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Perspective: Explicitly correlated electronic structure theory for complex systems

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The explicitly correlated approach is one of the most important breakthroughs in *ab initio* electronic structure theory, providing arguably the most compact, accurate, and efficient ansatz for describing the correlated motion of electrons. Since Hylleraas first used an explicitly correlated wave function for the He atom in 1929, numerous attempts have been made to tackle the significant challenges involved in constructing practical explicitly correlated methods that are applicable to larger systems. These include identifying suitable mathematical forms of a correlated wave function and an efficient evaluation of many-electron integrals. R12 theory, which employs the resolution of the identity approximation, emerged in 1985, followed by the introduction of novel correlation factors and wave function ansätze, leading to the establishment of F12 theory in the 2000s. Rapid progress in recent years has significantly extended the application range of explicitly correlated theory, offering the potential of an accurate wave-function treatment of complex systems such as photosystems and semiconductors. This perspective surveys explicitly correlated electronic structure theory, with an emphasis on recent stochastic and deterministic approaches that hold significant promise for applications to large and complex systems including solids. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4976974]

I. INTRODUCTION

The remarkable progress of *ab initio* quantum theory over the past 50 years has enabled the study of real atoms, molecules, and solids in terms of the most accurate, systematic, and reliable electronic structure methods ever established. This is particularly true for obtaining approximate solutions of the electronic Schrödinger equation, encompassing *the electron correlation* that is often of central importance in obtaining accurate descriptions and energetics of wave functions. Nevertheless, standard post-Hartree-Fock (post-HF) calculations in many-body perturbation theory (MBPT), configuration interaction (CI), and coupled-cluster (CC) theory employ orbital expansions and suffer from basis set problems. This is because the cusp conditions,[1,2] obeyed by the exact wave function Ψ, cannot be satisfied by expansions based on orbitals. The behavior of Ψ in the vicinity of the coalescence[3] is

$$\Psi = [1 + \frac{1}{2(k+1)} r_{12} + O(r_{12}^2)]\Phi, \tag{1}$$

where Φ is the eigenfunction of an unperturbed Hamiltonian in the absence of electron–electron interactions and k takes values of 0 and 1 for singlet and triplet states (i.e., s- and p-wave cusp conditions), respectively.[4] The linear r_{12} discontinuity arising from the singularity of the Coulomb interaction r_{12}^{-1} at the coalescence can hardly be represent by an orbital-based CI expansion from the single-determinant reference Φ. Therefore, it is essential to realize that the matrix element for the correlation energy $\langle\Phi|\,\hat{V}\hat{\Omega}\,|\Phi\rangle$ from the coalescence behavior (1),

$$I_{ij}^{kl} = \sum_{\alpha\beta}^{\infty} \langle ij|\, r_{12}^{-1}\, |\alpha\beta\rangle\, \langle\alpha\beta|\, r_{12}\, |kl\rangle\,, \tag{2}$$

is not a terminating series with the double summation over virtual orbitals, α and β, in the complete basis set (CBS). Indeed, their angular quantum numbers l can grow simultaneously, leading to a very slow convergence of the order $(l+\frac{1}{2})^{-4}$ in the increment or $(L+1)^{-3}$ in the truncation error at the maximum quantum number of the expansion L. For occupied orbitals $i,j,\ldots$, the convergence is very quick (one-electronically), terminating at L_{occ}. In the following, we present a brief overview of explicitly correlated electronic structure theory, which fundamentally ameliorates the root of the difficulty by explicitly including r_{12} dependencies into the wave function. For details of the advances until around 2012, readers can refer to the review articles.[5–11]

A survey of the history of the progressive development of explicitly correlated electronic structure theory is depicted in Fig. 1. In 1929, Hylleraas[12] introduced a wave function form containing a polynomial of r_{12} and obtained an extremely accurate energy of ground-state helium. Some 50 years after his death, the Hylleraas Symposium[13] was held in the winter of 2015 in honor of his profound influence. From that time, various extensions of the Hylleraas-type wave function, including

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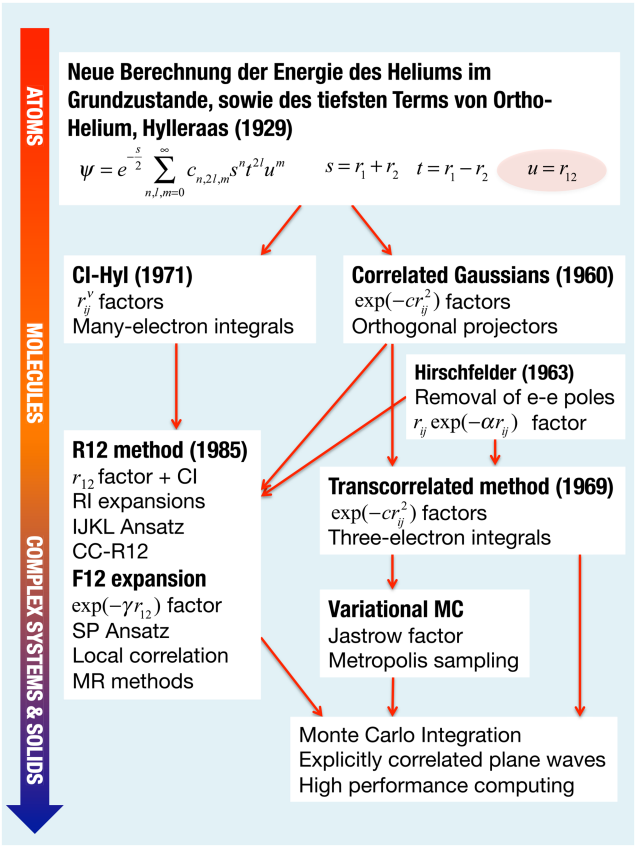

FIG. 1. A survey of the progress of explicitly correlated electronic structure theory. Constants and coefficients dependent on the spin-multiplicities of pair functions are omitted from the correlation factors for simplicity.

the combined CI and Hylleraas (CI-Hyl) methods, have been proposed for the study of multielectron atoms and diatomic molecules.[14–21] However, these expansions require the computations of difficult integrals involving products of correlation factors such as r_{12}^{μ}, $r_{12}^{\mu} r_{13}^{\nu}$, $r_{12}^{\mu} r_{13}^{\nu} r_{23}^{\lambda}$, $r_{12}^{\mu} r_{13}^{\nu} r_{14}^{\lambda}$, and so on. The complexity of these integrals has hindered applications to many-electronic and polyatomic systems, especially for the use of Slater-type orbitals.

The primal protocol for the significant progress of *ab initio* methods is the use of Gaussian-type orbitals (GTOs), as pioneered by Boys in 1950,[22] which enables very rapid computations of molecular integrals compared to those in $\exp(-ar_{iA})$. Ten years later, the extension to an explicitly correlated Gaussian (ECG) basis was developed independently by Boys and Singer,[23,24] where the correlation factors r_{ij}^{μ} are replaced by $\exp(-cr_{ij}^2)$. All necessary integrals of ECG can be calculated in closed-form algebraic expressions for molecules.[25] Boys and Singer also suggested linear expansions in MBPT and CI calculations containing only two-body correlators in the wave function, that is, Gaussian-type geminals (GTGs), as the fully correlated Gaussian ($\exp(-\sum_i a_i r_{iA}^2 - \sum_{ij} c_{ij} r_{ij}^2)$) in direct variational calculations is only feasible for small molecules. (ECG has been employed for the calculation of few-particle systems in atomic and nuclear physics. See, e.g., a review article.[26]) If the linear r_{12} behavior could be accurately reproduced by a linear combination of GTG in the vicinity of the coalescence,

$$r_{12} \approx \sum_g b_g \exp(-c_g r_{12}^2), \tag{3}$$

(2) could be approximated as

$$I_{ij}^{kl} \approx \sum_g b_g \langle ij| r_{12}^{-1} \hat{Q}_{12} \exp(-c_g r_{12}^2) |kl\rangle, \tag{4}$$

