

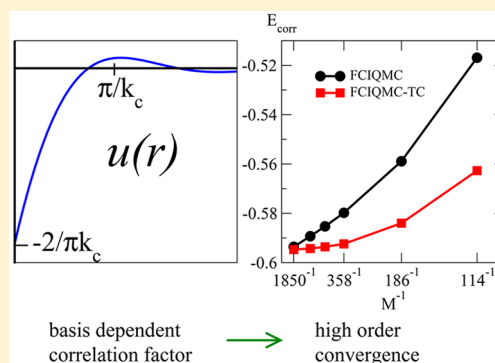
Combining the Transcorrelated Method with Full Configuration Interaction Quantum Monte Carlo: Application to the Homogeneous Electron Gas

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ABSTRACT: We suggest an efficient method to resolve electronic cusps in electronic structure calculations through the use of an effective transcorrelated Hamiltonian. This effective Hamiltonian takes a simple form for plane wave bases, containing up to two-body operators only, and its use incurs almost no additional computational overhead compared to that of the original Hamiltonian. We apply this method in combination with the full configuration interaction quantum Monte Carlo (FCIQMC) method to the homogeneous electron gas. As a projection technique, the non-Hermitian nature of the transcorrelated Hamiltonian does not cause complications or numerical difficulties for FCIQMC. The rate of convergence of the total energy to the complete basis set limit is improved from $O(M^{-1})$ to $O(M^{-5/3})$, where M is the total number of orbital basis functions.



1. INTRODUCTION

Electron correlation can be roughly classified into static and dynamic correlation. In conventional configuration descriptions of the many-body wave function, the two different types of electron correlation are treated in the same way, i.e., by linear expansion in terms of Slater determinants.¹ Although such a configuration description offers a natural and efficient way to deal with static correlation, it does not however treat dynamic correlation efficiently and thus usually leads to a slow convergence to the complete basis limit (CBL). The main problem is that, because of the Coulomb singularity of the electronic interaction, the short-range dynamic correlation introduces nonsmoothness into the many-body wave function, which cannot be approximated efficiently by orbital product expansions. This problem is even more severe for those methods aiming at high accuracy, such as full configuration interaction (FCI) methods and high-order coupled-cluster methods. On the other hand, the nonsmoothness of the many-body wave function can be locally resolved and is expressed as the well-known Kato cusp condition²

$$\left. \frac{\partial \Psi}{\partial r_{ij}} \right|_{r_{ij}=0} = \frac{1}{2} \Psi |_{r_{ij}=0} \quad (1)$$

Incorporating this property into the construction of many-body wave functions should in principle speed up convergence to the CBL.

One way of incorporating the cusp condition is to introduce explicitly correlated basis functions for the expansion of the many body-wave function. In the last few decades, various explicit correlation methods (e.g., R12 and F12 methods^{3–9}) have been

suggested and have achieved a high level of success. The main feature of these methods is that, instead of the conventional approximation of the cusp in terms of orbital product expansions, electron pair geminal functions are directly used in the construction of the basis of the many-body wave function. These geminal functions describe the cusps very efficiently, although they also make the involved calculations highly nonlinear. For example, in these calculations one has to deal with various kinds of orthogonality constraints, which lead to multielectron integrals (three, four, and even higher body electron integrals). These integrals are usually approximated by resolution of identity (RI) techniques.^{3–5,10}

Electron cusps can also be efficiently described by using the Jastrow ansatz¹¹

$$\Psi(\mathbf{R}) = e^{\tau(\mathbf{R})} \Phi(\mathbf{R}), \quad \mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (2)$$

where Φ is an antisymmetric reference function and τ is a symmetric pair correlation factor

$$\tau(\mathbf{R}) = \frac{1}{2} \sum_{i \neq j} u(\mathbf{r}_i, \mathbf{r}_j) \quad (3)$$

The correlation factor can be constructed to fulfill the cusp condition (1), and thus, the regularity of the reference function Φ is higher than that of the wave function Ψ . Fournais et al.¹² have proven that the correlation factor can improve the regularity of the wave function from $C^{0,1}$ to $C^{1,1}$. In Appendix A, we will show that this will lead to an acceleration of basis convergence for three-dimensional non-spin-polarized systems from M^{-1} to

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$M^{-5/3}$.¹³ For size consistency to be guaranteed, the correlation factor has to take an exponential form. This makes the Jastrow ansatz highly nonlinear, and any variational treatment leads to extremely high-dimensional integrals. Presently, the Jastrow ansatz is primarily used in various quantum Monte Carlo methods, such as variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods,^{16–18} where the involved integrals can be evaluated directly in the high dimensional space. The exponential correlation factor has also been treated by various expansions, such as the linked cluster expansion,^{19,20} random phase approximations (RPA),²¹ and Fermi hypernetted chain (FHNC) method.^{22,23} These sophisticated methods are highly nonlinear and difficult to implement in practical calculations.

For an efficient treatment of the exponential correlation factor, a relatively simple method, the transcorrelated (TC) method,^{24–31} was suggested by Boys and Handy roughly half a century ago. By using a similarity transformation, $e^{-\tau}\hat{H}e^{\tau}$, the exponential correlation factor is removed from the involved equations. The original TC method of Boys and Handy was designed for the single-determinant Jastrow ansatz and contains two equations for the calculation of the correlation factor τ and the orbitals, respectively. Initial calculations demonstrated that this method can efficiently recover much of the correlation energy. On the other hand, the resulting non-Hermitian effective Hamiltonian cannot prevent the energy from falling below the exact one. The lack of a variational bound is considered a severe problem and has hampered broad application of the TC method for quite a long time.

