Recovering Orbital Information from Orbital-Free Density Functional Theory

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Abstract: Linear-scaling orbital-free density functional theory (OF-DFT) is capable of calculating properties of large systems of thousands of atoms at quantum mechanical level. The major obstacles of OF-DFT lie in the computation of the kinetic energy and the nuclear-electron interaction energy. The latest linear-response based kinetic energy density functional can treat metallic materials in OF-DFT almost as accurate as Kohn-Sham (KS) DFT; however, the present best OF-DFT results for covalent materials still possess large unacceptable errors. We have developed a new linear-scaling method, called orbital-corrected OF-DFT (OO-DFT), to improve OF-DFT by solving the KS equations under a fixed KS effective potential, which is constructed from the electron density obtained from OF-DFT calculations. For covalent materials, OO-DFT corrects errors in OF-DFT with only one iteration of solving the KS equations. Our work paves the way for the general applications of OF-DFT on large systems.

Keywords: Orbital-free, Density functional theory, Kinetic energy density functional

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1 Introduction

In the original Hohenberg-Kohn theorems of density functional theory (DFT) [1], the total electronic energy of the system is formulated purely as a functional of the electron density $\rho(\mathbf{r})$:

$$E_v[\rho] = T_s[\rho] + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho] + \int \rho(\mathbf{r})v_{\mathrm{ne}}(\mathbf{r})\mathrm{d}\mathbf{r} \ . \tag{1}$$

Here, v_{ne} is the nuclear-electron Coulombic attraction potential, T_s is the electronic kinetic energy of a noninteracting system that has the same electron density as the interacting system, E_{H} is the classical Hartree electron-electron Coulombic repulsion energy, and E_{xc} is the exchange-correlation energy. One could calculate the ground-state density and other properties not explicitly dependent on the many-body wave function by directly minimizing the above total electronic energy functional under the constraint that $\rho(\mathbf{r})$ is properly normalized to N, the number of electrons in the system. This leads to the following Thomas-Fermi-Hohenberg-Kohn equation [2],

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\mathrm{H}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{\mathrm{xc}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\mathrm{ne}}(\mathbf{r}) = \mu \ , \tag{2}$$

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where μ is the Lagrange multiplier that guarantees the correct normalization of the electron density during the minimization of the total energy, $E_v[\rho]$. Eq. (2) can be solved in a nearly linear-scaling fashion. This constitutes the essence of orbital-free (OF) DFT [2], which has been used to study the dynamics of several thousand atoms near a metallic grain boundary [3] and nanoindentation in a multiscale model [4]. Such efforts demonstrate the power and efficiency of this OF-DFT method. On the other hand, the drawbacks of OF-DFT lie in the two necessary approximations for the kinetic energy and the nuclear-electron interaction [2]. The former relies on the kinetic energy density functional (KEDF), while the latter depends on the local pseudopotentials (LPSs). Recently, first-principles LPSs derived from a bulk environment (BLPSs) were shown to be quite accurate for treating covalent materials in KS-DFT [5]. The latest linear-response based KEDF can treat metallic materials in OF-DFT almost as accurate as KS-DFT [6]. However, the applications of OF-DFT on covalent materials using the combination of the above KEDF and BLPSs normally exhibit large errors, which were attributed mainly to the KEDF [7].

2   Orbital-Corrected OF-DFT (OO-DFT) Method

To remedy the drawbacks of OF-DFT in its current implementation, we have developed the following method. First, we solve Eq. (2) and obtain $\rho_{OF}(\mathbf{r})$. Then, we construct the KS effective potential $v_{eff}^{KS}[\rho_{OF}]$:

$$v_{eff}^{KS}[\rho_{OF}] = v_H[\rho_{OF}] + v_{xc}[\rho_{OF}] + v_{ne} \; . \tag{3}$$

Here, the interaction potential between nuclei and electrons, v_{ne}, could be modeled either by a LPS or by a nonlocal pseudopotential (NLPS), with the latter being ubiquitously exploited in KS-DFT. Next, we solve the KS equations under the fixed effective potential, $v_{eff}^{KS}[\rho_{OF}]$,

