Construction of Nonlocal Kinetic Energy Density Functional via Local Density Approximation Kernel for Isolated Systems

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Despite the large number of nonlocal kinetic energy density functionals (KEDFs) available for large-scale calculation of extended systems, these KEDFs based on the Lindhard response function, in many cases, are not suitable for the isolated systems, where deviate from the uniform electron gas scenario. In this manuscript, we proposed a generalized scheme to construct nonlocal KEDFs via the local density approximated kernel. This scheme can significantly improve the accuracy and generality of orbital-free density functional theory (OFDFT) to handle the isolated systems. We have implemented it into our developed ATLAS package under Dirichlet boundary condition and demonstrated the superior computational performances by several prototypical systems encompassing Mg, Si and GaAs clusters. The results show that the KEDFs constructed by our scheme can achieve high accuracy and numerical stability for simulations of isolated systems, applicable to design clusters and quantum dots containing a large number of atoms.
1. Introduction

Over the past few decades, *ab initio* calculation based on density functional theory (DFT) [1,2] has provided important insights into a variety of material systems and become a prevalent tool for materials discovery. Particularly, OFDFT has been recognized as a practical means for large-scale simulations, as exemplified by the calculations of Li and Mg, which contain millions of atoms in periodic simulated cell[3–5]. However, the accuracy of OFDFT heavily depends on an approximation of KEDFs since the kinetic energy has been proved to be dominant term. Therefore, the main barrier to widespread use of OFDFT is finding reliable KEDFs.

Over the past few decades, there has been great progress in development of KEDFs for periodic systems. Several nonlocal KEDFs such as Wang-Teter (WT)[6], Smargiassi and Madden (SM)[7], Perrot[8], Wang-Govind-Carter (WGC)[9,10], Huang-Carter (HC)[11] and Mi-Genova-Pavanello (MGP)[12] etc. have been proposed and successfully applied to simple metallic and semi-conducting periodic systems. However, most of these KEDFs derived from the homogeneous electron gas cannot be applied to isolated systems, in which electron density significantly deviates from the uniform electron gas scenario.

In the past decades, several attempts have been made to develop KEDFs for isolated systems. Initially, a semilocal KEDF was introduced by Chan et al.[13] and followed with several applications for metallic clusters[14–16]. Later, the advanced density dependent KEDFs have been proposed to enable OFDFT to simulate localized systems such as isolated atoms and molecules[17,18]. Recently, a family of non-local KEDFs named LX (X=WT, MGP0, MGP) were proposed using line integral and proved to achieve close to chemical accuracy for isolated systems[19]. Unfortunately, these KEDFs suffer from the numerical instability in some cases. Therefore, development of KEDF with high accuracy and numerical stability is still challenging and elusive for the isolated systems.

In this manuscript, a generalized scheme to construct KEDFs for isolated systems have been proposed via introduction of local density approximation kernel (LDAK) and applied to construct a family of nonlocal KEDFs. We have implemented these KEDFs
into ATLAS [20] for numerical solution of OFDFT under Dirichlet boundary condition (DBC). The high accuracy and numerical stability of these KEDFs are illustrated by successful reproduction of KSDFT results in several prototypical isolated systems.

The remainder of this manuscript is organized as follows. Section 2 briefly gives the OFDFT, followed by the details of KEDFs and their implementation into ATLAS under DBC. The computational details are provided in Section 3. The accuracy and numerical stability of the proposed KEDFs for isolated systems have been demonstrated in section 4. Finally, we give conclusions in Section 5.

2. Theory and Implementation

2.1 Orbital-free density functional theory

In OFDFT, the ground-state energy \( E_{GS} \) and electron density \( \rho_{GS} \) are obtained by minimizing the total energy functional \( E[\rho] \) of the \( N_e \)-electron system

\[
E_{GS}[\rho_{GS}] = \min_{\rho} \left\{ E[\rho] - \mu \left( \int \rho (\mathbf{r}) d^3 \mathbf{r} - N_e \right); \rho \geq 0 \right\},
\]

(1)

where \( \mu \) denotes the Lagrange multiplier, which is used to enforce the constraint that the total number of electrons \( N_e \). The total energy functional can be written as

\[
E[\rho] = T_s[\rho] + E_H[\rho] + E_{ie}[\rho] + E_{xc}[\rho] + E_{ii}(R),
\]

(2)

where \( T_s, E_H, E_{ie}, E_{xc}, E_{ii} \) and \( R \) denote terms of noninteracting kinetic energy, the Hartree energy, the ion-electron interaction energy, the exchange-correlation energy, the ion-ion repulsion energy and the ionic position, respectively. In contrast to the Kohn-Sham (KS) DFT, the local pseudopotentials and KEDF should be employed to describe the ion-electron interactions and non-interacting electron kinetic energy, respectively. Note that the kinetic energy, whose magnitude is comparable to total energy, is proved to be dominated among the terms of isolated systems. Therefore, construction of KEDFs with high accuracy plays a vital role in OFDFT simulations of isolated systems.