Recently, there has been renewed interest in the development of the TC method. Ten-no used the TC Hamiltonian in the perturbation and coupled electron-pair approximations.³² In this approach, the correlation factor τ is a fixed local geminal satisfying the cusp condition, and the reference function is treated by conventional configuration expansions. The reference function Φ is much smoother than the many-body wave function Ψ , and as a consequence, the configuration expansion of Φ converges much faster. The price to pay is the introduction of a three-body operator in the effective Hamiltonian as well as various numerical problems due to non-Hermiticity. The non-Hermiticity problem is more severe for self-consistent optimization methods. Hino et al. suggested using the biorthogonal basis to deal with the TC Hamiltonian.³³ Umezawa et al. optimized the orbitals by minimizing the energy variance.^{34,35} Luo has suggested a general variational method for simultaneous optimizations of the correlation factor and reference function.^{36,37} Yanai et al. used a truncated canonically transformed Hamiltonian to eliminate the non-Hermiticity of the effective Hamiltonian.^{38,39} Grüneis et al. recently offered a detailed discussion on the choice of correlation factors.⁴⁰

In this work, we incorporate the TC method into the full configuration-interaction quantum Monte Carlo (FCIQMC) method,^{41–43} aiming at highly accurate calculations on periodic systems. FCI in principle provides the most accurate description of the wave function, within an orbital representation, and the results are usually used to benchmark other calculation results. However, FCI methods are also extremely expensive with the computational cost scaling exponentially with respect to the system size. On the other hand, the extremely large FCI expansion is also very sparse so that the vast majority of expansion coefficients are essentially zero. This sparsity, however, usually has no regular pattern, especially for strongly correlated systems. The recently developed FCIQMC method

and its “initiator” adaptation (*i*-FCIQMC)^{42,44} offers a way to detect and make use of this sparsity. This method is based on Monte Carlo simulations of the dynamic evolution of the many-body wave function with imaginary time

$$\Psi(t) = e^{-(\hat{H}-E_0)t}\Psi(t=0) \quad (4)$$

which leads to the ground state wave function in the long-time limit $\Psi_0 = \Psi(t \rightarrow \infty)$. The FCI expansion coefficients are simulated by a set of walkers that evolve over imaginary time. In the long-time limit, a steady distribution of the walkers is reached, and the corresponding projection energy, in the large-walker limit, converges to the FCI energy. With this method, FCI quality calculations have been achieved on larger molecular systems⁴⁵ and even periodic systems.⁴³ F12 methods have also been combined with the FCIQMC technique^{45,46} as universal a posteriori corrections^{47,48} involving contractions of the one- and two-body matrices with F12 integrals.

For periodic systems, plane waves are usually the most appropriate basis functions. However, their smooth and nonlocal properties make the slow convergence in the description of electronic cusps an even more severe problem. This problem is tremendously enhanced in FCIQMC with large basis sets aiming to reach the CBL. In this work, we design an explicit correlation method to resolve this problem in such calculations. In FCIQMC, the matrix elements of the interaction operators (e.g., the two-body Coulomb operators, etc.) are used intensively and thus have to be either stored efficiently or calculated repeatedly on the fly. One advantage of the plane wave basis is that the two-body Coulomb matrix can be simply evaluated and need not be stored, alleviating the memory bottlenecks associated with storing the 4-index integrals of large systems. We would like to keep this advantage, so that the application of the intended explicit correlation method will not be limited to small systems. This requires that the involved effective potential and its matrix elements should be as simple as possible. In the next section, we will describe the new TC method designed for plane wave basis. In section 3, we will present our initial test calculations on three-dimensional homogeneous electron gas models, and this will be followed by some conclusions and discussion in section 4.

2. METHOD

Following the idea of Ten-no,³² for a given N electron system with a given basis set, we take a fixed correlation factor τ in the Jastrow ansatz (2) and try to determine the reference function Φ by approximately solving an eigenvalue equation

$$\hat{H}_{\text{TC}}\Phi = E\Phi \quad (5)$$

where the effective Hamiltonian, the transcorrelated Hamiltonian, has a finite Baker–Campbell–Hausdorff expansion, up to a double commutator, owing to the fact that the correlation factor $\tau(\mathbf{R})$ is purely a function of the spatial coordinates of the electrons

$$\begin{aligned} \hat{H}_{\text{TC}} &\equiv e^{-\tau}\hat{H}e^{\tau} \\ &= \hat{H} + [\hat{H}, \tau] + \frac{1}{2}[[\hat{H}, \tau], \tau] \\ &= \hat{H} - \sum_i \left(\frac{1}{2}\nabla_i^2\tau + (\nabla_i\tau)\cdot\nabla_i + \frac{1}{2}(\nabla_i\tau)^2 \right) \end{aligned} \quad (6)$$

Here, the TC Hamiltonian is non-Hermitian owing to the presence of the single commutator term $[\hat{H}_T, \tau]$. For any eigenvalue of such operators, the corresponding left and right eigenvectors are usually different. In solving this type of eigenvalue equation, approximations based on a variational treatment are usually troubled by the non-Hermitian nature of the matrix. Projection methods, however, such as the Power method, provide a route forward for such matrices.⁴⁹ Unlike standard FCI methods, the FCIQMC method is not a variational method but rather a stochastic version of the Power method. For the Jastrow ansatz, the time evolution of the wave function can be represented as

$$\Psi(t) = e^\tau \Phi(t) \quad (7)$$

$$\Phi(t) = e^{-t(\hat{H}_{TC} - E_0)} \Phi(t=0) \quad (8)$$

where eq 8 can be simply derived from eq 4.

$$\begin{aligned} \Phi(t) &= e^{-\tau} e^{-t(\hat{H} - E_0)} e^\tau \Phi(t=0) \\ &= \lim_{M \rightarrow \infty} e^{-\tau} \left(1 - \frac{t(\hat{H} - E_0)}{M} \right)^M e^\tau \Phi(t=0) \\ &= \lim_{M \rightarrow \infty} \left(e^{-\tau} \left(1 - \frac{t(\hat{H} - E_0)}{M} \right) e^\tau \right)^M \Phi(t=0) \\ &= \lim_{M \rightarrow \infty} \left(1 - \frac{t(\hat{H}_{TC} - E_0)}{M} \right)^M \Phi(t=0) \\ &= e^{-t(\hat{H}_{TC} - E_0)} \Phi(t=0) \end{aligned} \quad (9)$$

It is worth noting that eq 8 is not constructed based on the eigenvalue eq 5, where one may get frustrated due to the non-Hermiticity and lack of variational bounds on \hat{H}_{TC} . The equivalence of eq 4 and eq 8 reveals that methods based on these equations (such as FCIQMC) can handle properly the non-Hermiticity due to such a kind of similarity transformations. Following eq 8, the FCIQMC method can be directly used for the TC Hamiltonian \hat{H}_{TC} . The only difference is that here we are dealing with non-Hermitian operators such that the involved matrix elements are nonsymmetric. In calculations of these matrix elements, the operators should not be mixed up with their Hermitian conjugates (i.e., these operators should only be applied to the right-hand side).

