Self-consistent Density Functional Calculations without Diagonalization

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We develop a fully self-consistent first-principle calculation method based on the density functional theory. Comparing with the traditional Kohn-Sham method, the real-space distribution of electron density is obtained from the Hamiltonian without any diagonalization. In particular, a Fermi-Dirac filter applied on a random state combined with a time-evolution of the state vector is introduced to approximate the electron density. We show analytically that the average of electron densities calculated using different random states converges to the one obtained from diagonalization. Our approach is verified numerically in different systems including single atoms, diatomic molecules, clusters, and crystals. The computational costs (memory and time) scale linearly with the system size. Further electronic, optical, and transport calculations can be realized based on the ground state Hamiltonian using linear-scaled time-evolution methods. Our new approach for obtaining electron density without diagonalization provides a powerful strategy to solve problems in complex quantum systems.

First-principles calculation using the Density Functional Theory (DFT) is the most powerful computational method for multi-electron systems, and contribute extensively in physics, chemistry, and material science. DFT theorems prove that there is a one-to-one mapping between the ground-state wave function and the ground-state electron density [1]. In the mid-1960s, Kohn and Sham showed that the finding of the ground-state density can be determined by a set of single-electron equations (Kohn-Sham equations) [2], which is also known as KS-DFT. The iterative methods with the diagonalization of the KS-Hamiltonian are the most popular choices for realizing ground state calculations, and now many KS-DFT simulation packages are available [3–5]. However, KS-DFT suffers from a size limitation caused by the diagonalization, in which the computational cost exhibits a cubic scaling with the system size. Although many efforts such as iterative diagonalization schemes [6], preconditioned conjugate-gradient minimizations [7–9], and the Car-Parrinello method [10] have improved the scaling behavior for a relatively small system, it is still hard to handle systems of more than a few hundred atoms.

This size limitation has stimulated the development of linear-scaling DFT [11–24]. The first attempt can be traced back to the ‘divide and conquer’ method of Yang [14]. In 1992, Baroni and Giannozzi also proposed an algorithm that determines the electron density directly by using Green’s function [15]. In 1993, the density-matrix minimization approach was proposed by Li, Numes, and Vanderbilt [16]. Following these strategies, many linear-scaling DFT codes have been developed [13, 18–23]. Chebyshev filter method is another successful attempt to reduce the size of effective dimension of Hilbert space, but there are other non-linear factors dominated for large systems[25]. A linear-scaling algorithm using atomic orbitals (LCAO) basis sets [17] can be applied to suitable systems with clearly separated occupied and empty states [24]. Furthermore, the orbital-free DFT (OF-DFT) [26, 27] is a linear-scaling approach that avoids completely diagonalization, but the kinetic energy density functionals have not yet reached a good accuracy for many elements [28, 29].

In this letter, we develop a self-consistent first-principle calculation method based on DFT without any diagonalization. We use a statistical strategy with the average from different random states to update the electron density directly. We first construct a superposition state of all occupied orbitals by applying a Fermi-Dirac filter on a random state in real space. Then, we perform a time-evolution of the superposition state according to the time-dependent Schrödinger equation (TDSE), and the time-average of the wave function amplitude in real space will be an approximation of the electron density. We show analytically that the average of these approximations from different initial random states converges to the electron density obtained from the diagonalization method. We call our approach as Random-States DFT (RS-DFT). A detailed discussion of the method and the numerical verification in different systems, including single atoms, diatomic molecules, clusters, and crystals, will be presented in the following.

\textbf{Method.}— The common KS-DFT is realized iteratively with the diagonalization of the KS-Hamiltonian, which can be divided into four steps. In step (I), Kohn-Sham equation is constructed with an initial electron density $\rho(r)$:

$$[-\nabla^2 + V_{\text{ext}}[\rho(r)] + V_H[\rho(r)] + V_{\text{xc}}[\rho(r)]]\varphi_i(r) = \varepsilon_i \varphi_i(r),$$  