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v_{eff}^{KS}[\rho_{OF}] \right) \tilde{\phi}_i(\mathbf{r}) = \tilde{\epsilon}_i \tilde{\phi}_i(\mathbf{r}) \; , \tag{4}$$

and obtain $\tilde{\rho}(\mathbf{r})$ within one non-self-consistent iteration,

$$\tilde{\rho}(\mathbf{r}) = \sum_i f_i \left| \tilde{\phi}_i(\mathbf{r}) \right|^2 \; , \tag{5}$$

where $\tilde{\epsilon}_i$ and f_i are the eigenvalue and occupation number of the ith KS orbital $\tilde{\phi}_i$, respectively. Finally, we use the following Hohenberg-Kohn-Sham (HKS) functional to calculate the total electronic energy

$$E^{HKS}[\tilde{\rho}] = E_H[\tilde{\rho}] + E_{xc}[\tilde{\rho}] + \sum_i f_i \tilde{\epsilon}_i - \int \tilde{\rho}(\mathbf{r})(v_H[\rho_{OF}] + v_{xc}[\rho_{OF}])d\mathbf{r} \; . \tag{6}$$

We name the above scheme orbital-corrected OF-DFT (OO-DFT) method. Note that in the self-consistent KS-DFT, the number of iterations required to converge the calculation increases with the size of the system [8]. If at each iteration, the computational cost is $\mathcal{O}(N)$, where N is a measure of the system size, the overall computational cost cannot be truly linear due to the requirement of self-consistency [8]. Since OO-DFT involves only one non-self-consistent iteration, this bottleneck is removed. With many linear-scaling algorithms available for solving the KS equations under a fixed effective potential [9], OO-DFT can be implemented as an essentially linear-scaling method. We have applied OO-DFT method to the cubic diamond (CD) Si system, a covalent semiconducting material that poses difficulty for OF-DFT. In the following, we will compare the predicted static properties from OO-DFT to those from KS-DFT and OF-DFT.

3   Results for the CD Si

The OO-DFT and KS-DFT results are obtained from a modified *ABINIT* code [10]. Both the NLPS [11] and the BLPS [5] are employed. In our OF-DFT calculations, the Wang-Govind-Carter (WGC) KEDF [6] and the BLPS [5] are used to compute the kinetic energy and nuclear-electron interaction energy. Local density approximation (LDA) [12] is used in all the DFT calculations. The computational details are reported in Refs. [5] and [7].
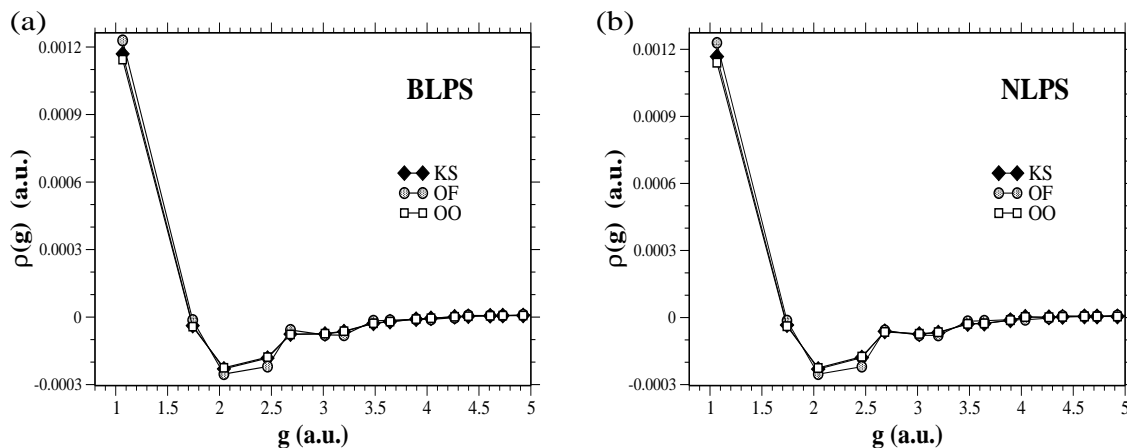

Figure 1: The electron densities in reciprocal space from a unit cell of the CD Si with lattice constant 5.40 Å, (a) from the BLPS and (b) from the NLPS, using KS (solid diamond), OF (opaque circles), and OO (open squares) DFT methods.