where $\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)$ is the strong orthogonality projector and $\hat{O}_n = \sum_i |i(n)\rangle \langle i(n)|$ is the projector on the occupied space. (Indeed, (3) has been employed to avoid the nonlinear optimization of GTG.[27,28]) The expression for the matrix elements (4) can be precisely evaluated from the two- and three-electron integrals over r_{12}^{-1}, $\exp(-cr_{12}^2)$, $\exp(-cr_{12}^2)/r_{12}$, and $\exp(-cr_{12}^2)/r_{13}$, providing much faster convergence than the orbital expansion (2) at the expense of the calculation of the three-electron integrals. Pan and King developed second-order Møller–Plesset (MP2) perturbation theory in the GTG basis and calculated pair energies for atoms including Ne.[29,30] However, the three- and four-electron integrals arising from $\hat{Q}_{12}$ in pair functions are so numerous that the application of the naive implementation of MP2-GTG is limited only to small molecules. To mitigate the problem of MP2-GTG, Szalewicz and coworkers developed the weak orthogonality functional (WOF) primarily to avoid four-electron integrals.[31–33] In WOF, $\hat{Q}_{12}$ is removed from the term involving the Fock operator in the Hylleraas energy functional, and a penalty term is added to enforce the strong orthogonality. The avoidance of four-electron integrals in CC singles and doubles (CCSD) is achieved by combining the superweak orthogonality projection with an approximate strong orthogonality projection (SWOP).[34] Recently, there has been a resurgence of interest in WOF, and Tew *et al.* proposed an improved functional within MP2-GTG, the so-called intermediate orthogonal functional (IOF).[35]

Another way to avoid four-electron integrals is to use a similarity-transformed Hamiltonian. This approach was first introduced by Hirschfelder to remove the electron–electron poles from the original Hamiltonian.[36] Based on the Hirschfelder transformation, Boys and Handy developed the transcorrelated (TC) method,[37,38] which was applied to polyatomic molecules in the correlated Gaussian basis.[39] The TC Hamiltonian contains interactions up to the three-body case from the commutator between the kinetic energy operators and correlation factors. More recently, the TC Hamiltonian has been combined with a preset frozen GTG,[40] and correlated methods based on biorthogonal reference wave functions have been developed.[41] In these methods, even three-electron integrals are avoided using the resolution of the identity (RI), similar to the technique employed in R12 theory (*vide infra*). Luo investigated the asymptotic behavior of the correlation factor for a homogeneous electron gas,[42] refining the earlier work of Armour.[43] For more complex systems, Ochi *et al.* developed an efficient algorithm for the TC Hamiltonian in plane waves. This has been successfully applied to the calculations of band structures and optical absorption spectra in solids.[44–46] Variational quantum Monte Carlo integration using Metropolis sampling[47] is another powerful technique for more complicated correlation factors, as will be discussed in Sec. II.

A conceptual breakthrough was introduced by Kutzelnigg in 1985.[48] On the basis of the observation that the energy increment in the standard CI expansions converges, at the worst, as $(l+\frac{1}{2})^{-6}$, except for the direct contribution $\sum_l \langle\Phi|\,(r_{12}^{-1})_l\,\frac{1}{2}(r_{12})_l\,|\Phi\rangle = \frac{1}{2}$ near the coalescence, Kutzelnigg proposed *a hybrid scheme to employ a CI wave function* χ *reinforced by a simple correlation factor* r_{12},

$$\Psi = (1+\frac{r_{12}}{2})\Phi + \chi. \tag{5}$$

For instance, the partial wave expansions of integrals like $\langle\Phi|\,r_{12}r_{13}^{-1}\,|\Phi\rangle$ and $\langle\Phi|\,r_{12}r_{23}^{-1}r_{34}\,|\Phi\rangle$ terminate at a finite L, and the increment of $\langle\Phi|\,r_{12}r_{23}^{-1}r_{13}\,|\Phi\rangle$ is of the order $(l+\frac{1}{2})^{-6}$.[48] Soon afterwards, the first molecular application of the corresponding MP2-R12 in Gaussian basis functions was performed by Klopper and Kutzelnigg[49] using the RI expansion as

$$\langle ij|\,r_{12}^{-1}\hat{O}_1 r_{12}\,|kl\rangle \overset{\text{RI}}{\simeq} \sum_{mp}\langle ij|\,r_{12}^{-1}\,|mp\rangle\,\langle mp|\,r_{12}\,|kl\rangle\,, \tag{6}$$

where the summation over p is strictly bound to $3L_{\text{occ}}$. in the one-center limit and converges very rapidly for molecules. The standard approximations (SA) were developed to avoid difficult integrals,[50] and CC theory combined with the R12 ansatz (CC-R12) was advanced by Noga and co-workers.[51,52] Note that the linear r_{12} behavior is unphysical at large inter-electronic distances, resulting in artificial solutions if we employ canonical orbitals to constitute pair functions. Klopper circumvented this problem by introducing additional amplitudes for $(ij)\neq(kl)$ to make the pair function unitary invariant,[53]

$$u_{ij,s}^{(\text{IJKL})} = \sum_{k\geq l} c_{ij,s}^{kl}\hat{Q}_{12}r_{12}\phi_{kl,s} + \chi_{ij,s}, \tag{7}$$

i.e., the unitary-invariant or IJKL ansatz, where $\phi_{kl,s}$ are the spin-free pair functions of occupied orbitals and $\chi_{ij,s}$ is a pair function spanned by virtual orbitals. Note that more flexible geminal basis functions involving virtual orbitals, e.g., $r_{12}\phi_{ak,s}$ and $r_{12}\phi_{ab,s}$, can be employed, as in the GGn model.[54] Although these extensions of the geminal basis further improve the convergence, the deterioration of the RI expansion (6), which *does not terminate* at $3L_{\text{occ}}$. in this case, necessitates an explicit evaluation of three-electron integrals.[55]

Explicitly correlated electronic structure theory was developed enormously in the 2000s, expanding its applicability considerably. Klopper and Samson introduced the auxiliary basis set (ABS) for the RI expansion that gives rise to a novel framework beyond SA.[56] The complementary ABS (CABS) approach of Valeev is the standard procedure to construct the RI basis.[57] Manby introduced robust density fitting (DF) into explicitly correlated theory to significantly reduce the computational cost of various two-electron integrals.[58] An alternative approximation C with novel intermediates was also derived.[59] Once RI is employed, linear r_{12} and $\exp(-cr_{12}^2)$ are not the only usable correlation factors for polyatomic molecules that can be combined with Gaussian orbital basis. In 2004, the Slater-type geminal (STG) correlation factor[60]

$$f_{12}^{(\text{STG})} = -\gamma^{-1}\exp(-\gamma r_{12}), \tag{8}$$

was proposed, and all necessary two-electron integrals over operators like $f_{12}\equiv f(r_{12}), f_{12}/r_{12}, f_{12}^2, [\nabla_1^2, f_{12}], \frac{1}{2}[[\nabla_1^2, f_{12}], f_{12}]$ for STG were calculated either by expanding f_{12} in a linear combination of GTGs (STG-nG) or written analytically in closed-form using the extended Boys function, $G_m(T,U) = \int_0^1 t^{2m}\exp[-Tt^2 + U(1-t^{-2})]dt$, $(m = -1, 0, 1, \ldots)$.[60,61] A Gaussian quadrature algorithm was developed for the integrals of genuine STGs.[62] The performance of correlation factors was thoroughly examined, such as the decisive work of Valeev employing extremely flexible expansions with up to nine GTGs, and a single STG proved to be near-optimal.[63–65] STG prevailed immediately in quantum chemistry, and corresponding orbital basis sets have been developed.[66] The use of nonlinear correlation factors in place of the linear r_{12} is often called F12 to distinguish it from R12 theory.