2.2 The nonlocal KEDFs for the isolated systems

Most of nonlocal KEDFs can be written in the generic form

\[
T_s[\rho] = T_{sp}[\rho] + T_{sw}[\rho] + T_{nl}[\rho],
\]

(3)
where \( T_{TF}[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \left\langle \rho^{5/3} (\vec{r}) \right\rangle \) [21–23] and \( T_{sw}[\rho] = \frac{1}{8} \left( \frac{\nabla \rho(\vec{r})}{\rho(\vec{r})} \right) \) [24] are the Tomas-Fermi and von Weizsäcker functionals, respectively. The last term in Eq. (3) is the nonlocal part of KEDFs. In this manuscript, a simplest form of nonlocal KEDFs with a density independent kernel \( w_{\alpha, \beta} \) is employed:

\[
T_{NL}[\rho] = \left\langle \rho^\alpha (\vec{r}) \right| w_{\alpha, \beta}(k^0_F, \vec{r} - \vec{r}') \left| \rho^\beta (\vec{r}') \right\rangle .
\]  
(4)

Note that the density independent kernel contains a constant Fermi wave vector of \( k^0_F = (\pi^2 \rho_0)^{1/3} \), which associates with the average density \( (\rho_0) \) in the unit cell for extended systems. Unfortunately, the average density in isolated systems is not well defined [25].

In view of the aforementioned problem, a simple scheme is proposed to reformulate the nonlocal term of KEDFs by introduction of a LDAK. Specifically, the constant \( k^0_F \) in density independent kernel of KEDFs of Eq. (4) is substituted by Fermi wave vectors of \( k_F(\vec{r}) = (\pi^2 \rho(\vec{r}))^{1/3} \) referred to the spatial electron density. In other words, a density dependent kernel dependent on the local electron density instead of average electron density is employed in our scheme. Within this scheme, the nonlocal terms of KEDFs in Eq. (4) are reformulated by

\[
T_{NL}^{\text{LDAK-Z}}[\rho] = \left\langle \rho^\alpha (\vec{r}) \right| w^X_{\alpha, \beta} \left[ k_F(\vec{r}), \vec{r} - \vec{r}' \right] \left| \rho^\beta (\vec{r}') \right\rangle ,
\]  
(5)

where \( X = \text{WT, SM, Perrot, MGP and MGP0} \). According to Eq. (5), the kinetic potentials are given by

\[
V_{T, NL}^{\text{LDAK-Z}}[\rho] = \alpha \rho^{\alpha-1}(\vec{r}) \int w^X_{\alpha, \beta} \left[ k_F(\vec{r}), \vec{r} - \vec{r}' \right] \rho^\beta (\vec{r}') d^3 r'
+ \rho^\alpha(\vec{r}) \int \frac{dw^X_{\alpha, \beta} \left[ k_F(\vec{r}), \vec{r} - \vec{r}' \right]}{d \rho(\vec{r})} \rho^\beta (\vec{r}') d^3 r'
+ \beta \rho^{\beta-1}(\vec{r}) \int w^X_{\alpha, \beta} \left[ k_F(\vec{r}'), \vec{r} - \vec{r}' \right] \rho^\alpha (\vec{r}') d^3 r'.
\]  
(6)

