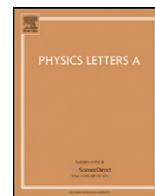




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Hybridized kinetic energy functional for orbital-free density functional method

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ABSTRACT

We propose a hybridized kinetic energy functional, $aT_{\text{TF}} + bT_{\text{vW}}$, where T_{TF} is the Thomas–Fermi functional and T_{vW} the von Weizsäcker functional while a and b are adjustable parameters. The new functional is implemented in orbital-free plane-wave density functional method, in which a conjugate-gradient line-search scheme of electronic minimization is incorporated. Calculations with the fitted a and b show that this kinetic energy functional can describe the structures of small Si, Al and Si–Al alloy clusters with reasonable accuracy.

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1. Introduction

The Kohn–Sham scheme [1] of the density functional theory (DFT) [2] has been widely used and becomes one of mainstreams in the modern first-principles calculation. However, this method involves order- N^3 scaling due to the orthogonality constraints on Kohn–Sham orbitals. In every self-consistent cycle, Kohn–Sham equations should be solved to get the orbital wave functions one by one. The computation of such method is limited up to hundreds of atoms with present computer resources. From the uprising of Hohenberg–Kohn theorem, the cornerstone of density functional theory, orbital-free method has been investigated persistently [3–5]. Without using the orbital wave function, all energy terms are expressed as the functionals of electron density. Therefore orbital orthogonality operation and k -sampling in Brillouin zone are avoided straightforwardly, leading to a linear-scaling of orbital-free method. These advantages enable the study of large systems and long simulation time with which the Kohn–Sham method is hard to handle. The studies of liquid dynamics and liquid–vapor interface, with systems including ~ 3000 atoms and simulation time of tens of picoseconds, have been reported recently [6,7]. The advantages of orbital-free method are not only its efficiency, but also its application to multiscale embedding method, as the density-based energy formulas are necessary to compute quantum interactions between two separated regions [8]. However, two problems

are involved in practical implementation. One is pseudopotential. Non-local pseudopotentials [9] are widely used in Kohn–Sham method because different l -component orbitals feel different pseudopotentials, while in orbital-free method, electron density is not l -dependent. The other one, even more difficult, is the non-interacting kinetic energy functional. In the Kohn–Sham method, non-interacting kinetic energy is calculated exactly via Kohn–Sham orbital. Unfortunately, no general kinetic energy functional of sufficient accuracy for orbital-free method is available so far. In the past several years, the computational advantage of orbital-free method has stimulated the development of proper kinetic energy functional and much progress has been made. For example, Carter and Madden [10–12] developed a family of kinetic energy functionals based on the linear response functional of homogeneous electron gas. Their work demonstrated that the proposed functional produced reasonable behaviors for metals with weak pseudopotential such as Na, in which electron gas was nearly homogeneous.

Many other kinetic energy functionals were also proposed [13–17], including $T_{\text{TF}} + \frac{1}{9}T_{\text{vW}}$, $T_{\text{vW}} + \lambda T_{\text{TF}}$ and the functional $F(N)T_{\text{TF}} + T_{\text{vW}}$ where N is the number of electrons and the N -dependent factor $F(N) = (1 - \frac{2}{N})(1 - \frac{1.314}{N^{1/3}} + \frac{0.0021}{N^{2/3}})$ [18,19] which was believed to be an appropriate functional for rapidly varying densities. It is well known that T_{TF} is exact in the limit of homogeneous electron density and T_{vW} is a good approximation for isolated system with a few electrons. However, the real system is usually in between. Stimulated by those previous works, we propose another hybridized kinetic energy functional $aT_{\text{TF}} + bT_{\text{vW}}$, where a and b are parameters. In the present work, attention is focused on the application of the ground states or energetically

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low lying structures of small clusters. Calculations on Si₄, Si₆, Si₈, Si₉, Al₇, Al₁₃, Al₁₃[−] and Si₅Al are carried out with the hybridized kinetic energy functional and their structures are compared with the results of Kohn–Sham method. The orbital-free method is implemented on the plane-wave method. In all the calculations, the local pseudopotential is used for Si [20,21] and LRV local pseudopotential [22] for Al, which had been found reasonable [23].

