

REVIEW ARTICLE

Orbital-Free Density Functional Theory for Molecular Structure Calculations

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Abstract. We give here an overview of the orbital-free density functional theory that is used for modeling atoms and molecules. We review typical approximations to the kinetic energy, exchange-correlation corrections to the kinetic and Hartree energies, and constructions of the pseudopotentials. We discuss numerical discretizations for the orbital-free methods and include several numerical results for illustrations.

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1. Introduction

In modeling either atomic or molecular systems, the most common strategy relies on approximate solutions of Schrödinger equations; and the so-called density functional theory (DFT) has been established as one of the most widely used first-principles methods in many fields. DFT may be dated back to 1927 [68, 74, 98, 113]. It was first realized by Thomas [91] and Fermi [25] that the electronic structure of solids in their ground states could be fully understood in terms of the electron density ρ alone. This fact, which gave the origin to the DFT, was later formalized by Hohenberg and Kohn [44] in 1964. It was proved in [44] that there exists a functional, $E(\rho)$, of the electron density ρ of the system, such that for any external potential V_{ext} , the exact ground state energy of the system is the global minimum value of $E(\rho)$, and the density ρ that minimizes $E(\rho)$ is the exact ground state density ρ_0 , namely

$$E(\rho_0) = \min \left\{ E(\rho) : \rho \geq 0, \int_{\mathbb{R}^3} \rho = N \right\}, \quad (1.1)$$

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where N is the number of the electrons and

$$E(\rho) = T(\rho) + E_{ee}(\rho) + \int_{\mathbb{R}^3} V_{ext} \rho \quad (1.2)$$

with $T(\rho)$ the kinetic energy and $E_{ee}(\rho)$ the electron-electron interaction energy. The problem remains how to evaluate the kinetic energy $T(\rho)$ and the electron-electron interaction energy $E_{ee}(\rho)$, which is of surpassing difficulty. In 1965, Kohn and Sham [56] invented an indirect approach to the kinetic energy, the so-called Kohn-Sham (KS) method. They proposed introducing a set of N wavefunctions $\{\psi_i\}_{i=1}^N$ and expressing the total energy of the system as [56]

$$E(\rho) = T_s(\{\psi_i\}) + E_H(\rho) + E_{xc}(\rho) + \int_{\mathbb{R}^3} V_{ext} \rho, \quad (1.3)$$

where $T_s(\{\psi_i\})$ is the exact kinetic energy of the system of non-interacting electrons with density ρ :

$$T_s(\{\psi_i\}) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \psi_i|^2, \quad \rho = \sum_{i=1}^N |\psi_i|^2. \quad (1.4)$$

Other terms in the right hand of (1.3) are the Hartree energy, the exchange-correlation energy and the external potential energy, respectively. The Hartree energy describes the repulsion Coulomb interactions between electrons

$$E_H(\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}. \quad (1.5)$$

The exchange-correlation energy $E_{xc}(\rho)$ introduces corrections to the energy that derive from using the non-interacting electron approximation for the Hartree and kinetic energies. Although the expression for the total energy in (1.3) is exact, $E_{xc}(\rho)$ is unknown. For a system with slow varying density, we can make the local density approximation (LDA) [55]:

$$E_{xc}(\rho) = \int_{\mathbb{R}^3} \varepsilon_{xc}(\rho) \rho, \quad (1.6)$$

where $\varepsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of a uniform electron gas of density ρ . The last term in (1.3), i.e., the integral term, represents the effect of an external potential. For a simple many-particle system without any electric and magnetic potentials, the external potential can be expressed by

$$V_{ext}(r) = - \sum_{\alpha=1}^M \frac{Z_\alpha}{|r - R_\alpha|}, \quad (1.7)$$

where M is the number of the atoms, Z_α is the charge of the α th atom and R_α is the position of the α th atom. It is apparent that there are singularities at the locations of the nuclei. And it is also observed that the strong Coulomb potential of the nucleus and the effects of the tightly bound core electrons could be replaced by an effective ionic potential acting on the valence electrons. In what follows we consider ρ to be the density of the valence electrons only. The core electrons and the nuclei are treated as unit which interacts with the valence electrons through V_{ext} , which usually is the pseudopotential.

The computation of the Kohn-Sham kinetic energy functional requires the calculation of the N non-interacting electron orbitals. By traditional variational methods, solving the problem (1.1) is equivalent to solving a nonlinear eigenvalue problem with N independent-particle eigenstates in \mathbb{R}^3 . The computational cost scales $\mathcal{O}(N^3)$ with the size of the system N by the traditional self-consistent matrix diagonalization techniques, which is due to the diagonalization process. Currently, this is not viable for large systems with thousands of atoms. To reduce the computational cost, a number of linear scaling methods are then proposed. The linear scaling methods are of two types: orbital-based and orbital-free methods.

1.1. Orbital-based methods

There are mainly three orbital-based (OB) linear scaling methods which have deep roots in physics [36, 70]: divide and conquer method, fermi operator expansion method, and density matrix minimization method. These linear scaling methods all basically exploit the general principle of locality or "nearsightedness" [54] for quantum many-particle systems: that the properties at one point can be considered independent of what happens at distant points. Note that in insulator, electrons are localized, even in metal, the total charge density is a superposition of the atomic charge densities with reasonable accuracy, where the linear scaling methods can be exploited.

The contents of the locality or "nearsightedness" principle are the decay properties of the density matrix and the Wannier functions. All the three linear scaling methods take advantages of the decay of the density matrix with distance and truncate it at some point. Even though there are long range Coulomb forces, there are various methods to sum the long range forces in time $\propto N$.

- *Divide and conquer method*: The first orbital-based linear scaling method was proposed by Yang [111] in 1991, which is based directly upon the argument that the interior of a large region depends only weakly upon the boundary conditions. The procedure termed "divide and conquer" [111] is to divide a large system into small subsystems, whose size is N_{small} . Each subsystem is called central region, and all regions around the central region are called buffer regions. The size of buffer determines the length of localization. For each of these systems one can solve for the electronic eigenstates using ordinary $\mathcal{O}(N^3)$ methods. For each small system, one must add buffer regions of size N_{buffer} large enough so that the density and the energy in the original small subsystem converge and are independent of the buffer

termination. The solution for the density and other properties is then kept only for the interior of each small region.

In many ways, the “divide and conquer” approach is a counterpart of using supercells. Although there is wasted computational effort, the approach is attractive because it uses standard methods and there is much experience in extracting information from small systems with well-chosen terminations. Using traditional methods, the cost is of $\mathcal{O}(N_{small} + N_{buffer})^3$ for each subsystem, which may be prohibitive, especially for three dimensional systems where N_{buffer} may need to be very large. Nevertheless, the method is $\mathcal{O}(N)$ essentially for large enough systems and it may be particularly applicable for long linear molecules with large energy gaps.