For periodic systems, the orbital basis functions to be used are plane waves

$$\phi_{\mathbf{p},\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_0}} e^{i\mathbf{p}\cdot\mathbf{r}} \quad (10)$$

where ω_0 is the formal volume of the infinite system. All operators in the effective Hamiltonian can then be represented in terms of second quantization.⁵⁰ The fixed correlation factor, assumed to be spin-independent, can be expressed as

$$\begin{aligned} \tau &= \frac{1}{2} \sum_{ij} u_0(\mathbf{r}_i - \mathbf{r}_j) \\ &= \frac{1}{2} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \langle \mathbf{p} - \mathbf{k}, \mathbf{q} + \mathbf{k} | u_0 | \mathbf{p}, \mathbf{q} \rangle a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \\ &= \frac{1}{2\Omega_0} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \tilde{u}_0(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \end{aligned} \quad (11)$$

where $\tilde{u}_0(\mathbf{k}) = \int e^{i\mathbf{k}\cdot\mathbf{r}} u_0(\mathbf{r}) d^3r$ is the Fourier transformation of u_0 . Here, the two-body correlation factor is assumed to be a function of $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ due to translational symmetry. Similarly, for the other required two-body operators, we have the following expressions

$$\hat{W} = \frac{1}{2\Omega_0} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \tilde{w}_0(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \quad (12)$$

$$\frac{1}{2} \sum_i \nabla_i^2 \tau = -\frac{1}{2\Omega_0} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} k^2 \tilde{u}_0(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \quad (13)$$

$$\sum_i (\nabla_i \tau) \nabla_i = \frac{1}{2\Omega_0} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} (\mathbf{p} - \mathbf{q}) \cdot \mathbf{k} \tilde{u}_0(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \quad (14)$$

where \hat{W} is the electronic (Coulomb) potential. The double commutator in eq 6 is more complicated and gives rise to a three-body operator and a two-body operator

$$\begin{aligned} \frac{1}{2} \sum_i (\nabla_i \tau)^2 &= \frac{1}{2} \sum_{ijk} \nabla_i u_0(\mathbf{r}_i - \mathbf{r}_j) \cdot \nabla_j u_0(\mathbf{r}_i - \mathbf{r}_k) \\ &\quad + \frac{1}{2} \sum_{ij} (\nabla_i u_0(\mathbf{r}_i - \mathbf{r}_j))^2 \\ &= \frac{1}{2\Omega_0^2} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{q}\mathbf{s}} \tilde{u}_0(\mathbf{k}) \tilde{u}_0(\mathbf{k}') \mathbf{k} \cdot \mathbf{k}' a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k}',\sigma'}^\dagger \\ &\quad a_{\mathbf{s}+\mathbf{k}-\mathbf{k}',\sigma}^\dagger a_{\mathbf{s},\sigma} a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma} \\ &\quad + \frac{1}{2\Omega_0} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \mathcal{F}((\nabla u_0)^2)(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma'} \end{aligned} \quad (15)$$

where \mathcal{F} denotes Fourier transformation. A complete treatment of the three-body operator would be expensive, and we would like to treat it only approximately.

Periodic systems are usually treated by the supercell approach¹⁸ where the infinite system is approximated by periodically arranged replicas of a finite cell $\Omega = L^3$. Because of this artificial periodic boundary condition, the \mathbf{p} vector of the plane wave basis (10) is discretized (i.e., $\mathbf{p} = \frac{2\pi}{L} \mathbf{n}$, $\mathbf{n} \in \mathcal{Z}^3$), and to make the basis finite, we take a cutoff $|\mathbf{p}| \leq k_c$.

In the supercell approach, u_0 and w_0 have to fulfill the periodic boundary conditions. The periodic w_0 is usually constructed via periodic summation.¹⁸ Following the same idea, we construct the periodic correlation factor u_0 by applying the periodic summation on a local function u

$$u_0(\mathbf{r}) = \sum_{\mathbf{n} \in \mathcal{Z}^3} u(\mathbf{r} + \mathbf{n}L) \quad (16)$$

However, such summations are not practically needed if we work in \mathbf{k} -space because

$$\frac{\tilde{u}_0(\mathbf{k})}{\Omega_0} = \frac{\tilde{u}(\mathbf{k})}{\Omega}, \quad \text{for } \mathbf{k} = \frac{2\pi}{L}\mathbf{m}, \quad \mathbf{m} \in \mathcal{Z}^3 \quad (17)$$

The only thing that needs to be taken care of is that the inverse Fourier transformation of u_0 does not exist, and instead, there is a Fourier series

$$u_0(\mathbf{r}_2 - \mathbf{r}_1) = \frac{1}{\Omega} \sum_{\mathbf{k}=2\pi\mathbf{m}/L} \tilde{u}(\mathbf{k}) e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)} \quad (18)$$

