Total energy evaluation in the Strutinsky shell correction method

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We analyze the total energy evaluation in the Strutinsky shell correction method (SCM) of Ullmo *et al.* [Phys. Rev. B **63**, 125339 (2001)], where a series expansion of the total energy is developed based on perturbation theory. In agreement with Yannouleas and Landman [Phys. Rev. B **48**, 8376 (1993)], we also identify the first-order SCM result to be the Harris functional [Phys. Rev. B **31**, 1770 (1985)]. Further, we find that the second-order correction of the SCM turns out to be the second-order error of the Harris functional, which involves the *a priori* unknown exact Kohn-Sham (KS) density, $\rho_{KS}(\mathbf{r})$. Interestingly, the approximation of $\rho_{KS}(\mathbf{r})$ by $\rho_{out}(\mathbf{r})$, the output density of the SCM calculation, in the evaluation of the second-order correction leads to the Hohenberg-Kohn-Sham functional. By invoking an auxiliary system in the framework of orbital-free density functional theory, Ullmo *et al.* designed a scheme to approximate $\rho_{KS}(\mathbf{r})$, but with several drawbacks. An alternative is designed to utilize the optimal density from a high-quality density mixing method to approximate $\rho_{KS}(\mathbf{r})$. Our new scheme allows more accurate and complex kinetic energy density functionals and nonlocal pseudopotentials to be employed in the SCM. The efficiency of our new scheme is demonstrated in atomistic calculations on the cubic diamond Si and face-centered-cubic Ag systems. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2755714]

I. INTRODUCTION

In density functional theory (DFT), the ground state electronic total energy is decomposed into following terms, with each term being a functional of the electron density,[1,2] $\rho(\mathbf{r})$,

$$E_v[\rho] = T_s[\rho] + E_H[\rho] + E_{XC}[\rho] + \langle \rho(\mathbf{r})v_{ne}(\mathbf{r})\rangle. \quad (1)$$

Here, 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 repulsion energy, E_{XC} is the exchange-correlation (XC) energy, and $\langle \rho(\mathbf{r})v_{ne}(\mathbf{r})\rangle$ is a shorthand notation for the nuclear-electron interaction energy, $\int \rho(\mathbf{r})v_{ne}(\mathbf{r})d\mathbf{r}$. In the original formulation of DFT, i.e., orbital-free DFT (OF-DFT),[3] there are no one-electron orbitals involved. Based on the variational principle, the density and the total energy are computed in OF-DFT by solving the following Thomas-Fermi-Hohenberg-Kohn (TFHK) equation:[4]

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_H[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} + v_{ne}(\mathbf{r})$$

$$= \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_H[\rho](\mathbf{r}) + v_{XC}[\rho](\mathbf{r}) + v_{ne}(\mathbf{r})$$

$$= \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_{eff}^{KS}[\rho](\mathbf{r}) = \mu, \quad (2)$$

where $v_H[\rho](\mathbf{r})$, $v_{XC}[\rho](\mathbf{r})$, and $v_{eff}^{KS}[\rho](\mathbf{r})$ are the Hartree, XC, and total Kohn-Sham (KS) effective potentials, respectively, and μ is the Lagrange multiplier to impose the correct

normalization of $\rho(\mathbf{r})$ during the minimization and corresponds to the chemical potential after the total energy is minimized. Note that the last equal sign holds only for the density that minimize the total energy functional.

With the modern fast Fourier transform technique,[5] OF-DFT can be implemented essentially as a linear-scaling method with computational cost of $\mathcal{O}(N \ln N)$.[4,6–13] Thus, it is capable of treating large systems (>1000 atoms) at a much lower cost than other orbital-based first-principles methods, such as Hartree-Fock[14] and KS-DFT (Ref. 15) methods. In the past decade, OF-DFT has attracted increasing interest[4] and the linear-scaling OF-DFT method has been applied to study the dynamics of several thousand atoms near a metallic grain boundary,[6] the metal-insulator transition in a two-dimensional array of metal nanocrystal quantum dots,[7] and in a multiscale model of nanoindentation.[8] Despite the encouraging advances in OF-DFT, its applications are mainly limited to simple metallic systems, in which electrons are nearly free-electron-like. The major unsolved problem in OF-DFT is that the exact KS kinetic energy density functional (KEDF), which corresponds to the first term in Eq. (1), is still unknown. Although many KEDFs have been developed in the past, all of them suffer from the accuracy problem to different extents and some of them cannot be evaluated with linear-scaling algorithms, which prevent OF-DFT from becoming a mainstream quantum mechanics method.[4,11,12] In the following, the KEDFs we will discuss refer to approximations of the exact KS KEDF at different levels.