The advent of STG, which operates over short ranges and provides the exact asymptotic behavior at short r_{12}, soon promoted the use of pair functions exploiting the s- and p-wave cusp conditions directly (SP ansatz),[67,68]

$$u_{ij,s}^{(\text{SP})} = \hat{Q}_{12}\hat{\mathcal{R}}_{12}\phi_{ij,s} + \chi_{ij,s}. \tag{9}$$

$\hat{\mathcal{R}}_{12} = f_{12}(\frac{3}{8} + \frac{1}{8}\hat{p}_{12})$ is the so-called *rational generator*[68] with the operator $\hat{p}_{12}$ to permute the spatial coordinates, applying different cusp conditions (1) for singlet and triplet pairs by means of the symmetry $\hat{p}_{12}\phi_{ij,s} = (-1)^s\phi_{ij,s}$. The pair function (9), which can be considered as the generalization of Kutzelnigg's original wave function for s-waves (5), is orbital-invariant, size-consistent, numerically robust, and avoids geminal basis set superposition errors.[69] The SP ansatz (also called the fixed amplitude or diagonal orbital invariant ansatz), in conjunction with STG, greatly simplifies the implementation and has been used in various CC models with Lagrangian functionals.[70–75] These have also been expanded into F12 adaptations in local correlation pictures, as we will outline later. Note the rational generator is a spin-free operator that does not contain the spin index s. This feature permits the application of $\hat{\mathcal{R}}_{12}$ to open-shell references involving unrestricted HF (UHF),[76,77] restricted open-shell HF (ROHF),[74,78,79] and multi-determinant[80–85] wave functions in the manner of spin-flipped geminal[73,77] and internally contracted[80] bases. The extended SP (XSP) ansatz for correlated pairs involving virtual orbitals was developed by Köhn for response properties, excited states, and perturbational triples.[86,87] More recent advances involve methods for large molecules, an explicit correlation for solids, and stochastic approaches, which we will describe in the following sections.

The superior use of the exponential form of the correlation factor (8) in F12 theory stems from the presence of the quadratic term $-(\gamma/2)r_{12}^2$ in the correlation factor related to the second-order Taylor expansion coefficient in higher-order cusp conditions.[88,89] This coefficient is not universal, but state-energy-dependent, yet the accuracy is insensitive to γ in the correlation of valence electrons. In contrast, correlations involving core electrons attenuate much faster, enlarging the optimum γ, especially for the SP ansatz. This does not usually become an obstacle in F12 calculations with core polarization functions for light elements,[61] as the fast convergence in $(L+1)^{-7}$ is guaranteed even in the R12 limit ($\gamma\to 0$).[50] However, if the CI description in the orbital part is unsatisfactory without tight polarization functions for heavier elements (or

even when it is necessary to drop χ entirely from (9) at the worst), we apparently need to optimize the geminal amplitudes or use a different γ for pairs with core orbitals.[90]

Similarly, there is controversy about the treatment of the long-range behavior that should scale as $1/r_{12}$ at large r_{12} accompanying pair-specific amplitudes.[8,68] Such long-range components have not been included in the F12 machinery to date because the standard CI expansion is particularly efficient for dispersion interactions that converge asymptotically only at $L_{\mathrm{occ.}} + 1$ in virtual functions. Therefore, it appears that the use of a correlation factor with a Coulombic decay for dispersion-type correlations is a roundabout choice that introduces additional computational costs for new integrals and manipulations arising from the strong orthogonality projector, at least for molecules with auxiliary CI expansions in atom-centered basis functions, which already contain $1/r_{12}$ correlations in perturbative wave functions. Nevertheless, the situation could be rather different for solid state calculations in plane waves, the number of which can grow intractably in proportion to the volume of the cell regardless of the number of atoms. When a very small basis set, e.g., double-zeta, is employed in F12 calculations, the principal source of the basis set error shifts from dynamic correlation to the HF energy, which can be corrected by single-electron excitations in the CABS space.[70,91] In this context, Nakatsuji and coworkers investigated the structure of the exact wave function in terms of the free-component wave function indicating a slower convergence of the coalescence behavior in the free-component wave function.[92–94]

In the following sections of this perspective, we mainly focus on the explicitly correlated developments in recent years, which enable applications to complex systems, i.e., stochastic explicitly correlated methods with Monte Carlo integration, F12 approaches for nanoscale applications, and explicitly correlated plane waves for solids. Finally, anticipated advances related to these topics will be discussed.

II. STOCHASTIC ALGORITHMS

A potentially highly scalable method of evaluating integrals entering the F12 correction is the Monte Carlo (MC) approach.[95] MC is a general and, in principle, efficient method of evaluating the definite integral of a D-dimensional function, say $f(\mathbf{x})$, approximately as

$$\int f(\mathbf{x})d\mathbf{x} = \int \frac{f(\mathbf{x})}{w(\mathbf{x})} w(\mathbf{x})d\mathbf{x} \approx \frac{1}{N}\sum_{n=1}^{N} \frac{f(\mathbf{x}^{[n]})}{w(\mathbf{x}^{[n]})}, \qquad (10)$$

where $\{\mathbf{x}^{[n]} | 1 \le n \le N\}$ is a set of D-dimensional coordinates distributed randomly but according to the weight function, $w(\mathbf{x})$. A random distribution according to any weight function is achieved by the Metropolis algorithm.[47] In a numerical integration with quadrature, to maintain the same accuracy, exponentially many (m^D) grid points are needed with increasing dimension, where m is the number of necessary grid points per dimension. In contrast, the error (statistical uncertainty) in the MC integral falls off as $N^{-1/2}$, regardless of the dimension.[96] This is because the Metropolis algorithm[47] can place more points in important dimensions, as well as in critical areas of each dimension, as dictated by the weight function. Therefore, MC is a sparse-integration method, which is known to outperform a typical deterministic numerical integration for $D \ge 8$.[97] The MC method also boasts extraordinary versatility in integrating virtually any mathematical form of the integrand, provided a suitable weight function is found.

Taking advantage of this versatility, quantum Monte Carlo (QMC) methods[96,98] have a long history of including the effects of explicit correlation, e.g., through the Jastrow factor.[99,100] This factor can describe three- as well as two-body correlations,[101] and is harder to use outside stochastic methods, with a notable exception of the TC method.[39] With modern supercomputers, which have hundreds of thousands or even millions of CPUs, the ease and efficiency of parallelizing stochastic algorithms is making QMC increasingly popular for conducting benchmark high-accuracy calculations for large and complex systems including solids.[98] Furthermore, the computational cost of QMC methods is typically cubic with respect to the system size,[96,98] and their memory cost is negligible. This also makes QMC more attractive than *ab initio* methods, whose algorithms are usually based on many dense matrix multiplications (e.g., the RI approximation with ABS in the context of F12 theory), which are less scalable with respect to both computer and system sizes.

The existing QMC methods are not without weaknesses. They are, in principle, "ground-state" methods, making it hard to extract reliably (without too much noise) energy differences such as correlation, excitation, ionization, and electron-attachment energies, as well as energy bands. Many QMC approaches suffer from the so-called sign problem, which necessitates, e.g., the fixed-node approximation in diffusion Monte Carlo (DMC).[96,98] They are also subjected to finite-size errors[98] in solid-state applications and have to invoke a thermodynamic extrapolation. These nonsystematic approximations often prevent QMC from reaching exact solutions of the Schrödinger equation, which systematic *ab initio* methods can demonstratively attain, albeit only for small molecules.[102]

There has been a surge of interest in combining *ab initio* methods with QMC,[103–110] aiming to retain the merits of the two while eradicating their demerits. Some techniques perform efficient stochastic sampling in the vast Hilbert space using molecular integrals evaluated by deterministic algorithms, whereas others consider random walks in real space and stochastically integrate all objects entering a target quantity.

