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We present an investigation into the use of an explicitly correlated plane wave basis for periodic wavefunction expansions at the level of second-order Møller-Plesset (MP2) perturbation theory. The convergence of the electronic correlation energy with respect to the one-electron basis set is investigated and compared to conventional MP2 theory in a finite homogeneous electron gas model. In addition to the widely used Slater-type geminal correlation factor, we also derive and investigate a novel correlation factor that we term Yukawa-Coulomb. The Yukawa-Coulomb correlation factor is motivated by analytic results for two electrons in a box and allows for a further improved convergence of the correlation energies with respect to the employed basis set. We find the combination of the infinitely delocalized plane waves and local short-ranged geminals provides a complementary, and rapidly convergent basis for the description of periodic wavefunctions. We hope that this approach will expand the scope of discrete wavefunction expansions in periodic systems. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818753]

I. INTRODUCTION

Despite huge advantages in terms of accuracy and systematic improvability, wavefunction-based quantum chemical methods are routinely used by only a small fraction of electronic structure theorists, in contrast to density functional theory (DFT) which dominates the community.[1] Nowhere is this more true than in the solid state, where application of high-level quantum chemistry methods are only beginning to emerge in a recently growing field.[2–17] The reason for this slow uptake is the computational cost of these methods, which generally scale as a high power of the system size, compared to the lower mean-field scaling of DFT. This is exacerbated in the solid state where increasing the size of the supercell to converge finite size effects is far more costly than for mean-field counterparts. Much of this expense originates from the need to expand out the many-electron wavefunction in terms of anti-symmetrized one-particle functions of a specified basis set. This itself must then be expanded and generally extrapolated to near completeness to obtain accurate results and justify the use of the high level of correlation treatment. Although methods more familiar to the solid state, such as DFT[18] and Diffusion Monte Carlo (DMC)[19] require a basis set, there is only a weak dependence since no many-electron wavefunctions are expanded in this basis.

The difficulty with the expansion of many-electron wavefunctions as antisymmetric products of one-particle basis functions (Slater determinants) has been known since the early days of electronic structure theory, and is due to the short-ranged or "dynamic" correlation between electron pairs. As the electrons coalesce, a derivative discontinuity or "cusp" must arise, so that a divergence in the kinetic energy operator cancels an opposite one in the potential. Within an expansion of Slater determinants the exact cusp is never obtained, and a quantitatively correct linear form at small interelectronic distances only arises with large basis sets of high momenta. A description of these cusps was initially formulated by Kato,[20–23] who found the wavefunction to be linear to first-order as a function of the interelectronic distance between the pairs (r_{12}). Moreover, the gradient of this linear behavior was found to be exactly a half (or quarter for triplet pairs), regardless of the form of the rest of the potential in the system. Higher order terms in r_{12} however are affected by the rest of the potential.[24]

For many years, methods were developed which tried to exploit this knowledge of the form of the exact wavefunction in the small r_{12} limit, but the methods which resulted, such as methods utilizing exponentially correlated Gaussians[25] and the transcorrelated method[26] among others, were generally expensive, plagued by many electron integrals, and limited to systems of only a small size. A major breakthrough was achieved in 1985 by Kutzelnigg,[27–29] where two electron geminal functions were introduced into the wavefunction which satisfied the electron cusps, and augmented a traditional Slater determinant expansion. This resulting wavefunction expansion was then used within the formulation of traditional quantum chemical methods, and crucially, an approximate resolution of identity (RI) was performed as a way to factorize the many-electron integrals into sums of products of at most two-electron quantities. A small set of these geminals dramatically improved the convergence of quantum

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chemical methods with respect to basis set size, since fewer high momenta functions were required for these energetically significant cusp regions. This dual basis of traditional determinants and strongly orthogonal geminals, and the methods for evaluating resultant expectation values, has been named F12 theory.

In the intervening years, this approach has matured, with important advances taking it from a promising technique to an indispensable tool for high-accuracy quantum chemical methods for large systems.[30–36] These advances include the introduction of a complementary auxiliary basis set in which to perform the RI,[37, 38] refinement of the approximations used in order to minimize the impact of the RI and maintain orbital invariance,[39–43] a more general function of the interelectronic coordinate to approximately capture longer range effects,[44, 45] and the introduction of specially designed basis sets for optimal efficiency.[46, 47] The result are methods which share the intrinsic accuracy of the complete basis set (CBS) limit of their parent method, but which approach this limit far more rapidly, thereby reducing the cost of the method. Combining this with density fitting,[48] local approximations,[49, 50] and multireference methods[51–62] has greatly extended the reach of quantum chemistry in recent years.

All F12 approaches to date have taken place within the framework of a traditional atom-centered Gaussian basis set. Although these functions are ubiquitous in gas-phase molecular quantum chemistry, where their local nature generally suits the wavefunction, it is unclear whether these are well suited for extended systems, especially when the wavefunction is intrinsically delocalized. These systems have been traditionally studied in a discrete basis of plane waves, chosen such that the boundary conditions at the edges of the unit cell are fulfilled, although this is by no means the only choice in solids. However, a plane wave basis confers many advantages in the solid state. There is a single basis set parameter (the orbital kinetic energy cutoff), which allows the CBS limit to be approached systematically and straightforwardly, without the need for basis set optimization. These basis functions are also strictly orthogonal, and therefore no issues with linear dependencies occur as the basis increases, in contrast to Gaussian functions.

However, for all these advantages of a plane wave basis, the features of electronic cusps are still missing, and are difficult to capture without including very high energy plane waves in the expansion which dramatically increases the cost. This convergence has been found to have the same scaling behavior as the Gaussian expansion,[63, 64] though generally requires many more functions to reach the complete basis limit.

In this paper, we attempt to overcome these difficulties by combining a plane wave basis with the explicitly correlated F12 approach, and evaluate energies at the level of second-order Møller–Plesset (MP2) theory to analyze the benefit. We first consider the 3D finite-electron uniform electron gas (UEG) for this approach, which has recently received attention as a model system for wavefunction-based quantum chemistry,[22, 63, 65–69] as well as long being an important model, especially in the development of density functional theory.[70, 71] As the simplest model for a fully periodic metallic system, it has many advantages. The plane waves in the

UEG are exact natural orbitals, but in addition they are also exact Hartree–Fock solutions, and kinetic energy eigenfunctions. This means that the generalized Brillouin condition (GBC) and the extended Brillouin condition (EBC) are exactly satisfied, which decouples the conventional and F12 energy contributions.[28, 37, 43]

In addition, all three-electron integrals have simple analytic forms, whose RI can be saturated completely with the addition of at most just a single auxiliary orbital. Tractable expressions for the electron repulsion integrals mean that extrapolation to the CBS limit is straightforward to derive and understand; these energies can be easily found and used as benchmarks.[63] We note in passing that the CBS limit is also well-defined for the MP2 energy of a finite system, even though the energy diverges in the thermodynamic limit.[9, 68] This is because the divergence is caused by low-momenta excitations in the large box limit, rather than the high-momenta basis functions responsible for converging the basis set incompleteness error.

The simple model Hamiltonian also allows us to calculate the exact MP1 wavefunction for the two electron UEG analytically, whose expansion about $r_{12} = 0$ we find to take a different form than the traditional Slater-type correlation factor now established in molecular F12 theory. We use this to compare the Slater-type form to a new correlation factor which we find to be optimal for the UEG, and which may have advantages in other solid-state (or even potentially molecular) systems. Finally, we apply the method to the most widely studied solid-state system with quantum chemical methods, rock salt lithium hydride crystal, to check the transferability of the findings into realistic *ab initio* solid state systems.

II. THEORY

This section outlines the theoretical methods that are employed in the present work to study the uniform electron gas simulation cell Hamiltonian. We briefly recapitulate MP2 perturbation theory, explicit correlation and the Hylleraas functional. Furthermore, we elaborate on the use of a plane-wave basis set in the many-electron wavefunction expansion and its implications for explicitly correlated methods. Analytical expressions for the integrals required in the above methods are derived and techniques to treat finite size effects as well as singularities are discussed. Finally, a new correlation factor that we term Yukawa-Coulomb correlation factor is derived.

A. Second-order Møller-Plesset perturbation theory

In MP2 theory, electron correlation is treated using many-body Rayleigh-Schrödinger perturbation theory, taking the N-electron Fock operator as the unperturbed Hamiltonian $H^{(0)}$.[72] The Hartree–Fock wave function $|\Psi^{(0)}\rangle$ both defines and is defined by the Fock operator. Formally, it is the ground state Slater determinant with occupied orbitals that are eigenstates of the 1-electron Fock operator

$$F|i\rangle = \epsilon_i|i\rangle. \tag{1}$$

In practical computations, however, the $|i\rangle$ are rarely true eigenstates of the Fock operator, since they are expressed

in a finite and in general, insufficient 1-electron basis. Nevertheless, these Hartree–Fock orbitals define $H^{(0)}$. For the UEG, which is the main focus of this work, the Hartree–Fock orbitals are determined by symmetry. They are therefore exact eigenstates and the generalized and extended Brillouin conditions are fulfilled. For the UEG, $|\Psi^{(0)}\rangle$ is the exact ground state of the zeroth-order Hamiltonian $H^{(0)}$.