The two-body operator $(\nabla u_0)^2$ is very important for the short-range correlation and is closely related to the infinite summation of all ladder diagrams in the linked cluster expansion.²⁰ By taking the periodic summation, $(\nabla u_0)^2$ can be expressed as

$$(\nabla u_0)^2 = -\frac{1}{\Omega^2} \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{k}\cdot\mathbf{k}' \tilde{u}(\mathbf{k}) \tilde{u}(\mathbf{k}') e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)} e^{i\mathbf{k}'\cdot(\mathbf{r}_2-\mathbf{r}_1)} \quad (19)$$

whose Fourier transformation is now

$$\mathcal{F}((\nabla u_0)^2)(\mathbf{k}) = -\frac{\Omega_0}{\Omega} \left(\frac{1}{\Omega} \sum_{\mathbf{k}'} (\mathbf{k} - \mathbf{k}') \cdot \mathbf{k}' \tilde{u}(\mathbf{k} - \mathbf{k}') \tilde{u}(\mathbf{k}') \right) \quad (20)$$

As explained before, the correlation factor τ is designed here mainly to capture the short-range cusp. In the short-range limit, we have the asymptotic solution⁵⁰

$$\tilde{u}(\mathbf{k}) = -\frac{4\pi}{k^4}, \quad \text{when } k \sim \infty \quad (21)$$

which is the cusp condition expressed in the k -space. This expression is derived for unlike spin pairs, whereas for electron pairs with the same spin $\tilde{u}(\mathbf{k}) \sim -\frac{2\pi}{k^4}$. In principle, we can use any kind of local function u in the TC calculation as long as it satisfies the cusp condition. However, because we intend to introduce approximations in the treatment of the three-body term, we want u to be small and to vanish in the CBL. Therefore, we design the following correlation factor

$$\tilde{u}(\mathbf{k}) = \begin{cases} -\frac{4\pi}{k^4}, & |\mathbf{k}| > k_c \\ 0, & |\mathbf{k}| \leq k_c \end{cases} \quad (22)$$

where k_c is the cutoff parameter of the basis set. The idea behind this construction is simple: because the wave function can already be described by a configuration description up to the given level of resolution (characterized by k_c), it is only needed to be improved in the finer region of resolution by means of the correlation factor. In real space, the above correlation factor becomes

$$u(r) = -\frac{r}{\pi} \left(\text{si}(k_c r) + \frac{\cos(k_c r)}{k_c r} + \frac{\sin(k_c r)}{(k_c r)^2} \right) \quad (23)$$

where $\text{si}(x) = -\int_x^\infty \frac{\sin x}{x} dx$ is the sine integral. A sketch of $u(r)$ is presented in Figure 1, which looks like a small “hole” with depth $= -2/\pi k_c$ and width $\sim \pi/k_c$. Taylor expansion of u in the small r region can be calculated for the leading terms

$$u(r) = -\frac{2}{\pi k_c} + \frac{r}{2} + \dots \quad (24)$$

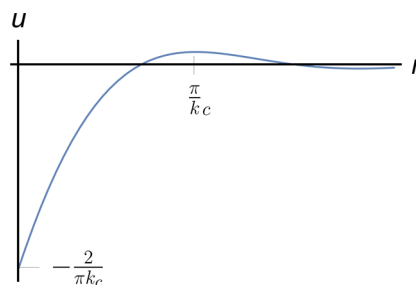


Figure 1. A sketch of the correlation factor $u(r)$.

where the second term satisfies the cusp condition for unlike spin pairs. In the large r region, the magnitude of $u(r)$ decays like $1/r^2$.

In principle, we can also use a spin-dependent correlation factor, namely to reduce the correlation factor for parallel spin pairs by one-half. However, the existence of exchange “holes” between parallel-spin electrons keeps them largely apart anyway, and as a consequence, the system energy is not very sensitive to the cusp between such pairs. Therefore, the use of spin-dependent correlation factors does not significantly improve the convergence rate of energy. Rather, spin-dependent Jastrow factors induce undesirable spin contamination⁵¹ into the wave function so that the wave function cannot be an eigenstate of S^2 .

With the above short-ranged correlation factor, we can largely ignore the complicated three-body operator in eq 15 and take only a simple RPA type contribution from it. This contribution is represented by a two-body operator

$$\frac{N-2}{2\Omega^2} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} k^2 \tilde{u}^2(\mathbf{k}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma} \quad (25)$$

which is generated by a contraction of the $a_{\mathbf{s}+\mathbf{k}-\mathbf{k}',\sigma'}^\dagger a_{\mathbf{s},\sigma'}$ pairs in eq 15 (i.e., by a summation of those terms where $\mathbf{k} = \mathbf{k}'$). This term makes the dominant contribution of the three-body operator to the long-range correlation and is closely related to the summation of all ring diagrams in the linked cluster expansion.^{52–54} In the current method, the correlation factor is short ranged, and therefore, the contribution of these terms will be very small. In the applications studied in this paper, namely the homogeneous electron gas in the r_s range from 0.5 to 5, this contribution was less than 1% of the total correlation energy. We nevertheless keep it in the method for two reasons: first, it partly recovers the three-body contributions, and second, it can be used to estimate the magnitude of error due to the missing three-body terms. Last but not least, the use of this term incurs almost no extra computational cost.

Putting all terms together, we have the following two-body effective potential

$$\hat{W}_{\text{eff}} = \frac{1}{2\Omega} \sum_{\sigma\sigma'} \sum_{\mathbf{k}\mathbf{p}\mathbf{q}} \tilde{w}_{\text{eff}}(\mathbf{k}, \mathbf{p}, \mathbf{q}) a_{\mathbf{p}-\mathbf{k},\sigma}^\dagger a_{\mathbf{q}+\mathbf{k},\sigma'}^\dagger a_{\mathbf{q},\sigma} a_{\mathbf{p},\sigma} \quad (26)$$

$$\begin{aligned} \tilde{w}_{\text{eff}}(\mathbf{k}, \mathbf{p}, \mathbf{q}) = & \tilde{w}(\mathbf{k}) + k^2 \tilde{u}(k) - (\mathbf{p} - \mathbf{q}) \cdot \mathbf{k} \tilde{u}(k) \\ & - \frac{N_e - 2}{\Omega} k^2 \tilde{u}^2(\mathbf{k}) + \frac{1}{\Omega} \sum_{\mathbf{k}'} (\mathbf{k} - \mathbf{k}') \cdot \mathbf{k}' \tilde{u}(\mathbf{k} - \mathbf{k}') \tilde{u}(\mathbf{k}') \end{aligned} \quad (27)$$

