i^2, f_{ij}]$ and $[[\nabla_i^2, f_{ij}], f_{ij}]$, and three-electron operators from $[[\nabla_i^2, f_{ij}], f_{ik}]$. Besides the purpose to determine C and D (which still requires the computation of awkward three-electron integrals), the use of a similarity transformation has drawn attention to eliminate the Coulomb singularities from the many-electron Hamiltonian to accelerate the convergence of a CI expansion. Hirschfelder [35] showed the explicit form of the similarity transformed Hamiltonian for the spherically symmetric correlation factor,

$$C = \prod_{i > j} \left[1 + \frac{1}{2} r_{ij} \exp(-\alpha r_{ij}) \right], \tag{12}$$

and the system of equation involving new operators as

$$-\frac{\mathbf{r}_{ij}}{r_{ij}} \cdot (\nabla_i - \nabla_j), \tag{13}$$

for cusp-less wave functions can be made regular. Similar discussions were made more recently [36–38], and second-order perturbation [39] and approximated coupled cluster methods [40, 41] were developed either with the usual HF reference or biorthogonal one-particle states for the similarity transformed Hamiltonian [39, 40]. It is also noted that the use of the transcorrelated Hamiltonian $\hat{H}_T$ in VMC (TC-VMC) is advantageous permitting the nodal optimization achieved by the self-consistent field calculation for $\hat{H}_T$ [42, 43]. (See also the recent paper of Luo et al. [44] for more applications of $\hat{H}_T$ in quantum Monte Carlo calculations.)

The use of explicitly correlated Gaussian (ECG) functions permits the computation of many-electron integrals inevitable in explicitly correlated calculations [45, 46]. Especially, on the basis of pair correlation theory of Sinanoğlu [47–49], various many-body perturbation theories have been developed using GTG basis [50–57] in the form,

$$\hat{Q}_{12} \exp\left(-\alpha r_{12}^2\right) \phi_i(1) \phi_j(2), \tag{14}$$

where $\hat{Q}_{12}$ is the strong orthogonality (SO) projection operator,

$$\hat{Q}_{12} = \left(1 - \hat{O}_1\right)\left(1 - \hat{O}_2\right), \tag{15}$$

with projectors onto the occupied orbitals,

$$\hat{O}_n = \sum_{i=1}^{\text{occ.}} |\phi_i(n)\rangle\langle\phi_i(n)|, \tag{16}$$

and the orbitals ϕ are also expanded into Gaussian-type functions. Several approaches with different functional

forms instead of the original use of SO were proposed to eliminate the requirement of high-dimensional objects like four-electron integrals. (For details involving ECG, see the recent review article on GTG [17].) Apparently, it is necessary to take a linear combination of GTG functions to approximate the cusp behavior as the first derivative of GTG is zero at the coalescence.

In the seminal paper of Kutzelnigg [12], partial wave expansion analyses for the S-state of He-like atoms were performed using the simple *Ansatz*,

$$\psi = \left(1 + \frac{1}{2} r_{12}\right)\psi_0 + \chi, \tag{17}$$

with a bare-nucleus wave function ψ_0 and a component expanded in products of one-particle functions, χ. It was demonstrated that the leading term of the partial wave increment of the correlation energy obtained with a linear combination of determinants alone [58, 59] going as $(l + \frac{1}{2})^{-4}$ is due to the basis set expansion of

$$\frac{1}{2} = \sum_{l=0}^{\infty} \langle\psi_0|(r_{12}^{-1})_l \left(\frac{1}{2} r_{12}\right)_l |\psi_0\rangle, \tag{18}$$

and a closed summation of the slowly converging contributions to the partial wave expansion can be accomplished by the introduction of the term $1 + \frac{1}{2} r_{12}$. This notion was realized for general molecules by the introduction of the resolution of the identity (RI) approximations for many-electron integrals [60]. (See the following section for RI approximations, and Sect. 3.3 of the review article [13] for elaborative discussions of RI.) Kutzelnigg and Klopper developed the so-called standard approximation (SA) for intermediates on the basis of analysis of partial wave expansion in R12 theory [61]. It is noted that the linear r_{12} behavior is not favorable for large distances, and Klopper introduced the unitary invariant *Ansatz* to mitigate this feature [62],

$$|w_{ij}\rangle = \frac{1}{2} \sum_{kl} c_{kl}^{ij} \hat{Q}_{12} r_{12} |\{kl\}\rangle, \tag{19}$$

where w_{ij} is the explicitly correlated part of the pair function for the noninteracting $\{ij\}$. (See Table 1 for definitions of orbitals indices.) The GTG and original R12 methods retain only the diagonal amplitudes c_{ij}^{ij} in (19) for spin-adapted pair functions, and the linear r_{12} *Ansatz* with delocalized orbitals leads to $c_{ij}^{ij} = 0$ in the dissociation limit. This problem can be avoided by introducing the off-diagonal amplitudes c_{kl}^{ij}. Furthermore, Noga et al. [63–65] developed coupled–cluster methods with the R12 *Ansatz* (CC-R12), which provides highly accurate results [66] at the same scaling of the standard CC calculations.