In MP2 theory, the standard route to obtaining the first-order wavefunction is to expand it in the basis of excited Slater determinants $|\Psi_{ij}^{ab}\rangle$,

$$|\Psi^{(1)}\rangle = \frac{1}{2} \sum_{ij}^{\text{occ.}} \sum_{ab}^{\text{virt.}} t_{ij}^{ab} E_{ij}^{ab} |\Psi^{(0)}\rangle, \qquad (2)$$

where i, j and a, b refer to occupied and unoccupied spatial Hartree–Fock orbitals, respectively, from the full set of M one-electron basis functions. E_{ij}^{ab} is the spin-free two electron excitation operator. The coefficients of the excited determinants t_{ij}^{ab} are readily calculated and read

$$t_{ij}^{ab} = \frac{\langle ij|ab\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \qquad (3)$$

In the above expression, ϵ_n corresponds to the one-electron HF eigenvalues, and $\langle ij|ab\rangle$ are the conventional electron repulsion integrals. The calculation of two-electron integrals will be outlined in Sec. II D. In Møller-Plesset perturbation theory, the second-order energy is the leading order correction to the correlation energy that can be obtained by calculating $\langle \Psi^{(0)}|H - H^{(0)}|\Psi^{(1)}\rangle$, which simplifies to

$$E_c^{\text{MP2}} = \sum_{ij}^{\text{occ.}} \sum_{ab}^{\text{virt.}} \frac{\langle ij|ab\rangle(2\langle ab|ij\rangle - \langle ba|ij\rangle)}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \qquad (4)$$

Both the energy and the equations that determine the first-order wavefunction separate into decoupled equations for each occupied pair. The pair correlation energy can alternatively be obtained by optimizing the first-order pair correlation function $|u_{ij}\rangle$ to minimize the Hylleraas energy functional

$$E_c^{ij} = \min[\langle u_{ij}|F_1 + F_2 - \epsilon_i - \epsilon_j|u_{ij}\rangle + 2\langle u_{ij}|\frac{1}{r_{12}}|ij\rangle]. \qquad (5)$$

This expression is useful in explicitly correlated methods. In conventional MP2 theory, the spinless first-order pair function and its contravariant counterpart, have the expansion

$$|u_{ij}\rangle = \frac{1}{2} \sum_{ab}^{\text{virt.}} t_{ij}^{ab}|ab\rangle, \qquad (6)$$

$$\langle u_{ij}| = \frac{1}{2} \sum_{ab}^{\text{virt.}} \langle ab|(2t_{ij}^{ab} - t_{ij}^{ba}). \qquad (7)$$

Figure 1 visualizes the zeroth-(HF) and first-order wavefunctions using the example of two electrons in a box with a homogeneous neutralizing background charge. The wavefunctions are plotted with respect to the interelectronic distance r_{12}. While the first-order wavefunction accounts for electronic correlation by decreasing the probability of finding both electrons at short interelectronic distances, the zeroth-order wavefunction does not exhibit this so-called
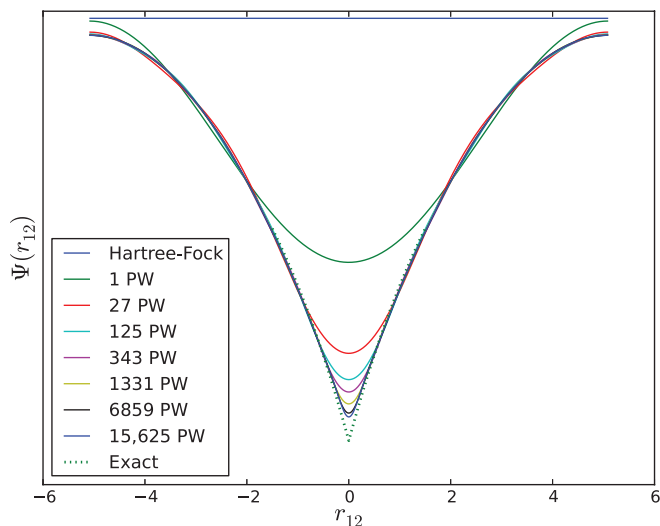

FIG. 1. The MP1 wavefunction for the two electron uniform electron gas at $r_s = 5$ a.u. with increasing plane wave orbital basis sets (OBS), up to a total basis of 15 625 plane waves. One electron is fixed at the center of the box, and the other is moved in a line through the coalescence point. This illustrates the slow convergence to the exact wavefunction as the interelectronic distance tends to zero. The Hartree–Fock wavefunction shows no variation with interelectronic distance, as only the average electronic potential is felt across the box. This demonstrates the same qualitative cusp convergence in plane waves as demonstrated elsewhere for molecular systems in Gaussian basis sets.[30,31]

correlation hole centered at the electron coalescence point ($r_{12} = 0$), and is depicted by a flat line. We note that the first-order wavefunction converges very slowly to a cusp in the complete basis set limit with respect to the number of employed virtual one-electron orbitals used in the expansion of $|\Psi^{(1)}\rangle$ [see Eq. (2)].

B. Explicitly correlated MP2

As outlined above and in Refs. 30, 31, and 63, the MP1 wavefunction converges frustratingly slowly to the complete basis set limit, with a M^{-1} dependence. Concomitantly, the correlation energy converges very slowly and usually requires the treatment of a large one-electron basis sets of high momenta, that result in significant computational effort. However, as shown in Figure 1, a large fraction of the basis is needed to describe the many-electron wavefunction in the vicinity of the electron-electron coalescence points. The first-order cusp condition defines the shape of the many-electron wavefunction close to the electron coalescence of singlet pairs[20]

$$\left. \frac{\partial \left(\frac{\Psi(\mathbf{r}_{ij})}{\Psi(0)} \right)}{\partial \mathbf{r}_{ij}} \right|_{\mathbf{r}_{ij}=0} = \frac{1}{2}. \qquad (8)$$

The above equation implies that the many-electron wavefunction exhibits a derivative discontinuity about $\mathbf{r}_{12} = 0$, with a linear behavior as you move from this point regardless of the external potential of the system, and as seen in Figure 1. Explicitly correlated methods fulfill the first-order cusp conditions exactly by augmenting the ansatz for the many-electron wavefunction with two-electron terms that depend on the

interelectronic distance of each electron pair. In explicitly correlated MP2-F12 theory,[41,73] the first-order pair functions $|u_{ij}^{F12}\rangle$ are expanded as

$$|u_{ij}^{F12}\rangle = \frac{1}{2}\sum_{ab}^{\text{virt.}} t_{ij}^{ab}|ab\rangle + t_{ij}\hat{Q}_{12}f_{12}|ij\rangle, \qquad (9)$$

where t_{ij} are geminal amplitudes determined by the universal cusp conditions, f_{12} is the correlation factor that models the shape of the correlation hole and is typically chosen to be a Slater-type function[44]

$$f_{12}^{\text{STG}} = e^{-\gamma r_{12}}. \qquad (10)$$

This choice ensures that the geminal functions included in the basis are linear with respect to r_{12} in the vicinity of the electron-electron cusp and decay to zero at large r_{12}, where the wavefunction is expected to vary smoothly and is generally well-represented by the conventional determinantal basis. We note that it is more common in explicitly correlated Gaussian implementations to approximate this functional form by a fixed combination of Gaussian type correlation factors to simplify integral evaluation over this kernel, however, this is not a problem here (see Sec. II D), and an exact Slater-type geminal function is used.

This form of the correlation factor is an empirical choice, and its longer-ranged decay is not motivated by an underlying theory, but rather intuition.[44] However, it has been shown to be accurate compared to various other alternatives in molecular systems.[45,74] In molecules, it is likely that the rapid exponential decay of the correlation factor to zero (the lack of long range structure) is an advantage because it separates out the long-range behavior which is not expected to be able to be modeled by a simple function of r_{12} due to the anisotropy of the external potential.[74] Furthermore, in Ref. 45 the function has been shown to not increase monotonically to a constant, but rather to reach a maximum and then decrease, due to the fact that the remaining molecular electron density is reduced at large interelectronic distances.

However, here we will also investigate a new correlation factor derived from perturbation theory that we term Yukawa-Coulomb correlation factor,

$$f_{12}^{\text{YC}} = \frac{2}{\gamma}\frac{1 - e^{-\gamma r_{12}}}{r_{12}}. \qquad (11)$$

The MP2-F12 theory outlined in this work is, however, independent from the specific form of f_{12}. Therefore, we will return to the discussion of f_{12}^{YC} in Sec. II E.