Instead of tackling the KEDF problem directly, the Strutinsky shell correction method[16,17] (SCM) tries to improve the accuracy of OF-DFT by introducing a non-self-consistent KS-DFT calculation (in Hartree atomic units),

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127, 064101-1

$$\left(-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}^{\text{KS}}[\rho_{\text{OF}}](\mathbf{r})\right)\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \tag{3}$$

where the input density, $\rho_{\text{OF}}(\mathbf{r})$, is obtained from an OF-DFT calculation and ϵ_i is the eigenvalue of the ith orbital, $\phi_i(\mathbf{r})$. The output density, $\rho_{\text{out}}(\mathbf{r})$, is generated from the orbitals via

$$\rho_{\text{out}}(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2, \tag{4}$$

where f_i is the occupation number of $\phi_i(\mathbf{r})$. On the other hand, many iterations are carried out in the self-consistent KS-DFT calculation until the output density is converged to the exact KS density, $\rho_{\text{KS}}(\mathbf{r})$. Then, the exact KS total energy, $E^{\text{KS}}[\rho_{\text{KS}}]$, is obtained as follows:

$$E^{\text{KS}}[\rho_{\text{KS}}] = \sum_i f_i \langle \phi_i^{\text{KS}} | -\tfrac{1}{2}\nabla^2 | \phi_i^{\text{KS}} \rangle + E_{\text{H}}[\rho_{\text{KS}}] + E_{\text{XC}}[\rho_{\text{KS}}]$$
$$+ \langle \rho_{\text{KS}}(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) \rangle, \tag{5}$$

where $\phi_i^{\text{KS}}(\mathbf{r})$ is the ith converged KS orbital. The computational cost of the SCM should be much lower than that of the iterative self-consistent KS-DFT calculation since the many iterations in the latter are eliminated. Thus, the SCM is potentially a powerful tool for treating large systems of thousands of atoms and provides impetus to further improve OF-DFT.[18]

Although the SCM has been applied to study a wide range of systems, including metallic clusters,[16] fullerenes,[19] metallic nanowires,[20] and quantum dots,[21,22] the accuracy of SCM calculations remains to be a critical issue. In the SCM, the Thomas-Fermi[3] (TF) or the extended TF KEDFs,[23] which contain the gradient expansion terms up to the fourth order, are usually employed in OF-DFT calculations.[16,17] Due to the approximate nature of the TF and the extended TF KEDFs, the resulting density from OF-DFT is usually an average of the exact KS density, smoothing out the atomic shell structure. After one iteration of the KS-DFT calculation, the output density from Eq. (4), $\rho_{\text{out}}(\mathbf{r})$, begins to show the shell structure. The SCM then assumes that the total electronic energy can be accurately evaluated from $\rho_{\text{OF}}(\mathbf{r})$ and $\rho_{\text{out}}(\mathbf{r})$. In different versions of the SCM,[16,17] several schemes for the total energy evaluation exist, which are closely related to the Hohenberg-Kohn-Sham[24] (HKS) and the Harris[25] functionals and their second-order corrections.[26] In this work, we examine the subtle differences among these schemes and propose practical improvements for them.

II. THE STRUTINSKY SHELL CORRECTION METHOD

In the SCM, the exact KS effective potential, $v_{\text{eff}}^{\text{KS}}[\rho_{\text{KS}}](\mathbf{r})$, can be written perturbatively as

$$v_{\text{eff}}^{\text{KS}}[\rho_{\text{KS}}](\mathbf{r}) = v_{\text{eff}}^{\text{KS}}[\rho_{\text{OF}}](\mathbf{r}) + \Delta v(\mathbf{r}), \tag{6}$$

where $\Delta v(\mathbf{r})$ represents a small quantum interference treated as a perturbation on the smooth potential from the OF-DFT calculation, $v_{\text{eff}}^{\text{KS}}[\rho_{\text{OF}}](\mathbf{r})$. Expansion of $\Delta v(\mathbf{r})$ in terms of $\Delta\rho(\mathbf{r})$,