- *Fermi operator expansion method*: The Fermi operator expansion method [37] is the most direct method to calculate the density matrix. It exploits the decay properties of the density matrix and of the Wannier functions to obtain the linear scaling methods for very large systems. The density matrix at zero temperature is a projection operator which projects onto the space of the occupied particle wavefunctions. We define the density matrix in r representation by [57, 70]

$$\mathcal{F}(r, r') = \sum_i \psi_i^*(r) n_i \psi_i(r'), \quad r, r' \in \mathbb{R}^3, \quad (1.8)$$

where the atomic orbits $\{\psi_i\}$ are used and $\{n_i\}$ are occupation numbers. Knowing \mathcal{F} one has therefore the complete information about the quantum mechanical system. One can either create a set of vectors that will span the space by applying \mathcal{F} to N linearly independent vectors, or calculate the total energy directly from the density matrix in a discretized version. The density matrix \mathcal{F} can be defined as a matrix functional of the Hamiltonian \mathcal{H} :

$$\mathcal{F} = f(\mathcal{H}).$$

The function f is the Fermi distribution

$$f(x) = \frac{1}{1 + e^{(x-\mu)/(k_B T)}},$$

where μ is the chemical potential, T the temperature, and k_B Boltzmann’s constant.

As was pointed out that the density matrix is a projection matrix that projects onto the space of the occupied independent particle orbitals. The problem in the content of $\mathcal{O}(N)$ algorithms is consequently to find a prescription to construct the density matrix to this system, namely to calculate the density matrix directly as a matrix functional of \mathcal{H} avoiding any reference to orbitals. In a localized basis set both \mathcal{H} and \mathcal{F} are sparse. The basic linear algebraic operations involving \mathcal{H} and \mathcal{F} such as matrix times vector multiplications can therefore be done with linear scaling.

A simple computational functional representation has been proposed by Goedecker and Colombo [37] in 1994, a polynomial Fermi operator expansion. The simple

minded polynomial representation

$$\mathcal{F} \approx p(\mathcal{H}) = c_0 I + c_1 \mathcal{H} + c_2 \mathcal{H}^2 + \cdots + c_n \mathcal{H}^n$$

is numerically unstable. The Fermi operator expansion method approximates f by a Chebyshev polynomial expansion \mathcal{T} , which is to compute

$$\mathcal{F} \sim f(\mathcal{H}) \sim \mathcal{T}(\mathcal{H}) = \frac{c_0}{2} I + \sum_{j=1}^{n_{pl}} c_j T_j(\mathcal{H}),$$

where n_{pl} is the degree of the polynomial needed to represent the Fermi distribution, and $T_j(\mathcal{H})$ is the Chebyshev polynomial:

$$\begin{aligned} T_0(\mathcal{H}) &= I, \\ T_1(\mathcal{H}) &= \mathcal{H}, \\ T_{j+1}(\mathcal{H}) &= 2\mathcal{H}T_j(\mathcal{H}) - T_{j-1}(\mathcal{H}). \end{aligned}$$

The linear scaling of computing band structure energy can be obtained by “nearsightedness” of $\mathcal{T}_j(\mathcal{H})$. For the k th column of the matrix $T_j(\mathcal{H})$, there is a localization region, which is centered at the atom to which the k th basis belongs. Therefore, a truncated Hamiltonian \mathcal{H} can be used to obtain the band-structure energy E_{BS} :

$$E_{BS} = \sum_k \sum_l (\mathcal{T}(\mathcal{H}))_{kl} \mathcal{H}_{lk} = \text{Tr}(\mathcal{T}(\mathcal{H})\mathcal{H}),$$

where $\text{Tr}(\mathcal{M})$ and \mathcal{M}_{kl} denote the trace and the (k, l) th entry of a density matrix \mathcal{M} , respectively [74]. Notice that the trace can not be used in numerical calculation because of a truncated Hamiltonian, although for simplicity it is still written as the trace.

The key idea of the Fermi operator expansion is that all operations can be done by repeated applications of \mathcal{H} to basis function, which amounts to repeated multiplication of a matrix and a vector. At each step one of the localized basis functions is treated. The Chebyshev expansion method can be a very efficient procedure if the basis set is small, e.g., in tight-binding models, where n_{pl} is only a factor larger than N .

- *Density matrix minimization method*: Minimization is one of the basic approaches in traditional electronic structure algorithms. Since the energy can always be written in terms of the density matrix, we can define and minimize a grand potential Ω in terms of the density matrix \mathcal{F} .

Li et al. [63] showed how to use a minimization method to drive the density matrix to its proper $T = 0$ form in 1993. The starting point is the “McWeeny purification” idea [71]: If \mathcal{F} is an approximate trial density matrix with eigenvalues between 0 and 1, then the matrix $3\mathcal{F}^2 - 2\mathcal{F}^3$ is always an improved approximation to the

density matrix with eigenvalues closer to 0 or 1. This can be illustrated by the function $y = 3x^2 - 2x^3$. It is easy to see that for $x < 1/2$, $y < x$, the occupation is closer to 0, whereas for $x > 1/2$, $y > x$, the occupation is closer to 1.

However, if one iterates the matrix using the purification equation

$$\Omega = Tr(\mathcal{F}\mathcal{H}) \rightarrow Tr\left((3\mathcal{F}^2 - 2\mathcal{F}^3)\mathcal{H}\right)$$

alone, there is no reason for the eigenvectors to correspond to the lowest energy states. In order to make a functional which yields the proper idempotent density matrix when the total energy is minimized, one can shift the Hamiltonian to obtain the modified "purified" form

$$\Omega = Tr(\mathcal{F}(\mathcal{H} - \mu I)) \rightarrow Tr\left((3\mathcal{F}^2 - 2\mathcal{F}^3)(\mathcal{H} - \mu I)\right), \quad (1.9)$$

where the term μI is to ensure that $Tr(\mathcal{F})$ equals the number of the electrons.[†] Since Ω is a minimum for the true density matrix, this functional can be minimized by iterative methods such as the conjugate-gradient method. Any matrix satisfying the physical conditions can be used as a starting point. The $\mathcal{O}(N)$ algorithm can be obtained by implying the locality or "nearsightedness" properties of the density matrix.

A principle difficulty with this method is that it requires explicit operations of multiplying matrices which are of the size of the basis N_{basis} . Thus it is appropriate for small bases such as in tight-binding, but not for large bases such as plane waves.

1.2. Orbital-free methods

In the spirit of the Thomas-Fermi (TF) approach, it is desirable to approximate the kinetic energy by a functional of the density alone, free of orbitals. Based on the TF type kinetic energy approximations, another group of linear scaling methods are then proposed, which is the so-called orbital-free density functional Theory (OF-DFT). The details of the OF-DFT methods will be discussed in the following sections.