(1)
where \(-\nabla^2/2\) is the kinetic energy, \(V_{\text{ext}}\) is the external potential, \(V_H\) is the Hartree potential, and \(V_{xc}\) is the exchange and correlation potential. In step (II), the Kohn-Sham equation is solved by exact diagonalization to obtain KS orbitals \(\{|E_n\}\) and corresponding energies \(E_n\). In step (III), an output electron density is constructed by the superposition of occupied KS orbitals \(\{|E_n\}\), namely 
\[
\rho(r) = \sum_{i} f(E_{n_i})|E_{n_i}|^2
\]
where \(f\) is the Fermi-Dirac function. In step (IV), new input electron density is constructed by a mixture of output and previous input densities. Then iterative calculations involving steps (I) to (IV) are continued until the total energy and electron density differences between two iterations are less than given thresholds. Here, the most time-consuming part is step (II). In principle, the energies \(E_n\) can be calculated by using the time-evolution method without diagonalization \[30, 31\] (a brief discussion will be presented later), but currently there is no other way except diagonalization to obtain KS orbitals \(\{|E_n\}\). It is thus critical to develop a new method to construct the electron density from KS-Hamiltonian without any diagonalization.

In the basis of real-space grid \(\{|r_j\}\), the wave functions of KS orbitals can be expressed as 
\[
E_n = \sum N a_i(E_n)|r_j\rangle,
\]
where \(N\) is the total number of grid points. Consider a random superposition state in the real-space: 
\[
|\varphi_0\rangle = \sum c_i|r_i\rangle,
\]
where \(c_i\) are random complex numbers. We apply a Fermi-Dirac (FD) filter on a random state \(|\varphi_0\rangle\) to obtain a superposition state of all occupied states 
\[
|\varphi\rangle_{FD} \equiv \sqrt{f(H)}|\varphi_0\rangle,
\]
where \(f(H) = 1/(e^{(H-\mu)/k_BT}+1)\), \(\mu\) is the Fermi level, and \(T\) is temperature. By using the properties \(\sum_n |E_n\rangle\langle E_n| = I\), 
\[
\sum_j |r_j\rangle\langle r_j| = I,
\]
and \(f(H)|E_n\rangle = f(E_n)|E_n\rangle\), we have
\[
|\varphi\rangle_{FD} = \sum_{i,j} \sum_n c_i a_i^*(E_n)f^{1/2}(E_n)a_j(E_n)|r_j\rangle. \tag{2}
\]
The intensity of \(|\varphi\rangle_{FD}\) at grid \(r_j\) can be expressed as 
\[
\langle \varphi|\varphi\rangle_{FD} = \sum_i \sum_{j\neq m} f^{1/2}(E_n)a_j(E_n)|r_j\rangle\langle r_j|a_i^*(E_n)f^{1/2}(E_n)|r_j\rangle
\]
\[
\sum_{i,j} \sum_{n\neq m} c_i^* a_i(E_n)f^{1/2}(E_n)a_j^*(E_n)c_j a_j(E_n)f^{1/2}(E_n)a_j(E_n). \tag{3}
\]

Consider a set of random states \(|\varphi_p\rangle = \sum c_{i,p}|r_i\rangle\), where \(p = 1, 2, ..., S\) and \(\{c_{i,p}\}\) are random complex numbers. According to the central limit theorem, for a large but finite number \(S\), we have \[30,\]
\[
\frac{1}{S} \sum_{p=1}^S \sum_{i=1}^N \sum_{i' = 1}^N c_{i,p} c_{i', p} = E(|c|^2)\delta_{i,i'} + O\left(\frac{1}{\sqrt{S}}\right), \tag{4}
\]
where \(E(|c|^2)\) is the expectation value of \(|c_i|^2\). Therefore, one can prove that
\[
\lim_{S \to \infty} \frac{1}{S} \sum_{p=1}^S \langle \varphi_p|\varphi\rangle_{FD} = E(|c|^2)\delta_{i,i'} + O\left(\frac{1}{\sqrt{S}}\right).
\]

Using the normalization property \(\sum_{i=1}^N a_i(E_n)a_i^*(E_n) = 1\) and the orthogonal property \(\sum_{i=1}^N a_i(E_n)a_m^*(E_m) = 0\), for \(n \neq m\). Eq. (5) suggests that \(\rho_{FD}(r_j) \equiv \frac{N}{S} \sum_{p=1}^S \langle \varphi_p|\varphi\rangle_{FD}|r_j\rangle^2\) is an approximation of the electron density at \(r_j\) with an error vanishes as \(1/\sqrt{S}\). In fact, it is also possible to approximate \(\rho(r_j)\) by introducing \(f(H)|\varphi_0\rangle\) instead of \(\sqrt{f(H)}|\varphi_0\rangle\). However, the sum will then involve all unoccupied states which leads to a much slower convergence of approximated \(\rho(r_j)\) (see detailed discussion in Supplemental Materials).