It is quite clear that the same forms of WT, SM, Perrot, MGP and MGP0 kernels are employed to construct the KEDFs by our scheme. For efficient linear-scaling calculations of \( T_{NL}^{\text{LDAK-Z}}[\rho] \) and the corresponding potentials \( V_{T, NL}^{\text{LDAK-Z}}[\rho] \), the integrals of

\[
P(\vec{r}) = \int w \left[ k_F(\vec{r}), |\vec{r} - \vec{r}'| \right] f(\vec{r}') d^3 r'
\]  
and
\[ Q(\vec{r}) = \int w[ k, (\vec{r}'), |\vec{r} - \vec{r}'|] f(\vec{r}') d^3 \vec{r}' \] in Eq. (5) and (6) are calculated by cubic Hermite spline interpolation technique and fast Fourier transform (FFT) [11]. It is important to note that the computational cost of Eq. (5) and (6) becomes intrinsic quasi-linear scaling \( O[mN \log N] \). Note that \( m \) and \( N \) are the number of the uniform interpolation nodes of Fermi wave vectors and FFT grids, respectively. The details of these techniques can also be found in Ref. [11] and references therein.

### 2.3 The implementation of OFDFT for isolated systems

Our KEDFs have been implemented in the ATLAS code, which is used for numerical solution of OFDFT in periodic systems. However, the periodic boundary conditions used in ATLAS limits its effectiveness in study of isolated systems. Especially, artificial supercell periodicity should be introduced for simulation of non-periodic systems, leading to suffering from high computation costs. Furthermore, a compensating background charge is also required for the charged systems[26], which may significantly affect the accuracy of physical properties. Here, we extend the capability of ATLAS to simulate isolated systems under DBC.

In general, all the interaction terms of OFDFT have quasi-linear scaling except for the ion-ion interaction term. The ion-ion interaction energy is defined as

\[ E_{ii}[R] = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Z_i Z_j}{R_{ij}}, \quad (7) \]

where \( R_{ij} = |\vec{R}_i - \vec{R}_j| \), \( \{\vec{R}_i\} \) and \( \{Z_i\} \) denote the ionic positions and charges, respectively. Obviously, a direct calculation of ion-ion interaction shows intrinsic square scaling with respect to the number of ions. In fact, the Eq. (2) can also be reformulated as [27]

\[ E[\rho] = T[\rho] + E_{xc} + E_{el}[\rho, R], \quad (8) \]
where \( E_{\text{ele}} \) denotes the electrostatic interactions and contains the ion-ion, ion-electron, and electron-electron interactions. The electrostatics can be expressed by [27–29]:

\[
E_{\text{ele}}[\rho, R] = \sup_{\rho_{\text{ele}}} \left\{ -\frac{1}{8\pi} \int \left[ \nabla V_{\text{ele}}(\vec{r}) \right] d^3 r + \int \left( \rho(\vec{r}) + b(\vec{r}) \right) V_{\text{ele}}(\vec{r}) d^3 r \right\} 
- E_{\text{self}}(R) + E_c(R) \tag{9}
\]

where \( V_{\text{ele}} \) is referred as the electrostatic potential, \( b \) is the total pseudo-charge density of the nuclei, \( E_{\text{self}} \) is the self-energy of nuclei, \( E_c \) is used to correct the error of ion-ion repulsive energy due to overlap of pseudo-ion density. The electrostatic potential \( V_{\text{ele}} \) in Eq. (9) is calculated by solving Poisson equation:

\[
\nabla^2 V_{\text{ele}}[n](\vec{r}) = -4\pi n(\vec{r}) \tag{10}
\]

The total density of \( n \) is defined as the sum of pseudo-ion density and electron density

\[
n(\vec{r}) = \rho(\vec{r}) + b(\vec{r}) \tag{11}
\]

The detailed calculations of \( b \), \( E_{\text{self}} \) and \( E_c \) can be found in Ref. [29].

We now describe the implementation in ATLAS for numerical solution of OFDFT under DBC. Real-space calculations are performed on grids, in which the values of the electron density distribution and electrostatic potential are given on discrete Cartesian grid points. Just as shown in Fig. 1(a), the radius \( R_{\max} \) of a spherical region is used to truncate the tail of charge density, whose value should be zero beyond the spherical region. In our practice, electrostatic potentials are directly represented on discretized grid points in cubic cell and evaluated by the finite difference method. Note that the side length of unit cell is defined as \( L = 2R_{\max} \). There are two types of grid points in our implementation as illustrated in Fig. 1(b). The electrostatic potentials on boundary points are calculated by the multipoles expansion method[30], whereas the electrostatic potentials on the internal points can be solved by conjugate gradient iteration with multigrid in real space[31]. The number of boundary layers is determined by the order of finite-difference employed. The nonlocal part of KEDFs in Eq. (6) is calculated by the FFT, whose computational cost scales quasi-linearly with the number of FFT
The ground-state electron density is obtained by minimizing the total energy using the truncated Newton method[32].