Although the study on OF-DFT has a much longer history than that on the Kohn-Sham type DFT (KS-DFT), it had not yet become a mainstream quantum mechanical method until recent years. It is noted that computational cost of the OF-DFT method scales essentially as $\mathcal{O}(N)$ while that of the KS-DFT method scales as $\mathcal{O}(N^3)$. The major obstacle of applying

[†]The diagonal part of $\mathcal{F}(r, r')$ is just the electron density [57, 70, 74]

$$\rho(r) = \sum_i \psi_i^*(r) n_i \psi(r) = \mathcal{F}(r, r), \quad r \in \mathbb{R}^3,$$

from which it is seen that

$$Tr(\mathcal{F}) = \int_{\mathbb{R}^3} \mathcal{F}(r, r) dr = \int_{\mathbb{R}^3} \rho(r) dr$$

equals the number of the electrons.

OF-DFT lies in the lack of a transferable kinetic energy density functional (KEDF) and an accurate local pseudopotentials to calculate the kinetic energy. However, the OF-DFT approach has many advantages over the KS-DFT methods, for instance

- The number of degrees of freedom is reduced.
- Without any orbital dependence, the complication and cost associated with orbital manipulation, including orbital orthonormalization and orbital localization (for linear scaling implementations) are avoided.
- For metals, the need for Brillouin-zone (k-point) sampling of the wavefunction is completely eliminated.
- The utilization of the fast Fourier transformation in solving the orbital-free model is essentially linear scaling with respect to the system size.

It should be pointed out that all above positive features will be realized only if one knows all functionals in (1.3) solely in terms of the density. Comparing to the high quality of exchange-correlation energy density functional, OF-KEDF's are still lacking accuracy and transferability for all kinds of systems. Only recently, better designed OF-KEDF's have begun to appear, along with highly efficient numerical implementations for large scale simulations [38, 101]. Orbital-free models thus permit to simulate much larger systems than Kohn-Sham models at the cost of a loss of accuracy.

The remainder of this paper is arranged as follows: In the coming two sections, typical kinetic energy functionals and exchange-correlation corrections are introduced, respectively. In Section 4, a couple of pseudopotentials used in orbital-free methods are addressed. In Section 5, some more details about the numerical implementations of orbital-free methods are discussed. Finally, some concluding remarks and future prospects are presented.

2. Kinetic energy functional approximation

To make OF-DFT methods practical in calculations, an accurate formulation of the kinetic energy as well as the potential energy contributions in terms of the electron density should be made. To this end, making direct approximations for $T(\rho)$ invests a great effort in developing orbital-free density functional theory.

2.1. Thomas-Fermi model

The first direct approximation for $T(\rho)$ is the TF model, which is exact for a uniform system:

$$T_{TF}(\rho) = C_{TF} \int \rho^{\frac{5}{3}}, \quad (2.1)$$

where

$$C_{TF} = \frac{3}{10}(3\pi^2)^{\frac{2}{3}}.$$

The TF model is derived from the local implementation of a uniform free electron gas model and is known to be exact when the number of electrons tends to infinity.

Although the TF model is simple in computation, it is only exact for free-electron gas. The formulation (2.1) has the following drawbacks:

- At the nucleus of the atom the density is incorrectly predicted to be infinite.
- No molecular system is stable relative to dissociation into constituent fragments.
- The electronic charge density does not exhibit shell structure in any form. The density does not decay exponentially in the classically forbidden region.
- The total energies predicted for atomic systems give at best an order of magnitude estimate, and can not be relied on for quantitative calculations.

2.2. The Thomas-Fermi-von Weizsäcker model

The limitations of the TF model have motivated a number of developments leading to systematic improvement of the TF kinetic energy functional. The first improvement to the functional was proposed by von Weizsäcker [96] in 1935, which incorporated the inhomogeneity of the electron density as a gradient correction about the uniform gas. The total kinetic energy is rewritten by

$$T_{TF\lambda W}(\rho) = T_{TF}(\rho) + \lambda T_W(\rho), \quad (2.2)$$

where the von-Weizsäcker correction term T_W is given by

$$T_W(\rho) = \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho}. \quad (2.3)$$

The value of the parameter λ is either determined empirically for getting good atomic energies or obtained by some semiclassical arguments. For example, it has been found that $\lambda = 1$ which is the original von Weizsäcker value works best in the case of rapidly varying densities. For slowly varying densities, the conventional gradient expansion with $\lambda = \frac{1}{9}$ yields improved results, which has been shown to give the correct second order gradient expansion correction [110] to the TF functional. The value like $\lambda = \frac{1}{5}$ has been found empirically by Tomishima and Yonei [92] which predicts rather accurate atomic ground state energy for a wide range of atoms.

The $T_{TF\lambda W}$ functional is exact for the ground state of a system with one or two electrons or in systems where one-electron wavefunctions have no overlap. However, the linear response (LR) behavior [82, 98] is still incorrect. It has been established that the correct LR behavior is the key point to

- reproducing the atomic shell structure;
- reproducing the near-neighbor oscillations and the asymptotic Friedel oscillations in the density for solid metals;
- permitting a much better flexibility for the density functionals to adjust to any local environment and chemical changes.

So further LR based corrections are needed to incorporate the LR behavior into the design of better OF-KEDF's.

2.3. Linear response correction model

The kinetic energy models above do not satisfy the exact LR behavior in the homogeneous limit and the simple local gradient correction used can not reproduce the oscillatory atomic shell structure. A modification of the kinetic energy functional which is a somewhat different combination of the TF term T_{TF} and the gradient correction given by von Weizsäcker T_W has been suggested as follows:

$$T(\rho) = F(N)T_{TF}(\rho) + T_W(\rho), \quad (2.4)$$

where N is the number of electrons and the factor $F(N)$ is

$$F(N) = \left(1 - \frac{2}{N}\right) \left(1 - \frac{A_1}{N^{1/3}} + \frac{A_2}{N^{2/3}}\right)$$

with optimized parameter values A_1 and A_2 . This kinetic energy functional is known to describe the response properties of the electron gas well and has yielded very good polarizabilities for various atomic systems [40]. It also provides an excellent representation of the kinetic energy of atoms [33, 34].

However, since only a truly nonlocal KEDF can satisfy the exact LR condition, we have to modify the kinetic energy by the nonlocal terms completely determined by the requirement that linear response is exactly satisfied.

In 1994, Perrot proposed another functional by adding a term to the TF and the von Weizsäcker functional with an integration kernel $K_\alpha(r - r')$ to incorporate the correct linear response [81]:

$$T(\rho) = T_{TF}(\rho) + T_W(\rho) + \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} dr dr' P(r) K_\alpha(r - r') P(r'), \quad (2.5)$$

where

$$P(r) = \frac{6}{5} \frac{\rho_\alpha + v \Delta \rho}{\rho} \left(\rho^{\frac{5}{6}} - \rho_\alpha^{\frac{5}{6}} \right)$$

with $v = \frac{5}{\sqrt{32}}$ and ρ_α the average electron density. This functional has the correct scaling for $\rho_\alpha \rightarrow 0$, incorporates the proper linear response for perturbations both small and large.