Besides the average from different random samples, an extra time-evolution can be introduced to fast the convergence of \(\rho_{FD}(r_j)\) to \(\rho(r_j)\). From Eq. (5), one can see that when making the average from different random samples, the numerical error is dominated by the second term with \(n \neq m\). Introducing \(|\varphi(t)\rangle_{FD} = e^{-iHt}\sqrt{f(H)}|\varphi_0\rangle\), and the time-evolution of \(|\varphi(t)\rangle_{FD}\) can provide a series of \(\rho_{FD}(r_j, t)\) at different time. One can prove that the time averaging of \(\rho_{FD}(r_j, t)\) reduces significantly the second term with \(n \neq m\) by using the property \(\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i(E_n - E_m)t} dt = \delta(E_n - E_m)\) (see details in the Supplemental Materials). With this advantage, the electron density at \(r_j\) is given by
\[
\rho_{FD}(r_j) = \frac{N}{S} \sum_{p=1}^S \int_{-\infty}^{\infty} ||\varphi_p(t)||_{FD}^2(r_j) dt. \tag{6}
\]

When using Eq. (6), the Fermi-level needs to be determined before applying the Fermi-Dirac filter. Next, we discuss briefly the calculations of energy spectrum \(\langle E_n\rangle\) and the Fermi-level \(\mu\).

In RS-DFT, the density of states (DOS) are calculated with the time-evolution method without diagonalization \[30, 31\]:
\[
D(\varepsilon) = \lim_{S \to \infty} \frac{1}{S} \sum_{p=1}^S \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\varepsilon t} \langle \varphi_p|e^{-iHt}|\varphi_p\rangle dt, \tag{7}
\]
here similarly, \(|\varphi_p\rangle\) is a random state and \(S\) is the number of random samples for the average. In general, the statistical error on this calculation vanishes with \(1/\sqrt{SN}\), and
FIG. 1: (a) DOS and Carrier density calculated from the time-evolution method of one He atom. The vertical dashed lines indicate the energies obtained from the diagonalization. (b) The output electron density after one iteration using diagonalization (black) and Fermi-Dirac filter on random states (red) from the same input electron density (blue). For He atom, due to the spherical symmetry, electron density is only a function of distance \( r \) from the center of the atom. (c) The converged ground-state electron density of He atom obtained from KS-DFT and RS-DFT. (d) The total energy as a function of bond length of molecular \( \text{H}_2 \) from obtained from KS-DFT and RS-DFT, respectively.

The energy resolution is determined by \( 1/N_i \tau \), where \( N_i \) is the number of time step and \( \tau \) is the time intervals \( dt \). The Fermi level \( \mu \) is determined using \( n_e = \int_{-\infty}^{\infty} D(\varepsilon) d\varepsilon \), where \( n_e \) is the total number of electrons in the system. The time-evolution operator \( e^{-iHt} \) and the Fermi-Dirac filter \( \sqrt{f(H)} \) are calculated numerically using the Chebyshev polynomials method [31], which is very efficient and accurate for sparse matrix \( H \). In the Chebyshev decomposition of the Fermi-Dirac filter, the temperature has to be finite, and we here fix it at 10K in all the calculations.

In the following, we show several examples of using RS-DFT in real systems. The kinetic energy in the KS-Hamiltonian (Eq. (1)) is approximated by using the higher-order finite-difference expansion for the Laplacian operator in a uniform real-space grid [32, 33]. The Hartree potential \( V_H \) is derived by solving the Poisson equation [33]. For exchange and correlation potential \( V_{xc} \), we use the local density approximation (LDA) [34]. The full ionic potential \( V_{ion} \) is effectively replaced by pseudopotential in Kleinman-Bylander forms [35].