The projector $\hat{Q}_{12}$ enforces strong orthogonality between $|\Psi^{(1)}\rangle$ and $|\Psi^{(0)}\rangle$, and it also enforces orthogonality between the standard and F12 contributions to the first-order wave function

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

where

$$O_1 = \sum_i^{\text{occ.}} |r_1'\rangle\langle r_1'|i\rangle\langle i|r_1\rangle\langle r_1|, \quad V_1 = \sum_a^{\text{virt.}} |r_1'\rangle\langle r_1'|a\rangle\langle a|r_1\rangle\langle r_1|.$$

In F12 theory, it is convenient to obtain the second-order correlation energy by optimizing $|u_{ij}^{F12}\rangle$ to minimize

the Hylleraas functional Eq. (5). The F12 contributions involve non-factorizable many-electron integrals, which increase the computational cost of evaluating $E_c^{\text{MP2-F12}}$ compared to E_c^{MP2}. The calculation of many-electron integrals can, however, be approximated by the introduction of resolutions of identity using the orbital basis, and an additional orthogonal complimentary auxiliary basis set (CABS). In this work, we employ unoccupied Hartree–Fock orbitals as CABS.

For calculations on the UEG, since the EBC is fulfilled, the contributions involving t_{ij}^{ab} do not depend on the F12 terms.[28,30,43] The energy then decomposes into the standard MP2 correlation energy and a F12 correction

$$E_c^{\text{MP2-F12}}(M) = E_c^{\text{MP2}}(M) + E_c^{\text{F12}}(M). \qquad (13)$$

The dependence of the above energies on M indicates that these energies are calculated using a finite orbital basis that is composed of M plane waves with a kinetic energy below a specified cutoff. The complete basis set limit is approached for $M \to \infty$. The expressions for E_c^{F12} have been derived elsewhere,[30,31,36,41] and are given here as

$$\begin{aligned} E_c^{\text{F12}}(M) = &2V_{mn}^{ij}\left(2t_{mn}^{ij} - t_{nm}^{ij}\right) \\ &+ t_{mn}^{kl}B_{kl}^{ij}\left(2t_{mn}^{ij} - t_{nm}^{ij}\right) \\ &- (\epsilon_m + \epsilon_n)t_{mn}^{kl}X_{kl}^{ij}\left(2t_{mn}^{ij} - t_{nm}^{ij}\right). \end{aligned} \qquad (14)$$

In the above expression, the indices i, j, k, l, m, and n refer to occupied HF orbitals, and Einstein summation convention is assumed. t_{kl}^{ij} are the geminal amplitudes that fulfill the first-order cusp condition and are kept fixed at the diagonal orbital-invariant ansatz of Ten-no,[40] which exactly satisfy the first order cusp-conditions of singlet and triplet electron pairs,

$$t_{ii}^{ii} = -\frac{1}{2}\gamma^{-1}, \qquad (15)$$

$$t_{ij}^{ij} = -\frac{3}{8}\gamma^{-1}, \qquad (16)$$

$$t_{ij}^{ji} = -\frac{1}{8}\gamma^{-1}. \qquad (17)$$

The intermediates V, X, and B are defined as

$$V_{mn}^{ij} = Y_{mn}^{ij} - R_{mn}^{pq}v_{pq}^{ij} - R_{mn}^{la'}v_{la'}^{ij} - R_{mn}^{a'l}v_{a'l}^{ij}, \qquad (18)$$

$$X_{mn}^{ij} = \bar{R}_{mn}^{ij} - R_{mn}^{pq}R_{pq}^{ij} - R_{mn}^{la'}R_{la'}^{ij} - R_{mn}^{a'l}R_{a'l}^{ij}, \qquad (19)$$

$$\begin{aligned} B_{mn}^{ij} = &\tau_{mn}^{ij} + \hat{S}_{12}\left(\frac{1}{2}\hat{S}_H\bar{R}_{mP}^{ij}h_n^P\right. \\ &- R_{mn}^{PQ}k_P^R R_{RQ}^{ij} - R_{mn}^{Pk}f_P^Q R_{Qk}^{ij} \\ &+ R_{mn}^{ka'}f_k^l R_{la'}^{ij} - R_{mn}^{pa}f_p^q R_{qa}^{ij} \\ &\left. - \hat{S}_H R_{mn}^{ka'}f_k^P R_{Pa'}^{ij} - \hat{S}_H R_{mn}^{a'b}f_{a'}^P R_{pb}^{ij}\right). \end{aligned} \qquad (20)$$

TABLE I. Index notation for different orbital subspaces of the complete one-electron basis. CABS refers to the complimentary auxiliary basis set,[38] and OBS refers to the orbital basis set over which the conventional MP1 amplitudes are defined.

	Occ. OBS orbitals	Virt. OBS orbitals	CABS
i, j, k, l, m, n	Yes	No	No
a, b	No	Yes	No
p, q	Yes	Yes	No
P, Q, R	Yes	Yes	Yes
a'	No	No	Yes

For this work, the B intermediate is calculated using approximation C.[39,75] Table I summarizes the meaning of the above indices. f_P^Q, h_P^Q, and k_P^Q refer to the Fock-, Hartree-, and exchange matrix. We note that $f_P^Q = h_P^Q - k_P^Q$. Section II C outlines their evaluation for the UEG. Y_{mn}^{ij}, R_{mn}^{ij}, $\bar{R}_{mn}^{ij}$, τ_{mn}^{ij}, and v_{mn}^{ij} correspond to two electron integrals defined as

$$Y_{mn}^{ij} = \langle \phi_m \phi_n | f_{12} v_{12} | \phi_i \phi_j \rangle, \tag{21}$$

$$R_{mn}^{ij} = \langle \phi_m \phi_n | f_{12} | \phi_i \phi_j \rangle, \tag{22}$$

$$\bar{R}_{mn}^{ij} = \langle \phi_m \phi_n | f_{12}^2 | \phi_i \phi_j \rangle, \tag{23}$$

$$\tau_{mn}^{ij} = \langle \phi_m \phi_n | (\nabla_1 f_{12})^2 | \phi_i \phi_j \rangle, \tag{24}$$

$$v_{mn}^{ij} = \langle \phi_m \phi_n | v_{12} | \phi_i \phi_j \rangle. \tag{25}$$

f_{12} and v_{12} is the correlation factor and the electron repulsion kernel, respectively. We will return to the evaluation of the above integrals in reciprocal space in Sec. II D, which is performed in the Vienna *ab initio* simulation package (VASP).[76] The operators $\hat{S}_{12}$ and $\hat{S}_H$ symmetrize four index quantities such that

$$\hat{S}_{12} T_{mn}^{ij} = T_{mn}^{ij} + T_{nm}^{ji}, \tag{26}$$

$$\hat{S}_H T_{mn}^{ij} = T_{mn}^{ij} + T_{ij}^{mn}. \tag{27}$$

We stress that the above expressions hold for general systems with real as well as complex electron repulsion integrals, so that the introduction of k-point symmetry in *ab initio* systems follows naturally.

C. The homogeneous electron gas in a plane wave basis set

In this work, we seek to apply explicitly correlated second-order Møller-Plesset perturbation theory to a finite-size (insulating) uniform electron gas model. The N-electron homogeneous electron gas simulation-cell Hamiltonian reads

$$\hat{H} = -\sum_\alpha \frac{1}{2} \nabla_\alpha^2 + \sum_{\alpha,\beta} \frac{1}{2} \hat{v}_{\alpha\beta}, \tag{28}$$

where α and β are electron indices and the two-electron Ewald interaction $\hat{v}_{\alpha\beta}$ is given by

$$\hat{v}_{\alpha\beta} = \frac{1}{\Omega} \sum_{\mathbf{G}} \frac{4\pi}{\mathbf{G}^2} e^{i\mathbf{G}(\mathbf{r}_\alpha - \mathbf{r}_\beta)}, \tag{29}$$

and Ω refers to the volume of the real-space simulation cell. For all calculations in the present work, we employ a cubic real-space unit cell with 54 electrons unless stated otherwise. The reciprocal lattice vectors $\mathbf{G}$ are defined as

$$\mathbf{G} = \frac{2\pi}{L} \begin{pmatrix} n \\ m \\ l \end{pmatrix}, \tag{30}$$

where n, m, and l are integer numbers and L is the real-space box length such that $L^3 = \Omega$. The one-electron orbitals are chosen to be plane waves

$$\phi_n(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_n \mathbf{r}}, \tag{31}$$

where $\mathbf{k}$ refers to the unique reciprocal lattice vector of the orbital. The one-electron Hartree–Fock Hamiltonian becomes diagonal in this orbital basis and reads

$$\langle \phi_n | H^{(0)} | \phi_m \rangle = f_n^m = \delta_{n,m}\left(h_n^m - k_n^m\right) = \epsilon_n,$$

where

$$h_n^n = \frac{1}{2} \mathbf{k_n}^2 \tag{32}$$

and

$$k_n^n = -\sum_i \langle ni | v_{12} | in \rangle. \tag{33}$$

D. Evaluation of the integrals in reciprocal space

It can be advantageous to calculate the electron repulsion integrals in reciprocal space if a plane-wave basis set is employed. This 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

$$\langle ij | v_{12} | ab \rangle = \sum_{\mathbf{G}} C_{ia\mathbf{G}} \tilde{v}_{\mathbf{G}} C_{bj\mathbf{G}}^*, \tag{34}$$

where

$$\sum_{\mathbf{G}} C_{ia\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} = \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r}). \tag{35}$$