$$\Delta\rho(\mathbf{r}) = \rho_{\text{KS}}(\mathbf{r}) - \rho_{\text{OF}}(\mathbf{r}), \tag{7}$$

and retention of only the first-order term yield

$$\Delta v(\mathbf{r}) \approx \int \frac{\delta v_{\text{eff}}^{\text{KS}}[\rho](\mathbf{r})}{\delta\rho_{\text{OF}}(\mathbf{r}')}\Delta\rho(\mathbf{r}')d\mathbf{r}' = 2\langle C(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}')\rangle, \tag{8}$$

where $C(\mathbf{r},\mathbf{r}')$ is given by

$$C(\mathbf{r},\mathbf{r}') = \frac{1}{2}\left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \frac{\delta v_{\text{XC}}[\rho](\mathbf{r})}{\delta\rho_{\text{OF}}(\mathbf{r}')}\right). \tag{9}$$

Here, we introduce the following notation:

$$\frac{\delta F[\rho]}{\delta\rho_{\text{OF}}(\mathbf{r})} = \left.\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})}\right|_{\rho=\rho_{\text{OF}}}, \tag{10}$$

for some functional or function of the electron density, $F[\rho]$.

With the SCM, Ullmo et al. developed a series expansion of the exact KS total energy, based on perturbation theory (see Ref. 17 for the detailed derivation) as follows:

$$E^{\text{KS}} \approx E^{\text{SCM}} = E^{\text{OF}} + \Delta E^{(1)} + \Delta E^{(2)}, \tag{11}$$

$$\Delta E^{(1)} = \sum_i f_i \epsilon_i - \{T_s[\rho_{\text{OF}}] + \langle \rho_{\text{OF}}(\mathbf{r}) v_{\text{eff}}^{\text{KS}}[\rho_{\text{OF}}](\mathbf{r})\rangle\}, \tag{12}$$

$$\Delta E^{(2)} = \tfrac{1}{2}\langle R[\rho_{\text{OF}}](\mathbf{r})\Delta v(\mathbf{r})\rangle = \langle R[\rho_{\text{OF}}](\mathbf{r})C(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}')\rangle, \tag{13}$$

where E^{OF} is the total energy from the OF-DFT calculation,

$$E^{\text{OF}} = T_s[\rho_{\text{OF}}] + E_{\text{H}}[\rho_{\text{OF}}] + E_{\text{XC}}[\rho_{\text{OF}}] + \langle \rho_{\text{OF}}(\mathbf{r})v_{\text{ne}}(\mathbf{r})\rangle, \tag{14}$$

$R[\rho_{\text{OF}}](\mathbf{r})$ is the density residual,

$$R[\rho_{\text{OF}}](\mathbf{r}) = \rho_{\text{out}}(\mathbf{r}) - \rho_{\text{OF}}(\mathbf{r}), \tag{15}$$

and the second equal sign in Eq. (13) comes from Eq. (8).

Note that the above formalism also applies to the iterative KS-DFT calculation,[27] in which $\rho_{\text{OF}}(\mathbf{r})$ is replaced by the input density, $\rho_{\text{in}}(\mathbf{r})$, of each iteration. Thus, the SCM can be deemed as a shortcut to the iterative self-consistent KS-DFT. To be more general, we replace $\rho_{\text{OF}}(\mathbf{r})$ with $\rho_{\text{in}}(\mathbf{r})$ hereafter, except for the discussion of the second-order correction, $\Delta E^{(2)}$, from Eqs. (22)–(26). Moreover, our derivation hereafter applies to any general XC and KEDF models.