where $\tilde{w}(\mathbf{k})$ is the original Coulomb potential

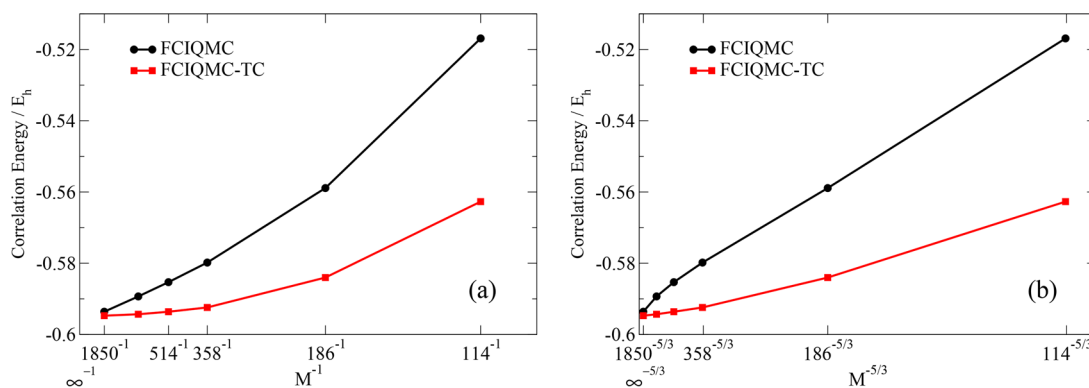


Figure 2. (a) Total correlation energy as a function of M^{-1} calculated by FCIQMC and FCIQMC-TC methods for the 14 electron system with $r_s = 0.5$. (b) The same results but presented as a function of $M^{-5/3}$.

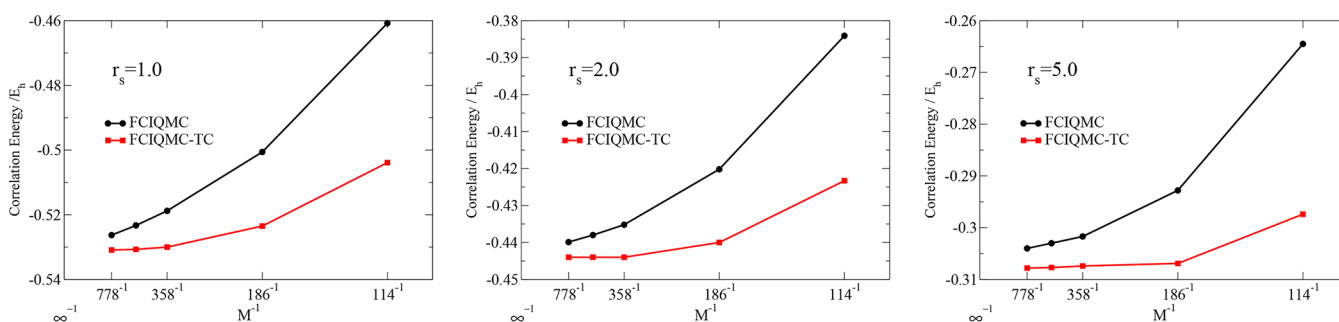


Figure 3. Total correlation energy as a function of M^{-1} calculated by FCIQMC and FCIQMC-TC methods for the 14 electron system with $r_s = 1.0, 2.0$, and 5.0 , respectively.

$$\tilde{w}(\mathbf{k}) = \begin{cases} \frac{4\pi}{k^2}, & \mathbf{k} \neq \mathbf{0} \\ 0, & \mathbf{k} = \mathbf{0} \end{cases} \quad (28)$$

In eq 27, the last term coming from $\mathcal{F}((\nabla u)^2)(\mathbf{k})$ is only a function of \mathbf{k} and can be easily prepared and stored before the FCIQMC simulation. Unlike other terms, this term is nonzero at $\mathbf{k} = \mathbf{0}$. Practical implementation of this TC method in FCIQMC calculations is straightforward. We need only to replace the pure electronic Coulomb potential \tilde{w} with the TC effective potential \tilde{w}_{eff} and this requires only a very small modification of the existing code. Because calculation of the Coulomb potential makes up only a very small portion of the total computational cost of the FCIQMC method, use of the effective potential will not make the computations more expensive.

3. RESULTS

Homogeneous electron gases (HEG) are important models for the investigation of electron correlation in solids. They also play a fundamental role in the development of density functional theory (DFT).⁵⁵ These models have been intensively studied by variational and diffusion quantum Monte Carlo simulations.^{56–60}

The DMC method is very efficient and can be applied to fairly large systems. On the other hand, this method does not solve the problem completely, owing to the fixed-node approximation, even though this can be reduced by means of back-flow and multideterminant techniques. The FCIQMC method contains in principle no bias and offers a way to investigate the fixed node error. Recently, the FCIQMC method has been used to investigate the three-dimensional HEG model.^{61–63} Because of the cusp singularity of the wave functions, the calculation suffers

from slow convergence with respect to the basis size with the error of the calculated energy being proportional to M^{-1} , M being the total number of basis functions. Extrapolations based on this M^{-1} behavior are used to estimate the results in the CBL. For an accurate result, calculations need to be performed on fairly large basis sets to reach the M^{-1} regime, and the computational cost increases sharply with basis size.