The Fourier components of the integral kernels in Eqs. (22) and (25) read

$$\tilde{f}_{\mathbf{G}}^{\text{STG}} = \mathcal{FT}\left(f_{12}^{\text{STG}}\right) = \frac{4\pi}{(\mathbf{G}^2 + \gamma^2)^2}, \tag{36}$$

$$\tilde{f}_{\mathbf{G}}^{\text{YC}} = \mathcal{FT}\left(f_{12}^{\text{YC}}\right) = \frac{4\pi}{(\mathbf{G}^2 + \gamma^2)\mathbf{G}^2}, \tag{37}$$

$$\tilde{v}_{\mathbf{G}} = \mathcal{FT}\left(v_{12}\right) = \frac{4\pi}{\mathbf{G}^2}. \tag{38}$$

We note that if the orbitals correspond to plane waves, as it is the case in the UEG, momentum conservation applies. $\langle ij|v_{12}|ab\rangle$ is non-zero only if $\mathbf{k}_i + \mathbf{k}_j = \mathbf{k}_a + \mathbf{k}_b$. Moreover, in the UEG all orbital codensities, and therefore two-electron integrals can be defined uniquely from the momentum transfer vector $\mathbf{k}_i - \mathbf{k}_a$ such that

$$\langle ij|v_{12}|ab\rangle = \tilde{v}_{\mathbf{k}_i - \mathbf{k}_a}. \tag{39}$$

1. Treatment of singularities in reciprocal potentials

The reciprocal kernels in Eqs. (37) and (38) diverge at $\mathbf{G} = 0$. Although these singularities become only problematic for integrals $\langle vw|vw\rangle$ (due to the orthogonality of the orbitals), a direct numerical evaluation of the $\mathbf{G} = 0$ contribution to the electron repulsion integrals according to Eq. (39) is not possible. The singularities are, however, integrable and well-known solutions to this problem have already been proposed.[77] We will employ a technique that introduces a Gaussian charge distribution $C_{\mathbf{G}}$ whose integral over the reciprocal space with the corresponding kernels can be calculated analytically as

$$\frac{1}{\Omega}\sum_{\mathbf{G}} C_{\mathbf{G}}\tilde{v}_{\mathbf{G}} \rightarrow \int d\mathbf{G}\, e^{-\alpha \mathbf{G}^2}\tilde{v}_{\mathbf{G}}, \tag{40}$$

where

$$C_{\mathbf{G}} = e^{-\alpha \mathbf{G}^2}. $$

α is chosen such that the charge distribution decays to zero at the boundary of the employed plane wave grid and is constant in the vicinity of $\mathbf{G} = 0$. Adding and removing this Gaussian charge distribution to $C_{ia\mathbf{G}}C^*_{bj\mathbf{G}}$ on the right-hand side of Eq. (34) gives

$$\frac{1}{\Omega}\sum_{\mathbf{G}}(C_{nn\mathbf{G}}C^*_{mm\mathbf{G}} - C_{\mathbf{G}} + C_{\mathbf{G}})\tilde{v}_{\mathbf{G}}$$
$$= \underbrace{\frac{1}{\Omega}\sum_{\mathbf{G}}(C_{nn\mathbf{G}}C^*_{mm\mathbf{G}} - C_{\mathbf{G}})\tilde{v}_{\mathbf{G}}}_{\mathbf{G}=0 \text{ contribution vanishes}} + \underbrace{\frac{1}{\Omega}\sum_{\mathbf{G}}C_{\mathbf{G}}\tilde{v}_{\mathbf{G}}}_{\text{analytical integration}}. \tag{41}$$

The difference between the Gaussian and orbital charge distribution vanishes for $\mathbf{G} = 0$, removing the $\mathbf{G} = 0$ contribution from the sum in the first term on the right-hand side of the above equation. The last term on the right-hand side can be integrated analytically. Depending on the kernel, we obtain the following results for the integrals:

$$\frac{1}{\Omega}\sum_{\mathbf{G}} C_{\mathbf{G}}\tilde{v}_{\mathbf{G}} \rightarrow \int d\mathbf{G}\frac{4\pi e^{-\alpha \mathbf{G}^2}}{\mathbf{G}^2} = 2\pi\sqrt{\frac{\pi}{\alpha}}, \tag{42}$$

$$\frac{1}{\Omega}\sum_{\mathbf{G}} C_{\mathbf{G}}\tilde{f}_{\mathbf{G}}^{\text{YC}} \rightarrow \int d\mathbf{G}\frac{4\pi e^{-\alpha \mathbf{G}^2}}{(\mathbf{G}^2 + \gamma^2)\mathbf{G}^2} = \frac{2\pi^2 e^{\alpha\gamma^2}\text{Erfc}\left(\sqrt{\alpha}\gamma\right)}{\gamma}. \tag{43}$$

Practically speaking, the $\mathbf{G} = 0$ component is computed once per kernel and stored. This one-time effort does not require significant optimization.

2. Convolution of integral kernels in reciprocal space

We compute the reciprocal kernels for the integrals in Eqs. (21), (23), and (24) using the convolution theorem with

$$\mathcal{FT}(f_{12}v_{12}) = \frac{1}{\Omega}\sum_{\mathbf{G}'}\tilde{v}_{\mathbf{G}-\mathbf{G}'}\tilde{f}_{\mathbf{G}'}, \tag{44}$$

$$\mathcal{FT}\left(f_{12}^2\right) = \frac{1}{\Omega}\sum_{\mathbf{G}'}\tilde{f}_{\mathbf{G}-\mathbf{G}'}\tilde{f}_{\mathbf{G}'}, \tag{45}$$

$$\mathcal{FT}((\nabla_1 f_{12})^2) = \frac{1}{\Omega}\sum_{\mathbf{G}'}\tilde{f}_{\mathbf{G}-\mathbf{G}'}\tilde{f}_{\mathbf{G}'}(\mathbf{G}\cdot\mathbf{G}' - \mathbf{G}'\cdot\mathbf{G}'). \tag{46}$$

The integral kernels are calculated using the convolution theorem in order to treat finite-size effects in the B intermediate consistently and obtain the correct limiting behavior for the F12 contributions away from the large box-size limit. We stress that E_c^{F12} must vanish in the complete basis set limit ($M \rightarrow \infty$) in a non-trivial way, since the conventional determinant amplitudes recover the CBS energy in this limit. Specifically, the contributions of the V, X, and B intermediates to E_c^{F12} must all vanish individually. In the following, we will discuss this behavior for the V intermediate that reads

$$V_{mn}^{ij} = Y_{mn}^{ij} - R_{mn}^{pq}v_{pq}^{ij} - R_{mn}^{la'}v_{la'}^{ij} - R_{mn}^{a'l}v_{a'l}^{ij}. \tag{47}$$

The first term in the above equation on the right hand side must cancel with the others as the employed basis set approaches completeness. The contraction over the orbital indices in the last three terms corresponds to a resolution of identity between the Coulomb potential (present in the v_{pq}^{ij} integrals) and the correlation factor (present in the R_{mn}^{pq} integrals). Thus, it is important that the three different integral kernels ($\frac{1}{r}$, $e^{-\gamma r}$, and $\frac{e^{-\gamma r}}{r}$) are treated in a consistent manner, which is achieved via the convolution theorem.