As shown in Ref. 16, to first order, E^{SCM} is just the Harris functional,[25] E^{Harris},

$$E^{\text{Harris}}[\rho_{\text{in}}, \rho_{\text{out}}] = \sum_i f_i \epsilon_i - E_{\text{H}}[\rho_{\text{in}}] + E_{\text{XC}}[\rho_{\text{in}}]$$
$$- \langle \rho_{\text{in}}(\mathbf{r})v_{\text{XC}}[\rho_{\text{in}}](\mathbf{r})\rangle. \tag{16}$$

Furthermore, the second-order correction, $\Delta E^{(2)}$, is simply the second-order error of E^{Harris}, as derived by Finnis,[26]

$$E^{\text{Harris}} - E^{\text{KS}} = \langle R[\rho_{\text{in}}](\mathbf{r})C(\mathbf{r},\mathbf{r}')[\rho_{\text{in}}(\mathbf{r}') - \rho_{\text{KS}}(\mathbf{r}')]\rangle$$
$$= -\Delta E^{(2)}, \tag{17}$$

which involves the a priori unknown $\rho_{\text{KS}}(\mathbf{r})$. Apart from E^{Harris}, another widely used total energy density functional is the HKS functional,[24] E^{HKS},

$$E^{\mathrm{HKS}}[\rho_{\mathrm{in}},\rho_{\mathrm{out}}] = \sum_i f_i \epsilon_i + E_{\mathrm{H}}[\rho_{\mathrm{out}}] - \langle \rho_{\mathrm{out}}(\mathbf{r}) v_{\mathrm{H}}[\rho_{\mathrm{in}}](\mathbf{r}) \rangle$$
$$+ E_{\mathrm{XC}}[\rho_{\mathrm{out}}] - \langle \rho_{\mathrm{out}}(\mathbf{r}) v_{\mathrm{XC}}[\rho_{\mathrm{in}}](\mathbf{r}) \rangle. \quad (18)$$

Following Finnis,[26] the second-order error in the HKS functional is given by

$$E^{\mathrm{HKS}} - E^{\mathrm{KS}} = \langle R[\rho_{\mathrm{in}}](\mathbf{r}) C(\mathbf{r},\mathbf{r}')[\rho_{\mathrm{out}}(\mathbf{r}') - \rho_{\mathrm{KS}}(\mathbf{r}')] \rangle. \quad (19)$$

Taking the difference between Eqs. (19) and (17), we have

$$E^{\mathrm{HKS}}[\rho_{\mathrm{in}},\rho_{\mathrm{out}}] - E^{\mathrm{Harris}}[\rho_{\mathrm{in}},\rho_{\mathrm{out}}]$$
$$= \langle R[\rho_{\mathrm{in}}](\mathbf{r}) C(\mathbf{r},\mathbf{r}') R[\rho_{\mathrm{in}}](\mathbf{r}') \rangle. \quad (20)$$

Interestingly, if $\rho_{\mathrm{KS}}(\mathbf{r})$ is replaced by $\rho_{\mathrm{out}}(\mathbf{r})$ in Eq. (13), the total energy from the SCM is the same as that from the HKS functional since $\Delta E^{(2)}$ will be the difference between E^{HKS} and E^{Harris}. As far as we are aware, this relationship has not been identified before in all existing versions of the SCM.

In order to obtain an accurate $\Delta E^{(2)}$, a high-quality approximation for $\rho_{\mathrm{KS}}(\mathbf{r})$ is required. Ullmo *et al.* proposed the following scheme to obtain $\Delta \rho(\mathbf{r})$ [see Eq. (7)] approximately, by invoking an auxiliary system in the framework of OF-DFT,[17]

$$\frac{\delta T_s[\rho]}{\delta \rho'_{\mathrm{KS}}(\mathbf{r})} + v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{\mathrm{KS}}](\mathbf{r}) = \mu'_{\mathrm{KS}}, \quad (21)$$

which corresponds to an OF-DFT calculation with a fixed effective potential $v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{\mathrm{KS}}](\mathbf{r})$. Here, the output density $\rho'_{\mathrm{KS}}(\mathbf{r})$ is different from $\rho_{\mathrm{KS}}(\mathbf{r})$ due to the approximate nature of the KEDF, $T_s[\rho]$. Thus, Eq. (21) is non-self-consistent. For convenience, we rewrite Eq. (2) as

$$\frac{\delta T_s[\rho]}{\delta \rho_{\mathrm{OF}}(\mathbf{r})} + v_{\mathrm{eff}}^{\mathrm{KS}}[\rho_{\mathrm{OF}}](\mathbf{r}) = \mu_{\mathrm{OF}}. \quad (22)$$