To study the efficiency of the new TC method, we have performed calculations on the same 3D HEG systems as investigated in the previous studies.^{61,62} Two different supercell sizes are used, containing 14 and 54 electrons, respectively. For the 14 electron cell, calculations are carried out on four different densities with Wigner–Seitz radius $r_s = 0.5, 1.0, 2.0$, and 5.0 , respectively. For the 54 electron cell, we can only obtain converged results for $r_s = 0.5$ and 1.0 because the required total number of walkers increases rapidly with r_s . We use the initiator-FCIQMC (*i*-FCIQMC) method with the initiator parameter set to 3.0. In addition, we used the semistochastic method⁶⁴ using the $|D| = 10000$ leading determinants in the deterministic space⁶⁵ as implemented in the NECI code.⁶⁶

In Figure 2(a), the total correlation energy as a function of M^{-1} is presented for the 14 electron system with $r_s = 0.5$, where the two different results are calculated by FCIQMC method with the effective TC Hamiltonian (FCIQMC-TC) and the original FCIQMC method, respectively. Here, M , the number of spin orbital basis functions, is chosen to be 114, 186, 358, 514, 778, and 1850, respectively. The FCIQMC result shows an asymptotic linear convergence with respect to M^{-1} , whereas the result of FCIQMC-TC has a higher order of convergence. According to the theoretical analysis in Appendix A, the best asymptotic convergence we can expect is $M^{-5/3}$. We also present the same results in Figure 2(b) as functions of $M^{-5/3}$. The result

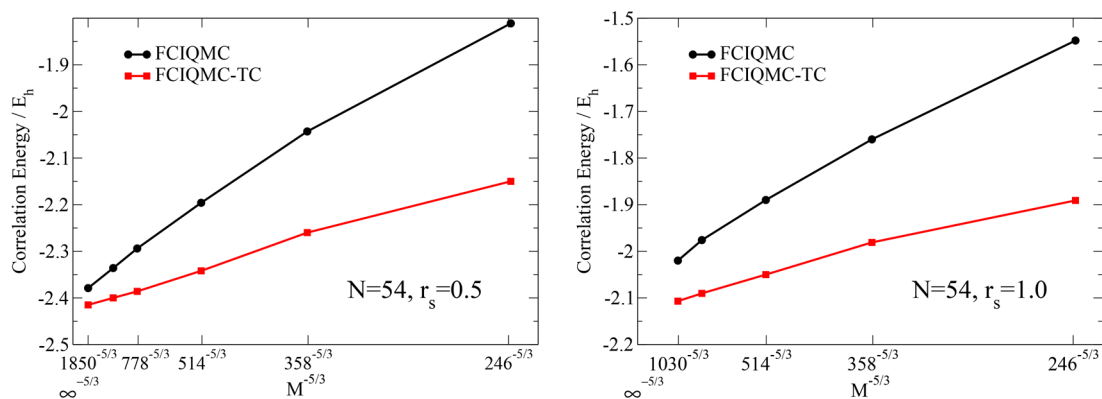


Figure 4. Total correlation energy as a function of $M^{-5/3}$ calculated by FCIQMC and FCIQMC-TC methods for the 54 electron systems with $r_s = 0.5$ and 1.0.

of FCIQMC-TC shows a roughly linear behavior in the large M region, and in the small M region, the convergence is faster. The asymptotic $M^{-5/3}$ convergence behavior offers a possibility of extrapolations to the CBL in case of need. For the result in Figure 2, such an extrapolation is not necessary because $1850^{-5/3}$ is already very close to the origin ($\infty^{-5/3}$) and the FCIQMC-TC result has already converged at 0.1 millihartree (mE_h) level.

Similar behaviors are observed for other densities of the 14 electron system. In Figure 3, the convergence with respect to M^{-1} of the two different calculations are presented for $r_s = 1.0, 2.0,$ and $5.0,$ respectively, in three plots. It turns out that, for larger r_s , the result converges faster. For $r_s = 1.0$, the FCIQMC-TC energy has converged within a millihartree error at $M = 514$, whereas for $r_s = 2.0$ and 5.0 , such a convergence can already be reached at $M = 358$ and 186 , respectively. However, this does not mean that simulations for larger r_s 's are easier because the required number of walkers (N_w) increases sharply with r_s to reduce the initiator error. For $r_s = 0.5-2.0$, calculations are performed mostly with $N_w = 10^7 \sim 10^8$, whereas for $r_s = 5.0$, we need $N_w = 10^9$ already at $M = 114-358$ and even $N_w = 10^{10}$ at $M = 514$ and 778 . For such systems, to demonstrate the $M^{-5/3}$ asymptotic convergence, we have to deal with larger basis sets, which will require even larger N_w 's, but on the other hand, such difficult calculations are not needed for our accuracy requirement.

Computations on the 54 electron systems are much more expensive, and with present computational resources, we can only obtain converged results for $r_s = 0.5$ and 1.0 . For $r_s = 0.5$, calculations are performed with six different basis sets with $M = 246 \rightarrow 1850$, where $N_w = 10^8$ is found to be sufficient for all of them. For $r_s = 1.0$, we can obtain converged results for M up to 1030 . For $M = 246, 358,$ and 514 , the number of walkers N_w is taken to be 10^{10} , whereas for $M = 778$ and 1030 , we need $N_w = 2 \times 10^{10}$. In Figure 4, the results for 54 electron systems are presented as functions of $M^{-5/3}$ for $r_s = 0.5$ and 1.0 . The asymptotic behaviors are clearer than those of the 14 electron systems for the FCIQMC-TC results, and extrapolations are used to evaluate the results in the CBL.

