Supplemental Material for Angular Momentum Dependent Orbital Free Density Functional Theory

Youqi Ke[1], Florian Libisch[1], Junchao Xia[1], Lin-Wang Wang[2] and Emily A. Carter[1]

[1] Department of Mechanical and Aerospace Engineering, Program in Applied and Computational Mathematics, and Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, USA
[2] Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

HYBRID SCHEME

In the following, we present the details of our hybrid scheme for implementing OFDFT. We partition the system into atom-centered spheres and an interstitial region (see Fig. 1(a) in the main manuscript). Within this muffin tin (MT) geometry, ρ is written as a sum of contributions from the MT spheres and the interstitial region [Fig. 1(c)],

$$\rho(\vec{r}) = \sum_R \rho_R(\vec{r}_R) + \rho_I(\vec{r}), \tag{1}$$

where $\rho_R(\vec{r}_R)$ is the electron density inside the MT sphere centered on site $\vec{R}$, $\rho_I(\vec{r})$ is the interstitial electron density which is 0 inside the spheres and $\vec{r}_R = \vec{r} - \vec{R}$. To explicitly include the angular momentum dependence in E^{OF}, we introduce fixed atom-centered basis functions [Fig. 1(b)] to express ρ_R as

$$\rho_R(\vec{r}_R) = \sum_{lm,l'm'} N_{R,lm,l'm'} \psi^*_{R,lm}(\vec{r}_R) \psi_{R,l'm'}(\vec{r}_R). \tag{2}$$

We omit spin indices for simplicity. N_R is the on-site density matrix. The fixed atom-centered basis functions $\psi_{R,lm}(\vec{r}_R) = \phi_{R,l}(r_R) Y_{lm}(\hat{\vec{r}}_R)$, where $\phi_{R,l}(r_R)$ is the radial wave function and $Y_{lm}(\hat{\vec{r}}_R)$ are the spherical harmonics. Using Eqs. (1)-(2) the general total energy functional of OFDFT can be rewritten as

$$E^{\mathrm{OF}}[\rho(\vec{r})] = E^{\mathrm{OF}}[\{N_R\}, \rho_I(\vec{r})], \tag{3}$$

where the on-site density matrices $\{N_R\}$ and the interstitial electron density ρ_I become the basic independent variables.

DERIVATION OF THE NONLOCAL ENERGY

We now derive analytical expressions for the nonlocal energy term E^{NL} we introduce in the main manuscript. We begin by considering in more detail the kinetic energy error $\Delta T_s = T_s - T_s^{\mathrm{KEDF}}$. After neglecting ΔT_s in the interstitial region as justified in the main text, we introduce a smooth scaling function $f(r)$ in the energy density of $T_s - T_s^{\mathrm{KEDF}}$ to make the KE density continuous at the sphere boundary. ΔT_s then becomes

$$\Delta T_s \simeq \sum_R \int_{\mathrm{MT}} [\tau_s(\vec{r}_R) - \tau_s^{\mathrm{KEDF}}(\vec{r}_R)] d\vec{r}_R$$

$$\simeq \sum_R \int_{\mathrm{MT}} f(r_R)[\tau_s(\vec{r}_R) - \tau_s^{\mathrm{KEDF}}(\vec{r}_R)] d\vec{r}_R \tag{4}$$

where f is spherical inside the spheres and $0 \leq f \leq 1$, and τ_s and τ_s^{KEDF} are the exact and approximate KE densities, respectively. $f = 0$ at the sphere boundary and in the interstitial region, ensuring the KE density is continuous everywhere. When combining Eq. 4 with the KEDF in Eq.(1) of the main manuscript, we arrive at a rigorous hybrid KE model for the AMD-OFDFT total energy as follows,

$$T_s^{\mathrm{hybrid}} = T_s^{\mathrm{KEDF}} + \Delta T_s$$

$$= \int \tau_s^{\mathrm{KEDF}}(\vec{r}) d\vec{r} + \sum_R \int_{\mathrm{MT}} f(r_R)[\tau_s(\vec{r}_R) - \tau_s^{\mathrm{KEDF}}(\vec{r}_R)] d\vec{r}_R$$

$$= \int [1 - f(\vec{r})] \tau_s^{\mathrm{KEDF}} d\vec{r} + \int f(\vec{r}) \tau_s(\vec{r}) d\vec{r} \tag{5}$$

Inside the MT spheres, a part of the KEDF is replaced by the exact KE, correcting different types of errors due to the KEDF in the core region. Thus, the accuracy of OFDFT can be enhanced. This hybrid KE model provides us with a sophisticated basis to find a solution for E^{NL}. However, determining the optimal $f(r_R)$ on a large number of grid points is extremely challenging, even though we know f values at and beyond the MT boundary. Thus, in the following, we proceed further to derive a general form for E^{NL} in terms of the on-site density matrix N_R and a small set of on-site, angular-momentum-dependent energies, yielding an easily applicable scheme.