2. Numerical scheme

The total energy of many-electron system in DFT is given by (Hartree atomic units is used throughout this Letter)

$$E[\rho, R_n] = T[\rho] + \int \rho(r) V_{ps}(r) dr + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho] + E_{II}[R_n], \quad (1)$$

where the terms on the right are the kinetic energy for a non-interacting electron gas, the interaction energy between valence electrons and pseudopotential, the classical Coulomb energy between electrons, the exchange-correlation energy and ion-ion interaction energy. It is obvious that the Kohn–Sham method and orbital-free method have the same energy expression except for kinetic energy. Kinetic energy functional $T[\rho] = T_{TF}[\rho] + \lambda T_{vW}[\rho]$ has been investigated in previous work [24,25] and produced several desirable properties. Different λ have been proposed, such as $\lambda = \frac{1}{9}$ corresponding to the limit of very slowly varying electron density system and $\lambda = \frac{1}{5}$ with better behavior for convergence [16]. Present work shows that the results could be improved by adding another parameter to Thomas–Fermi term. The hybridized kinetic energy functional has the form

$$T[\rho] = aT_{TF}[\rho] + bT_{vW}[\rho] \quad (2)$$

where T_{TF} is the Thomas–Fermi kinetic energy functional [26,27], exact in the limit of homogeneous electron density,

$$T_{TF}[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int_{\Omega} \rho(r)^{5/3} dr, \quad (3)$$

and T_{vW} is the von Weizsäcker term [28],

$$T_{vW}[\rho] = \frac{1}{8} \int_{\Omega} \frac{|\nabla \rho(r)|^2}{\rho(r)} dr, \quad (4)$$

which is exact in one or two electron system.

Considering non-negativity of electron density, it is convenient to choose $\psi(r)$ as the basic variable, which satisfies $\rho(r) = |\psi(r)|^2$. The ground state energy is obtained by minimizing $E[\rho, \{R_n\}]$ with respect to the electron density ρ for a given structural configuration $\{R_n\}$; the variation principle leads to equation

$$\left[-\frac{b}{2} \nabla^2 + \frac{5}{3} a C_{TF} \rho^{2/3}(r) + V_{eff}^{KS}(r) \right] \psi(r) = \epsilon \psi(r) \quad (5)$$

for

$$\frac{\delta T_{vW}[\rho]}{\delta \rho(r)} = -\frac{1}{2} \frac{\nabla^2 \psi(r)}{\psi(r)}, \quad (6)$$

$$V_{eff}^{KS}(r) = V_{ps}(r) + \int \frac{\rho}{|r-r'|} dr' + \frac{\delta E_{xc}}{\delta \rho(r)}, \quad (7)$$

where $\psi(r)$ is subject to the normalization constraints $\int |\psi(r)|^2 dr = N$. The above equation is solved self-consistently until convergence reached and Hellman–Feynman force is obtained for structural configuration $\{R_n\}$,

$$F_I = -\frac{d}{dR_I} E[\rho, \{R_n\}], \quad (8)$$

which is similar to Kohn–Sham method. Starting from an initial homogeneous electron density guess, a conjugate-gradient optimization method [29] is applied for electronic minimization. At the i th iteration, the steepest-descent vector is calculated as

$$\eta^{(i)} = \mu^{(i)} - H^{(i)} |\psi^{(i)}\rangle \quad (9)$$

with $\mu^{(i)} = \langle \psi^{(i)} | H^{(i)} | \psi^{(i)} \rangle$. The conjugate-gradient vector is

$$|\varphi_1^{(i)}\rangle = |\eta^{(i)}\rangle + \gamma^{(i)} |\varphi_1^{(i-1)}\rangle, \quad (10)$$

where

$$|\gamma^{(i)}\rangle = \frac{\langle \eta^{(i)} | \eta^{(i)} \rangle}{\langle \eta^{(i-1)} | \eta^{(i-1)} \rangle} \quad (11)$$

and $\gamma^{(1)} = 0$. The conjugate-gradient direction is then orthogonalized to ψ and normalized accordingly to total electron number N ,

$$|\varphi_2^{(i)}\rangle = \left(1 - \frac{|\psi^{(i)}\rangle \langle \psi^{(i)}|}{N} \right) |\varphi_1^{(i)}\rangle, \quad (12)$$

$$|\varphi_3^{(i)}\rangle = |\varphi_2^{(i)}\rangle \left(\frac{N}{\langle \varphi_2^{(i)} | \varphi_2^{(i)} \rangle} \right)^{1/2}. \quad (13)$$