**Single Atom.**— Let us first consider a single Helium atom. In step (I), we construct a KS-Hamiltonian (Eq. (1)) based on an initial electron density with a gaussian distribution, as shown in Fig. 1(b). In step (II), we obtain DOS \( D(\varepsilon) \) by using the time-evolution method (Eq. (7)) without the diagonalization of the Hamiltonian matrix, and subsequently determine the Fermi level \( \mu \) (see Fig. 1(a)). As a comparison, the energies of KS orbitals from the diagonalization are also shown in Fig. 1(a), which agree very well with our results. In step (III), as there is only one occupied state, one can just use \( \rho_{FD} \) to obtain the electron density without time-evolution (because there is no second term in Eq. (3)). As a comparison, we also calculate the electron density \( \rho_{diag} \) based on the occupied KS orbital obtained from the diagonalization of KS-Hamiltonian, and plot together with \( \rho_{FD} \) in Fig. 1(b). We see that with only \( S=10 \) random samples, \( \rho_{FD} \) converges to \( \rho_{diag} \) with an error of \( \Delta(\rho_{FD} - \rho_{diag}) = 8.06 \times 10^{-5} \), where \( \Delta(\rho_{FD} - \rho_{diag}) = \sum_{j=1}^{N} |\rho_{FD}(\mathbf{r}_j) - \rho_{diag}(\mathbf{r}_j)|/N \). In step (IV), we use \( \rho_{FD} \) as the new input electron density, and perform the next iteration. The self-consistent iterations including step (I) to (IV) are continued until a given threshold is reached.

In our approach, since the space resolution (determined by \( N \)) is much larger than the energy resolution (determined by \( N_1 \)), it is more accurate to use the electron density instead of the total energy to define the convergence criterion. The ground-state electron density obtained from RS-DFT without any diagonalization agrees well with the one from the common KS-DFT with diagonalization, and both are plotted in Fig. 1(c) for comparison. More examples on other single atoms can be found in Supplementary Materials.

**Molecules.**— For molecular systems, we consider a diatomic model \( \text{H}_2 \). The iterative calculations are similar as in the case of single atom. Here we verify our approach by calculating the total energies for different H-H bond lengths, and compare the results from our RS-DFT approach and the common KS-DFT in Fig. 1(d). The two methods lead to similar total energies for a given H-H bond length. The bond lengths in the ground state obtained from both methods are the same (74 pm), which agree with the well-known result [36].

**Clusters.**— We further extend our calculations to large atomic clusters of fullerenes \( C_{60} \), \( C_{540} \) and \( C_{1500} \). The iterations are performed in the same way as previous cases except using \( \hat{\rho}_{FD} \) instead of \( \rho_{FD} \) to fast the convergence of the electron density. Pulay mix is used to optimize the new input density and accelerate the convergence [37]. The real-space distribution of electron density in the ground state are visualized by VESTA [38] in Fig. 2. Since the size is too large for the diagonalization using our package, we use VASP (Vienna Ab initio Simulation Package) [3] to represent the common KS-DFT method. VASP is a very efficient and widely used commercial KS-DFT package, but \( C_{1500} \) is still too large for VASP in our local cluster. The densities of \( C_{60} \) and \( C_{540} \) are calculated using VASP and we show here the result of \( C_{540} \) in Fig. 2(d) for comparison. For both molecular fullerenes, the electron density distributions obtained
from RS-DFT and VASP are very similar. One should notice that as VASP uses different functionals and different pseudo-potentials, the results from two different DFT packages can not match exactly.

**Crystals.**— At last, we consider three-dimensional crystals and check the scaling behavior of our approach. The non-diagonal elements of KS-Hamiltonian are from the kinetic energy and non-local pseudopotentials in Eq. (1), leading to a highly sparse Hamiltonian matrix due to the locality. The number of the non-zero elements in the matrix scales linearly with the number of atoms in the system. In RS-DFT, the basic and absolutely dominated calculations are the multiplications between the Hamiltonian matrix and a state vector, in which the number of operations scales linearly with the nonzero elements in the matrix. Therefore, the total computational load (CPU time) and memory cost of RS-DFT are both linearly dependent on the number of atoms in the system. These linear-scaling behaviors are verified in three-dimensional crystal calculations shown in Fig. 3 (a-b). We performed RS-DFT calculations of graphite with 42, 264, 2202, 5040, and 11440 carbon atoms, respectively. In all cases, we used the same calculation parameters such as the same real-space grid density and the same accuracy for the Chebyshev decompositions of the time-evolution operator and the Fermi-Dirac filter. As benchmark tests, we perform complete ground state calculations of graphite with 5040 and 11440 carbon atoms, respectively. The converge of $\Delta(\rho_{in} - \rho_{out})$ as a function of iterative steps is plotted in Fig. 3 (c-d). One should notice that, for 11440 carbon atoms, the total memory cost is only 16 GB. To the best of the authors knowledge, this memory cost per atom is far beyond all available self-consistent KS-DFT packages. Furthermore, due to the linear-scaling behavior, a self-consistent calculation of millions of atoms should be possible for computer clusters with Terabytes (TB) memory.