Taking the difference of the above two equations and expanding $T_s[\rho]$ to second order, we get

$$\Delta v(\mathbf{r}) + \int \frac{\delta^2 T_s[\rho]}{\delta \rho_{\mathrm{OF}}(\mathbf{r}) \delta \rho_{\mathrm{OF}}(\mathbf{r}')} [\rho'_{\mathrm{KS}}(\mathbf{r}') - \rho_{\mathrm{OF}}(\mathbf{r}')] d\mathbf{r}'$$
$$= \mu'_{\mathrm{KS}} - \mu_{\mathrm{OF}} = \Delta \mu. \quad (23)$$

Then, the density residual, $R[\rho_{\mathrm{OF}}](\mathbf{r})$, is used to approximate the difference between $\rho_{\mathrm{KS}}(\mathbf{r})$ and $\rho'_{\mathrm{KS}}(\mathbf{r})$ as follows:[17]

$$\rho_{\mathrm{KS}}(\mathbf{r}) - \rho'_{\mathrm{KS}}(\mathbf{r}) \approx \rho_{\mathrm{out}}(\mathbf{r}) - \rho_{\mathrm{OF}}(\mathbf{r}) = R[\rho_{\mathrm{OF}}](\mathbf{r}). \quad (24)$$

Consequently, we have

$$\rho'_{\mathrm{KS}}(\mathbf{r}) - \rho_{\mathrm{OF}}(\mathbf{r}) = [\rho_{\mathrm{KS}}(\mathbf{r}) - \rho_{\mathrm{OF}}(\mathbf{r})] - [\rho_{\mathrm{KS}}(\mathbf{r}) - \rho'_{\mathrm{KS}}(\mathbf{r})]$$
$$\approx \Delta \rho(\mathbf{r}) - R[\rho_{\mathrm{OF}}](\mathbf{r}). \quad (25)$$

Substitution of Eqs. (8) and (25) into Eq. (23) leads to

$$\Delta \mu = \int \frac{\delta^2 T_s[\rho]}{\delta \rho_{\mathrm{OF}}(\mathbf{r}) \delta \rho_{\mathrm{OF}}(\mathbf{r}')} \{\Delta \rho(\mathbf{r}') - R[\rho_{\mathrm{OF}}](\mathbf{r}')\} d\mathbf{r}'$$
$$+ \int \frac{\delta v_{\mathrm{eff}}^{\mathrm{KS}}[\rho](\mathbf{r})}{\delta \rho_{\mathrm{OF}}(\mathbf{r}')} \Delta \rho(\mathbf{r}') d\mathbf{r}', \quad (26)$$

which corresponds to Eq. (38) in Ref. 17 and serves as the basic equation for solving $\Delta \rho(\mathbf{r})$.[17]

The above approach has several drawbacks. First, the central approximation of this scheme, Eq. (24), is not well justified. Even if a high-quality KEDF is employed, which will result in a small $\Delta \mu$ in Eq. (23), both sides of Eq. (24) are not necessarily close to each other at each point in real space although they can be small in magnitude. Whether this approximation is sound for densities resulting from OF-DFT using various KEDFs and of systems under different chemical environment needs to be further investigated. Second, the above scheme implies that the external potential is of local form; otherwise, some inconsistency will arise and further degrade the approximation in Eq. (24). Indeed, the above scheme has been applied on systems described by a local external potential,[17,21,22] whose transferability and quality are clearly not optimal.[11–13] Finally, due to the necessity of evaluating the second derivative of the KEDF in Eq. (26), only the simplest TF KEDF (Ref. 3) is employed in the applications of the SCM of Ullmo *et al.*, while other more accurate and complex KEDFs are excluded.[17,21,22] A different path is taken below to avoid such difficulties.

It is clear that an accurate approximation for $\rho_{\mathrm{KS}}(\mathbf{r})$ plays a vital role in the evaluation of the SCM total energy. In fact, this is also the main objective in the development of high-quality density mixing schemes for iterative KS-DFT calculations.[27] At each step, the input density for the next iteration is generated by optimally mixing the current-step input and output densities in reciprocal space,

$$\rho_{\mathrm{in}}^{i+1} = \rho_{\mathrm{in}}^i + \mathbf{G} R[\rho_{\mathrm{in}}^i], \quad (27)$$