The new wave function ψ resulting from the i th iteration is

$$|\psi^{(i+1)}\rangle = |\psi^{(i)}\rangle \cos \theta_{\min} + |\varphi_3^{(i)}\rangle \sin \theta_{\min} \quad (14)$$

the value of θ which minimizes E is

$$\theta_{\min} = \frac{1}{2} \tan^{-1} \frac{B}{A}, \quad (15)$$

where

$$A = \frac{E(0) - E(\theta_0) + B \sin(2\theta_0)}{1 - \cos(2\theta_0)}, \quad (16)$$

$$B = \frac{1}{2} \frac{\partial E}{\partial \theta} \Big|_{\theta=0}. \quad (17)$$

In present work, θ_0 is chosen as $\frac{\pi}{600}$ and the normalization constraints are intrinsically kept. The traditional conjugate-gradient method above has been proved to behave well in the present plane-wave orbital-free method.

3. Results and discussion

Present orbital-free calculations were performed in reciprocal space and the structures of the clusters were optimized with the parameters $a = 0.95$ and $b = 0.40$, which were obtained by comparing the orbital-free results and Kohn–Sham results. Since a global minimum of total energy is not guaranteed in electronic minimization due to nonlinear property of Thomas–Fermi terms [30], a uniform electron density is chosen as the initial guess, which has been proved to be reliable near homogenous limit. For many cases of present cluster calculations, the energy minimum yielded by initial guess of Kohn–Sham self-consistent result and uniform electron density is the same. As shown in Fig. 1, Si₄, Si₆, Si₈, Si₉ and Al₁₃ show almost the same structures from Kohn–Sham method and orbital-free method with the hybridized kinetic energy functional. For comparison, the results for the parameter $a = 1.00$ and $b = 0.20$ are also shown in Fig. 1. Fig. 2 shows the relative deviations of average bond lengths and binding energies derived by orbital-free method compared to Kohn–Sham results. It is encouraging that the bond lengths of clusters of different element Al and Si could be well predicted with the same parameters in the hybridized kinetic energy functional. However, the structures of Al₇ obtained by Kohn–Sham and orbital-free method are distinguishable. It indicates that the orbital-free method prefers the higher symmetry because of the failure in describing the Jahn–Teller effect which is based on electron orbital