**Conclusion and Discussion.**—In summary, we developed a linear-scaled self-consistent first-principle calculation method. In RS-DFT, a Fermi-Dirac filter on a random state and subsequently a wave propagation according to the time-dependent Schrödinger equation are introduced to approximate the space distribution of the electron density. We showed analytically how the average of electron density from different random states converges to the result of standard DFT calculations. We also verified our theory numerically in different systems including single atoms, diatomic molecules, clusters, and crystals. The main advantage of RS-DFT is that there is no diagonalization of Hamiltonian matrix in the whole process, and both the memory cost and computational...
time are linearly dependent on the system size. A calculation of a system with millions of atoms should be possible for computer clusters with Terabytes memory. Furthermore, after obtaining the ground-state Hamiltonian, many physical properties can be calculated by using the time-evolution methods as these developed in the tight-binding model [31, 39–41]. These methods are also linear-scaled and based on the single-particle approximation. They mainly use the random state technology and the linear-response theory for the calculations of electronic, optical and transport properties without any diagonalization. RS-DFT provides new possibility to study large-scale systems from first-principle, and can be used widely in physics, chemistry, biology and material science. Furthermore, our approach to obtain the electron density without any diagonalization is applicable to other problems in quantum systems beyond DFT.

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Supplementary Materials: Self-consistent Density Functional Calculations without Diagonalization

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1. Higher-order Finite-difference Pseudopotential Method

Within non-relativistic Kohn–Sham DFT, the ground state of a system of N electrons subject to an external potential can be obtained by solving a set of one-particle equations, the Kohn–Sham equations (atomic units will be used throughout):

\[ -\nabla^2/2 + V_{KS}[\rho(r)]\varphi_i(r) = \varepsilon_i\varphi_i(r) \tag{1} \]

where Kohn-Sham potential \( V_{KS}[\rho(r)] \) is usually divided as:

\[ V_{KS}[\rho(r)] = V_{ext}[\rho(r)] + V_H[\rho(r)] + V_{xc}[\rho(r)] \tag{2} \]

where \( V_{ext} \) is the external potential, \( V_H \) is the Hartree potential, and \( V_{xc} \) is the exchange and correlation potential. In this paper, we implement real-space finite-element methods, resulting in \( V_{KS}[\rho(r)] = V_{KS}(r) \).

In our letter, we impose a simple, uniform orthogonal three-dimensional (3D) grid where the points are described in a finite domain by \((x_i, y_j, z_k)\) \[1\]. Kinetic-energy operator can be described by high-order finite-element difference method \[2\],

\[ \frac{\partial^2 \varphi}{\partial x^2} = \sum_{n=-N}^{N} C_n \varphi(x_i + nh, y_j, z_k) + O(h^{2N+2}) \tag{3} \]

where \( h \) is the grid spacing and \( N \) is the order of finite-element difference. Expansion coefficients \( C_n \) for a uniform grid are given in Table. S1.

The hartree energy density and potential are given by:

\[ \varepsilon_H(r) = \frac{1}{2} \int d\mathbf{r'} n(\mathbf{r'}) / |\mathbf{r} - \mathbf{r'}| \tag{4} \]

\[ V_H(r) = \int d\mathbf{r'} n(\mathbf{r'}) / |\mathbf{r} - \mathbf{r'}| \tag{5} \]

The Hartree potential \( V_H \) could be obtained by solving Poisson’s equation.