Table 1 Convention of orbital indices

$p, q, r, \ldots$	Orbitals in the given basis set (GBS)
$i, j, k, \ldots$	Occupied orbitals
$a, b, c, \ldots$	Virtual orbitals in GB
$\kappa, \lambda, \mu, \ldots$	Orbitals in the complete basis set (CBS)
$\alpha, \beta, \gamma, \ldots$	Virtual orbitals in CBS
$\alpha', \beta', \gamma', \ldots$	Orthogonal complement of GBS
$p', q', r', \ldots$	Auxiliary basis set (ABS)

Corresponding capital indices are used for spatial orbitals

3 Explicitly correlated theory using cusp conditions

The linear r_{12} correlation factor is valid in the vicinity of the coalescence point where the cusp conditions hold. However, one can easily confirm that the behavior cannot be applied for distant pairs. The second-order interaction energy of the He dimer with the HF reference in the dissociation limit is

$$
U^{(2)} = -4 \sum_{\substack{m \neq 0 \\ n \neq 0}} \frac{|\langle np_A mp_B | r_{12}^{-1} | 1s_A 1s_B \rangle|^2}{E_m^A + E_n^B - E_{1s}^A - E_{1s}^B}.
\tag{20}
$$

The standard binomial Taylor expansion of the Coulomb interaction $|\mathbf{R} + \mathbf{a} - \mathbf{b}|^{-1}$ gives the well-known limit of the first-order amplitude,

$$
\psi_{np_A mp_B}^{(1)} = -\frac{\langle np_A mp_B | r_{12}^{-1} | 1s_A 1s_B \rangle}{E_m^A + E_n^B - E_{1s}^A - E_{1s}^B} \propto R^{-3},
\tag{21}
$$

while the expansion of $|\mathbf{R} + \mathbf{a} - \mathbf{b}|$ leads to a different asymptotic behavior,

$$
\langle np_A mp_B | r_{12} | 1s_A 1s_B \rangle \propto R^{-1}.
\tag{22}
$$

Fortunately, the usual CI expansion is effective for dispersion coefficients because the virtual orbitals only with $\Delta l = \pm 1$ with respect to the occupied orbitals contribute to the C_6 coefficients.

There are two ways to eliminate the unphysical long-range behavior for distant pairs. One is to employ extra geminals that cancel the unfavorable contribution as in the unitary invariant *Ansatz* (19) (See also more general GGn ($n = 0, 1, 2$) *Ansätze* [67] including virtual orbitals in pair functions), and the other is to introduce a short-range correlation factor f_{12} in place of r_{12}. The introduction of the RI approximation and other decomposition methods for many-electron integrals allows us to employ more efficient correlation factors, as far as the two-electron integrals over $f_{12}, f_{12}/r_{12}, f_{12}^2, [\hat{T}_1, f_{12}]$, and $\frac{1}{2}\big[[\hat{T}_1, f_{12}], f_{12}\big]$ can be calculated. Short-range correlation factors were parameterized with a contracted GTG (CGTG),

$$
f_{12}^{(\text{CGTG})} = \sum_G^{N_G} c_G \exp(-\zeta_G r_{12}^2).
\tag{23}
$$

approximating the linear r_{12} behavior at short distances with suitable weight functions [68–72]. It has been well known in the community that the necessary integrals can be calculated efficiently with $F_m(T)$-based algorithms such as McMurchie–Davidson and Obara–Saika ones [73–77] for a correlation factor represented by any linear combination of GTG functions (23). Samson et al. also examined the Gaussian-damped r_{12} factor aiming at low-scaling R12 calculations [78, 79]. The Slater-type geminal (STG) function [80],

$$
f_{12}^{(\text{STG})} = -\frac{1}{\gamma} \exp(-\gamma r_{12}),
\tag{24}
$$

has been exclusively employed in F12 methods. (F12 refers to the choice of non-linear correlation factor instead of R12.) The necessary integrals can be calculated either by approximating $f_{12}^{(\text{STG})}$ in terms of an n-component CGTG (STG-nG) or using analytic expressions involving the generalized Boys function [80, 81],

$$
G_m(T, U) = \int_0^1 t^{2m} \exp[-Tt^2 + U(1 - t^{-2})]dt,
\tag{25}
$$

in place of $F_m(T)$ for the usual electron repulsion integrals. (Recently, the Dupuis–Rys–King algorithm [82] was extended to calculate integrals over $e^{-\gamma r_{12}}$ and $\frac{e^{-\gamma r_{12}}}{r_{12}}$ for F12 [83].) The efficiency of STG has been confirmed in MP2-F12 [84–87], and CC-F12 methods have been developed within SA [88], beyond SA with the linear approximation CCSD(F12) [89, 90], perturbative inclusion of explicitly correlated terms [91], and using automated code synthesis [92–95]. The short-range correlation factors are relevant to the explicitly correlated local methods [96–100], and F12 basis sets have been developed based on STG as well [101–103].