In Table 1, the complete basis limit results are presented for all calculated systems. The results for the 14 electron systems are simply taken from those of the largest basis sets used. Within the given error bars, these results are already converged to the CBL. The results for $N = 54$ are obtained by extrapolation based on the $M^{-5/3}$ convergence rate. Compared with the previous FCIQMC results, the new results agree well for the 14 electron systems with the differences in total energies $\leq 1 mE_h$. The new results are also in good agreement with the recent high-order coupled-cluster

Table 1. Total Correlation Energies in the Complete Basis Limit for a Variety of N and r_s Calculated with the FCIQMC-TC Method^a

r_s (a.u.)	N	E_{corr} (a.u.)			
		FCIQMC-TC	FCIQMC ⁶²	FCIQMC ⁶³	BF-DMC
0.5	14	-0.5948(2)	-0.5959(7)	-0.59467(9)	
	54	-2.425(1)	-2.435(7)		-2.387(2)
1.0	14	-0.5309(2)	-0.5316(4)	-0.5313(2)	
	54	-2.134(2)	-2.124(3)		-2.125(2)
2.0	14	-0.4440(3)	-0.444(1)		
	5.0	14	-0.3078(3)	-0.307(1)	

^aExtrapolation based on $M^{-5/3}$ behavior is used for the 54 electron systems. The results are compared with the previous FCIQMC results^{62,63} and back-flow DMC results.⁵⁹

study of the $N = 14$ electron system by Neufeld and Thom.⁶³ The small differences between the FCIQMC results of Shepherd et al.⁶² and Neufeld and Thom⁶³ for the 14 electron systems arise because of the use of different extrapolation formulas to the infinite-basis set limit, the former being based on M^{-1} , whereas the latter includes higher order terms ($b_0 + b_1 M^{-1} + b_2 M^{-2}$). This allows the use of a larger number of points in the extrapolation procedure (with smaller M) and leads to somewhat higher extrapolated correlation energies, the implication being that a simple M^{-1} extrapolation tends to overshoot the exact result unless a sufficiently large M has been reached. Although the differences are not large, this indicates that the precise form of extrapolation is indeed consequential and provides further motivation to try to minimize basis-set errors through analytic means as far as possible.

For $N = 54$, the new transcorrelated result at $r_s = 0.5$ is $10 mE_h$ above the previous FCIQMC result of Shepherd et al.⁶¹ based on M^{-1} extrapolation. At this density, the FCIQMC-TC result is $\sim 40 mE_h$ below the back-flow DMC result,⁵⁹ and this indicates that the fixed-node error of the BF-DMC result is still quite large for $r_s = 0.5$. For $r_s = 1.0$, the previous FCIQMC result for $N = 54$ is roughly the same as the BF-DMC result, whereas the new result is $\sim 10 mE_h$ below the BF-DMC result. This reveals the fixed nodes error decays very rapidly with r_s , and we expect that at even larger r_s the fixed-node error of BF-DMC will be even smaller and hence can be ignored.

The effective TC potential in eq 27, now denoted as $\tilde{w}_{\text{eff}}(\mathbf{k}, \mathbf{p}, \mathbf{q}) = \tilde{w}(\mathbf{k}) + \tilde{w}_{\text{TC}}[\tilde{u}](\mathbf{k}, \mathbf{p}, \mathbf{q})$, is constructed with $\tilde{u}(\mathbf{k})$ defined in eq 22. Because $\tilde{u}(\mathbf{k})$ contains only high frequency terms, it might

be expected that the effective potential \tilde{w}_{TC} has a weak coupling to the low frequency basis space, and thus, this potential behaves roughly like a constant potential in the dynamic evolution. If this would be the case, it should be expected that the energy difference produced by \tilde{w}_{TC}

$$\Delta E(t) = E_{\text{FCIQMC}}(t) - E_{\text{FCIQMC-TC}}(t) \quad (29)$$

should be approximately independent of imaginary time. In Figure 5, such energy differences for the 14 electron systems with

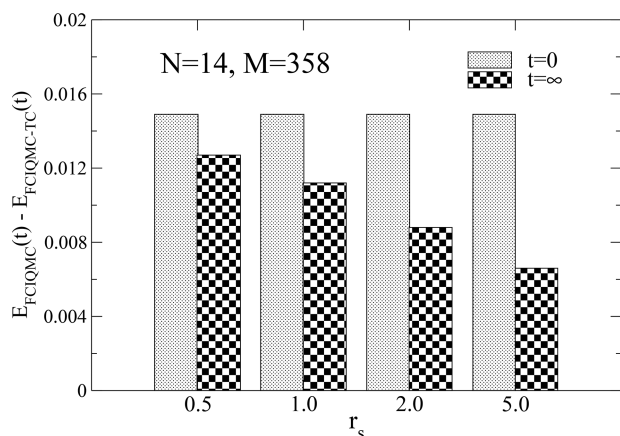


Figure 5. Energy differences $\Delta E(t)$ at $t = 0$ and $t = \infty$ for 14 electron systems with $M = 358$ presented for all different densities $r_s = 0.5$ – 5.0 .

$r_s = 0.5$ – 5.0 and on the basis $M = 358$ is presented for $t = 0$ and ∞ . In the calculation, the initial wave function is always chosen as the Hartree–Fock (HF) wave function. It can be seen that, at high density, $\Delta E(0)$ is close to $\Delta E(\infty)$, but at low density, they are quite different. This indicates that the effective potential \tilde{w}_{TC} does have a coupling to the wave function, especially in the low density region. It turns out that, for a given number of particles N and a given basis size M , $\Delta E(0)$ is independent of r_s . This can be easily understood by scaling arguments. At the HF level, the kinetic energy $\propto r_s^{-2}$ and the exchange energy $\propto r_s^{-1}$, because the corresponding operators $-\frac{1}{2} \sum_i \nabla_i^2$ and $\sum_{ij} 1/r_{ij}$ scale like r_s^{-2} and r_s^{-1} , respectively. By referring to eq 6, we get the expression of $\Delta E(0)$

$$\Delta E(0) = \langle \Phi_{\text{HF}} | \frac{1}{2} \sum_i (\nabla_i \tau)^2 | \Phi_{\text{HF}} \rangle \quad (30)$$

On the basis of eqs 11 and 23, it is not difficult to find that $\sum_i (\nabla_i \tau)^2$ scales as a constant of r_s and, therefore, $\Delta E(0)$ does not depend on r_s .