with the aid of the preconditioning matrix $\mathbf{G}$ to reduce the density residual $R[\rho_{\mathrm{in}}]$.[27] Naturally, one can simply use the optimal density from the high-quality density mixing scheme, such as the Pulay method,[28] to approximate the exact KS density, and the second-order SCM correction in Eq. (13) can be computed via

$$\Delta E^{(2)} = \langle R[\rho_{\mathrm{in}}^i(\mathbf{r})] C(\mathbf{r},\mathbf{r}') [\rho_{\mathrm{in}}^{i+1}(\mathbf{r}') - \rho_{\mathrm{in}}^i(\mathbf{r}')] \rangle, \quad (28)$$

which will be used to evaluate the total energy in the SCM in the next section. Note that the form of the preconditioning matrix, $\mathbf{G}$, in the Pulay method can admit nonzero off-diagonal elements in reciprocal space and a detailed illustration on various density mixing schemes in a plane-wave basis set can be found in Ref. 27. Finally, Eq. (28) involves the functional derivative of the XC potential, $\delta v_{\mathrm{XC}}[\rho(\mathbf{r})]/\delta \rho_{\mathrm{in}}(\mathbf{r}')$, which is a highly undesirable quantity to compute since it is complicated for some sophisticated XC functionals and the cost is quite high.[29,30] Fortunately, Eq. (8) provides a simpler scheme to evaluate Eq. (28) by recognizing the following approximation:
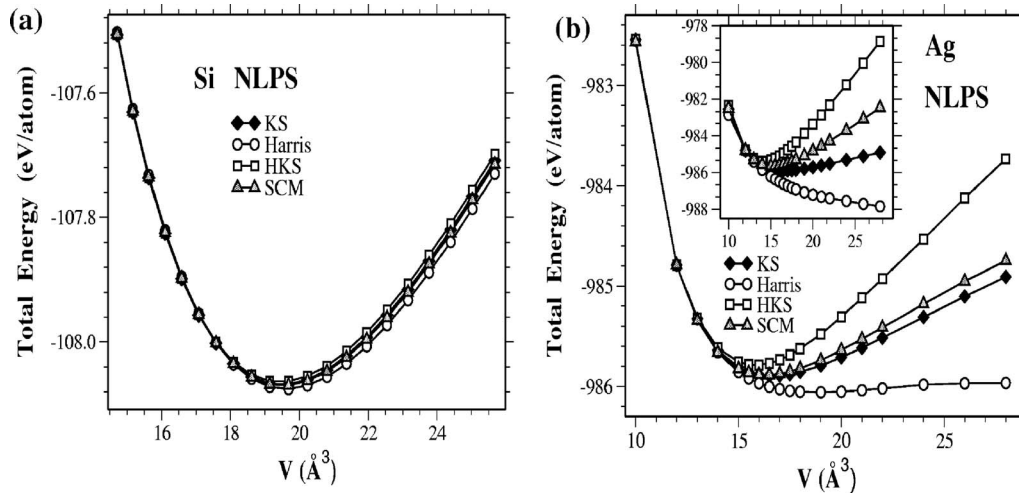
FIG. 1. LDA total energies (in eV/at.) vs cell volume V (in Å³) for (a) the CD Si and (b) the fcc Ag. The results from the Harris functional (open circle), the HKS functional (open square), and the SCM (opaque triangle) are compared with those from KS-DFT (solid diamond). In (b), both the first iteration (see the inset) and the second iteration results are illustrated.

$$\left\langle R[\rho_{in}(\mathbf{r})]\frac{\delta v_{XC}[\rho(\mathbf{r}')]}{\delta \rho_{in}(\mathbf{r})}\right\rangle \approx v_{XC}[\rho_{out}](\mathbf{r}') - v_{XC}[\rho_{in}](\mathbf{r}'),$$

(29)

which only introduces numerical errors higher than second order.