Once a correlation factor with correct asymptotical behaviors both in the short and long distance limits becomes available, a transparent *Ansatz* of wave function is conceivable. The cusp conditions (3) and (4) through $l = 1$ are expressed in terms of $f_{12} = r_{12} + O(r_{12}^2)$ as

$$
\psi = (1 + \hat{\mathcal{R}}_{12})\psi_0,
\tag{26}
$$

where ψ_0 is the unperturbed wave function ($\lambda = 0$), and $\hat{\mathcal{R}}_{12}$ is the rational generator [71],

$$
\hat{\mathcal{R}}_{12} = f_{12}\left(\frac{3}{8} + \frac{1}{8}\hat{p}_{12}\right).
\tag{27}
$$

with a permutation operator $\hat{p}_{12}$ of electronic positions, i.e. $\hat{p}_{12}\psi = \psi$ for singlet, and $= -\psi$ for triplet. It is noted that

the usual spin-dependent Jastrow factor J_n without $\hat{p}_{12}$ does not satisfy the s- and p-wave cusp conditions simultaneously to lead to a spin-contaminated solution. The most important indication of the rational generator in Eq. (26) is the cancelation of the Coulomb singularity in the Schrödinger equation as

$$\left[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2)\hat{\mathcal{R}}_{12} + r_{12}^{-1} \right]\psi_0 = O(r_{12}^0)\psi_0, \tag{28}$$

for regular singlet and triplet pairs of any block of orbital products $\psi_0 = \{ij\}$, $\{i\alpha\}$, and $\{\alpha\beta\}$.

General applications of the rational generator in MBPT can be formulated with the partitioning,

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{29}$$

where the zeroth-order Hamiltonian is

$$\hat{H}_0 = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 + v(\mathbf{r}_i) + \hat{U}_i \right], \tag{30}$$

with the external field $v(\mathbf{r}_i)$, and the potential $\hat{U}_i$ can be either local or nonlocal as in the Møller–Plesset perturbation theory. Wave operators are obtained by means of the linked diagram theorem [104, 105],

$$\left[\hat{H}_0, \hat{\Omega}^{(n)} \right] = -\hat{Q}\left\{ \hat{V}\hat{\Omega}^{(n-1)} \right\}_{\text{linked}}, \tag{31}$$

i.e., the wave operator diagrams of the order n are obtained by operating on the wave operator diagrams of $n-1$ with the perturbation $\hat{V}$ keeping only linked diagrams, where $\hat{Q}$ is the projector onto the space orthogonal to the unperturbed wave function $\hat{Q} = 1 - |\Psi_0\rangle\langle\Psi_0|$. We introduce the *Ansatz* for the wave operator

$$\hat{\Omega}^{(n)} = \hat{\omega}^{(n)} + \hat{\chi}^{(n)}, \tag{32}$$

which is a sum of the explicitly correlated part in the form,

$$\hat{\omega}^{(n)} = \hat{Q}\left\{ \hat{\mathcal{R}}\hat{\Omega}^{(n-1)} \right\}_{\text{C}}, \tag{33}$$

and its is residual $\hat{\chi}^{(n)}$, where C denotes connected diagrams. $\hat{\mathcal{R}}$ is the particle block of the rational generator,

$$\hat{\mathcal{R}} = \frac{1}{4}\sum_{\kappa\lambda}\sum_{\alpha\beta}\bar{\mathcal{R}}_{\alpha\beta}^{\kappa\lambda}\left\{ \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger \hat{a}_\lambda \hat{a}_\kappa \right\} \tag{34}$$

with $\mathcal{R}_{\alpha\beta}^{\kappa\lambda} = \langle\alpha\beta|\hat{\mathcal{R}}_{12}|\kappa\lambda\rangle$, the overbar stands for anti-symmetrization $\bar{\mathcal{R}}_{\alpha\beta}^{\kappa\lambda} = \mathcal{R}_{\alpha\beta}^{\kappa\lambda} - \mathcal{R}_{\beta\alpha}^{\kappa\lambda}$, and the curly brackets {} denote normal ordering. Substituting $\hat{\Omega}^{(n)}$ of (33) into (31) and using the relation $[\hat{H}_0, \hat{Q}] = 0$, we establish the setoff between the Coulomb singularity in the connected terms of $\hat{Q}\{\hat{V}\hat{\Omega}^{(n-1)}\}_{\text{linked}}$ and $\overbrace{\hat{H}_0\{\hat{\mathcal{R}}\hat{\Omega}^{(n-1)}\}}_{\text{C}}$ in each order in an analogous manner to the two-electronic case. (Thus, $\hat{\mathcal{R}}$ is first order in $\hat{V}$.) Starting from the initial condition,

$\hat{\omega}^{(0)} = 0$ and $\hat{\chi}^{(0)} = 1$, we can perform an order-by-order expansion of the wave operator.

The above formalism does not lead to a proper factorization of the wave operator like the absence of $\frac{1}{2}(\hat{\omega}^{(1)})^2$ in $\hat{\Omega}^{(2)}$ with a finite basis expansion of $\hat{\chi}^{(n)}$, albeit the correct energy scaling is guaranteed by the linked diagram expansion. This problem can be easily settled by exponentiating the *Ansatz*,

$$\hat{\Omega} = \exp(\hat{S}) = \exp(\hat{T}' + \hat{T}), \tag{35}$$

with the explicitly correlated cluster operator as indicated by Köhn [115]