The conclusion that the effective potential \tilde{w}_{TC} couples to the wave function can also be verified by looking at the difference of the final solutions of the wave function between the two different methods. In Figure 6, the CI coefficient of the Hartree–Fock determinant (C_0) in the final solutions of the wave function with the two different methods is presented for different basis sets. The results are calculated for the 14 electron system with $r_s = 2.0$. C_0 of the FCIQMC-TC result is found to be clearly larger than that of the FCIQMC result. This also serves as evidence that the effective potential does couple to the wave function space. In Figure 6, it can be found that both curves show a rough $1/\sqrt{M}$ convergence. For the FCIQMC result, this can be easily understood based on variational argument, that because the energy converges like M^{-1} , the wave function should converge

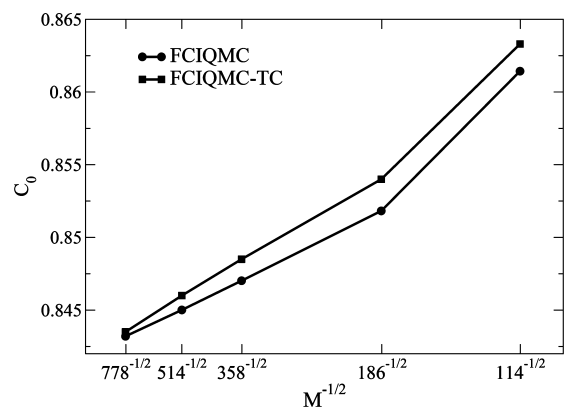


Figure 6. CI coefficient of the Hartree–Fock determinant in the final solutions of wave function with the two different methods presented for different basis sets. The results are calculated for the 14 electron system with $r_s = 2.0$.

like $1/\sqrt{M}$. As for the FCIQMC-TC result, where the energy converges like $M^{-5/3}$, the variational argument cannot be applied because the Hamiltonian is not fixed and itself depends on the basis.

4. CONCLUSIONS

In this work, we have designed a simple but efficient transcorrelated method for plane wave basis functions. The effective Hamiltonian contains only several two-body operators and thus can be easily implemented. To systematically reduce the error due to the neglect of the three-body operator in the original transcorrelated Hamiltonian, the correlation factor is constructed in a natural and systematic way according to the basis set. As an initial test, this simple effective Hamiltonian is used in FCIQMC calculations of homogeneous electron gas models. The results demonstrate that, with the same computational cost, this simple method can improve the FCIQMC convergence rate from $O(M^{-1})$ to $O(M^{-5/3})$.

We have also demonstrated that the effective transcorrelated Hamiltonian does couple to the wave function and changes the dynamic evolution of the FCIQMC simulations. This means that the FCIQMC-TC results cannot be precisely estimated based on an a posteriori use of the effective Hamiltonian.

The effective Hamiltonian, in principle, can also be applied to other projection methods such as the coupled cluster method. Because of the simple structure of the effective Hamiltonian, its implementation should be easier than that of the usual F12 methods. We are currently working on this implementation.

Generalization of this method to other types of basis is straightforward, and the basis-dependent correlation factors can be constructed as follows: first, take a usual F12 factor, for example a Slater type geminal $f(r_{12}) = \exp(-\gamma r_{12})$; then, the correlation factor can be constructed by projection against the current (orthonormal) basis set $\{\phi_i, i = 1, \dots, M\}$

$$u(\mathbf{r}_1, \mathbf{r}_2) = f(|\mathbf{r}_1 - \mathbf{r}_2|) - \sum_{ij} F_{ij} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) \quad (31)$$

$$F_{ij} = \int f(|\mathbf{r}_1 - \mathbf{r}_2|) \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) d^3r_1 d^3r_2 \quad (32)$$

The effective two-body transcorrelated potential can then be calculated with this correlation factor. Comparing with the plane wave basis, the expressions may become redundant. Therefore,

the induced one-body and two-body matrix elements have to be prepared and stored. We plan to work on this in the near future.

APPENDIX

A Regularities and Convergence Rates

The regularity of many body wave functions Ψ is $C^{0,1}$, and the non-smoothness comes largely from the cusps between electron pairs. (In the present analysis, we concentrate only on the electronic cusps and ignore the electron-nuclear cusps.) For an understanding of the relation between the regularity and the convergence rate, it is enough to take the example of a two-electron system, which is essentially a one-body problem in the center of mass coordinate. Because of the electronic cusp, the short range behavior of the exact wave function for a three-dimensional non-spin-polarized system looks like $|\tilde{\psi}(\mathbf{k})| \propto k^{-4}$ for $k \rightarrow \infty$. This means that, for a finite plane wave basis with a cutoff at k_c , the error of the wave function due to the missing resolution for the cusp can be estimated as

$$\delta\tilde{\psi}(\mathbf{k}) \propto \begin{cases} \frac{1}{k^4}, & |\mathbf{k}| > k_c \\ 0, & |\mathbf{k}| \leq k_c \end{cases} \quad (33)$$

The error of a variational energy can then be approximated as (ignoring any change of normalization)

$$\begin{aligned} \delta E &\approx \langle \delta\psi | \hat{H} | \delta\psi \rangle \\ &\approx \frac{1}{2} \int \delta\tilde{\psi}(\mathbf{k}) k^2 \delta\tilde{\psi}(\mathbf{k}) d^3k \\ &\propto \frac{1}{k_c^3} \end{aligned} \quad (34)$$

where we have used that fact that the leading contribution comes from the kinetic energy. By using a Jastrow factor, the regularity of the wave function is improved to $C^{1,1}$, which means that now the first order derivatives of ψ are in $C^{0,1}$. This leads to an asymptotic short range behavior of the gradient of the reference function $|\nabla\phi(\mathbf{k})| \propto k^{-4}$, for $k \rightarrow \infty$. Similarly, the energy error for a finite basis set can be estimated as

$$\begin{aligned} \delta E &\approx \frac{1}{2} \int |\delta\nabla\phi(\mathbf{k})|^2 d^3k \\ &\propto \frac{1}{k_c^5} \end{aligned} \quad (35)$$

Because the basis size $M \propto k_c^3$, we see that the Jastrow factor improves the convergence rate from $O(M^{-1})$ to $O(M^{-5/3})$.

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Notes

The authors declare no competing financial interest.

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