E. A new MP2-F12 correlation factor: Yukawa-Coulomb

The optimal correlation factor maximizes the convergence rate of the MP2-F12 correlation energy to the CBS limit with respect to the employed orbital basis set. All MP2-F12 implementations have so far been confined to molecular systems, where different choices of correlation factors have been investigated but did not yield an improvement over the conventional Slater-type correlation factor.[45] In this work, we seek to investigate a correlation factor motivated by analytic results for two electrons in a box with a neutralizing and uniform background charge.[22,78,79] The amplitudes of the first-order wavefunction for two electrons with opposite spins in a box are given by

$$t_{ii}^{ab} = \frac{\langle ii|ab\rangle}{\epsilon_i + \epsilon_i - \epsilon_a - \epsilon_b}, \tag{48}$$

where $|i\rangle = \Omega^{-1/2}$ is the spatial orbital at the gamma point $\mathbf{G} = 0$. In this case, the kinetic energy of the occupied orbitals are zero and momentum conservation of all two-electron excitations requires that $\mathbf{k}_b = -\mathbf{k}_a$. Therefore, the denominator of Eq. (48) can be approximated by

$$\epsilon_i + \epsilon_i - \epsilon_a - \epsilon_b \approx -\mathbf{k}_a^2 + \tilde{\gamma}. \qquad (49)$$

In the above equation, we have approximated the contributions of the exchange k_a^a [see Eq. (33)] to the HF one-electron energies by a constant $\tilde{\gamma}$. We note that in the limit $\mathbf{k}_a \to \infty$, the denominator will be dominated by contributions of the kinetic energy whereas the exchange contributions to ϵ_a will decay as $1/\mathbf{k}_a^2$. Inserting the definition of the electron repulsion integrals and noting that $\mathbf{k}_a$ in this instance is also equal to the momentum transfer vector of the excitation, the above approximation gives

$$t_{ii}^{ab} = -\frac{1}{\Omega} \frac{4\pi}{\mathbf{k}_a^2(\mathbf{k}_a^2 - \tilde{\gamma})}. \qquad (50)$$

A sum over all orbital products in the reciprocal lattice to obtain the wavefunction form then allows for an analytic inverse Fourier transform of the electron pair function to real space, to yield the first-order pair function

$$|u_{ii}\rangle = -\frac{2}{\gamma^2} \frac{1 - e^{-\gamma r_{12}}}{r_{12}} \frac{1}{\Omega} \qquad (51)$$

with $\gamma^2 = \tilde{\gamma}$. The corresponding correlation factor consistent with Eqs. (9) and (15) is

$$f_{12}^{\text{YC}} = \frac{2}{\gamma} \frac{1 - e^{-\gamma r_{12}}}{r_{12}}. \qquad (52)$$

The above correlation factor, that we denote Yukawa-Coulomb correlation factor, becomes linear in r_{12} for $r_{12} \to 0$ and decays to zero for large r_{12}. We note that the Yukawa-Coulomb correlation factor is similar to the two-body Jastrow factor used in previous studies of the homogeneous electron gas with transcorrelated methods.[80] This correlation factor may equivalently be derived directly in real space, starting from the differential equation for the first-order wave function for doubly occupied pairs in a UEG,

$$(F_1 + F_2 - \epsilon_i - \epsilon_j)Q_{12}f(r_{12})\frac{e^{i2\mathbf{k}_i\mathbf{s}}}{\Omega} + Q_{12}\frac{1}{r_{12}}\frac{e^{i2\mathbf{k}_i\mathbf{s}}}{\Omega} = 0, \qquad (53)$$

where $\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and we have asserted that the first-order pair function can be exactly represented by the product of the ij orbital pair with an isotropic function of r_{12}. Since the GBC and EBC are fulfilled, $[Q_{12}, F_1] = 0$ and we can therefore solve for $f(r_{12})$ without considering Q_{12}. Approximating $F_1 + F_2 \approx T_1 + T_2 + \tilde{\gamma} = -\nabla_{r_{12}}^2 - \frac{1}{4}\nabla_s^2 + \tilde{\gamma}$ gives

$$\left(-\nabla_{r_{12}}^2 + k_i^2 - \epsilon_i - \epsilon_j + \tilde{\gamma}\right)f(r_{12}) + \frac{1}{r_{12}} = 0, \qquad (54)$$

which has the solution $f(r_{12}) = -f_{12}^{\text{YC}}/2\gamma$ with $\gamma^2 = k_i^2 - 2\epsilon_i + \tilde{\gamma}$.

The main difference between Eq. (52) and the Slater-type function is in the longer-ranged behavior, as f^{YC} decays to

zero as $1/r_{12}$ for $r_{12} \to \infty$ as opposed to an exponential decay for the Slater-type correlation factor in Eq. (10) commonly used in F12 theories. From consideration of the correct van der Waals description of a minimal basis helium dimer, the same long range $1/r_{12}$ form was deduced in Ref. 40. However, since this long-range part of the correlation function is continuous and able to be captured in single reference theories by basis functions of angular momentum of $L_{\text{occ}} + 1$, it was not deemed necessary there to include this asymptotic behavior in the form of the correlation factor. In this paper, we will show clear improvements from the Yukawa-Coulomb correlation factor in the case of the UEG where the correlation is isotropic, however, it remains to be seen if any advantages are transferable to *ab initio* solid state or extended molecular systems, where the longer range behavior in the geminals may be projected out by the determinantal expansion in the presence of significant inhomogeneity in the potential.

Although we use simple perturbative arguments to motivate correlation functions of the uniform electron gas – the prototypical example of a metallic system where simple perturbation theory will fail – it should be noted that for a two electron system the model is highly insulating and metallic behavior and divergent results only arise on approach to the thermodynamic limit.[68] In addition, this long-range $1/r_{12}$ tail for the pair correlation function can also be motivated from the random phase approximation in this thermodynamic limit, where Gaskell[78, 79] found the *exact* long-range behavior of the uniform electron gas to be

$$\lim_{r_{12} \to \infty} u(r_{12}) \propto r_{12}^{-(D-1)/2}, \qquad (55)$$

where D is the dimension of the model, and $e^{-u(r_{12})}$ then gives the exact solution to the two-body Schrödinger equation. This gives confirmation that the form of the correlation factor given in Eq. (52) is *exactly* correct for both long and short distances in the two-body correlation, although not necessarily between. This is also true in the strongly correlated regime, although there higher body effects are obviously increasingly important. This knowledge has informed the choice of Jastrow factors within the quantum Monte Carlo community,[81] whose simplest functional form of

$$u(r_{12}) = e^{-\frac{r_{12}}{2(1+br_{12})}}, \qquad (56)$$

also has the correct long-ranged $1/r_{12}$ behavior, and is used as standard for two-body correlation in both molecular and extended systems.[26, 82–84] These Jastrow factors, which can be constructed to have increasing numbers of variational parameters, additionally in higher particle number coordinates[85] capture all correlation effects of variational Monte Carlo methods.[19]

III. RESULTS

This section discusses MP2 and MP2-F12 results of the finite simulation cell uniform electron gas model. Section III A recapitulates the well-known basis set extrapolation procedures used in MP2 theory to obtain accurate complete basis set limit reference energies. Section III B investigates the convergence of the MP2-F12 correlation energy with

respect to the employed computational parameters such as the size of the CABS space, the variational parameter γ used in the correlation factors, and the orbital basis set. Having established CABS convergence, Sec. III C examines the variation in the optimal parameter γ governing the extent of the correlation hole, as the electron density of the system is changed. Section III D explores the potential benefit of a pairwise optimization of the correlation factor in order to accelerate the correlation energy convergence with respect to the employed basis set even further. Finally, Sec. III E investigates the relative accuracy in finite basis set MP2 and MP2-F12 correlation energies as a function of the electron density.

A. Basis set convergence in MP2 theory

Accurate complete basis set limit MP2 correlation energies are an indispensable prerequisite for the investigation of the quality of our MP2-F12 results. To this end, we outline the calculation of the MP2 complete basis set limit energies below. Figure 2 shows the convergence of the MP2 correlation energy with respect to the employed basis set for 54 electrons in a box at a density corresponding to $r_s = 5.0$ bohrs, a typical electron density, e.g., potassium metal. As derived and discussed thoroughly in Ref. 63, the MP2 correlation energy converges only as $1/M$ to the complete basis set limit, where M corresponds to the number of plane waves. This rate of convergence results directly from the convergence of the first-order cusp condition by the wavefunction. In the present work, we employ this functional behavior ($1/M$) to extrapolate to the complete basis set limit ($M \rightarrow \infty$). The extrapolations were carried out using several MP2 energies obtained for orbital cutoffs yielding 5887–9171 orbitals. The inset in Figure 2 confirms that the MP2 correlation energies for these basis sets converge as $1/M$ to the complete basis set limit. In the following, we will employ extrapolated complete basis set limit energies as reliable comparisons for MP2-F12 results.
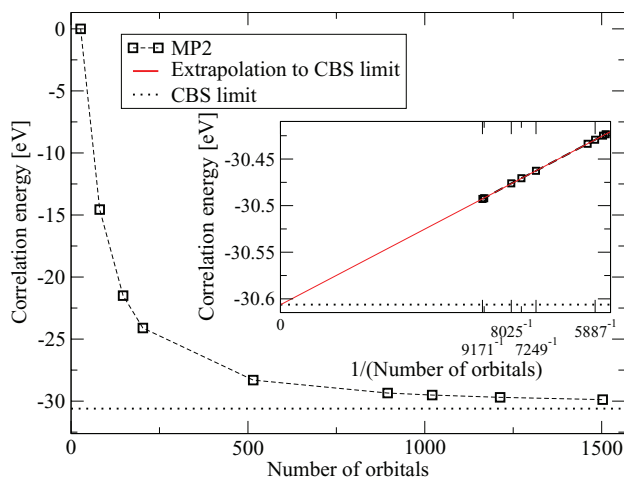
B. Computational parameters in MP2-F12 theory

1. CABS convergence

To avoid the explicit evaluation of three- and four-electron integrals in F12 calculations, a CABS is introduced.[38] By insertion of the RI, many-electron integrals can be replaced with products of two electron integrals contracted over the union of the orbital basis and the CABS (e.g., $\langle mnl|f_{12}f_{23}|lji\rangle \rightarrow \sum_P \langle mn|f_{12}|lP\rangle\langle Pl|f_{12}|ji\rangle$). In this work, the CABS space is trivially constructed as a set of higher momentum plane waves to those in the orbital basis, and is therefore automatically orthogonal. Figure 3 demonstrates a rapid convergence of the MP2-F12 energy with respect to the number of CABS orbitals used in the RI, and crucially, the rate of this convergence is independent of the orbital basis size. This is because the occupied orbitals do not include components of higher momentum as the orbital basis increases, and therefore the quality of the RI for a fixed number of electrons is independent of the size of the virtual basis, and only depends on the size of the complete basis set (the union of OBS and CABS). In addition, we note that the MP2-F12 energy changes by less than 50 meV if the number of basis functions in the RI increases from 587 to 1503. As indicated in Sec. I, due to conservation of momentum, the RI for three-electron integrals in the uniform electron gas can in fact be saturated with a single function, obviating the need for a full RI in these cases. However, in order to maintain generality, this approach will not be considered further here.