$$\hat{T}' = (\hat{\mathcal{R}}\hat{\Omega})_{\text{C}}, \tag{36}$$

in which we retain only particle-hole excitation operators. In Fig. 1, we show representative diagrams of $\hat{T}'$. For the first-order wave operator $\hat{\Omega}^{(1)}$, d2:00 is the only term in $\hat{T}'$, and the s- and p-wave cusp conditions are automatically fulfilled by the rational generator for all pair functions (SP *Ansatz*) [71, 81]. The SP *Ansatz* is sometimes referred to as the diagonal orbital-invariant (DOI) or FIXED amplitude *Ansatz* and has led to efficient perturbation and CC-F12 methods [106–112]. For the ground state around the equilibrium geometry, the contribution of other diagrams associated with $\hat{S}$ would be small with a reasonable size of basis set. d2:20 and d3:20 appear in $\hat{\Omega}^{(2)}$ to contribute to the third- and fourth-order energies, respectively. The explicitly correlated connected triples with d3:20 have been investigated by Köhn for the first time under the name of the extended SP (XSP) *Ansatz* [113], and the geminal contributions are analyzed perturbationally [114]. The diagrams d2:10 and d2:11 will be significant when $\hat{T}_1$ is large as in a non-HF reference. For excitation energies in linear response theory, dominant occupations are induced in the virtual space, and the inclusion of d2:10 is crucial [115, 116]. Alternatively, the cusp behavior in the virtual-occupied block can be dealt with by a partial augmentation of the geminal basis within the unitary invariant *Ansatz* [117].

Another important consequence of the rational generator is on the treatment of open-shell molecules. The permutation operator in (27) causes a spin-flipped geminal basis (SFG),

$$f_{12}\hat{p}_{12}\{I_\uparrow J'_\downarrow\} = f_{12}\{J'_\uparrow I_\downarrow\}. \tag{37}$$

SFG, which is absent in traditional geminal *Ansatz* as (19), should be included explicitly to satisfy the cusp conditions for different orbitals for different spins. The MP2-F12 method with SFG was implemented for the unrestricted HF (UHF) reference [118], and simplified CCSD(T)-F12x methods were extended to the case of restricted open-shell
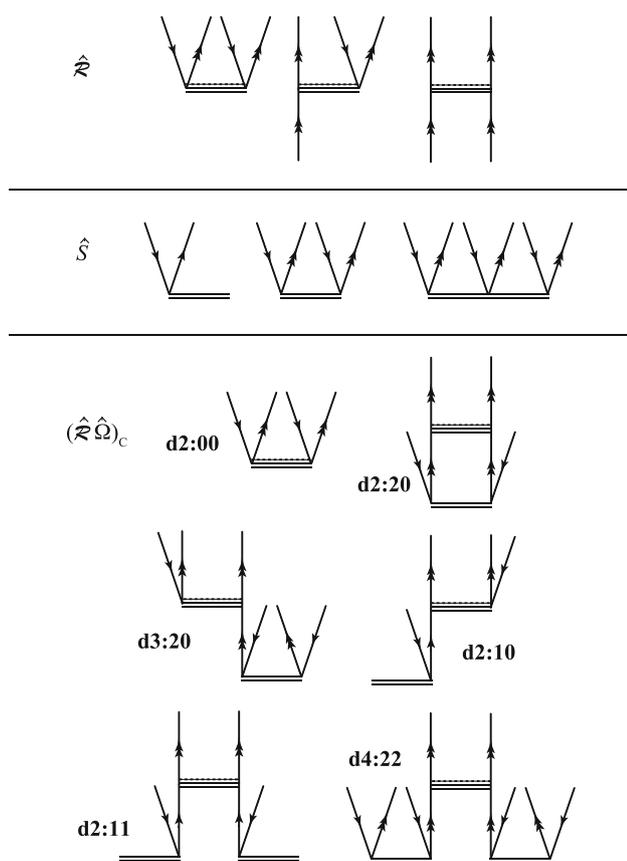
Fig. 1 Diagrammatic representations of $\hat{\mathcal{R}}$, $\hat{S}$, and representative operators in $(\hat{\mathcal{R}}\hat{\Omega})_C$. The diagram for $\hat{T}'_\kappa$ of the contraction $(\hat{\mathcal{R}}\hat{S}_\mu\hat{S}_\nu)_C$ is labeled as dκ:$\mu\nu$. The *single* and *double up-going arrows* denote particle lines in GBS and CBS, respectively

HF (ROHF) reference functions similarly [119]. More recently, a Z-averaged perturbation theory with the rational generator was studied by Wilke et al. [120], and several *Ansätze* for open-shell molecules have been discussed in detail by Tew et al. [121]. For more general open-shell systems, multireference (MR) treatments are required, and the internally contracted geminal basis $\hat{\mathcal{R}}_{ext}|\text{CAS}\rangle$ was employed in explicitly correlated multireference perturbation theory [122], where $\hat{\mathcal{R}}_{ext}$ is the external excitation part of the rational generator on the complete active space self-consistent field (CASSCF) reference function [123] regarded as a generalized closed-shell vacuum. MR perturbation and MRCI methods with internally contracted basis have been developed [124–127]. The use of the internally contracted basis is more advantageous computationally than the earlier implementation of MRCI-R12 [128, 129], in which the unitary invariant *Ansatz* is applied for each determinantal state in the reference wave function. More recently, explicitly correlated Brillouin–Wigner (BW) MRCC methods [130, 131] with a modified Jeziorski–Monkhorst