For the exchange-correlation part, we use local-density approximation (LDA):

\[ E_{xc}[n] = \int d\mathbf{r} n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) \tag{6} \]

The most accurate formulae for the exchange-correlation functional were obtained by fitting the QMC results for the Jellium model. Various parametrizations are available. We use one of the most popular choices proposed by Vosko-Wilk \[3\]. From the Jellium model we know that the local part of the exchange is given by:

\[ \varepsilon_x = -\frac{3}{4} \left( \frac{3}{2\pi} \right)^{2/3} \frac{1}{r_s}, \quad V_x = \left( \frac{3}{2\pi} \right)^{2/3} \frac{1}{r_s}. \tag{7} \]

For \( V_{ext}(r) \), we use full ionic potential \(-\hat{Z}\) for the cases of single atoms. For other systems, we implement pseudopotential operator to reduce the computational demand. We use the projection scheme of the pseudopotential operator suggested by Kleinman and Bylander \[4\]:

\[ V_{ps}(r) = \sum_{a=1}^{N} \left[ V_{loc,a,ps}(r) + \frac{\langle \Delta V_{a,ps}^{l}(r) \varphi_{lm}^{a}(r) \rangle}{\langle \varphi_{lm}^{a}(r) \varphi_{lm}^{a}(r) \rangle} \right] \tag{8} \]

where the total pseudopotential can be divided into non-local and local part \( \Delta V_{a,ps}^{l}(r) \equiv V_{a,ps}^{l}(r) - V_{loc,a,ps}(r) \). \( V_{loc,a,ps} \) is the local part with specific angular momentum l component of atom a, which differs from zero only in the region smaller than cutoff radius \( r < r_c \). \( \varphi_{lm}^{a}(r) \) is the atomic pseudo wave function with \( lm \) quantum angular momentum numbers. It is worth noticing that the pseudopotential operator only needs to be calculated once at very beginning since it only depends on the atomic configuration. Taking pseudopotential of carbon atom as an example. We use program ATOM \[5\] to generate its pseudopotential. The type of pseudopotential is chosen as local density approximation (LDA) \[6\] and plotted in Fig. S1. In Fig. S2, we show the atomic pseudo wave-function, and indeed it is same as full-potential wave-function in the range of \( r > r_s \) where \( r_s \) is the cutoff radius. The construction of charge density has been described in the main context.
TABLE S1: Expansion coefficients $C_n$ for higher-order finite-difference expressions of the second derivative.

| $N$ | $C_1$ | $C_{i+1}$ | $C_{i+2}$ | $C_{i+3}$ | $C_{i+4}$ | $C_{i+5}$ | $C_{i+6}$ |
|-----|-------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1   | -2    | 1         |           |           |           |           |           |
| 2   | $-\frac{5}{2}$ | 2        | 1         |           |           |           |           |
| 3   | $-\frac{45}{12}$ | 3        | 2        | 1         |           |           |           |
| 4   | $-\frac{205}{24}$ | 4        | 3        | 2        | 1         |           |           |
| 5   | $-\frac{5269}{50}$ | 5        | 4        | 3        | 2        | 1         |           |
| 6   | $-\frac{1800}{72}$ | 6        | 5        | 4        | 3        | 2        | 1         |

FIG. S1: Pseudopotential of carbon atom generated by program ATOM [5].

FIG. S2: Atomic wavefunction (Red dashed curve) and pesudo-wavefunction (black solid curve) of carbon.

2. The detailed discussion of the methods used in RS-DFT

In this part, we show details of the methods used in RS-DFT. First, we construct a random superposition state in a uniform real-space grid as an initial state, in which the number of grid is $N$,

$$|\varphi_0\rangle = \sum_{i=1}^{N} c_i |r_i\rangle$$

where $\{r_i\}$ are the real space basis states and $\{c_i\}$ are random complex numbers. Assuming that

$$|E_n\rangle = \sum_{i} a_i (E_n) |r_i\rangle,$$

we have

$$|\varphi_0\rangle = \sum_{i=1}^{N} c_i \sum_{n=1}^{N} |E_n\rangle \langle E'_n| r_i\rangle$$

$$= \sum_{i=1}^{N} \sum_{n=1}^{N} c_i a_i^* (E_n) |E_n\rangle$$

$$= \sum_{i=1}^{N} \sum_{n=1}^{N} \sum_{n' = 1}^{N} c_i a_i^* (E_n) |r_j\rangle \langle r_j|E_{n'}\rangle$$

$$= \sum_{i=1}^{N} \sum_{n=1}^{N} \sum_{n' = 1}^{N} c_i a_i^* (E_n) a_j (E_{n'}) |r_j\rangle.$$

Here we consider another type of Dirac-Fermi filter different from the one introduced in the main text:

$$|\varphi\rangle_{fd} \equiv f(H)|\varphi_0\rangle$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{n'=1}^{N} c_i a_i^* (E_n) f(E_n) a_j (E_{n'}) |r_j\rangle$$