This invariance with respect to orbital basis size will not be strictly true for *ab initio* systems, and so the question of convergence with respect to the auxiliary basis will need to be readdressed at a later date. In addition, even for the uniform electron gas, the convergence will change with number of electrons, as the formal requirement for saturation of the auxiliary basis for three-electron integrals includes plane waves with momenta $3 \times k_{occ}$, where k_{occ} is the maximum momenta of the occupied orbitals.[28,29] However, errors may be sufficiently small such that the RI basis can be truncated well before this limit, and the computational cost for
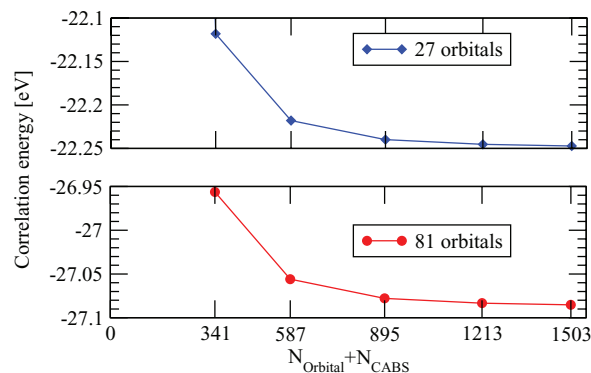

FIG. 2. Convergence of the MP2 correlation energy for the 54 electron UEG simulation cell ($r_S = 5.0$ bohrs) with respect to the employed number of orbitals M. The inset shows that the correlation energy behaves as $1/M$ using a very large orbital basis set, which allows for the extrapolation to the complete basis set limit.

FIG. 3. Convergence of the MP2-F12 correlation energy for the 54 electron UEG simulation cell ($r_s = 5$ bohrs) with respect to the employed number of basis functions in the orbital basis and the CABS. A Slater-type correlation factor and $\gamma = 0.67$ Å^{-1} was used. The number of basis functions in the orbital space was fixed to 27 (upper panel) and 81 (lower panel). The CABS convergence rate does not change as the number of virtual orbitals is increased.

increasing the basis is only $\mathcal{O}[M^2]$. This issue will be returned to in the context of *ab initio* systems at a later date.

2. γ optimization

As discussed in Sec. II, the f_{12}^{STG} and f_{12}^{YC} correlation factors depend on the parameter γ that describes how quickly the correlation factor decays to zero with increasing inter-electronic distance, modeling the physical extent of the correlation hole. The Hylleraas energy functional Eq. (5) is variational and allows optimization of γ through energy minimization. Figure 4 shows the dependence of the MP2-F12 energy on γ for the Slater and Yukawa-Coulomb correlation factors. The Yukawa-Coulomb and Slater-type correlation factors minimize the MP2-F12 correlation energies when $\gamma = 1.04$ Å^{-1} and $\gamma = 0.67$ Å^{-1}, respectively.

It is instructive to compare the behavior of the two correlation factors by contrasting their series expansion about $r_{12} = 0$, which gives

$$-\frac{f_{12}^{\text{STG}}(r_{12})}{\gamma} = -\frac{1}{\gamma} + r_{12} - \frac{\gamma r_{12}^2}{2} + \mathcal{O}(r_{12}^3), \qquad (57)$$

$$-\frac{f_{12}^{\text{YC}}(r_{12})}{\gamma} = -\frac{2}{\gamma} + r_{12} - \frac{\gamma r_{12}^2}{3} + \mathcal{O}(r_{12}^3). \qquad (58)$$

The zeroth-order terms on the right hand side of the above equations are constant. Constant shifts in the correlation factors are, however, always removed by the projector $\hat{Q}_{12}$ defined in Eq. (12) and yield no contribution to the MP2-F12 correlation energy. The first-order terms agree in both correlation factors, and are linear as required by the first-order cusp condition. Inserting the optimized γ's to calculate the coefficients for the second-order terms in r_{12} from Eqs. (57) and (58) yield 0.347 Å^{-1} and 0.335 Å^{-1} for the Yukawa-Coulomb and Slater-type correlation factor, respectively. This comparison shows that both correlation factors give in fact very similar results at the cusp position for the present system. However, the Yukawa-Coulomb correlation factor yields an improved minimum energy for the system, which is lower by approximately 100 meV compared to the Slater-type correlation factor, indicating its superior suitability for the system as expected.

We also note that the MP2-F12 energy becomes identical for both correlation factors in the limits $\gamma \to \infty$ and $\gamma \to 0$. For $\gamma \to \infty$, the MP2-F12 energy converges to the conventional MP2 energy in the respective orbital basis set. In the limit $\gamma \to 0$, both correlation factors become r_{12}. As such, the latter limit corresponds to the MP2-R12 correlation energy.

3. Basis set convergence

As a further test of the quality of the MP2-F12, we consider the convergence with respect to the orbital basis using the Slater-type correlation factor, and compare to the extrapolated CBS limit results outlined in Sec. III A and in Ref. 63. Figure 5 confirms that the correct CBS limit correlation energy (30.61 eV) is recovered in the large basis limit of our MP2-F12 implementation. As anticipated, we find that the rate of convergence for the MP2-F12 results is greatly improved compared to conventional MP2 theory. The inset in Figure 5 shows that the MP2-F12 correlation energy converges approximately as $1/M^{\frac{7}{3}}$, significantly faster than the $1/M$ convergence of MP2. This can be rationalized from the optimal convergence of a principal expansion of the wavefunction with terms linear in r_{12}, which can be shown to be $(L + 1)^{-7}$ where L is the largest momentum in the expansion.[29]

Figure 6 shows the convergence of the MP2 and MP2-F12 correlation energies with respect to the employed basis set for the Slater-type and Yukawa-Coulomb correlation factors. We stress that a logarithmic scale is used on the horizontal axis. As expected, both correlation factors converge to the correct CBS limit. Furthermore, the Yukawa-Coulomb correlation factor exhibits a slightly faster rate of convergence indicating that the $1/r$ decay of f^{YC} captures longer-ranged, important correlation effects that are neglected by the exponentially decaying Slater-type correlation factor. The results
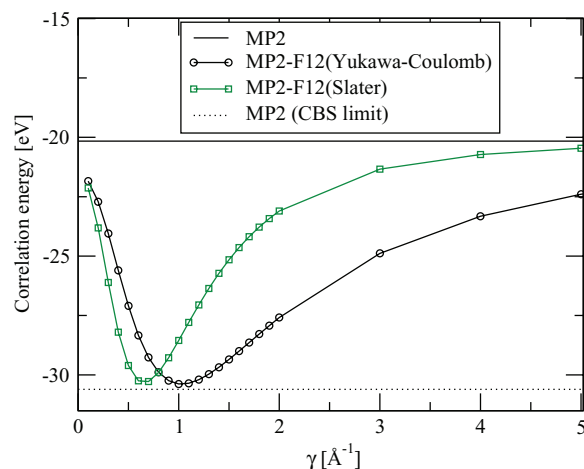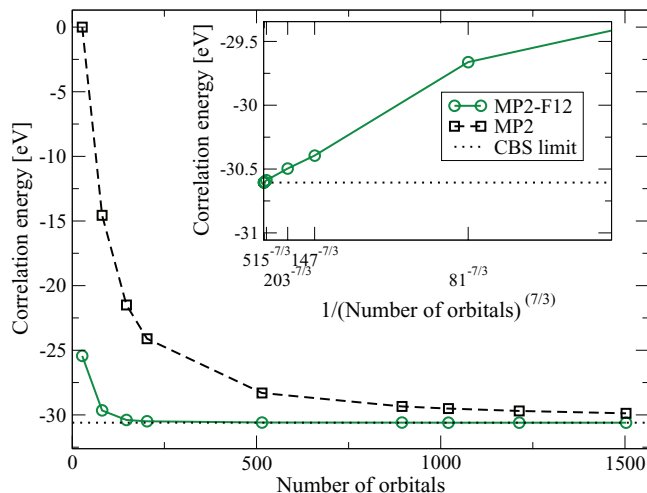

FIG. 4. The variation in the MP2-F12 energy with respect to the γ parameter in the Slater- and Yukawa-Coulomb correlation factors, with the optimal γ giving the lowest MP2-F12 energy. We employed 123 orbitals with 724 CABS basis functions for the 54 electron system at a density of $r_s = 5$ bohrs.