The correction term of the TF and the von Weizsäcker functional can also be formed by Wang and Teter [97]. The Wang-Teter kinetic energy is determined by

$$T_{WT}(\rho) = T_{TF}(\rho) + T_W(\rho) + F_{WT}(\rho), \quad (2.6)$$

where

$$F_{WT}(\rho) = -\frac{32C_{TF}}{25} \int_{\mathbb{R}^3} \rho^{\frac{5}{3}} + \frac{4C_{TF}}{5} \int_{\mathbb{R}^3} \rho^{\frac{5}{6}} K_{WT} * \rho^{\frac{5}{6}}. \quad (2.7)$$

The convolution kernel K_{WT} is given in Fourier space in terms of the Lindhard susceptibility function, which is already available for a nearly free electron gas system [98]:

$$\widehat{K}_{WT}(\eta) = \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right)^{-1} - 3\eta^2 + \frac{3}{5}.$$

Furthermore, there exists an important group of KEDF's based on linear response theory which contain the Wang-Teter model. These functionals take the form

$$T_s(\rho) = T_{TF}(\rho) + T_W(\rho) + T_K(\rho), \quad (2.8)$$

where the kernel term $T_K(\rho)$ is expressed as

$$T_K(\rho) = C_{TF} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho^\alpha(r) \omega(r, r') \rho^\beta(r') dr dr'. \quad (2.9)$$

Obviously different functionals of this class are determined by the constants α and β and the kernel function ω . A standard treatment based on the linear response of the noninteracting electron gas leads to a simple expression in reciprocal space for ω when it is taken to be density-independent. It is shown in [98] that the choice

$$\alpha = \frac{5 + \sqrt{5}}{6}, \quad \beta = \frac{5 - \sqrt{5}}{6}$$

or

$$\alpha = \frac{5 - \sqrt{5}}{6}, \quad \beta = \frac{5 + \sqrt{5}}{6}$$

was optimal for the density-independent kernel.

The latter improvements were recently developed by Wang, Govind and Carter (WGC) [99], who generalize (2.9) to density-dependent kernels. These KEDF's will be denoted by WGC-DI and WGC-DD for the density independent and density-dependent kernel functionals, respectively.

Another kind of approximation for kinetic energy functionals has been proposed by Ludena group, within the local scaling transformation version of the DFT [69]. The theory seeks to develop well-defined procedures for the construction of N -representable density functionals, expressed in terms of one particle density. It turns out that these functionals then necessarily depend upon the number of particles N and on the symmetry of the system. A few applications to single atom and clusters implemented by Kanhere et al. [51] have shown promising results.

The KEDF's mentioned above indicate that the field is alive and in future one should hope to obtain more accurate kinetic energy functionals for orbital-free molecular structure calculations.

3. Exchange-correlation corrections

As the same as the KS method, the exchange-correlation correction expressed as a functional, $E_{xc}(\rho)$, of the density ρ is also a crucial quantity in the orbital-free methods for the kinetic energy and the Hartree energy terms in (1.3).

The first obvious exchange-correlation correction to the basic TF theory, which adds an exchange term to the total energy carries the name Thomas-Fermi-Dirac (TFD) [22] in 1930. But this model can actually be worse [74] because the most important correction to TF theory is the inclusion of the cusp condition near the nucleus, which makes the electronic density finite there. The cusp term may arise from a gradient correction term. However, the exchange-correlation corrections work especially well combined with the LR-based kinetic energy models described above.

To particularize the exchange-correction energy term in (1.6), we introduce a simple approximation of $E_{xc}(\rho)$ by LDA which assumes that the exchange-correlation energy functional is purely local. It consists in taking

$$E_{xc}^{LDA}(\rho) = \int_{\mathbb{R}^3} \rho \varepsilon_{xc}^{LDA}(\rho) = \int_{\mathbb{R}^3} \rho \left(\varepsilon_x^{LDA}(\rho) + \varepsilon_c^{LDA}(\rho) \right), \quad (3.1)$$

where ε_{xc}^{LDA} is the exchange-correlation energy per particle in a uniform electron gas of density ρ . Several parameterizations exist for the exchange-correlation energy of a homogeneous electron gas, all of which lead to similar total energy results. One of the widely used interpolation formulas is [80]

$$\varepsilon_x^{LDA}(\rho) = -\frac{3}{4} \left(\frac{3\rho}{\pi} \right)^{\frac{1}{3}},$$

$$\varepsilon_c^{LDA}(\rho) = \begin{cases} 0.0311 \ln r_s - 0.0480 + 0.0020 r_s \ln r_s - 0.0116 r_s & \text{if } r_s < 1, \\ -0.1423 / (1 + 1.0529 \sqrt{r_s} + 0.3334 r_s) & \text{if } r_s \geq 1, \end{cases}$$

where $r_s = \left(\frac{3}{4\pi\rho} \right)^{\frac{1}{3}}$.

There are additional improvements of the exchange-correlation functional. The first step consists in introducing spin dependent densities $\rho_+(x)$ and $\rho_-(x)$ in order to discriminate between spin-up and spin-down electrons and in building local spin density approximation (LSDA). Then the exchange-correlation functional can be expressed in the form of

$$E_{xc}^{LSDA}(\rho_+, \rho_-) = \int_{\mathbb{R}^3} \rho \varepsilon_{xc}^{LSDA}(\rho_+, \rho_-). \quad (3.2)$$

From a theoretical point of view, there is no need to introduce explicit spin dependence in the picture. The reason why LSDA usually gives better results than LDA is that the spin-dependent approximate local exchange-correlation functionals are better than the spin-independent ones.

The second step is to take into account density inhomogeneities in the evaluation of E_{xc} via a local expansion of the exchange-correlation energy density in terms of ρ_{\pm} and $\nabla\rho_{\pm}$ as follows:

$$E_{xc}^{GGA}(\rho_+, \rho_-) = \int_{\mathbb{R}^3} f(\rho_+, \rho_-, \nabla\rho_+, \nabla\rho_-), \quad (3.3)$$

which is the so-called GGA expression. The acronym GGA stands for Generalized Gradient Approximation. The most commonly used two representatives of this category are the exchange-correlation energy of Perdew and Wang [79] in 1986 and Perdew, Burke, and Ernzerhof [78] in 1996. Both of them are non-empirical in the sense that the determination of the function f does not use any experimental data. They are based on a fine analysis of the so-called exchange-correlation hole [78].