The most prominent example in the first category is full configuration interaction quantum Monte Carlo (FCIQMC).[106] This implements an algorithm analogous to DMC, but its walkers represent discrete configurations (as opposed to electrons in continuous real space), avoiding the fixed-node approximation, although the sign problem persists.[111] A similar imaginary-time-evolution method was independently developed by Ohtsuka and Nagase,[105] whose technique does not involve an imaginary-time integration. These methods have been extended to include F12 corrections.[112,113]

Here, we briefly review the Monte Carlo many-body perturbation (MC-MP) method,[114] which is in the second category and seems particularly well suited to an F12 extension,[115,116] taking its second-order variant (MC-MP2) as an example. The MP2 correlation correction to the restricted HF energy of a

closed-shell molecule is given by

$$E^{(2)} = \sum_{i,j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \frac{\langle ij|ab\rangle(2\langle ab|ij\rangle - \langle ab|ji\rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \tag{11}$$

in the standard notation. This is a long sum of products of dense matrices, whose evaluation requires significant disk I/O and careful organization for an efficient parallel execution (for large molecules). However, the actual hotspot of MP2 exists in the preceding step of the transformation of two-electron integrals from atomic orbitals (AOs) to molecular orbitals (MOs). This step is both expensive, incurring an $\mathcal{O}(n^5)$ operation cost (where n is the number of AOs or MOs), and not well-suited to a data-local layout, which is necessary for efficient serial and parallel executions. This difficulty is caused by the completely different characteristics of AOs (localized and asymmetric) and MOs (delocalized and symmetric).

The transformation of the integrals (as well as their evaluation and storage) can be avoided altogether as follows. Using Almlöf's Laplace transformation of the denominator,[117] followed by an interchange of the order of summations and integrations, we can rewrite Eq. (11) as

$$E^{(2)} = \iiiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4), \tag{12}$$

with

$$\begin{aligned} f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = -\int_0^\infty d\tau \frac{1}{r_{12} r_{34}} G^+(\mathbf{r}_3, \mathbf{r}_1, \tau) G^+(\mathbf{r}_4, \mathbf{r}_2, \tau) \\ \times \{2G^-(\mathbf{r}_1, \mathbf{r}_3, -\tau) G^-(\mathbf{r}_2, \mathbf{r}_4, -\tau) \\ - G^-(\mathbf{r}_2, \mathbf{r}_3, -\tau) G^-(\mathbf{r}_1, \mathbf{r}_4, -\tau)\}, \end{aligned} \tag{13}$$

where G's denote the traces of the real-space, imaginary-time, zeroth-order Green's functions,

$$G^-(\mathbf{r}_p, \mathbf{r}_q, \tau) = \sum_i^{\text{occ.}} \varphi_i(\mathbf{r}_p) \varphi_i^*(\mathbf{r}_q) \exp(-\epsilon_i \tau), \tag{14}$$

$$G^+(\mathbf{r}_p, \mathbf{r}_q, \tau) = \sum_a^{\text{vir.}} \varphi_a(\mathbf{r}_p) \varphi_a^*(\mathbf{r}_q) \exp(-\epsilon_a \tau). \tag{15}$$

Equation (12) is a single 12-dimensional integral that can be evaluated by MC integration, completely bypassing the evaluation, storage, or transformation of two-electron integrals either in the AO or MO basis (the one-dimensional integral over τ can be evaluated by quadrature[114]). A suitable weight function is a product of the integrands of the HF Coulomb energy of electron density $\rho(\mathbf{r})$ or a similar quantity, converting Eq. (12) to

$$E^{(2)} \approx \frac{1}{N} \sum_{n=1}^{N} \frac{f(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}, \mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})}{w(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}) w(\mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})}, \tag{16}$$

with

$$w(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2E_J} \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}. \tag{17}$$

Hence, the four-electron coordinates $(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}, \mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})$ are randomly distributed according to the 12-dimensional weight function $w(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_3, \mathbf{r}_4)$. This function is analytically integrable (E_J being the HF Coulomb energy), has identical and therefore mutually canceling singularities to the integrand, and is strictly nonnegative everywhere. MC integration does not have a sign problem from the outset. The operation cost of evaluating the quotient in Eq. (16) in each MC step grows only linearly with the system size, and the memory requirement is minimal.

After adopting the best practices of modern F12 theory, i.e., the SP ansatz[68] and strong orthogonality projector, the F12 correction to the MP2 correlation energy is a sum of two- through six-electron integrals. The GBC and EBC approximations[56] can be used to reduce the dimension of integrals to 15 (five electrons). These few high-dimensional integrals are directly evaluated by the MC integration in the MC-MP2-F12 methods[115,116] without the RI approximation or an ABS. For instance, one of the four-electron (4e) integrals in the F12 correction is evaluated as

$$\begin{aligned} E_{4e} &= \frac{5}{8} \sum_{i,j,k,l}^{\text{occ.}} \langle ijkl| \frac{f_{34}}{r_{12}} |klij\rangle \\ &= \iiiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 f_{4e}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &\approx \frac{1}{N} \sum_{n=1}^{N} \frac{f_{4e}(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}, \mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})}{w(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}) w(\mathbf{r}_3^{[n]}) w(\mathbf{r}_4^{[n]})}, \end{aligned} \tag{18}$$

with

$$\begin{aligned} f_{4e}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \frac{5}{8} \frac{f_{34}}{r_{12}} G^-(\mathbf{r}_1, \mathbf{r}_3, 0) G^-(\mathbf{r}_2, \mathbf{r}_4, 0) \\ \times G^-(\mathbf{r}_3, \mathbf{r}_1, 0) G^-(\mathbf{r}_4, \mathbf{r}_2, 0). \end{aligned} \tag{19}$$

Note that this single 12-dimensional integral is analytically factorable into the sum of products of $O(n^4)$ 6-dimensional integrals, $\langle ij|r_{12}^{-1}|kl\rangle$ and $\langle kl|f_{12}|ij\rangle$, but the former is preferred over the latter by the MC method, whose advantage over a deterministic numerical integration grows with dimension. The integrand $f_{4e}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ has the $1/r_{12}$ singularity but is analytic in the other dimensions. Therefore, the same weight function as Eq. (17) with the $1/r_{12}$ singularity is used for $\mathbf{r}_1$ and $\mathbf{r}_2$, whereas a simple s-type Gaussian-type orbital is adopted as $w(\mathbf{r}_3)$ and $w(\mathbf{r}_4)$.

MC-MP2 and MC-MP2-F12 can calculate the correlation and F12 corrections directly (allowing an inexpensive HF or small-basis MP2 calculation to be performed separately and deterministically) without any bias (reproducing the corresponding deterministic results). The operation costs of MC-MP2 and MC-MP2-F12 for a given accuracy (relative statistical error) were observed to be $\mathcal{O}(n^3)$ and $\mathcal{O}(n^4)$, respectively, where n is the number of orbitals.[116,118] The memory cost is negligible. With the redundant-walker convergence acceleration scheme,[119] the method can easily achieve >90% of the perfect parallel scalability up to thousands of CPUs, and an unprecedented speedup by a factor of tens of thousands (relative to one CPU core) on hundreds of GPUs.[118] These are by virtue of completely eliminating two-electron integral evaluations and transformations, and by foregoing the conventional dense-matrix algorithms in favor of more scalable stochastic ones.