3. Computational details

The OFDFT calculations were carried out by ATLAS under DBC. A grid spacing of 0.2 Å and 8th finite-difference order gave well-convergence of total energies less than 1 meV/atom. The KSDFT calculations were performed by in-house developed ARES software[33] and double checked using CASTEP[34]. A grid spacing of 0.2 Å and 16th finite-difference order in ARES and kinetic energy cutoff of 940 eV for CASTEP are sufficient for a well-converged total energy (1 meV/atom). The bulk-derived local pseudopotentials[35] and local density approximate exchange and correlation as parametrized by Perdew and Zunger [36] were employed to estimate the ion–electron and the exchange-correlation interactions for all the considered systems. The structures of Mg₈, Mg₅₀, Ga₂₅As₂₅, Ga₄As₄ and Si₅₀ were randomly generated by
CALYPSO[37,38]. The settings of $R_{\text{max}} = 9.5$ Å for Mg$_8$ and Ga$_4$As$_4$ and $R_{\text{max}} = 13.0$ Å for Mg$_{50}$, Ga$_{25}$As$_{25}$, Si$_{50}$ and Si$_{60}$ yielded good convergence of total energy. The number of interpolation nodes of 40 for LDAK-X gave well convergence of total energies within 20 meV/atom for all the considered systems.

4. Results and Discussion

To assess the performance of our scheme, we firstly construct a family of KEDFs and perform the energy optimization of Mg$_8$ using OFDFT with these KEDFs. For comparison, we also include the results of LX (X=WT, MGP0 and MGP, etc.). Just as shown in Fig. 2, our LDAK-X shows a significant improvement of numerical stability in comparison with LX, as illustrated by well convergence for LDAK-X. For example, it requires 7 iterations to give well-convergence of total energies less than 1 meV/atom for OFDFT calculation with LDAK-MGP, whereas it fails to converge using LMGP. The finding of convergence failure with LX functionals is also in agreement with the reports in Ref. [19].

Fig. 2. The comparison of total energy convergence for Mg$_8$ between LDAK-X and LX, where X denotes (a) WT, (b) MGP0 and (c) MGP, respectively.

To uncover the underlying causes of different converged behaviors for LDAK-X and LX functionals, we put emphasis on comparative analysis of their differences. Despite the similar framework for construction of KEDFs shared for both schemes, namely,
introduction of the local density dependent kernel, the completely different strategies are employed to construct the KEDFs. In LX scheme, the local density dependent kinetic potential is firstly calculated by spline interpolation[19]

$$V_{T,NL}^{LX}[\rho](\vec{r}) = \rho^{-1/6}(\vec{r}) \sum_{i=1}^{m} c_i [\rho(\vec{r}),\vec{r}] \int \mathcal{w}_{NL}^{LX}[\rho,\vec{r} - \vec{r}'] \rho^{5/6}(\vec{r}') d^3r, \quad (12)$$

where \( \{c_i\} \) denote the spline interpolation coefficients. In principle, those coefficients should depend on, at each point in space, local density \( \rho(\vec{r}) \). However, a simple approximation with constant the density independent coefficients is employed to obtain the analytical nonlocal KEDFs in LX scheme. It is quite clear that the approximation is so strong that the derivative relation between KEDFs and KEDVs cannot be strictly satisfied, leading to inaccurate KEDFs, which consequently suffer from numerical instabilities during energy optimization. In contrast, KEDFs are constructed by direct introduction of local density dependent kernel within our scheme and the corresponding KEDVs are obtained by derivative of KEDFs. It is, therefore, derivative relation between KEDFs and KEDVs can be strictly satisfied, making the OFDFT calculations with LDAK-X functionals fast total energy convergence during energy optimization.