There are also some further improvements of the exchange-correlation functionals which involve dependence on the Kohn-Sham density matrix [7] or orbital-dependent interactions [4, 5]. However, this kind of functions may not be available in OF-DFT model which is independent of the wavefunctions. The construction of more sophisticated exchange-correlation functionals which are able to describe fine phenomena such as hydrogen bonding of van der Waals forces, is still an active field of research.

4. Pseudopotentials for OF-DFT model

Solving the kinetic energy problem does not, however, mean that full OF-DFT calculations are immediately possible. The other terms in (1.3) should be considered.

The interactions between nuclei and electrons represented by the last term in (1.3) are described by pseudopotential. The pseudopotential removes the core electrons and replaces them and, the strong ionic potential by a weaker pseudopotential. Note that OF-DFT methods are purely based on the density, the lack of orbitals requires that the pseudopotential must be independent of angular momentum character, but a function of the radius only. Most modern pseudopotentials such as norm-conserving or ultra-soft pseudopotential contain several angular momentum contributions. They are described nonlocally and can not be used in the OF methods. Hence, local pseudopotentials (LPS) are needed.

For example, in the crystal electronic structure calculation by plane wave basis, the valence electron-ion interaction can be written as

$$E_{ext}(\rho) = \int V_{ext}\rho,$$

where $\rho(r)$ is the valence density at the point r and V_{ext} is the electron-ion interaction potential

$$V_{ext}(r) = \int v_{ps}(|r - r'|) \sum_i \delta(r' - R_i) dr' = \int e^{-ik \cdot r} S(k) v_{ps}(k) dk$$

with $v_{ps}(r)$ the pseudopotential for one atom, R_i the position of the i th ion, and $S(k)$ the "structure factor" $\sum_i e^{ik \cdot R_i}$.

A more particular pseudopotential called Goodwin-Needs-Heine (GNH) pseudopotential which describes the electron-ion interactions was introduced in [39] in 1990. The pseudopotential for a single atom can be formulated as

$$V_a(\tilde{r}) = \frac{2}{\pi} \int_0^\infty \frac{\sin(\tilde{r}t)}{\tilde{r}t} \left((Z - AR) \cos(Rt) + A \frac{\sin(Rt)}{t} \right) e^{-(t/R_c)^6} dt, \quad (4.1)$$

where Z is the valence, the parameters R_c , A and R are given in [39] and \tilde{r} is the distance between the electrons and the ion. Once the pseudopotential for a single atom is computed, the pseudopotential for a system with N_a atoms located at $\{R_i\}_{i=1}^{N_a}$ can be evaluated as

$$V_{ext}(r) = \sum_{i=1}^{N_a} V_a(|r - R_i|). \quad (4.2)$$

Although the empirical local pseudopotentials such as (4.1) have been used, the most widely used way to treat the problem of the lack of accurate transferable local pseudopotentials is to construct suitable pseudopotentials from first-principles (*ab initio* pseudopotential), on the basis of KS all-electron calculations on atoms [16, 100, 102, 116].

The Hohenberg-Kohn theorem, which states that the external potential is one-to-one mapped to the ground state electron density, is exploited. By employing a scheme for inverting the KS equations due to Wang and Parr [100], the KS effective potential V_{eff} can be iteratively solved until it reproduces a target density. We start from the KS equation

$$\left(-\frac{1}{2}\Delta + V_{eff} \right) \phi_i = \varepsilon_i \phi_i,$$

which leads to an exact expression for the local KS effective potential

$$V_{eff} = \frac{\rho + \sum_i^{occ.} f_i \phi_i^* (\frac{1}{2}\Delta) \phi_i / \varepsilon_i}{\bar{\rho}}, \quad (4.3)$$

where

$$\rho = \sum_i^{occ.} f_i \phi_i, \quad \bar{\rho} = \sum_i^{occ.} \frac{f_i \phi_i}{\varepsilon_i},$$

and f_i is the occupation number of the orbital ϕ_i . Note that from the KS iteration process

$$\left(-\frac{1}{2}\Delta + V_{eff}^{n-1} \right) \phi_i^n = \varepsilon_i^n \phi_i^n, \quad (4.4)$$

we have an approximation for the local potential in an iterative form:

$$V_{eff}^n = V_{eff}^{n-1} + \frac{\rho - \rho^n}{\bar{\rho}^n}. \quad (4.5)$$

And one of the widely used *ab initio* pseudopotential for bulk environment is then proposed in [116]. Based on the Wang-Parr approach for the local potential, a global LPS for the entire system can be derived from V_{eff} . This global LPS is then further decomposed to obtain an atom-centered LPS. It is shown that the LPS derived from bulk environments is substantially more transferable than those derived from atoms alone [116].

In conclusion, since the valence orbitals are usually slowly varying and fewer basis functions are needed to approach the model limit, the use of local pseudopotentials can reduce the computational cost remarkably. Moreover, the accuracy for the recently proposed non-local LR-based OF-DFT methods can be improved because the resulting pseudopotential is weaker, and hence is more applicable in the LR regime, where the theory is designed to be accurate.

5. Numerical discretizations

Now that each term in (1.2) has been explicated, especially the theoretical foundation for the OF-KEDF's has been laid, the energy functional in minimization problem (1.1) can be formulated clearly in terms of the density functional. Mathematically, the total energy functional can be minimized in the admissible class

$$\mathfrak{A} = \left\{ \rho \geq 0 : \int_{\mathbb{R}^3} \rho = N, \rho^{-\frac{1}{2}} \nabla \rho \in L_2(\mathbb{R}^3) \right\}, \quad (5.1)$$

where $L_2(\mathbb{R}^3)$ represents the set of square integrable functions. And it is not so easy to obtain either existence or uniqueness of the minimization solution (see, e.g., [8, 14, 57, 58, 64, 65] and references cited therein).

As in the case of the KS problem, there are mainly two types of approaches to solve the minimization problem (1.1) numerically, the direct minimization method and the variational optimization method. Here we will introduce these two methods respectively in addition to the Car-Parrinello dynamic method.

5.1. Direct minimization method

We will first introduce the method that searches the electronic state that minimizes the total energy functional (1.1) under the constraint (5.1) directly.

The simplest approach is the steepest-descent method, which moves the initial point in the negative gradient direction. Though the steepest-descent method is simple to implement, it is a well known poor minimization algorithm especially when the region around the minimum forms a long narrow valley.

The most widely used method for the energy minimization is the conjugate-gradient method. Such a method for the KS problem is well developed in plane wave *ab initio* modeling of semi-conductor material system [77, 90]. Indeed, it is an efficient method for the OF method, too. Starting from an initial guess, a conjugate-gradient algorithm for a numerical optimization problem usually involves three steps:

- Step 1: Calculate the steepest descent vector;
- Step 2: Construct the conjugate-gradient vector;
- Step 3: Update the optimization variables by moving along the conjugate vector direction for a certain distance that is determined either by an exact line search or by approximations. Note that the normalization constraint is imposed at each step for optimization [49].