Fig. 1 depicts the electron density in reciprocal space, $\rho(\mathbf{g})$, of the CD Si with the BLPS and the NLPS. Discrepancies between $\rho_{KS}(\mathbf{g})$ and $\rho_{OF}(\mathbf{g})$ are obvious. In both cases, the value of $\rho_{OF}(\mathbf{g})$ at the first Bragg vector is too high, while those at some intermediate $\mathbf{g}$ vectors are too low. The density with the BLPS is notably improved by the one-iteration OO-DFT and $\rho_{OO}(\mathbf{g})$ is getting very close to $\rho_{KS}(\mathbf{g})$. Even when the NLPS is used, the error in $\rho_{OO}(\mathbf{g})$ is significantly reduced. This illustrates that the error in OF-DFT density is mainly due to the less optimal KEDF.

The equation of state (EOS) for the CD Si is computed in KS-DFT, OO-DFT , and OF-DFT. In order to obtain the static structural properties, we fit the EOS data to Murnaghan's EOS [13] for an arbitrary volume V,

$$E_{\text{tot}}(V) = \frac{B_0 V}{B_0'} \left[\frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] + \text{constant} , \qquad (7)$$

where B_0 and B_0' are the bulk modulus and its pressure derivative at the equilibrium volume V_0, respectively.

Table 1 displays the resulting equilibrium volumes V_0, equilibrium bulk moduli B_0, and equilibrium energies E_0. The combination of the WGC KEDF and the BLPS in OF-DFT generates results containing large errors, with V_0 too large by *ca.* 20%, B_0 too small by *ca.* 70%, and E_0 too low by *ca.* 0.1%. In contrast, OO-DFT produces results very close to those from KS-DFT with the errors of the three properties reduced to 0.4%, 1.5%, and 0.01%, respectively. We further use the NLPS to test the accuracy of OO-DFT. The data in Table 1 shows that the KS-DFT results are very well reproduced by OO-DFT.

Table 1: OF (BLPS), OO (NLPS and BLPS), and KS (NLPS and BLPS) LDA predictions of the CD Si equilibrium bulk properties: V_0, B_0, and E_0.

	Property	OF	OO	KS
BLPS	V_0 (Å^3)	23.966	19.356	19.431
	B_0 (GPa)	25.8	97.0	95.6
	E_0 (eV/atom)	-110.345	-110.228	-110.236
NLPS	V_0 (Å^3)		19.393	19.489
	B_0 (GPa)		94.8	92.6
	E_0 (eV/atom)		-108.059	-108.067

4 Summary and Conclusions

We have developed an effective linear-scaling OO-DFT method by combining OF-DFT and KS-DFT via a density connection. OO-DFT offers remarkable improvements over the OF-DFT results and achieves comparable accuracy as KS-DFT at the cost of performing only a single non-self-consistent iteration of KS calculation under a fixed KS effective potential. We anticipate OO-DFT to venture into domains beyond the limits of other first-principles quantum mechanical methods.

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References

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] Y. A. Wang and E. A. Carter, in *Theoretical Methods in Condensed Phase Chemistry*, Chapter 5 (Kluwer, Dordrecht, 2000), pp. 117-184.

[3] S. C. Watson and P. A.Madden, Phys. Chem. Commun. **1**, 1 (1998).

[4] M. Fago, R. H. Hayes, E. A. Carter, and M. Ortiz, Phys. Rev. B **70**, 10010 (2004).

[5] B. Zhou, Y. A. Wang, and E. A. Carter, Phys. Rev. B **69**, 125109 (2004).

[6] Y. A. Wang, N. Govind, and E. A. Carter, Phys. Rev. B **60**, 16350 (1999).

[7] B. Zhou, V. L. Lignères, and E. A. Carter, J. Chem. Phys. **122**, 044103 (2005).

[8] J. F. Annett, Comput. Mater. Sci. **4**, 23 (1995).

[9] S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999).

[10] X. Gonze *et al.*, Comput. Mater. Sci. **25**, 478 (2002).

[11] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[12] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[13] F. D. Murnaghan, Proc. Nat. Acad. Sci. USA **30**, 244 (1944).