FIG. 5. Convergence of the MP2 and MP2-F12 correlation energies for the 54 electron UEG simulation cell ($r_S = 5.0$ bohrs) with respect to the employed number of orbitals M using the optimum γ (see Figure 4).
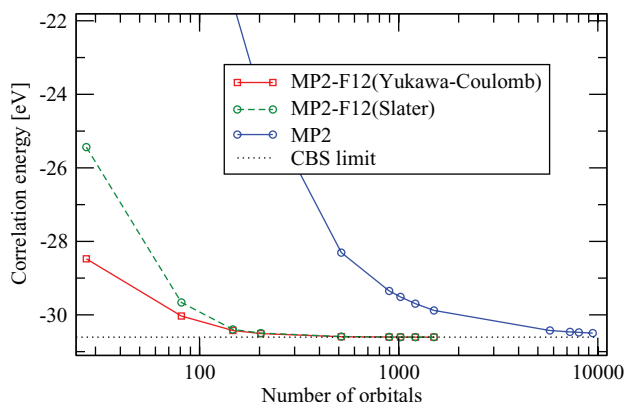
FIG. 6. Convergence of the MP2-F12 correlation energy for the Slater- and Yukawa-Coulomb correlation factors at $r_s = 5.0$ bohrs with respect to the employed number of orbitals compared to the MP2 energy and the CBS limit. It can be seen that MP2-F12 converges far quicker than MP2.

shown in Figure 6 suggest that MP2-F12 allows for a reduction of the size of the orbital basis by approximately an order of magnitude, although often more. Even though more investigation is required, and this factor will certainly not be fixed for different systems, this suggests savings in the orbital space could be on the whole larger than those generally achieved for molecular systems within a Gaussian orbital basis.

C. Variation of γ_{opt} with electron density

The physical extent of the correlation hole will change with the density of electrons, which in the electron gas model we are considering is inversely proportional to the r_s parameter. Therefore, we expect the optimal γ for the correlation factors to increase for higher densities. This is indeed observed, as can be seen in Figure 7, which shows an approximately linear relationship between the optimal γ and the electron density ($1/r_s$) for both correlation factors. This linear relationship allows for the determination of an approximately optimal γ in advance of any calculation, without the need for an explicit optimization of the parameter with respect to the MP2-F12 energy.
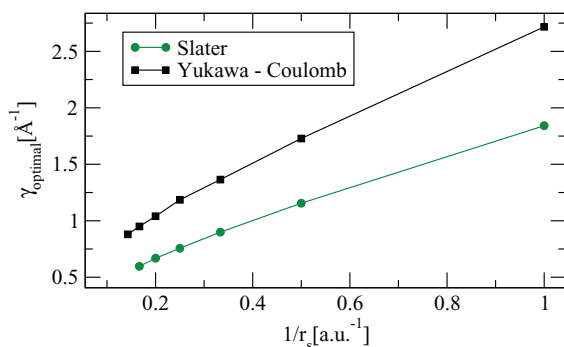
D. Pairwise γ optimization

We now seek to investigate the potential improvement in the basis set convergence rate of MP2-F12 by optimizing the correlation factor for each pair of electrons. The correlation factor in MP2-F12 theory is known to depend on the orbital eigenvalues[24] and indeed our derivation of f_{12}^{YC} for doubly occupied pairs also reveals a dependence of γ on ϵ_i, although this dependence is weak since it is partially canceled by k_i^2. Since MP2 theory is an independent electron pair approximation, one is free to use different correlation factors for each electron pair. Figure 8 shows the F12 correlation energy contributions as a function of γ for three different classes of electron pairs: (i) a core-core electron pair, (ii) a core-valence electron pair, and (iii) a valence-valence electron pair, as defined by the kinetic energy of the electrons and their plane wave momenta, rather than their density since all plane waves have a uniform density across the computational cell. Core and valence orbitals correspond to the plane wave orbitals with zero and the highest possible kinetic energy for the present 54 electrons in a cubic box system.

The energy contributions are variational with respect to γ and the respective minima are depicted by vertical lines. The optimal γ is found to be larger for core-core electron correlation than for valence-valence and core-valence electron correlation. As such it would seem beneficial to employ pairwise-optimized correlation factors. However, the contribution of the core-core correlation energy in the present system is small compared to the contribution of the valence-valence electron pair energy. Furthermore, the additional correlation energy gained by the optimized correlation factor for the core-core electron pair is almost negligible. To this end, we conclude that a pairwise optimization of the electron correlation factor is not a particularly worthwhile pursuit for the uniform electron gas. Furthermore, this observation indicates that the remaining errors in the finite-basis MP2-F12 calculations using optimized γ values arise from the violation of higher-order cusp conditions.

FIG. 7. Change in optimal γ parameter for the Slater- and Yukawa-Coulomb correlation factors as the density ($\propto r_s$) of the electron gas is varied, for the 54 electron simulation cell.
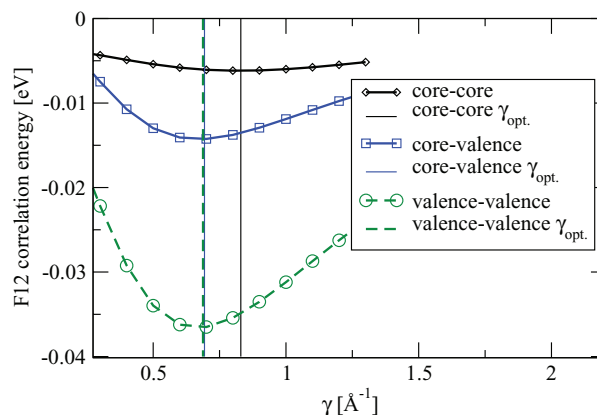

FIG. 8. Pairwise optimization of γ used for the Slater-type correlation factor shown for a core-core, core-valence, and valence-valence electron pair at $r_s = 5.0$ bohrs.

E. Relative errors in plane wave MP2-F12 theory

Although a rapid convergence of the absolute correlation energy with respect to the employed basis set is advantageous for the study of real solid state systems, it can be equally important that the *rate of convergence* does not change significantly in the investigated coordinate space. The latter allows for the calculation of properties such as lattice constants, bond lengths, or reaction energies in the complete basis set limit without having to converge the underlying absolute correlation energies, since absolute errors are relatively constant, and therefore a cancellation of these errors yield accurate energy differences. In the present system, the errors in the MP2(-F12) correlation energies for a range of electron densities with respect to a fixed basis set size, provides a good test case to investigate the issues described above.

Figure 9 shows the MP2(-F12) correlation energy as a function of r_s in the complete basis set limit and for a range of finite basis sets. We find that the correlation energy increases in the limit of higher densities and that finite as well as complete basis set limit results exhibit the same qualitative behavior for increasing r_s. However, a more instructive plot is shown in Figure 10, where the errors compared to the CBS result are given at each electron density. This shows that the non-parallelity errors (the difference between the maximum and minimum basis set errors over the electron densities considered) in finite basis conventional MP2 converge frustratingly slowly. Employing 203 orbitals yields MP2 non-parallelity errors of approximately 2 eV over this density range, which roughly corresponds to the range of realistic solid-state electron densities.

In contrast to conventional MP2, MP2-F12 exhibits non-parallelity errors that converge much faster with respect to the basis set size. Figures 11 and 12 show the MP2-F12 errors compared to the complete basis set limit for the same range of densities, for the Slater-type correlation factor and Yukawa-Coulomb correlation factor, respectively. In contrast to the conventional MP2 result, 203 plane-wave orbitals

FIG. 10. Basis set error of conventional MP2 correlation energies compared to the CBS limit, as a function of the Wigner-Seitz radius r_s.