Figure 2 is a result of the MC-MP2-F12 calculation for tetrahydrocannabinol using the cc-pVDZ basis set.[116] The F12 correction is substantial, exceeding 1 E_h, and is reasonably converged in the sense that the difference between the vari-

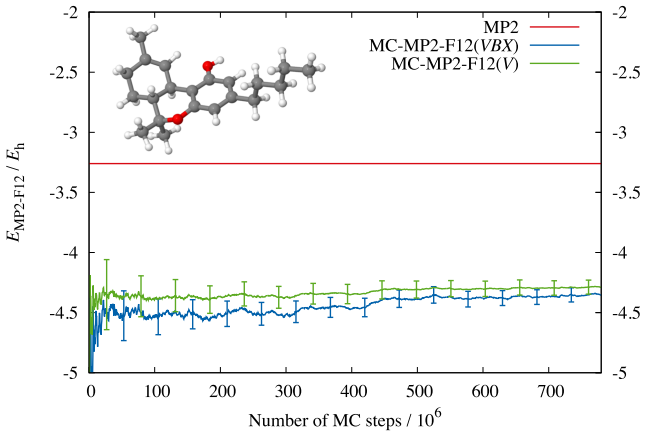

FIG. 2. Convergence of the MP2 correlation energy of tetrahydrocannabinol ($n = 472$) in the cc-pVDZ basis set with respect to the number of MC steps. The error bars correspond to the statistical uncertainty. Reprinted with permission from C. M. Johnson *et al.*, J. Chem. Phys. **145**, 154115 (2016). Copyright 2016 AIP Publishing.[116]

ational (*VBX*) and nonvariational (*V*) formulations or their statistical uncertainties is much smaller than the correction itself. Note the performance of MC-MP2-F12 is unaffected by diffuse function augmentation that is essential for accurate F12 results.

MC-MP2-F12 can use any differentiable correlation factor. The six correlation factors listed in Table I, all satisfying the cusp conditions,[1,2] have been tested for the total and relative correlation energies of small molecules.[116] The Slater-type geminal[60,61] was found to be the best performer (see Table I), whereas the "Gauss" function (not to be confused with GTG, which does not satisfy the cusp condition) is the poorest, possibly because it has the wrong shape in the intermediate domain of r_{12}. With the second- and higher-order cusp conditions being system- and state-dependent,[88,89] it seems unlikely that the observed relative performance of correlation factors can be explained or predicted purely mathematically. Numerical characterization is, therefore, valuable for an exhaustive list of correlation factors, and such a study is easily possible and well underway for MC-MP2-F12. Other approaches that have the same flexibility include the QMC methods,[96,98] GTG expansions,[65] and plane-wave-based methods,[120,121] with which excellent accuracy of the so-called Yukawa–Coulomb geminal was observed for a homogeneous electron gas (HEG).[120] To a lesser extent, the mixed Gaussian-basis-set and multicenter-grid method[68] also lifts some of the constraints on the mathematical form of the correlation factor to be used. Silkowski et *al.*[122] proposed a McMurchie–Davidson-type recursion equation for all necessary integrals for range-separated geminals.

TABLE I. The average error (in mE_h) in the MC-MP2-F12(*VBX*) correlation energies from the MP2 correlation energies in the CBS limits for 17 small molecules.[116] For each correlation factor, a respective suitable value of γ was used. The statistical errors are no greater than 0.7 mE_h.

Function	Name	aug-cc-pVDZ	aug-cc-pVTZ
$f_{12}^{(1)} = (1 - e^{-\gamma r_{12}})/\gamma$	Slater	6.9	3.5
$f_{12}^{(2)} = (1 - e^{-\gamma r_{12}^2})/(\gamma r_{12})$	Gauss	63.4	21.9
$f_{12}^{(3)} = \gamma r_{12}/(\gamma + r_{12})$	Rational	8.7	4.0
$f_{12}^{(4)} = \ln(1 + \gamma r_{12})/\gamma$	Logarithm	12.3	4.6
$f_{12}^{(5)} = \arctan(\gamma r_{12})/\gamma$	Arctangent	12.1	3.2
$f_{12}^{(6)} = f_{12}^{(1)}/2 + f_{12}^{(3)}/2$	Hybrid	7.2	3.2

The MC algorithm has been applied to third-order many-body perturbation (MP3)[123] and second-order many-body Green's function (GF2)[124] methods, with an extension of the latter to the F12 correction being underway, using the formulation of the deterministic counterpart.[125] GF methods[126,127] can compute correlated ionization and electron-attachment energies directly, which are key quantities in redox, electrocatalytic, and biochemical processes as well as in optoelectronic materials. Hence, MC-GF methods and their F12 extension may be even more useful than MC-MP and MC-MP2-F12.

MP and GF are rigorously (diagrammatically) size consistent, and can thus be applied to solids without a finite-size error or thermodynamic extrapolation. The MC-MP2 and GF2 methods have been implemented for one-dimensional solids,[128] the latter providing quasiparticle (electron-correlated) energy bands in the entire Brillouin zone as nearly continuous functions of the wave vector, a difficult feat for any existing QMC method.[98] A deterministic MP2-F12 method for one-dimensional solids[129] is already available, and this should be extensible to an MC algorithm.

The MC-MP and GF methods are best viewed as types of variational Monte Carlo (VMC) integration.[96,98] Therefore, they share the same extraordinary flexibility in handling any integrand, i.e., any Hamiltonian, wave functions, basis sets, and correlation factors. Their F12 extensions can, in principle, be free of any approximation except for the SP ansatz. They share the same difficulty, however, in terms of optimizing their wave functions; the MC-MP and GF methods are limited to one-shot evaluations of integrals and cannot be readily extended to iterative *ab initio* methods such as CC theory or analytical gradients. By the same token, MC-MP2-F12 cannot at present be used to solve geminal amplitude equations iteratively and, in this sense, it is the SP ansatz[68] that makes MC-MP2-F12 possible. Another important difference between the MC-MP and GF methods and VMC is that the latter has the so-called zero-variance property, whereas the former do not.

Apart from the flexibility of the correlation factor, the MC-MP, GF, and F12 methods essentially give the same results as their deterministic counterparts, but with inevitable statistical noise. Therefore, their usefulness ultimately hinges on their ability to perform grand-challenge calculations on the largest supercomputers that are not feasible with the best deterministic implementations. The calculation of Fig. 2 cannot be said to have demonstrated the unique capacity of MC-MP2-F12; a much larger application is still warranted.

III. LARGE MOLECULES

Explicitly correlated theory is now a rather mature technology for molecules containing up to several dozen atoms, and has been applied to investigate, e.g., reaction barriers of enzymatic reactions combined with molecular mechanics.[130] However, its application to molecules consisting of more than a hundred atoms is still challenging because of the steep scaling

of the computational cost with the system size. To overcome this difficulty, F12 theory has been incorporated into cultivated methodologies for large molecules, e.g., the local correlation approaches initiated by Pulay and Sæbø,[131,132] as seen in the earlier local adaptations of GTG[133] and F12.[134] A detailed explanation of local correlation methods is beyond the scope of this perspective, and we only outline the milestone local treatments in conjunction with explicitly correlated theory in the last decade. Readers can find more comprehensive publication lists elsewhere.[135,136] In addition, we will explain other solutions for large molecules using massively parallel computing techniques.

Local correlation approaches restrict the excitations from each pair of localized occupied orbitals to localized virtual orbitals spanned by projected atomic orbitals (PAOs) within finite domains, utilizing the short-range nature of the dynamical electron correlation.[137] The scaling of a correlated method can be reduced by such a treatment, whereas the local approximation appears to introduce the serious problem of irregular domain errors. A large domain size is required to reduce these domain errors. Werner demonstrated that the F12 correction improves not only the basis set incompleteness but also the PAO domain errors in a local version of MP2-F12 (LMP2-F12) using pair-specific strong orthogonality projectors.[138] Further developments involving local CCSD(T) (LCCSD(T)) with local DF and RI have enabled their quantitative applications to biochemical molecules and their reactions.[139] Nevertheless, one still needs to pay attention to the choice of the domain size to obtain energies comparable to those from a nonlocal treatment.[139]

The domain-size problem can be largely alleviated using Meyer's pair natural orbitals (PNOs),[140] as revived by Neese *et al.*,[141] because the accuracy can be controlled *a priori* by a single occupation number threshold for the truncation of PNOs. The steep scalings needed to generate PNOs can be avoided using local variants that employ intermediates with PAO domains or the orbital-specific virtuals (OSVs)[142] often generated from extended PAO domains to attain asymptotic linear scalings.[135,143,144] Among the choices of virtual orbitals, PNOs provide the most compact representation of domains with high accuracy. Krause and Werner proposed a scheme to combine the advantages of OSV and PNO.[143] Independently, Hättig, Tew, and co-workers developed a hybrid OSV-PNO scheme for F12 using auxiliary PNOs (X-PNOs) and reported PNO-CC-F12 implementations.[144,145] The recent development of the domain-based local PNO MP2-F12 (DLPNO-MP2-F12) for the $\mathcal{O}(N)$ scaling exhibits subquadratic scaling for quasi one-dimensional n-alkanes.[146] All of these implementations employ DF in their local representations to reduce the computational cost and memory requirement. Although PNOs have large linear dependencies amongst pairs, their use leads to only dense operations over pairs and appears to be suitable for parallel implementations in distributed memory.[136,147]

Other explicitly correlated methods utilizing localities involve explicitly correlated CCSD(T)[148,149] in the incremental scheme of Stoll[150] and Divide-Expand-Consolidate MP2-F12 (DEC-RIMP2-F12)[151] with simpler structures for F12 implementations to complement the domain-based approaches.