The conjugate-gradient algorithm for OF calculation is very close to the band-by-band direct minimization conjugate-gradient method used in Kohn-Sham calculations [48, 90]. There is however one critical difference. In the KS calculation, one might orthogonalize the steepest vectors and conjugate-gradient vectors to other bands in every iteration step, where the computational cost scales $\mathcal{O}(N^3)$. In contrast, there is no orthogonalization process in the OF method described above which dramatically reduces the computation efforts [49]. And it is found to be more stable and accurate by this conjugate-gradient method compared with the conventional variational method.

Note that there are many other efficient numerical ways for minimization problems with constraints, such as Truncated-Newton methods [21, 66, 73] and projected gradient methods [9, 61, 84]. These tools can also be applied to the electronic structure calculations by OF methods. In practice, currently, the minimization problems are often discretized by plane wave methods. Nonetheless, finite difference and finite element methods can also be used in the minimization discretization (see, e.g., [30, 32, 109] and references cited therein).

5.2. Variational method

In this subsection, we will introduce the conventional variational method. Given the total energy in (1.2), one can write down a general density functional $L(\rho)$ for a system with a fixed number of electrons N :

$$L(\rho) = E(\rho) - \mu \left(\int_{\mathbb{R}^3} \rho - N \right), \quad (5.2)$$

where μ is a Lagrange multiplier. $L(\rho)$ will be minimized with respect to ρ to determine the ground state of the system:

$$\frac{\delta L(\rho)}{\delta \rho} = 0, \quad (5.3)$$

which leads to

$$\frac{\delta T(\rho)}{\delta \rho} + V_{eff} = \mu. \quad (5.4)$$

In (5.4), $V_{eff} = V_{ne} + V_H + V_{xc}$, where V_{ne} denotes the static total electron-ion potential, V_H is the Hartree potential of the electrons, and V_{xc} is the exchange-correlation potential

$$V_{xc} = \frac{\delta E_{xc}(\rho)}{\delta \rho}. \quad (5.5)$$

Now we can obtain the electron density ρ of the system by solving (5.4) under the constraint (5.1). However, one would rather work with a new variational variable φ satisfying $\rho = \varphi^2$ to ensure a positive ρ during the entire minimization process. Another advantage of using φ instead of ρ is that the presence of ρ in the denominator in the kinetic energy (2.3) can result in numerical instabilities [30].

Using the TF-von Weizsäcker (TFvW) kinetic energy functional (2.3) where $\lambda = 1$, a more regular expression for the energy can be obtained. Noting that

$$\frac{\delta T_W(\rho)}{\delta \rho} = \frac{1}{8} \frac{|\nabla \rho|^2}{\rho^2} - \frac{1}{4} \frac{\nabla^2 \rho}{\rho}$$

and

$$\frac{1}{8} \frac{|\nabla \rho|^2}{\rho^2} = \frac{1}{2} \frac{|\nabla \sqrt{\rho}|^2}{\rho},$$

from which we can obtain that

$$\frac{\delta T_W(\rho)}{\delta \rho} = -\frac{1}{2} \frac{\nabla^2 \sqrt{\rho}}{\sqrt{\rho}}. \quad (5.6)$$

Thus, one can easily reach the Thomas-Fermi-Hohenberg-Kohn (TF-HK) equation in a fully equivalent quasi-orbital form [98]

$$\left(-\frac{1}{2} \nabla^2 + \frac{\delta T_{TF}(\rho)}{\delta \rho} + V_{eff}^{KS} \right) \varphi = \mu \varphi. \quad (5.7)$$

Note that in the conventional equation, $\sqrt{\rho}$ is used instead of φ . However, this φ function is more general than the $\sqrt{\rho}$ formulation, because φ behaves truly like an orbital, with positive and negative regions, while $\sqrt{\rho}$ is semipositive everywhere. Some theorems presented in [30] promise that the two minimization problems over $\sqrt{\rho}$ and φ are coincidental and they have the same energy minimum. Therefore, the constraint $\varphi \geq 0$ does not affect the Euler-Lagrange equation.

It is also important to notice that (5.7) can closely resemble (2.4), (2.5) or (2.6). The KEDF forms we got in Section 2.3 are to be used to derive the other forms of the TF-HK equations. Note that the OF TF-HK equations have the same form as the KS equations, but much simplified since there is only one "orbital" to be solved. As in the KS equation, this nonlinear eigenvalue problem has to be solved in a self-consistent way.

The procedure requires an initial guess for the electronic charge density, from which the Hartree potential and the exchange-correlation potential can be calculated. The Hamiltonian matrices must be constructed and diagonalized to obtain the eigenstate φ . This eigenstate will normally generate a different charge density to construct the electronic potentials, and hence a new Hamiltonian matrix can be constructed using the new electronic potentials. The eigenstate of the new Hamiltonian is then obtained, and the process is repeated until the solutions are self-consistent. In practice the new electronic charge density is taken to be a combination of the electronic charge densities generated by the old

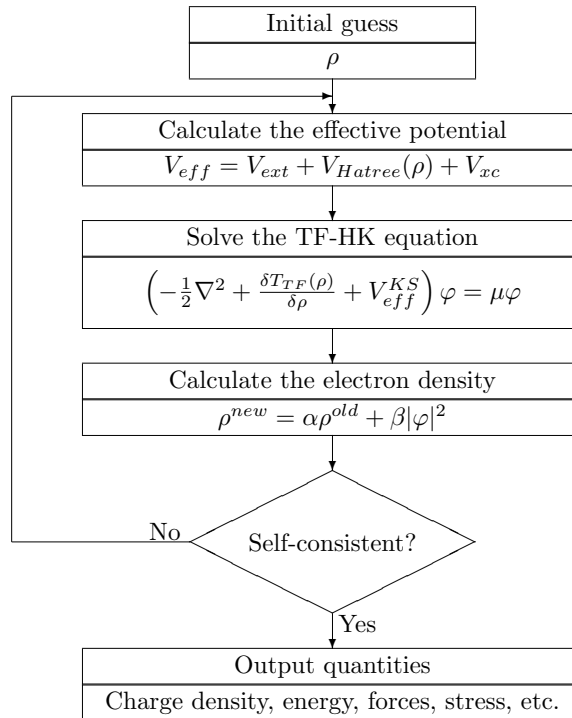


Figure 1: Self-consistent loop for TF-HK equation.

and the new eigenstate, since this speeds the convergence to self-consistency. The whole self-consistent procedure are summarized in the flow chart in Fig. 1.