Ansatz [132] have been reported. Although a standard MRCC model has not been established in this field, the use of the similarity transformed Hamiltonian with the rational generator,

$$\hat{H}_R = \exp(-\hat{\mathcal{R}}_{ext})\hat{H}\exp(\hat{\mathcal{R}}_{ext}). \qquad (38)$$

on top of MRCC would be promising for the inclusion of F12 effects. Although the problem of redundant variables is known in internally contracted MRCC [133], the use of the SP *Ansatz* bypasses the determination of F12 amplitudes. $\hat{H}_R$ with the rational generator is more advantageous than the transcorrelated Hamiltonian, $\hat{H}_{TC}$ in view of the cusp conditions. In this case, the correlation factor, f_{12}, in the rational generator is not necessarily a spherically symmetric function [71]. Even more drastic approximation is the replacement of $\hat{\mathcal{R}}_{ext}$ by

$$\hat{\mathcal{R}}'_{ext} = \frac{1}{4}\sum_{pq}\sum_{\alpha'\beta'}\bar{\mathcal{R}}^{pq}_{\alpha'\beta'}\left\{\hat{a}^\dagger_{\alpha'}\hat{a}^\dagger_{\beta'}\hat{a}_q\hat{a}_p\right\} \qquad (39)$$

in $\hat{H}_R$, which gives rise to only the double contraction $\overset{\frown}{\hat{H}\hat{\mathcal{R}}'_{ext}}$ consuming the complementary orbitals α', β'. This similarity transformed Hamiltonian has been employed to accelerate the basis set convergence in a projector Monte Carlo (PMC) method based on Slater determinants [Ohtsuka (in preparation), 134]. Despite its simple implementation, $\hat{\mathcal{R}}'_{ext}$ resembles *Ansatz* 1 of standard MP2-R12 and CC-R12, which is not as accurate as *Ansatz* 2. This feature was also noted by Torheyden and Valeev in their work on MR R12 method [124].

In Table 2, we compare all-electron correlation energies of Ne from CCSD(F12), CCSD(T)(F12), VMC, and diffusion MC (DMC) calculations. VMC recovery of the correlation energy is 91% despite the inclusion of the four-body three-electron-nucleus (e3-n) Jastrow factor. This relatively poor performance is partially attributed to the deficient form of the Jastrow factor for cusp conditions. The error in DMC from the fixed-node approximation amounts to a few % of the correlation energy. One can obtain highly accurate correlation energies with CC-F12 methods. The CC-F12 energy with connected triples in aug-cc-pCVQZ basis set [5–7] is accurate to 1 mE_h, and a similar accuracy can be attained for general polyatomic molecules.

On closing this section, some thoughts to refine the use of cusp conditions in explicitly correlated wave functions would be mentioned. Firstly, an optimum way to determine the length-scale parameter γ in STG has not been established, albeit it has been known that the result is less sensitive to γ especially for valence electronic states. Within the SP *Ansatz*, γ is connected to the second-order coefficients of cusp conditions, and Rassolov–Chipman

Table 2 All-electron correlation energies of the Ne atom obtained in CC-F12 and quantum Monte Carlo methods

Method	E_c (mE_h)	(%)
VMC[a]	355.8	91.1
DMC[a]	377.2	96.6
CCSD(F12)[b]	382.9	98.1
CCSD(T)(F12)[b]	389.2	99.7
CCSDT-R12[c]	390.1	99.9
Exact[d]	390.5	100.0

[a] QMC results with Jastrow factor through 3e-n, Ref. [135]

[b] F12 calculation with aug-cc-pCVQZ basis.

[c] F12 calculation with aug-cc-pCV5Z basis, Ref. [95]

[d] Estimated exact correlation energy, Ref. [136]

[137] and Tew [138] investigated the behavior of the coalescence conditions. In either case, energy dependences enter the second-order coefficients. More recently, MP2-F12 and CCSD(T)-F12 methods with orbital-pair-specific Slater-type geminals have been proposed by Werner et al. [139]. Different geminal exponents are used for different correlations of core–core, core–valence and valence–valence orbital pairs for improved correlation energies and molecular properties for a number of diatomic molecules involving d-shell correlation. Secondly, the F12 methods have exclusively employed spherically symmetric correlation factors. Nevertheless, the logarithmic behavior at the triple-point coalescence point [28–30] indicates the possibility of a partial introduction of position dependence in f_{12} for an improved accuracy. Investigation will be also made for unnatural parity singlet pairs [26, 27] whose rate of convergence is much faster than the natural pairs. Relativistic effects are of importance as well since the partial wave increment of the leading term of the relativistic correction goes as $(l + \frac{1}{2})^{-2}$; the slow rate can be also removed by the F12 *Ansatz* [140].