In contrast to the context for inert molecules, the aforementioned local correlation methods are much less effective for excited states, large aromatic molecules in nanoscale, and metallic systems. One effective approach for large-scale calculations without exploiting the orbital locality is to employ massively parallel computers. However, the standard algorithms for electron correlation methods involve successive 4-index integral transformations, and the communication costs hinder efficient implementations as the number of processes in the message passing interface (MPI) increases. This is particularly evident for the F12 treatment containing various intermediates for many-electron integrals. An alternative F12 approach uses real-space numerical quadratures developed in the field of density functional theory instead of the RI expansion.[61,68] All two-, three-, and four-electron molecular integrals in MP2-F12 are generated using numerical integrations directly from 2-index MO amplitudes and 3-index MO integrals over quadrature points. The numerical quadrature technique significantly eases the MPI parallelization in evaluating the 3-index intermediates and the OpenMP parallelization in the summation over grid points with efficient matrix–matrix multiplication libraries. Details of the implementation are explained elsewhere.[152,153]

A typical application of the canonical F12 implementation is the assessment of the binding energy (BE) between a bulky N-heterocyclic carbene and C_{60} fullerene in a Lewis acid-base adduct,[154] as depicted in Fig. 3. The RHF BEs are +0.4 kcal mol^{-1} and −23.2 kcal mol^{-1}, respectively, for the imidazolin-2-ylidene-C_{60} and IDipp)-C_{60} adducts, contradicting experimental observations.[154] The corresponding MP2-F12 BEs are +20.9 and +48.1 kcal mol^{-1}, indicating that the London dispersion force from the bulky ligand accelerates the formation of the IDipp-C_{60} adduct exceeding the steric repulsion.[155]

The F12 ansatz similarly accelerates the convergence of the frequency-independent GF2 ionization energies (IEs), which possess contributions from partial sums of MP2 pair energies.[125] The IEs of GF2 in near-CBS quality can be obtained using GF2-F12 in the aug-cc-pVTZ basis set. Despite its rather simple theoretical framework, GF2-F12 reproduces experimental IEs for conjugated systems quite well,[125] and is considered to be practically useful to investigate IEs of organic functional materials. Figure 4 shows the calculated first IEs of oligofurans from monomer to 15-mer, along with fits to several analytic functions in $1/n$. The evolution of the IEs for

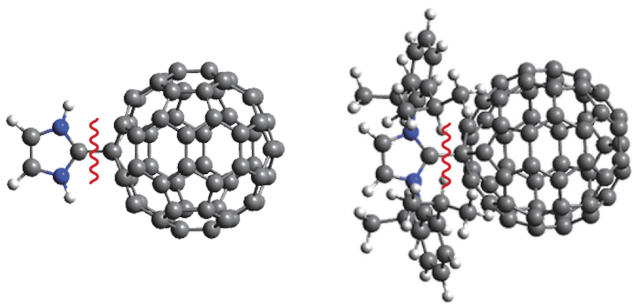

FIG. 3. Geometries of imidazolin-2-ylidene-C_{60} (left) and 1,3-bis(diisopropylphenyl)imidazol-2-ylene(IDipp)-C_{60} (right) adducts. Geometries are optimized at ωB97X-D/6-31G(d) and MP2-F12 energies are calculated in aug-cc-pVTZ with counterpoise corrections.

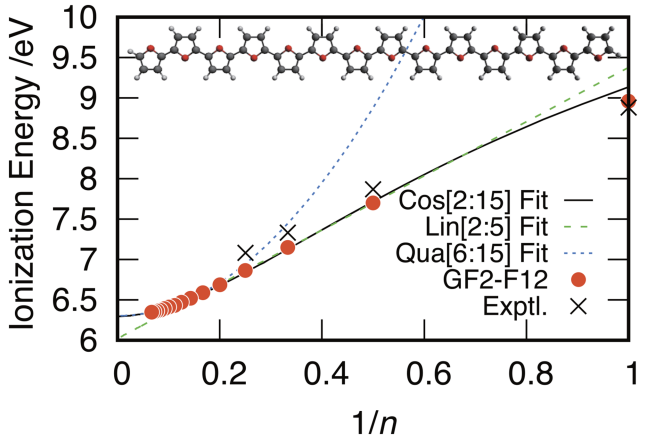

FIG. 4. The vertical IEs (eV) of oligofurans up to 15-mer calculated from GF2-F12/aug-cc-pVTZ as a function of the reciprocal of the number of rings n. The black solid line is the result of fitting to $A + B\cos[\pi/(n+1)]$ using the data in the range of n = [2,15]. The green dashed line is the $A + B/n$ fit for n = [2,5] and the blue short dashed line is the $A + B/n^2$ fit for n = [6,15]. All geometries are optimized with ωB97X-D/6-31G(d). Experimental values from Ref. 157.

these (quasi) 1-dimensional systems is well-represented by the $\cos[\pi/(n+1)]$ function derived from the Hückel theory compared with the empirical cases, the $1/n$ sometimes employed for short oligomers and the $1/n^2$ that is only valid for longer chains. Note that the ΔDFT method without long-range corrections cannot reproduce this behavior, but exhibits much slower $1/n^{0.7}$ behavior for flat oligothiophene.[156]

IV. EXPLICITLY CORRELATED PLANE WAVES

Explicitly correlated theory in a plane wave basis set is a computationally efficient means for the study of periodic solids, because (i) the required many-electron integrals, including three-electron integrals, can be calculated efficiently, and (ii) the correlation factor can be expressed using plane wave coefficients, providing a systematically improvable machinery for a solid-state research. Despite these advantages, there are many technical challenges in implementing explicitly correlated methods in plane waves. This is one reason why there have been relatively few studies on explicitly correlated methods including TC implementations for solids.[42,44,45,120,121,158] Alternatively, it is possible to employ Gaussian basis sets in explicitly correlated theory for solids.[129,159] The main advantage of this approach is that one can exploit the framework developed in F12 theory for many-electron integrals in conjunction with the local correlation techniques described in Sec. III.[159] Furthermore, the linear dependency problem of GTOs usually faced in the studies of solids is mitigated by the inclusion of explicit electron correlation. More recent developments such as the aforementioned stochastic F12 methods could also be applied to solids, either in plane wave or Gaussian basis sets.[116]

In this section, we briefly review an implementation of explicitly correlated perturbation theory within the framework of the projector augmented wave (PAW) method. This implementation employed the Vienna *ab initio* simulation package.[160] In the PAW method, the all-electron orbitals ($|\psi_n\rangle$) are obtained from the pseudo-orbitals ($|\tilde{\psi}_n\rangle$) by means of the linear transformation,[161]

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle)\left\langle \tilde{p}_i|\tilde{\psi}_n\right\rangle. \tag{20}$$