(12)

In the inner product of $\langle \varphi_0|\varphi\rangle_{fd}$ at grid $r_j$ can be calculated by using Eq. (11) and Eq. (12),

$$0\langle \varphi|r_j\rangle |\varphi_{fd}\rangle$$

$$= \sum_{i=1}^{N} \sum_{n,m=1}^{N} c_i a_i (E_n) a_j^* (E_m)c_i' a_i' (E_{m'}) f(E_m) a_j (E_m)$$

$$+ \sum_{i=1}^{N} \sum_{n',m=1}^{N} c_i a_i (E_n) a_j^* (E_m)c_i' a_i' (E_{n'}) f(E_{n'}) a_j (E_{n'})$$

$$+ \sum_{i=1}^{N} \sum_{n,m=1}^{N} c_i a_i (E_n) a_j^* (E_m)c_i' a_i' (E_{m'}) f(E_m) a_j (E_{m'})$$

$$+ \sum_{i=1}^{N} \sum_{n',m=1}^{N} c_i a_i (E_n) a_j^* (E_m)c_i' a_i' (E_{n'}) f(E_{n'}) a_j (E_{n'})$$

(13)
According to the central limit theorem, for a large but finite number \( S \) of the random states \( |\varphi_p\rangle = \sum_i c_{i,p} |r_i\rangle \), we have

\[
\frac{1}{S} \sum_{p=1}^{S} \sum_{i=1}^{N} \sum_{i'=1}^{N} c_{i,p} c_{i',p} = E(c^2) \delta_{i,i'} + O\left(\frac{1}{\sqrt{S}}\right). \tag{14}
\]

Therefore, one prove that

\[
\lim_{S \to \infty} \frac{1}{S} \sum_{p=1}^{S} \langle \varphi_p | r_j \rangle \langle r_j | \varphi_p \rangle = \frac{N}{N} \sum_{i=1}^{N} E(|c|^2) f(E_n) |a_i(E_n)|^2 |a_j(E_n)|^2 + \frac{N}{N} \sum_{i \neq m} E(|c|^2) f(E_m) a_i(E_m) a_i^\ast(E_m) a_j(E_m) a_j(E_m)
\]

\[
= \frac{N}{N} \sum_{i=1}^{N} |a_i(E_n)|^2 \sum_{n=1}^{N} E(|c|^2) f(E_n) |a_j(E_n)|^2
\]

\[
= \frac{1}{N} \sum_{n=1}^{N} f(E_n) |a_j(E_n)|^2
\]

\[
= \frac{1}{N} \rho_{diag}(x_j)
\]

(15)

Here we used the normalization property of KS orbitals \( \sum_{i=1}^{N} |a_i(E_n)|^2 = 1 \) and the orthogonal property \( \sum_{i=1}^{N} a_i(E_n) a_i^\ast(E_m) = 0 \) for \( m \neq n \). Eq. (15) indicates that \( \rho_{fd}(r_j) \equiv \frac{1}{N} \sum_{p=1}^{S} \langle \varphi_p | r_j \rangle \langle r_j | \varphi_p \rangle f_d \) is an approximation of the charge density at \( r_j \) with an error vanishes as \( 1/\sqrt{S} \), which can be verified in the zoom-in figure of SFig. S3.

However, as we mentioned in the main text, the convergence of \( \rho_{fd}(r_j) \) is slower than the one introduced in the main text. The reason is that, in Eq. (13), the sum in the second term \( (n \neq m) \) involves all unoccupied states associated with the index \( n \), and their number is several orders larger than the number of occupied states because \( N \gg n_e \). To overcome this difficulty, we introduce \( |\varphi\rangle_{FD} = \sqrt{f(H)} |\varphi\rangle_0 \), the one used in the main context. The main advantage of using \( |\varphi\rangle_{FD} \) is that the sums in the second term \( (n \neq m) \) of Eq. (3) of the main context includes only occupied states, leading to a much faster convergence compared with Eq. (13) (see SFig. S3).

The accuracy of \( |\varphi\rangle_{FD}(r_j) \) can be effectively improved by averaging over more different random samples (see SFig. S6). Besides averaging over different random samples, error induced by \( \langle E_n | E_m \rangle \) can also be reduced by introducing an extra time evolution of \( |\varphi\rangle_{FD} \) or \( |\varphi\rangle_{fd} \) according to the time-dependent Schrodinger equation.