Among the numerical discretization methods used in the self-consistent loop to solve (5.7), the most widely used methods are the linear combination of atomic orbitals (LCAO)–usually Gaussian-type orbitals (GTO), plane waves (PW), finite differences (FD), and finite elements (FE). Of these methods, the FD and FE methods are the most recent and less common. In a FD method, the kinetic energy Laplacian operator is evaluated from values of the function as a set of grid points. And there are a number of working FD algorithms applied to the electronic structure calculation which involve full “ab initio” self-consistent process [18, 19, 53, 60, 95]. In contrast, the FE method forms a localized basis in which the variational calculations can be done, unlike the FD method which simply approximates the Laplacian. Examples of the strictly localized basis for the electronic structure calculations are piecewise linear functions [1, 85], piecewise cubic functions [75, 76], a B-spline basis [41], and piecewise third-order polynomials [94].

General fully 3D grid-based electronic structure representation using the FD and FE methods as approximate numerical schemes for partial differential equations have started being used in the last decades only. However, the FD and FE approaches have already shown to be an efficient tool in a substantial number of large scale electronic structure calculations. There are many reasons why the FD and FE methods for electronic structure calculation are robust.

- In recent years, large parallel supercomputers have become an essential tool in first-principles molecular dynamics simulations. In a real space approach, all the expensive operations can be done locally to compute matrix elements between wavefunctions. And the local contributions can be summed up after being computed on every processing element.
- Since arbitrary boundary conditions are available, the real space methods can treat a model that corresponds to the actual experiment. In addition, simulation in which an electric or magnetic field is applied is possible.
- Since all of the calculations are carried out in real space, it is easy to incorporate the orbital localized in a finite region which is required for the $\mathcal{O}(N)$ calculation.
- Another key element in the development of efficient grid-based real space approaches is the multigrid method. The real space large scale *ab initio* calculations involve large sparse matrices and multigrid methods, either as solvers or as preconditioners, allow to design very efficient scalable algorithms.
- Other advantages of FD and FE methods over PW approaches include the use of local mesh refinements. As a result, adaptive computational algorithms may be devised.

Indeed, electronic structure calculations using the FE discretizations have been successfully applied to many problems, including clusters and other finite systems (see, e.g., [6, 20, 24, 31, 32, 62, 67, 75, 76, 85, 86, 93, 94, 104, 112] and references cited therein). Recently, in particular, some mathematical analysis of finite dimensional approximations for the ground state solution of a molecular system have been presented on the TFvW-type setting, and several convergence and upper error bounds of the approximations have been obtained in [113], which provided a mathematical justification of finite dimensional approximations in both the directly minimizing method and the variational method.

5.3. Car-Parrinello method

The Car-Parrinello molecular dynamics (MD) method stands out as one of the most efficient methods for computing the properties of materials for electronic equations, which can be also used in the OF-DFT methods [52]. The approach by Car and Parrinello [11, 12] combines MD and DFT into one unified algorithm for electronic states, self-consistency and nuclear movement. In this scheme, nuclear and electronic dynamics are considered together so that the ionic and electronic degrees of freedom are relaxed simultaneously. Altogether, there are four obvious advances of the Car-Parrinello method used in the electronic structure calculation:

- optimization methods instead of variational equations;
- equations of motion instead of matrix diagonalization;
- fast Fourier transforms instead of matrix operations;
- a trace of occupied subspace instead of eigenvector operation.

Note that in the orbital-free approach, the total energy is a functional of charge density only. We may apply the Car-Parrinello technique to this energy functional, too (see, e.g., [52]). Let the pseudo-Lagrangian be defined by

$$L = T_e + T_a - E(\rho, R_n) + \lambda \left(\int_{\mathbb{R}^3} \rho - N \right), \quad (5.8)$$

where N is the number of the electrons and R_n denotes the coordinates of the n th nuclear. The first term representing the fictitious kinetic energy associated with the electronic degrees of freedom is

$$T_e = \mu \int_{\mathbb{R}^3} \dot{\varphi}^2,$$

where $\dot{\varphi} = d\varphi/dt$, $\varphi^2 = \rho$, and the fake mass μ is the parameter to model classical motion of charge density analogous to that of electronic orbital motion. The second term in the Lagrangian is the kinetic energy of nuclei

$$T_a = \frac{1}{2} \sum_n M_n |\dot{R}_n|^2,$$

where M_n is the mass of the n th nucleus. The third term in (5.8) is the total electronic energy of the combined system of electrons and ions. The above Lagrangian leads to the MD equations for both classical ionic degrees of freedom $\{R_n\}$

$$M_n \ddot{R}_n(t) = -\nabla_n E \quad (5.9)$$

and electronic degrees of freedom $\varphi(r, t)$

$$\mu \ddot{\varphi}(r, t) = -\frac{\partial E}{\partial \varphi(r, t)} + \lambda \varphi(r, t), \quad (5.10)$$

respectively, under the constraint that the total charge density of the system is conserved:

$$\int_{\mathbb{R}^3} \varphi^2 = N.$$

In general, the numerical solution of (5.9) is obtained by the Verlet algorithm. That is, we can update the ionic positions for the next time instant from the ionic positions at the previous two time steps

$$R_n(t + \Delta t) = 2R_n(t) - R_n(t - \Delta t) + \frac{(\Delta t)^2}{M_n} \left(\frac{\partial E}{\partial R_n}(t) \right) \quad (5.11)$$

and the velocities for calculating the kinetic energy of the ions

$$\dot{R}_n(t) = \frac{R_n(t + \Delta t) - R_n(t - \Delta t)}{2\Delta t}.$$

Similarly, the motion of electronic degrees of freedom (5.10) is simulated by updating the root charge density from the charge densities at previous two time instants

$$\varphi(t + \Delta t) = 2\varphi(t) - \varphi(t - \Delta t) + \frac{(\Delta t)^2}{\mu} \left(\frac{\partial E}{\partial \varphi}(t) + \lambda\varphi(t) \right)$$

and the velocities of electrons are

$$\dot{\varphi}(t) = \frac{\varphi(t + \Delta t) - \varphi(t - \Delta t)}{2\Delta t},$$

where the time step for evolving the ionic and electronic are identical.

The time step Δt and the fake mass μ should be chosen carefully such that the dynamics of electrons remains adiabatic, which means that the system should remain in its electronic ground state during the motion. Choosing a small value of μ will make the dynamics adiabatic, but the time step Δt is governed by the value μ to be small since the frequency associated with the electronic system $\omega = 2\pi/\Delta t$ scales as $\mu^{-\frac{1}{2}}$, and such a small time step is not very profitable for long computational runs. Furthermore, a long time step may cause a slow upward drift in the energy. So one needs to choose an optimum value of Δt and μ such that the dynamics is stable.

However, this method does not guarantee to reach the global minimum of the system, the conjugate-gradient methods can not be employed to achieve this purpose neither. To reach the global minimum of a system, one has to span the configuration space extensively. For example, the simulated annealing technique is one of the most useful methods to overcome this difficulty. The atomic structure of clusters was usually obtained by minimizing the orbital-free energy by varying the nuclear coordinates using a simulated annealing procedure.