The index n, labelling the orbitals ψ, denotes the band index and the Bloch wave vector k_n, whereas the index i is shorthand for the atomic site R_i, the angular momentum quantum numbers l_i and m_i, and an additional index ϵ_i denoting the linearization energy. The wave vector is conventionally chosen to lie within the first Brillouin zone. The pseudo-orbitals, the variational quantities in PAW, are expanded in reciprocal space using plane waves, $\langle \mathbf{r}|\tilde{\Psi}_n\rangle = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{g}} C^n_{\mathbf{g}} e^{i(k_n+\mathbf{g})\mathbf{r}}$. Two-electron repulsion integrals are evaluated as

$$\langle ij|r_{12}^{-1}|ab\rangle = \sum_{\mathbf{G}} C_i^a(\mathbf{G})\tilde{v}(\mathbf{G})C^{*j}_{\ b}(\mathbf{G}), \tag{21}$$

where $\tilde{v}$ is the Coulomb kernel. The translational invariance of the integral kernel reduces the computational effort from a six-dimensional integral in real space to a three-dimensional sum in reciprocal space over the Fourier components of the given electron pair codensities. In this PAW implementation, the Fourier transformed codensities $C_i^a(\mathbf{G})$ are approximated using Eq. (2.87) of Ref. 162, as originally implemented by Kresse and Harl for the correlation energies of the random phase approximation.[163] Alternatively, the integrals can be evaluated by summing over different contributions on the plane wave grid and a radial atom-centered grid.[164] Note that keeping all contributions on the plane wave grid is more efficient for the three-electron integrals required for the explicitly correlated implementation.

Using the above expressions, it is possible to calculate the necessary two-electron integrals for the correlation energy of an arbitrary post-HF method, e.g., MP perturbation and CC. The standard expression for the correlation energy, which is dependent on the determinantal coefficients and two-electron integrals, can be rewritten by rearranging the nested summations over orbital and plane wave indices[165] as

$$E_c = \sum_{\mathbf{G}} S(\mathbf{G})\tilde{v}_{\mathbf{G}}. \tag{22}$$

This expression clarifies the source of the error in achieving the basis set and supercell size convergences. Figure 5 depicts

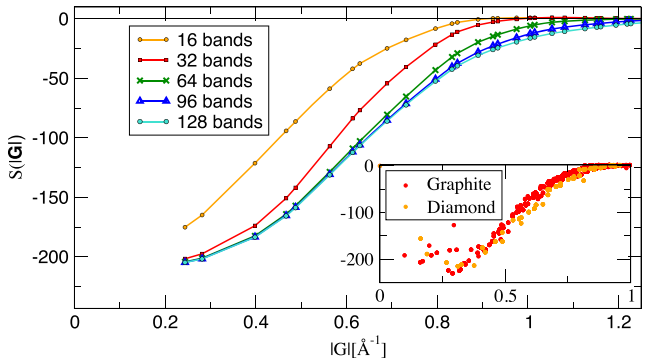

FIG. 5. The convergence of spherically averaged $S(\mathbf{G})$ for an increasing number of virtual bands using $2 \times 2 \times 2$ k-point mesh. $S(\mathbf{G})$ has been calculated using second-order Møller-Plesset perturbation theory. The vertical axis has been rescaled. Inset: Non-spherically averaged $S(\mathbf{G})$ for carbon diamond and graphite (ABC) using 32 bands per k-point and a $3 \times 3 \times 3$ k-point mesh. $S(\mathbf{G})$ has been calculated using second-order Møller-Plesset perturbation theory. The vertical axis has been rescaled.

the spherical average of $S(\mathbf{G})$ for the carbon diamond crystal by changing the size of the orbital basis set. The greater the number of virtual orbitals, the slower $S(\mathbf{G})$ decays to zero as $|\mathbf{G}|$ increases. This indicates that the slow convergence with respect to the number of virtual orbitals (as a result of the cusp behavior of the exact wave function at short $\mathbf{r}$) is reflected in the profile of $S(\mathbf{G})$ at large plane wave vectors $\mathbf{G}$ in the reciprocal space. It can also be noted that a sharp truncation of $S(\mathbf{G})$ at small $\mathbf{G}$ implies the presence of a convergence problem with respect to the given supercell size, which can be mitigated by interpolating $S(\mathbf{G})$ at small plane wave vectors.[165] It is a common practice in QMC to calculate the electronic structure factor by performing a similar interpolation.[166,167] Nevertheless, the structure factor of QMC does not represent such slow convergence with respect to the number of parameters, as the correct shape of the wave function at short inter-electronic distances is already captured by the employed Jastrow factors. Explicitly correlated plane waves attain a more rapid basis set convergence by augmenting a post-HF wave function with terms containing a two-electron correlation factor.

We now turn to the discussion of evaluating the many-electron integrals that occur in explicitly correlated theory for solids. It is generally advantageous to employ a plane wave basis set, in which various types of three- and four-electron integrals can be calculated efficiently. We give an example for the three-electron integrals over $f_{12}r_{23}^{-1}$ required for the so-called V intermediate in explicitly correlated MP2 theory. Using a series of forward and backward Fourier transforms, the integrals can be calculated in the following manner:[121]

$$\begin{aligned} y_{jil}^{lji} &= \langle jil|f_{12}r_{23}^{-1}|lji\rangle, \\ \tilde{\chi}_j^l(\mathbf{G}) &= C_j^l(\mathbf{G})\tilde{f}(\mathbf{G}), \\ \chi_{ijl}(\mathbf{r}) &= \mathcal{FT}^{-1}[\tilde{\chi}_j^l(\mathbf{G})]C_i^{*j}(\mathbf{r}), \\ \tilde{\chi}_{jil}(\mathbf{G}) &= \mathcal{FT}[\chi_{jil}(\mathbf{r})], \\ y_{jil}^{lji} &= \sum_{\mathbf{G}} \tilde{\chi}_{jil}(\mathbf{G})\tilde{v}(\mathbf{G})C_l^i(\mathbf{G}). \end{aligned} \tag{23}$$

The relatively fast decay of the Fourier coefficients for the correlation factor ($\lim_{|\mathbf{G}|\to\infty}\tilde{f}(\mathbf{G}) \propto \frac{1}{\mathbf{G}^4}$) means that the required size of the plane wave grids does not significantly increase from that employed for two-electron integrals.[121] Ochi *et al.* have also shown that integrals for the kernel $\nabla_1 u_{12}\cdot\nabla_1 u_{13}$ can be efficiently computed using plane wave basis sets.[44] This kernel appears in both TC and explicitly correlated F12 theories.[44,61] In contrast to the direct evaluation of three-electron integrals using atom-centered Gaussian basis sets in GTG theory, plane wave basis sets benefit greatly from the computational efficiency of Fourier transformations and the translational invariance of the employed kernels. Another advantage of using plane wave basis sets is that the Fourier coefficients of the correlation factor in the above expression can be easily modified to further improve the rate of convergence of the wave function expansion.

We now discuss the possible flexibility of correlation factors. In the vast applications of recent explicitly correlated theory, correlation factors are dependent on a single parameter γ, which models the decay of the correlation hole in the STG factor.[60] However, the pairwise ansatz for the first-order wave function enables us to employ orbital-pair-dependent parameters γ_{ij} to increase the accuracy. This enables better modeling for the optimum correlation factors of core and valence electrons.[90] In the case of the uniform electron gas, such a correlation factor strongly depends on the average density of the valence electron gas.[120] The optimum γ increases with the gas density when modeling a strongly confined electron correlation hole. This observation suggests that the correlation factor can be parametrized as a function of the average valence electron gas density. Such a parametrization can work very efficiently, especially for properties that require an accurate estimate of the correlation hole dependent on electron density, e.g., equilibrium volumes and bulk moduli of solids.[121]