FIG. S3: The difference between the output density obtained from KS-DFT \( \rho_{diag} \) and RS-DFT as a function of the number of random samples \( S \). In RS-DFT, the results are obtained by using \( \rho_{FD} \) (Eq. (3) in the main context) or \( \rho_{fd} \) (Eq. (13)).

FIG. S4: Comparisons of ground-state charge density calculated by KS-DFT based on diagonalization and RS-DFT of single atoms.

FIG. S5: The ground-state charge density calculated by RS-DFT and VASP, respectively.
Define $|\varphi(t)\rangle_{FD} = e^{-iHt}\sqrt{f(H)}|\varphi\rangle_0$, we have

$$F_D\langle \varphi(t) | r_j \rangle \langle r_j | \varphi(t) \rangle_{FD}$$

$$= \sum_{i,i'} \sum_{n,m} c_i^* a_i(E_n) c_{i'} a_{i'}^*(E_n) f(E_n) a_j^2(E_m)$$

$$+ \sum_{i,i'} \sum_{n \neq m} c_i^* a_i(E_n) f_2(E_n) a_{i'}^*(E_n) c_{i'} a_{i'}^*(E_m) f_2(E_m)$$

$$a_j(E_m) e^{-i(E_n - E_m)t}.$$  \hfill (16)

Therefore

$$\int_{-\infty}^{\infty} F_D\langle \varphi(t) | r_j \rangle \langle r_j | \varphi(t) \rangle_{FD} dt$$

$$= \sum_{i,i'} \sum_{n=1}^{N} c_i^* a_i(E_n) c_{i'} a_{i'}^*(E_n) f(E_n) a_j^2(E_n),$$

in which we used the property,

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(E_n - E_m)t} dt = \delta(E_n - E_m).$$  \hfill (18)

The effects of this extra time-evolution in real calculations are shown in SFig. S7.

In the numerical calculation, the operators $\frac{1}{\sqrt{e^{i(H_p+1)}}}$ and $e^{-iHt}$ are approximated by using the Chebyshev polynomial method. In general, a function $f(x)$ whose values are in the range [-1,1] can be expressed as,

$$f(x) = \frac{1}{2} c_0 T_0(x) + \sum_{k=1}^{\infty} c_k T_k(x)$$  \hfill (19)

where $T_k(x) = \cos(k \arccos x)$ and the coefficients $c_k$ are

$$c_k = \frac{2}{\pi} \int_{-1}^{1} \frac{dx}{\sqrt{1-x^2}} f(x) T_k(x)$$  \hfill (20)

if we let $x = \cos \theta$, then $T_k(x) = T_k(\cos \theta) = \cos k\theta$, and

$$c_k = \frac{2}{\pi} \int_{0}^{\pi} f(\cos \theta) \cos k\theta d\theta$$

$$= \Re \left[ \frac{2}{N} \sum_{n=0}^{N-1} f \left( \cos \frac{2\pi n}{N} \right) e^{2\pi i nk/N} \right],$$  \hfill (21)

which can be calculated by the fast Fourier transform (FFT). We normalize $H$ such that $\tilde{H} = H/\|H\|$ has eigenvalues in the range [-1,1] and put $\beta = \|\beta\|$. Then

$$f(\tilde{H}) = \sum_{k=0}^{\infty} c_k T_k(\tilde{H})$$  \hfill (22)

where the Chebyshev polynomial $T_k(x)$ is the Chebyshev polynomial of the first kind. $T_k(x)$ obeys the following recurrence relation:

$$T_{k+1}(x) + T_{k-1}(x) = 2x T_k(x)$$

with

$$T_0(x) = 1, T_1(x) = x$$

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FIG. S6: The charge density of C\textsubscript{60} calculated from average over different number of random samples without time evolution.

(a) time intervals $dt = \pi$

(b) time intervals $dt = 32\pi$

FIG. S7: The charge density of C\textsubscript{60} calculated from one random state averaging over from time evolution for 32, 64, 96, 128 steps with $dt = \pi$ (a) and $dt = 32\pi$ (b).
FIG. S8: $\Delta (\rho_{in} - \rho_{out})$ as a function of iterative steps for A-B stacked graphite calculated by RS-DFT. The insets indicate the converged ground state densities.