4 Computational aspects for many-electron integrals

The penalty in explicitly correlated theory is the introduction of many-electron integrals. Efficient treatment of the many-electron integrals is the key for wide applicability of theory. The geminal-based methods require three-electron integrals over $f_{12} r_{13}^{-1}$, $f_{12} r_{23}^{-1} f_{13}$, and $[\nabla_1^2 + \nabla_2^2, f_{12}] f_{13}$, and four-electron integrals over the operators as $r_{12}^{-1} f_{13} f_{14}$, and $r_{12}^{-1} f_{23} f_{34}$. All many-electron integrals can be expressed in closed form algebraic expressions using the Gaussian correlation factor [50, 51]. The three- and four-electron integrals are so numerous that the key to any practical method lies in the efficient handling of the integrals. The weak-orthogonality

projector was invented to avoid four-electron integrals in the GTG theory. The use of the transcorrelated Hamiltonian also requires only three-electron integrals over $(\nabla_1 f_{12}) \cdot (\nabla_1 f_{13})$. Recurrence relations have been developed for efficient evaluation of three-electron integrals [38].

RI introduced in the pioneering work of Kutzelnigg and Klopper [60, 61] approximates the primary three-electron integrals as

$$\langle ijk|f_{12} r_{13}^{-1}|lmn\rangle \simeq \sum_{p'} F_{ij}^{p'm} G_{p'k}^{ln}, \tag{40}$$

$$F_{ij}^{p'm} = \langle ij|f_{12}|p'm\rangle, \tag{41}$$

$$G_{p'k}^{ln} = \langle p'k|r_{12}^{-1}|ln\rangle. \tag{42}$$

In the atomic case, the expansion is saturated at the RI basis p' up to the angular momentum quantum number $l = 3l_{\text{occ}}$, because each of the two-electron integrals $F_{ij}^{p'm}$ and $G_{p'k}^{ln}$ vanishes beyond the range for the spherically symmetric operators f_{12} and r_{12}^{-1}. Although the expansion of the cyclic integrals,

$$\langle ijk|f_{12} r_{23}^{-1} f_{13}|lmn\rangle \simeq \sum_{p'q'r'} F_{ij}^{p'q'} G_{q'k}^{mr'} F_{p'r'}^{ln}, \tag{43}$$

does not terminate due to the two RI indices in each 4-index object, the partial wave increment of the integrals goes as $(l + \frac{1}{2})^{-6}$ which is regarded as "an acceptable rate of convergence" [12]. As a result, slowly convergent two-electron objects as $\langle ij|f_{12} r_{12}^{-1}|kl\rangle$ are calculated analytically, and all many-electron integrals are approximated by RI in R12/F12 theories. The RI approximation is also employed for the three-electron integrals in the transcorrelated method [37], and it was shown that the commutator form is more accurate than the simple application of RI to the vector product $(\nabla_1 f_{12}) \cdot (\nabla_1 f_{13})$ [41]. The standard approximation (SA) for various correlated methods in earlier R12 theory employs the same basis set for orbital expansion and RI. More flexible expansions using an auxiliary basis set (ABS) were introduced by Klopper and Samson in 2002 [141], and Valeev proposed the use of a union of the given basis for orbitals and its orthogonal component, complementary ABS (CABS) for RI to improve the accuracy of ABS [142]. The ABS and CABS approaches enabled us to use a compact basis set in R12/F12 methods, and various methods beyond SA have been developed for the last decade.

The computational cost for the requirement of a large basis set in ABS and CABS approaches has been reduced by the use of density fitting (DF). DF expands an orbital product into a fitting basis,

$$\rho_{pq}(\mathbf{r}) = \phi_p(\mathbf{r}) \phi_q(\mathbf{r})$$
$$\simeq \tilde{\rho}_{pq}(\mathbf{r}) = \sum_A c_{A,pq} \Xi_A(\mathbf{r}), \tag{44}$$

and has provided fast self-consistent field (SCF) and correlated methods [143–149]. (DF is often referred to as RI, but we use the terminology of DF to avoid the confusion with the RI in R12/F12 methods.) Manby introduced DF in explicitly correlated theory [150, 72]. All two-electron integrals are replaced by those of the robust formula, the error in which is quadratic in the errors in the fitted densities [151], and efficient methods have been developed in conjunction with local approximations [96–100]. DF was also employed to increase the accuracy of the RI approximation [152]. "A momentum transfer" by grouping the orbitals at the coordinate joining operators in three-electron integrals before the application of RI,

$$\langle ijk|f_{12}r_{13}^{-1}|lmn\rangle \simeq \langle \tilde{\rho}_{il}jk|f_{12}r_{13}^{-1}|1mn\rangle$$
$$\simeq \sum_{p'A} c_{A,il}F_{Aj}^{p'm}G_{p'k}^{1n}, \qquad (45)$$

reduces the requirement of the RI basis from $3l_{\text{occ.}}$ to $2l_{\text{occ.}}$, where 1 denotes unity instead of an orbital. This reduction will be significant for molecules with heavy elements especially of occupied f-shells. Further development would be possible to eliminate the remaining four-index integrals as $F_{Aj}^{p'm}$ using DF with the robust formula.

The central idea of breaking up many-electron integrals in the contemporary explicitly correlated electronic structure methods was actually suggested about 20 years earlier than the emergence of RI. Boys and Handy pointed out that a couple of 3-D integrals in the special kind of 9-D three-electron integrals of the transcorrelated Hamiltonian,

$$\int F(1,2)G(1,3)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \qquad (46)$$

can be evaluated without interference, and the final 3-D integration can be performed on the results of them [34]. Moreover, efficient 3-D numerical quadratures (QD) have been developed for exchange-correlation contribution in density functional theory [153–157].