For a uniform electron gas, the optimal correlation factor deviates from the Slater-type function over longer ranges. For two electrons in a box, it can be shown analytically and observed numerically that the exponential behavior of the Slater-type function is not optimal at large inter-electronic distances,[120] but the decay should be $1/r_{12}$.[68] This long-range $1/r_{12}$ tail for the pair correlation function is also suggested by the random phase approximation in the thermodynamic limit, where Gaskell[100,168] found the *exact* long-range behavior of the uniform electron gas to be $\lim_{r_{12}\to\infty} u(r_{12}) \propto r_{12}^{-(D-1)/2}$ for a D-dimensional model. Therefore, a good approximation to the optimal correlation factor for the homogeneous electron gas at both short and long ranges is the Yukawa–Coulomb correlation factor[120]

$$f_{12}^{(\mathrm{YC})} = \frac{2}{\gamma^2}\frac{\exp(-\gamma r_{12})-1}{r_{12}}, \tag{24}$$

employed in QMC and TC calculations.[42,100,158] However, for real inhomogeneous systems such as simple solids, it has been found that the Yukawa–Coulomb correlation factor does not improve upon the Slater-type correlation factor.[121] One possible explanation for this observation is that the coefficients of the long-range $1/r_{12}$ tail for the correlation function are generally pair dependent.[68]

For real solids with inhomogeneity and anisotropy, a large degree of flexibility for correlation factors would be desirable to further improve the efficiency of explicitly correlated theories. Note that plane waves can also be used as basis functions to expand the Jastrow factors in VMC.[169] Such Jastrow factors with augmented variational parameters along with higher particle number correlations[101] have been employed to capture the entirety of correlation effects in VMC calculations.[98] As an example for anisotropic correlation effects, we show $S(\mathbf{G})$ from the MP2 theory for the carbon diamond and graphite crystals in the inset of Fig. 5. A comparison of the respective structure factors at $|\mathbf{G}| \approx 0.25$ Å^{-1} reveals a significantly larger dispersion for graphite (red circles) than that for diamond (yellow circles). We attribute this broadening of S($\mathbf{G}$) to the larger anisotropy in graphite compared with that in diamond. Prendergast *et al.* have shown that VMC recovery in the correlation energy increases for graphite if the Jastrow factors contain additional degrees of freedom for inhomogeneous and anisotropic correlation effects.[169] Therefore, it is likely that a similar parameterization would further improve explicitly correlated wave functions.

To conclude this section, we present a practical application of explicitly correlated MP2 theory to the lattice constant

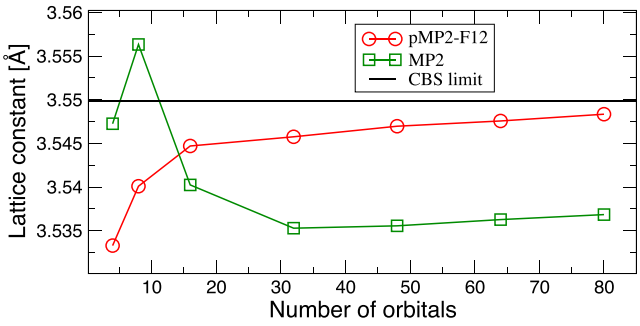

FIG. 6. Convergence of the carbon diamond lattice constant calculated using (explicitly correlated) MP2 theory and a $4 \times 4 \times 4$ k-point mesh with respect to the total number of orbitals per k-point. Note that this system has four occupied orbitals per k-point in the frozen core approximation and that we employ a two atomic unit cell.

of the carbon diamond crystal. The equilibrium lattice constant is obtained by minimizing the energy with respect to the volume of the unit cell. Figure 6 shows the convergence of the calculated (explicitly correlated) MP2 lattice constant with respect to the number of orbitals. It is clear that the convergence of the lattice constant from F12 theory is significantly faster than that of MP2 without F12 corrections. The pMP2-F12 method,[121] which corresponds to the MP2-F12 approximation in the V-term only, has been employed for these calculations, along with the Yukawa–Coulomb correlation factor parametrized for the average electronic density using results obtained for the uniform electron gas simulation cell.[121] We stress that the computational cost of pMP2-F12 with respect to the system size scales as $\mathcal{O}(N^5)$, like MP2 without F12 corrections. In this way, the inclusion of explicitly correlated terms makes wave-function-based theories significantly more efficient and accurate for the properties of solids.

V. FUTURE CHALLENGES

The use of explicitly correlated methods has significantly expanded the scope of both the studies of molecules and complex systems such as solids over recent decades. The essential ingredients would appear to be present for at least medium-sized molecules within the standard *ab initio* framework represented by the F12 approach, yet several challenges remain, e.g., efficient algorithms for many-electron integrals with general correlation factors,[170] relativistic treatment of explicit electron correlation,[171–174] especially beyond the Dirac–Coulomb Hamiltonian, composite schemes,[175] and three-body correlation factors for the triple-point coalescence.[176] Above all, the requirement of manifold integrals with CABS indices for nuclear derivatives has complicated the implementation of analytical energy gradients even for MP2-F12.[177] Constructing extended geminal spaces including virtual orbitals[86,178] for excited states and response properties is also nontrivial especially with high-angular-momentum contributions of geminal basis to make the RI expansion less effective. Moreover, the developments in this field of research will also help pave the way towards other, more efficient wave function expansions in different areas of electronic structure theory, where slowly converging wave function expansions need to be dealt with, including auxiliary field QMC (AFQMC)[179] and FCIQMC theories for both ground and excited states.[106,108,110] In this sense, possible conjunctions with strong correlation theories are of great importance, as they may enable the treatment of transition metal complexes that play the central role in biological water splittings.[180]

Another branch of research in explicitly correlated theories that will be continued in the future is the introduction of more flexibility in the employed correlation factors. This would help to further improve the rate of convergence in wave function expansions with little or even no assistance from CI expansions. This aim is shared by QMC, where a Jastrow correlation factor with a small number of parameters explicitly captures a majority or even the entirety of electronic correlation effects. This would require a powerful and universally transferable correlation factor with an increased flexibility that is capable of including correlation effects in higher particle numbers, e.g., the electron–electron–nucleus factor for inhomogeneous correlation effects. Various methods to optimize a correlation factor with additional parameters can be envisioned, including (i) minimization of the Hylleraas functional, (ii) employing hybrid techniques that use VMC to optimize the correlation factors and quantum chemical wave function theories for the energy calculation, and (iii) combining Green's function-based theories such as the random-phase approximation to the electronic correlation with explicitly correlated wave functions. When one attempts to capture the entirety of correlation effects by a correlation factor (including Slater-type geminal and Yukawa–Coulomb geminal, which share an exponential structure), the resulting explicitly correlated method may be similar to CC theory with a generalized operator.[181] It would be interesting to know whether such a cluster operator is largely dictated by these factors satisfying the cusp conditions. This also touches upon the fundamental question of partitioning and treating dynamic and static (possibly even strong) correlation effects on a different, but more accurate, footing than currently possible.

The field of explicitly correlated theories for the study of solids has only emerged over the last few years. Many of the techniques accumulated in *ab initio* quantum chemistry still need to be transferred to the study of solid states. One major technical challenge is to avoid different many-electron integrals in explicitly correlated theories, as these are expensive, increasing the computational cost compared with their parent methods for electron correlation. Many promising approaches to overcome these problems have already been proposed for large or periodic systems, including Monte Carlo techniques,[115,116] local explicitly correlated methods,[136,145,146] and plane wave basis set techniques.[44,121] These methods exhibit a trade-off between computational cost and accuracy that is strongly dependent on the system size, dimensionality, and possibly the band gap. In addition, a significant portion of the total correlation energy comes from the accumulation of long-range dispersion in a solid. A full understanding of the long-range dispersion in the CBS limit is therefore essential for predictive simulations of solids. It may be worth investigating whether a good correlation factor for electron pairs in essentially atomic environments remains so for itinerant

electron pairs in metallic solids. In this regard, a numerical study of various correlation factors (including many-particle correlation effects) in different electronic environments should be conducted. Finally, with the significantly deeper understanding of explicit correlation obtained over the last decade, one may revisit the question of whether the F12 correction can substantiate a systematic density functional. An affirmative answer may lead to a method that simultaneously achieves accuracy and efficiency and is particularly attractive for solids.

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