To evaluate the accuracy and transferability of LDAK-X, we applied LDAK-X functionals to metallic cluster of Mg₈. total energies of 100 random structures are evaluated by OFDFT with various KEDFs including LDAK-WT, LDAK-MGP0, LDAK-MGP, LDAK-SM, LDAK-Perrot, LWT, LMGP0 and LMGP functionals. The calculated OFDFT energies in comparison with that of KSDFT are shown in Fig. 3 (a). The general trend in total energies obtained by KSDFT is reasonable reproduced by
OFDFT with all eight KEDFs. However, LDAK-MGP and LMGP show a significant improvement in computational accuracy compared to other functionals and successfully reproduce KSDFT results across a wide window of energy spanning several eV per atom. To quantify the computational accuracy of our functionals, the mean-unsigned-error (MUE) of OFDFT energies with respect to KSDFT results for 100 random structures of Mg$_8$ are listed in Table 1. It is obvious that LDAK-MGP outperforms other KEDFs and yields the smaller MUE of 0.164 eV/atom, which is much lower than that of LMGP (0.313 eV/atom). These results indicate that LDAK-MGP has a considerable improvement over other KEDFs.

Fig. 3. The total energies of 100 random clusters calculated by OFDFT with a variety of KEDFs in comparison with the reference KSDFT results for (a) Mg$_8$, (b) Ga$_4$As$_4$ and (c) Si$_{50}$, respectively.

Table 1. The mean-unsigned-error of OFDFT energies with respect to the KSDFT results for 100 random structures of Mg$_8$.

| Scheme | LDAK-X | LX |
|--------|--------|----|
| X      | WT     | MGP0 | MGP | SM | Perrot | WT | MGP0 | MGP |
| MUE(eV/atom) | 1.295 | 0.650 | **0.164** | 2.406 | 1.969 | 1.444 | 0.501 | 0.313 |

In order to further validate the accuracy of LDAK-MGP, the total energies of 100 random structures of Ga$_4$As$_4$ and Si$_{50}$ are evaluated with KSDFT and OFDFT with LDAK-MGP and LMGP. Note that we only focus on the LDAK-MGP and LMGP in
following tests because they show a superior performance compared to other KEDFs. The OFDFT total energies of Ga$_4$As$_4$ and Si$_{50}$ using LDAK-MGP and LMGP compared against KSDFT are shown in Fig. 3(b) and (c), respectively. It should be noted that LDAK-MGP show superior performance to LMGP, evidenced by smaller MUE of LDAK-MGP in comparison with LMGP for Si$_{50}$ and Ga$_4$As$_4$ (see Table 2). Furthermore, it should be stressed that energy optimization with LDAK-MGP gives well-convergence for all the random structures in considered systems and the convergence rate approaches 100%, which is superior to that of LX in Ref.[19].

| System | Ga$_4$As$_4$ | Si$_{50}$ |
|--------|-------------|-----------|
| KEDF   | LDAK-MGP    | LMGP      | LDAK-MGP | LMGP |
| MUE(eV/atom) | 0.765 | 1.604 | **0.085** | 0.419 |

It is well-known that the total energy of OFDFT is expressed completely in terms of the electron density. However, it is an extremely difficult to predict accurate electron densities using KEDFs for isolated systems, where the electron density is not fully in the slowly varying regime. We also evaluate electron densities of Mg$_{50}$, Ga$_{25}$As$_{25}$, Si$_{50}$ and Si$_{60}$ using LDAK-MGP in comparison with those estimated by LMGP, as well as KSDFT. The detailed structural information and the corresponding directions for each structure are presented in Support Information. As shown in Fig. 4, the electron density distributions predicted by LDAK-MGP and LMGP share the similar general shapes with KSDFT. But, LMGP gives quit different distributions for the bonding regions and near core regions, whereas electron densities predicted by LDAK-MGP almost overlap.
with KSDFT benchmarks in all regions. It is important to note that LDAK-MGP successfully reproduces the tiny density oscillation obtained by KSDFT in the bonding region for Si$_{50}$, as evidenced by insert of Fig.4 (c). These results reveal that LDAK-MGP gives more accurate results than that obtained by LMGP.

Fig. 4. The electron densities calculated by LMGP (blue dot), LDAK-MGP (red short dash) and KSDFT (black solid line) for (a) Mg$_{50}$ (b) Ga$_{25}$As$_{25}$ (c) Si$_{50}$ and (d) Si$_{60}$ along the specific bond orientation.

5. Conclusion

In summary, a scheme derived from the local density approximation is developed and implemented into ATLAS package under Dirichlet boundary condition. A family of nonlocal KEDFs have been proposed within the scheme and show superior computational performance with extremely high accuracy and numerical stability for isolated systems. This accurate and transferable new KEDFs make OFDFT accessible
for simulations of large-scale isolated systems, therefore open the door to computer-aided materials design such as cluster and quantum dots.

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