QD introduced in F12 theory [71, 81] decomposes the three-electron integrals

$$\langle ijk|f_{12}r_{13}^{-1}|lmn\rangle \simeq \sum_g \bar{\phi}_i(\mathbf{r}_g)\phi_l(\mathbf{r}_g)F_{jm}^g G_{kn}^g, \qquad (47)$$

with only three-index objects,

$$F_{jm}^g = \int d\mathbf{r}\,\phi_j(\mathbf{r})f_{12}\phi_m(\mathbf{r}), \qquad (48)$$

$$G_{kn}^g = \int d\mathbf{r}\,\phi_k(\mathbf{r})r_{12}^{-1}\phi_n(\mathbf{r}), \qquad (49)$$

and orbital amplitudes, $\bar{\phi}_i(\mathbf{r}_g)$ and $\bar{\phi}_i(\mathbf{r}_g) = \phi_i(\mathbf{r}_g)w_g$ with the quadrature weights w_g. "The momentum transfer" as in DF holds in (47) from the beginning since the orbital

amplitudes are decoupled at a grid point. Thus, the numerical integration is saturated at $2l_{\text{occ.}}$ of the angular grid in the atomic case. The four-electron and cyclic three-electron integrals can be treated by the hybrid QD/RI approximation [81] analogous to the ABS/RI approach of Klopper [158]. The Coulomb interaction in those many-electron integrals is arising from the exchange operator in the Fockian as,

$$\langle ijk|\hat{K}_1 f_{12} f_{13}|lmn\rangle \simeq \sum_{p'g} \langle i|\hat{K}_1|p'\rangle \bar{\phi}_{p'}(\mathbf{r}_g)\phi_l(\mathbf{r}_g)F_{jm}^g F_{kn}^g. \qquad (50)$$

The summation over p' can be replaced by the given basis set (GBS) since the RI expansion should converge much faster than $l = 3l_{\text{occ.}}$ as indicated from the rare gas case. In this case, the four-electron integrals in the special form can be calculated explicitly without the hybrid approximation,

$$\langle ijk|\hat{K}_1 f_{12} f_{13}|lmn\rangle \simeq \sum_g K_i(\mathbf{r}_g)\bar{\phi}_l(\mathbf{r}_g)F_{jm}^g F_{kn}^g, \qquad (51)$$

in terms of the exchange operator in the physical space,

$$K_i(\mathbf{r}_g) = \sum_j \bar{\phi}_j(\mathbf{r}_g)G_{ij}^g. \qquad (52)$$

The cyclic integrals are canceled out by other terms within the hybrid QD/RI approximation, otherwise the RI basis can be replaced by ABS. One can calculate even two-electron integrals using QD optionally, and the reduction of the scaling of intermediates from quartic to cubic is effective for large-scale correlated calculations. The best MP2 energy of Benzene in the near basis set limit, $-1.0575(5)$ E_h, was obtained by performing MP2-F12 calculations with this method through aug-cc-pV6Z basis set in a fractional computational time of the SCF calculation [159].

We explore possibilities of further improved methods for many-electron integrals. Is it possible to mitigate the numerical integration using ABS? We introduce the overlap metric over ABS,

$$s_{p'q'} = \sum_g \phi_{p'}(\mathbf{r}_g)w_g\phi_{q'}(\mathbf{r}_g). \qquad (53)$$

The matrix $\mathbf{s}$ is positively definite for the usual numerical quadratures and is an identity matrix in the limit of the exact numerical integration. Using the symmetric orthogonalization matrix for $\mathbf{s}$,

$$\mathbf{x} = \mathbf{s}^{-\frac{1}{2}} = \mathbf{U}\mathbf{d}^{-\frac{1}{2}}\mathbf{U}^+, \qquad (54)$$

we define the renormalized orbital amplitudes

$$R_{gp} = \sum_{p'q'} \phi_{p'}(\mathbf{r}_g)x_{p'q'}\langle q'|p\rangle, \qquad (55)$$

where **d** is the diagonal matrix with the eigen values of the metric **s**, and $\langle q' \mid p \rangle = \delta_{q'p}$ for ABS consisting of GB and its orthogonal components (CABS). The numerical integration with the renormalized quadrature (rQD) is given by

$$\langle p|\hat{A}|q\rangle \simeq \sum_g \bar{R}_{gp}\hat{A}(\mathbf{r}_g)R_{gq}, \qquad (56)$$

with $\bar{R}_{gp} = R_{gp}w_g$. One can easily conform that rQD integrates ABS exactly for $\hat{A}(\mathbf{r}_g) = 1$.