III. NUMERICAL RESULTS AND DISCUSSION

We test different total energy evaluation schemes in the application of the SCM on the cubic diamond (CD) Si and the face-centered-cubic (fcc) Ag systems. The local density approximation[31] (LDA) is used in all DFT calculations. In OF-DFT calculations, the nuclear-electron interaction energy is computed with the local pseudopotential (LPS) derived from a bulk environment.[11,13] In the previous applications of the SCM,[16,17,19–22] the TF (Ref. 3) or the extended TF KEDFs (Ref. 23) are usually employed. These KEDFs do not exhibit the linear response behavior of the free electron gas[32] and lead to large errors in OF-DFT calculations.[4] In contrast, the Wang-Govind-Carter (WGC) KEDF (Ref. 10) allows the correct linear response behavior[32] of the free electron gas to be imposed and is one of the most accurate state-of-the-art KEDFs for the simple metallic and the covalent systems.[4,10–12] In this work, The WGC KEDF with the optimized parameters[12] is used for the CD Si. For the fcc Ag, the von Weizsäcker-ξ-Thomas-Fermi[13,33] KEDF, which incorporates a partial contribution from the TF KEDF (Ref. 3) into the full von Weizsäcker KEDF (Ref. 34), is employed. The optimal value for the parameter ξ in the von Weizsäcker-ξ-Thomas-Fermi KEDF is found to be 0.4, which allows the density from the KS-DFT calculations to be more accurately reproduced by the OF-DFT density.[13] In our OF-DFT calculations, the optimal density is solved from the TFHK equation [see Eq. (2)] variationally via a second-order damped dynamics method[4,10] and no analytic form is assumed for the density. Since the WGC KEDF suffers from the convergence problem,[12] the convergence criterion of the total energy is set to 0.125 meV/atom for the CD Si system.

A modified ABINIT code[35] is used to run the SCM and KS-DFT calculations, in which the standard Troullier-Martins nonlocal pseudopotentials[36] (NLPSs) are employed. Fermi-surface smearing with a width of 54 meV is used in the SCM and KS-DFT calculations for the metallic fcc Ag. For both systems, we use Kerker's preconditioning matrix,[37]

$$\mathbf{G}(q) = A\frac{q^2}{q^2 + q_0^2},$$

(30)

to generate the optimal density at the end of the first iteration. Here, q is the reciprocal space wave vector, and A =0.8 and q_0=1.5 Å⁻¹ from the recommendation of Ref. 27. A second iteration is carried out for the fcc Ag and Pulay's density mixing scheme[28] is employed to generate the optimal density at the end. Those optimal densities are used to evaluate the second-order SCM correction through Eq. (28).

In Fig. 1, the equations of state (EOSs) of the CD Si and the fcc Ag produced from the SCM, Harris, and HKS functionals are compared with that from KS-DFT. As illustrated in Fig. 1(a), the EOSs of the CD Si from the Harris and HKS functionals closely resemble that from KS-DFT. However, they degrade slightly at large cell volumes, where the total energy is underestimated by the Harris functional and overestimated by the HKS functional. This indicates that the densities from OF-DFT also degrade with the increase of the cell volume. With the optimal density generated from Kerker's preconditioning matrix, the SCM almost exactly reproduces the EOS from KS-DFT. The improvements achieved by our SCM upon the Harris functional (the first-order SCM result) demonstrate the importance of the inclusion of the second-order correction.

Turn to the inset of Fig. 1(b), we see that at the first iteration, the EOSs from both the HKS and Harris functionals contain large errors, especially at large cell volumes. This is not surprising because the highly localized density distribution of the d electrons of Ag poses even harder challenges for OF-DFT. Nonetheless, it is clear that these large errors in the Harris and HKS functionals are significantly reduced by the SCM. At the second iteration, both the Harris and HKS

functionals yield much better EOSs, but significant deviations still exit at large cell volumes. It is very encouraging that the SCM reproduces the EOS from KS-DFT very well and the total energy at large cell volumes are only slightly overestimated. For both iterations, the negative errors in the first-order SCM results, i.e., the Harris functional, are significantly reduced by the addition of the second-order correction.

IV. CONCLUSIONS

In conclusion, we have analyzed the relationship between the total energy evaluations in the SCM and the widely used Harris and HKS functionals. It is clear that in the SCM, the second-order correction for the total energy plays a key role and its accuracy depends on how well the exact KS density is approximated. Our new implementation of the SCM utilizes the optimal density from high-quality density mixing method. Apparent advantages of our scheme over that by Ullmo *et al.* include that our scheme allows more accurate KEDFs and NLPSs to be employed and its implementation requires very little extra effort. As shown by the numerical tests, our SCM achieves further improvements upon the widely used Harris and HKS functionals. Finally, our new scheme can also be employed in iterative KS-DFT calculations to facilitate the convergence of the total energy.

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