FIG. 11. Basis set error of 54 electron MP2-F12 correlation energies compared to the CBS limit as a function of the Wigner-Seitz radius r_s, for the Slater-type geminal correlation factor. From about 203 orbitals, the non-parallelity errors are almost negligible.
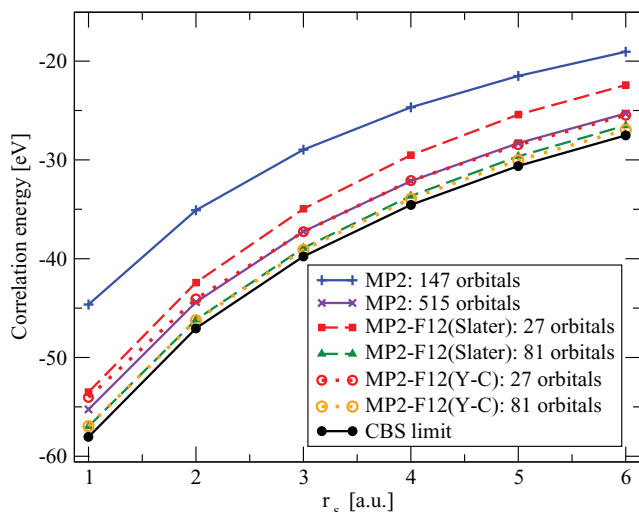

FIG. 9. MP2(-F12) correlation energies obtained using the optimal γ over a range of densities given by the Wigner-Seitz radius r_s for 54 correlated electrons, compared to the CBS result.
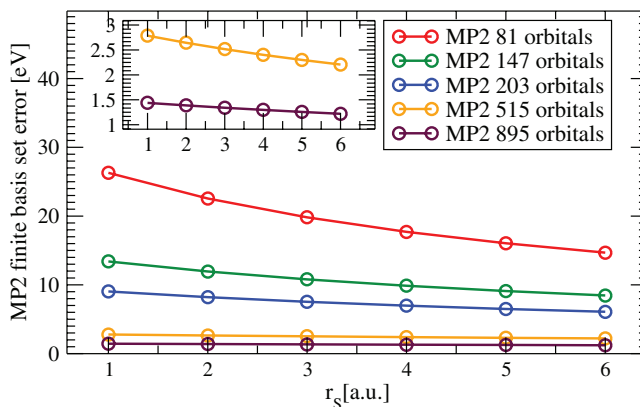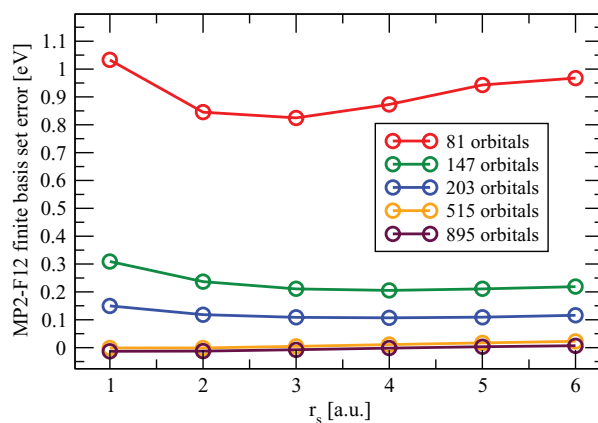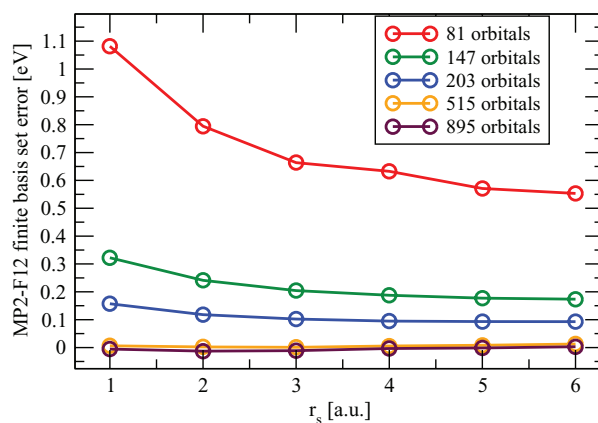

FIG. 12. Basis set error of 54 electron MP2-F12 correlation energies compared to the CBS limit as a function of the Wigner-Seitz radius r_s, for the Yukawa-Coulomb geminal correlation factor. From about 203 orbitals, the non-parallelity errors are almost negligible.

suffice to obtain non-parallelity errors over this density range below 100 meV in the correlation energy, a reduction in the relative errors by over an order of magnitude for the same basis size.

We note that the non-parallelity errors for all finite basis set results lead to a relative over-correlation at lower densities, where longer ranged, non-dynamic correlation is more important, and therefore the basis set convergence is seen to be faster. The only exception to this observation is seen in the non-parallelity of the MP2-F12 energy using the Slater-type correlation factor with 81 orbitals, as shown in Figure 11. In this case, the MP2-F12 basis set error exhibits a minimum at $r_s = 3$ a.u. We believe that this indicates that the Slater-type correlation factor is less efficient for lower densities where the long-range behavior of the correlation factor is energetically more significant.

IV. CONCLUSIONS AND OUTLOOK

In summary, we have shown that explicitly correlated MP2 theory can be used in conjunction with a plane-wave basis set for three-dimensional fully periodic systems. The combination of infinitely delocalized plane waves and a two-electron correlation factor centered at the electron coalescence points spans a very efficient and rapidly convergent basis set for the many-electron wavefunction expansion. This allows for the accurate evaluation of the electronic correlation energy close to the complete basis set limit. Our results for the uniform electron gas show that the reduction in the size of the employed one-electron basis set is similar to the corresponding findings in Gaussian orbital based molecular systems, although tentatively we suggest that the reduction could be even larger, perhaps due to the slower convergence of the original plane wave basis compared to an optimized Gaussian-type orbital expansion.

We have introduced a novel correlation factor that is termed Yukawa-Coulomb correlation factor, which in contrast to other employed correlation factors, is derived from analytic results for two electrons in a box. The Yukawa-Coulomb correlation factor differs from the Slater-type correlation factor in the long range and shows a faster rate of convergence with respect to the employed basis set. We believe that this novel correlation factor may be useful for the study of solid state systems and potentially large molecules with relatively isotropic interactions within explicitly correlated theories.

The change in the optimal variational parameter γ_{opt} was investigated for a range of densities. We found that γ_{opt} increases linearly for larger electron densities, which indicates that the correlation hole becomes more localized in this limit. A close to optimal γ can be determined solely from the density of the system and the expectation is that even in *ab initio* systems, a γ optimization will not always be necessary.

Furthermore, we have investigated the pairwise optimization of the correlation factor for core-core, core-valence, and valence-valence electron pairs. Our findings show that although γ_{opt} for the core-core electron pairs differs significantly from γ_{opt} for valence-valence electron pairs, the gain in the absolute correlation energy using pairwise optimized correlation factors is negligible. As such, we believe that it is not
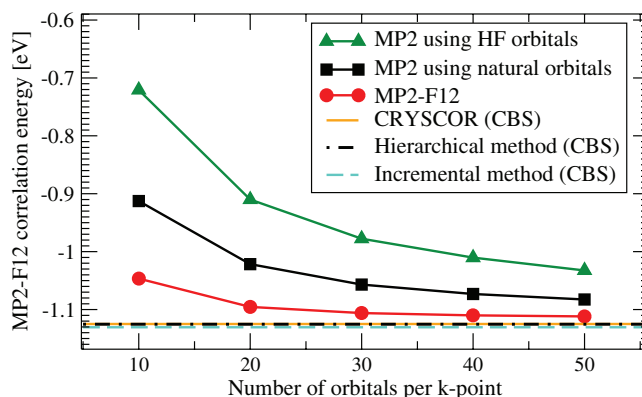

FIG. 13. Basis set convergence of the MP2 valence-only cohesive energy contribution to LiH. Our calculations were done using a $4 \times 4 \times 4$ k-mesh and norm-conserving pseudo-potentials in the framework of the PAW method.[76] The LiH unit cell volume was set to 17.03 Å^3. The MP2 calculations were done using HF and approximate natural orbitals.[12] Our MP2 and MP2-F12 (using a STG) results converge to the same complete basis set limit results obtained using local MP2 (CRYSCOR, from Ref. 13), the hierarchical method (from Ref. 8), and the incremental scheme (from Ref. 14).

beneficial to optimize the correlation factor for each electron pair individually.

Finally, we have studied the convergence of the non-parallelity error from the complete basis set limit using MP2-F12 and MP2 for a range of densities and basis sizes. This is expected to provide a good test case for the convergence of lattice constants and other energy differences in solid state systems with respect to the employed basis set. As expected, the convergence of MP2-F12 clearly outperforms MP2 and also allows for a reduction by approximately an order of magnitude in the employed basis set.

We hope that the findings of the present work will translate both to alternative UEG models,[86,87] *ab initio* systems, and to other explicitly correlated methods in the solid state such as CCSD-F12[32,33,88–90] or FCIQMC-F12,[2,61,91–94] where the additional computational cost for calculating the F12 contribution becomes negligible in comparison to these more expensive parent methods. The application of the methods outlined in this work to real, *ab initio* solid state systems is expected to significantly expand the scope of the whole range of quantum chemical wave function based methods. Figure 13 shows a preliminary application of the MP2-F12 implementation for the LiH crystal confirming our findings for the uniform electron gas that explicitly correlated MP2 theory allows for a substantial reduction in the basis set. We will expand on these results in a forthcoming paper.

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