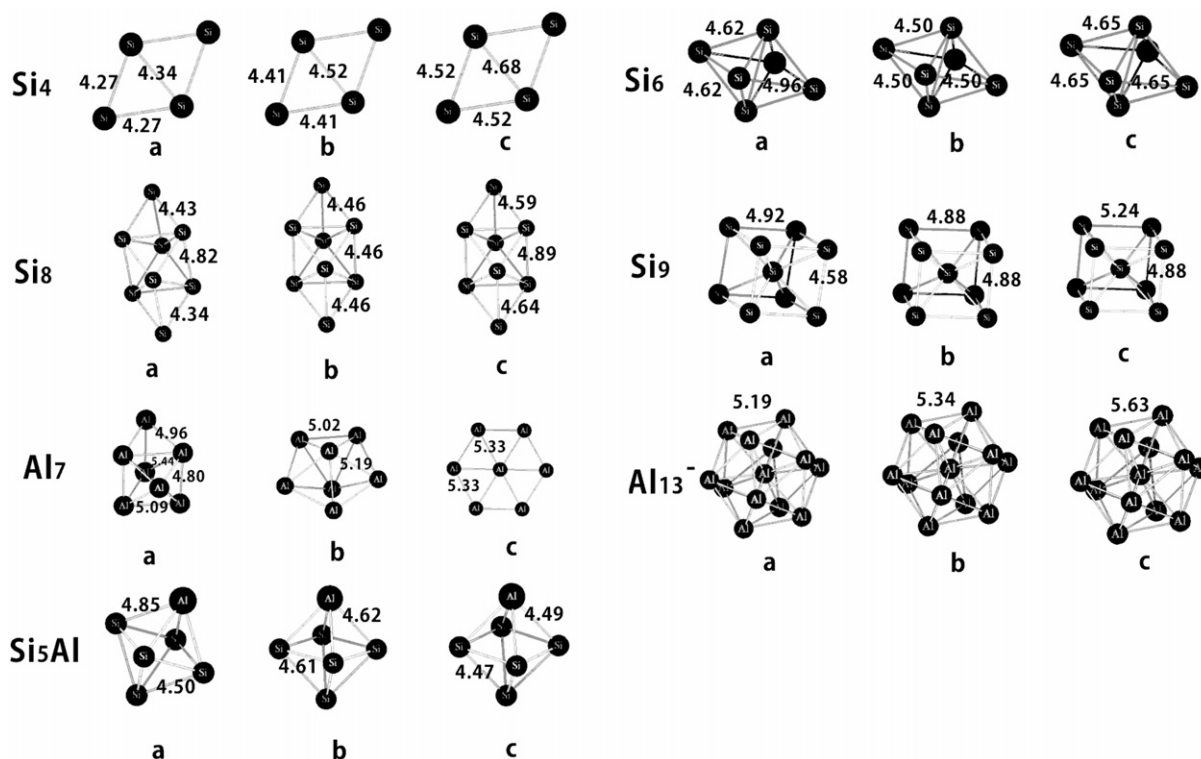


Fig. 1. The energetically low lying structures of clusters Si_4 , Si_6 , Si_8 , Si_9 , Al_7 , Al_{13}^- and Si_5Al . Structures a are the results of Kohn-Sham method. Structures b and c are the results of orbital-free method with kinetic energy functional $0.95T_{\text{TF}} + 0.40T_{\text{VW}}$ and $T_{\text{TF}} + 0.2T_{\text{VW}}$, respectively.

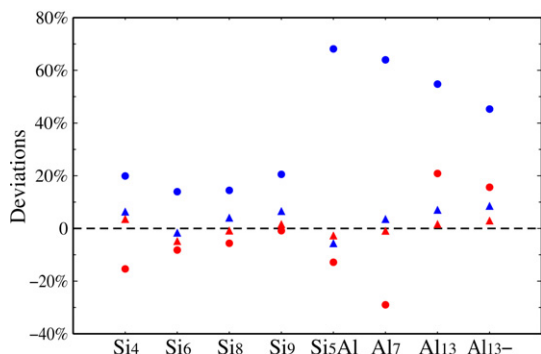


Fig. 2. The relative deviations to Kohn-Sham results of averaged bond lengths (labeled as triangles) and binding energies (labeled as circles) of clusters Si_4 , Si_6 , Si_8 , Si_9 , Si_5Al , Al_7 , Al_{13} and Al_{13}^- , resulting from orbital-free method with kinetic energy functionals $0.95T_{\text{TF}} + 0.40T_{\text{VW}}$ (red) and $T_{\text{TF}} + 0.2T_{\text{VW}}$ (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

theory. When adding one more electron on Al_{13} , the Jahn-Teller effect disappeared in Kohn-Sham method and the high symmetry structures restored.

From Fig. 2, it can be clearly seen that the $aT_{\text{TF}} + bT_{\text{VW}}$ functional with $a = 0.95$ and $b = 0.40$ improves the traditional $T_{\text{TF}} + \lambda T_{\text{VW}}$ functional with $\lambda = 0.20$. Generally, the orbital-free method with the present kinetic energy functional results in only about 4% errors in the bond lengths, much smaller than what from the traditional functional proposed earlier. As it is not sufficient to incorporate only Thomas-Fermi and von Weizsäcker terms in kinetic energy functional, the present functional could not give the correct linear response behavior [2] for most real systems. However, the hybridized kinetic energy functional $aT_{\text{TF}} + bT_{\text{VW}}$ is better than the existing similar functional, such as $T_{\text{TF}} + \lambda T_{\text{VW}}$. The traditional functional $T_{\text{TF}} + \lambda T_{\text{VW}}$ was proposed [17] based on the modification of homogeneous electron gas and $T_{\text{VW}} + \lambda T_{\text{TF}}$ as mentioned

above [15] was for electron density rapid-varying system. It is expected that our hybridized kinetic energy functional with $a < 1$ and $b > \lambda$ works for isolated clusters in which the distribution of electron density is in between. Present studies also show that with increasing parameter a , the bond length increases and decreases with increasing parameter b . This behavior is determined by general properties of two kinetic energy functionals. Comparing to the previous proposed functional, we obtain a large parameter b which indicates that the electrons in clusters are more isolated. Since the T_{VW} term has more contribution, the T_{TF} term should be less important, leading to the parameter a smaller than one, which is also different from the conventional functional.

4. Summary

By taking advantages of Thomas-Fermi and von Weizsäcker kinetic energy functional, a hybridized kinetic energy functional is proposed. The obtained parameter b is much larger than the value proposed previously and a is smaller than one. By using these parameters, the orbital-free DFT can correctly predicts the structure of Si and Al clusters. The errors in the bond length are within $\sim 4\%$ and the agreements of binding energies with Kohn-Sham results are better than results of traditional functional. The present studies provide a clue to improve the kinetic energy functional in the orbital-free density functional method.

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