5.4. Numerical examples

In this subsection we will illustrate the OF-DFT method by some numerical examples in literature. Both the variational method and the direct minimization method will be considered.

First, we take a nearly free-electron-like metal (solid Aluminum) as an example. For periodic systems, such as solid state systems, the KS-DFT scales as $\mathcal{O}(N_k \cdot N^3)$, where N_k is the number of the \mathbf{k} points used for the Brillouin-zone (BZ) sampling, and N is the number of atoms which can be the number of order 100. For metallic systems, this BZ sampling is very expensive, and N_k can be on the order of 1000. The use of OF-DFT, however, can eliminate such a sampling, and is computationally more suitable to study very large systems especially metallic systems than KS-DFT. The empirical GNH pseudopotential (4.1) for Aluminum and the Wang-Teter kinetic energy (2.6) were applied to compute the lattice parameter. It is shown by the numerical experiments in [16, 39] that this LR-based model performs well and agrees with the experimental value and the KS-DFT.

The OF calculations on the solid Aluminum have also been performed by the real space methods. Carlos [30] minimized the energy of 365 Aluminum atoms in a face-centered-cubic (FCC) lattice by a FD method and a modified Truncated-Newton method. Gavini

et al. [32] discretized the problem (1.2) by a FE method and used a nested sequence of iterative conjugate-gradient solvers. The cluster consisting of $9 \times 9 \times 9$ FCC unit cells with 3730 atoms was simulated and the accurate numerical results obtained illustrated the efficiency of this algorithm.

Solid Silicon can be computed in a similar way. Similar conclusions were obtained when an LR-based OF-DFT model with WGC kinetic energy functional and the BLPS were used [16, 116].

To test the performance of the conjugate-gradient optimization OF methods and the OF molecular dynamic methods, we enumerate several examples. Jiang and Yang considered a Sodium cluster, Na_{216} in [48]. By using the LR-based OF model, they compared the efficiency of some direct minimization methods, the steepest-descent method (SD), the sequential conjugate-gradient method (SCG) and the concurrent conjugate-gradient method (CCG). It is seen from [48] that the convergence behavior of the conjugate-gradient methods for this realistic system can be obtained in about 50 iterations. Because there is no work for orbital orthogonalization during the iterations, the conjugate-gradient method for OF model can save a lot of work in large scale problems. Using orbital-free molecular dynamics, Kanhere and Shah gave a walk through the Li_7Al_5 cluster. The calculations were performed in a unit cell of 35 a.u. with a $64 \times 64 \times 64$ mesh, and started by choosing a random initial geometry, the total energy minimization was performed by the method of conjugate-gradients. By cooling run of the system, they carried out a calculation to find a possible global minimum for the cluster, and the configuration was obtained at the end of the cooling run. More computational results can be found in [52]. It should be pointed out that the OF molecular dynamic method would be more useful for geometry configuration of the cluster when the present kinetic energy functionals are incorporated.

6. Concluding remarks

The main advantage of using OF-DFT is the ability to construct linear scaling implementation by avoiding orbital orthogonalization. Although it is not good for total energy due to the KEDF terms, it is somehow good for the electron density and the structure [16, 26]. With present workstation computational resources, systems of thousands of atoms can be studied [46, 47, 103]. Such a size is inconceivable for the present OB *ab initio* and DFT methods. In fact, the OF-DFT scheme is purely restricted by the grid size, not by the number of electrons, and certainly has clear advantages over the OB methods. With the help of linear scaling Ewald summation techniques [2, 43], even significantly larger systems can be modeled dynamically within the DFT description using current computational power.

The OF method has become favorable due to its linear scaling. It is noted that there are a number of issues that require future investigations and there are many ongoing works which try to make the method more applicable and accurate in modeling atoms and molecules, including

- *Development of more reliable orbital-free kinetic energy functionals:* The poor quality of the OF-KEDF's had somehow weaken the further interest of the OF methods. If better high-quality nonlocal density approximation OF-KEDF's were invented, the

OF-DFT scheme would gradually regain its popularity. In previous studies of OF-DFT, conclusions were usually drawn from the results on specific systems studied by KEDF's with empirical parameters fit to those systems. Therefore, these conclusions may not be generally applicable. In [16], the work has presented an attempt to apply the same LR-based OF-DFT to study a very wide range of systems: atoms, molecules, and solids. This provides a severe test for any such theory, and helps uncover deficiencies in the present formulation. Further work along these lines could lead to a generally accurate OF-DFT.

- *Making the OF-DFT scheme entirely linear scaling:* In the formulation of KEDF's (2.5) and (2.6), one could try to reduce the computational cost from the typical quadratic scaling (from the nonlocal terms) to linear scaling. Now in the TF-HK equation, all the potential terms can be set up by conventional plane-wave-basis techniques with essentially linear scaling [77, 98, 105]. However, for very large systems with more than 5000 nuclei, the computational cost associated with the nuclear-nuclear Coulomb repulsion energy becomes the major bottleneck. In this case, linear scaling Ewald summation techniques should be utilized [2, 43].
- *Combination of the OF methods and the KS methods:* A new implementation named orbital-corrected orbital-free DFT has been developed by Zhou and Wang [114]. The work provides a new impetus to further improve OF-DFT methods and presents a robust means to significantly lower the cost associated with general applications of linear scaling KS-DFT methods on large systems of thousands of atoms. The OF-DFT combining with KS methods can remedy the drawbacks of the OF methods which lacks a transferable KEDF and accurate LPSs.
- *Multi-level computer simulations:* As an important application, OF-DFT can be used in the multi-level computer simulations which describe the complex system of different length scales by different basic physical principles. In the simulation, the orbitals of the subsystem described at the orbital level are obtained from the KS like equations with a multiplicative effective potential. This effective embedding potential is expressed by means of the electron density of the environment. Based on a mixed description of the whole system by means of embedded orbitals and electron density, a non-empirical formalism was introduced in [108]. This formalism makes it possible to link the orbital-level description with any other type of theory provided that it yields the electron density of the environment and is referred to as "orbital-free embedding formalism". The representative works concerning multi-level computer simulations using the orbital-free embedding potential can be found in [13, 45, 72, 106–108].
- *Quasicontinuum (QC) method:* The OF methods have been proven to be an efficient method applied to the QC method. The QC method proposed by Tadmor et al. [89] is a first-principles multiscale modeling approach which retains atomic resolution only where necessary and grades out to a continuum finite elements description elsewhere. The OF methods can be performed at the atomic scale where the effect of the electrons can not be omitted [24, 31, 32]. Such QC-OFDFT methods supply a

fundamental description of the material with defects like vacancies, dislocations and cracks that require quantum mechanical resolutions and are sensitive to long range continuum stresses.

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