As a preliminary application, we show errors in numerical MP2 energies of water approximating electron repulsion integrals $(ai|bj)$ using QD and rQD in Fig. 2. The cc-pVXZ and aug-cc-pVXZ basis sets [5–7] labeled by the cardinal numbers as X and aX for GB are used, and ABS are formed from the GB and the uncontracted cc-pVQZ basis set as CABS. The numbers of quadrature points are 1,440 (72 angular and 20 radial) and 9,216 (268 angular and 32 radial) per atom for the coarse and medium grids, respectively. In either case, the rQD errors are one order of magnitude smaller than the corresponding ones of QD. rQD with the medium grid is accurate to 1 μE_h. The use of rQD in F12 methods is straightforward. The calculation of derivatives of ABS amplitudes required for the B-intermediate can be bypassed by the use of the approximation C [160]. The additional computational costs for the application of rQD to F12 methods are negligibly small since the most time-consuming steps involving three-index objects coincide with the original QD method. The detail of the use of rQD in F12 theory will be discussed in more detail elsewhere. It is noted that rQD is closely related with the pseudospectral (PS)
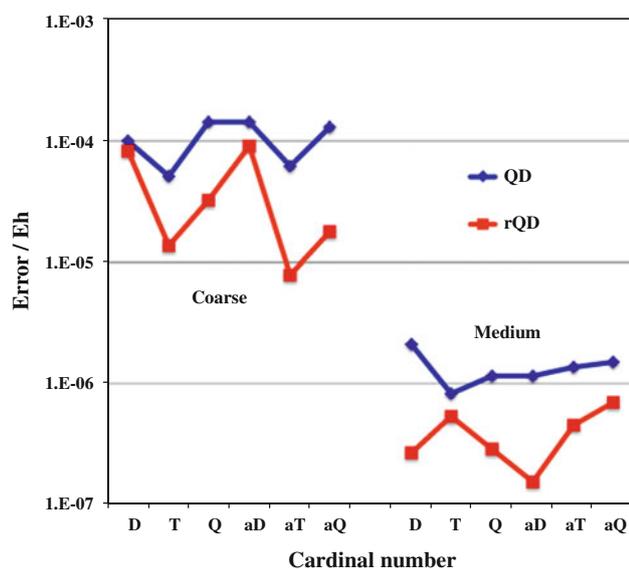
methods [161–165], which employ more parametrized grids and dealiasing functions. PS typically uses only ca. 100 grid points with a fair accuracy. This fact indicates that there is a possibility of further improvement of the performance of rQD using integral corrections and length scales algorithms employed in PS [163].

More recently, a message passing interface (MPI) and open multi-processing (OpenMP) hybrid parallel algorithm for MP2 calculations using QD have been developed [166]. High parallel efficiency is attained by distributing QD points and virtual molecular orbital pairs. The communication of the three-index objects and the assembly of electron repulsion integrals of them scale as OVG and O^2V^2G, for the numbers of occupied MOs, virtual MOs, and quadrature points, O, V, and G, respectively, and the parallel efficiency is increased for large molecules. The CPU timing of all-electron correlated calculations for coronene with the aug-cc-pCVTZ basis set is shown in Fig. 3. Calculations were performed on SGI Altix ICE 8400EX (CPU: Intel Xeon X5570 2.93GH, 8 CPU cores/node, Memory: 24 GB/node, Network: Enhanced Hypercube with $4 \times$ QDR InfiniBand) at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo with eight threads per process generated in hybrid parallel calculations. Another calculation of fullerene (C_{60}) with the same basis set (3,540 basis functions) was also completed in ca. 4.8 h on 8,192 cores without invoking molecular symmetry. The hybrid parallel algorithm can be applied to QD-based F12 methods, and massively parallel algorithms involving higher-order correlation will be presented in the near future.

Fig. 2 Errors in numerical MP2 energoes of QD and rQD methods for the water molecule (E_h)
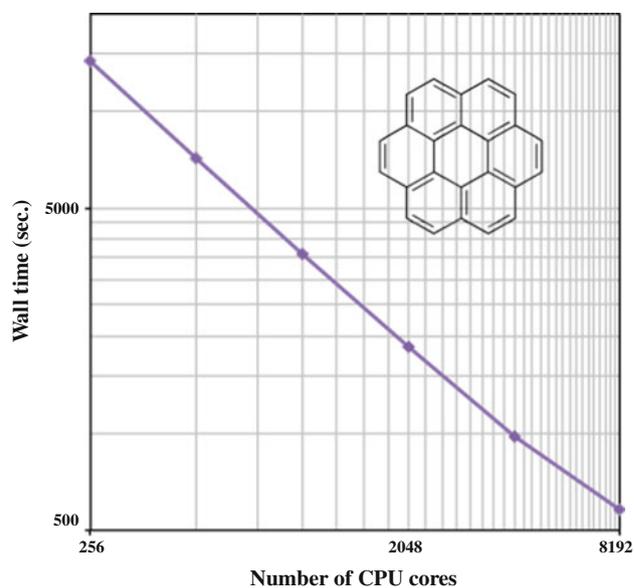
Fig. 3 Parallel efficiency of numerical MP2 calculation of coronene. All electrons are correlated, and the number of grid points per atom is 9,216. Point group symmetries are not employed

5 Summary

In this overview, we have summarized milestones in the history of explicitly correlated wave functions since the Hylleraas expansion for the He ground state in 1929. The latest methods utilize short-range correlation factor, mostly the Slater-type geminal function, which enables us to use the rational generator for cusp conditions to eliminate the electron–electron Coulomb singularity from the entire Schrödinger equation to grant improved basis set convergence. There remain issues to hone the present strategy on the inclusions of higher-order cusp conditions, triple-point coalescence conditions, and relativistic effects, which will be investigated extensively before long. At the same time, efficient computational schemes to realize accurate calculations of explicitly correlated methods rest with the treatment of many-electron integrals. This aspect has been also discussed with a perspective.

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