After neglecting the KE error in the interstitial region and introducing a scaling function for the KE density within the MT spheres, the approximated nonlocal energy term E^{NL} becomes

$$
\begin{aligned}
E^{\text{NL}} &\simeq E^{\text{NLPS}}_{i-e} + \Delta T_s \\
&= E^{\text{NLPS}}_{i-e} + \sum_R \left[\int_{\text{MT}} f(r_R)\tau_s(\vec{r}_R)d\vec{r}_R - \int_{\text{MT}} f(r_R)\tau_s^{\text{KEDF}}(\vec{r}_R)d\vec{r}_R \right] \\
&= E^{\text{NLPS}}_{i-e} + [\tilde{T}_s]_{\text{MT}} - [\tilde{T}_s^{\text{KEDF}}]_{\text{MT}},
\end{aligned}
\tag{6}
$$

where $[\tilde{T}_s]_{\text{MT}}$ and $[\tilde{T}_s^{\text{KEDF}}]_{\text{MT}}$ are the exact KE and KEDF inside the MT spheres, scaled by the function $f(r)$.

In the following, we give a term-by-term derivation of the nonlocal energy E^{NL} presented in Eq. 6. As we know, the contributions of the nonlocal parts of the pseudopotential and the exact noninteracting kinetic energy to $E^{\text{NL}}[N_R]$ depend linearly on the total occupation number of each l channel,

$$
\begin{aligned}
E^{\text{NLPS}}_{i-e}[N_R] &= \sum_{R,lm} N_R^{lm} \langle \psi_{R,lm} | V_{i-e}^l | \psi_{R,lm} \rangle_{\text{MT}} \\
&= \sum_{R,l} N_{R,l}^{\text{total}} \int_0^{Ws} \phi_{R,l}^*(r) V_{i-e}^l(r) \phi_{R,l}(r) r^2 dr \int Y_{lm}^* Y_{lm} d\Omega \\
&= \sum_{R,l} N_{R,l}^{\text{total}} \int_0^{Ws} \phi_{R,l}^*(r) V_{i-e}^l(r) \phi_{R,l}(r) r^2 dr \\
&= \sum_{R,l} N_{R,l}^{\text{total}} E_R^{l,\text{NLPS}},
\end{aligned}
\tag{7}
$$

where $\psi_{R,lm}(\vec{r}) = \phi_{R,l}(r)Y_{lm}(\hat{\vec{r}})$, and we have introduced the shorthand notation $N_R^{lm} = N_{R,lm,lm}$, and

$$
\begin{aligned}
[\tilde{T}_s]_{\text{MT}} &= -\frac{1}{2} \sum_{R,lm} N_R^{lm} \langle f\psi_{R,lm} | \nabla^2 | \psi_{R,lm} \rangle_{\text{MT}} \\
&= -\frac{1}{2} \sum_{R,l} N_{R,l}^{\text{total}} \int_0^{Ws} f(r)\phi_{R,l}^*(r) \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} \right] \phi_{R,l}(r) r^2 dr \int Y_{lm}^* Y_{lm} d\Omega \\
&= -\frac{1}{2} \sum_{R,l} N_{R,l}^{\text{total}} \int_0^{Ws} f(r)\phi_{R,l}^*(r) \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2} \right] \phi_{R,l}(r) r^2 dr \\
&= \sum_{R,l} N_{R,l}^{\text{total}} E_R^{l,T_s},
\end{aligned}
\tag{8}
$$

where $N_{R,l}^{\text{total}} = \sum_{m=-l}^{l} N_R^{lm}$, and $E_R^{l,\text{NLPS}}$ and E_R^{l,T_s} are constants, only depending on the shape of the basis functions of each l channel. Consequently, a linear term in E^{NL} can easily accommodate the AMD effects of $E_{i-e}^{\text{nonlocal}}$ and $[T_s]_{\text{MT}}$. Our task is therefore to find the linear and major nonlinear errors of the KEDF used to describe the system, so that we can make corrections for these errors to generate correct occupations and physical properties.

We start by considering a KEDF of the general form $T_s^{\text{KEDF}}[\{\rho_R\}] = T_s^{\text{KEDF}}[\{N_R\}]$, where ρ_R is given by Eq. (2). We make a Taylor expansion around the average occupation numbers $N_{R,l}^0 = N_{R,l}^{\text{total}}/(2l+1)$ of each l channel to obtain

$$
\begin{aligned}
\tilde{T}_s^{\text{KEDF}}[\{N_R\}] &= \tilde{T}_s^{\text{KEDF}}[\{N_{R,l}^0\}] + \sum_{R,lm} \left.\frac{\partial \tilde{T}_s^{\text{KEDF}}}{\partial N_R^{lm}}\right|_{\{N_{R,l}^0\}} \Delta N_R^{lm} + \frac{1}{2} \sum_{R,lm,l'm'} \left.\frac{\partial^2 \tilde{T}_s^{\text{KEDF}}}{\partial N_R^{lm}\partial N_R^{l'm'}}\right|_{\{N_{R,l}^0\}} \Delta N_R^{lm}\Delta N_R^{l'm'} \\
&+ \frac{1}{6} \sum_{R,lm,l'm',l''m''} \left.\frac{\partial^3 \tilde{T}_s^{\text{KEDF}}}{\partial N_R^{lm}\partial N_R^{l'm'}\partial N_R^{l''m''}}\right|_{\{N_{R,l}^0\}} \Delta N_R^{lm}\Delta N_R^{l'm'}\Delta N_R^{l''m''} + O(\Delta N_R^4),
\end{aligned}
\tag{9}
$$

where $\Delta N_R^{lm} = N_R^{lm} - N_{R,l}^0$. The contribution of off-diagonal elements of the density matrix is neglected because of the small hybridization of different l-channels in the core region. At the average occupation $N_R^{lm} = N_{R,l}^0$, the electron density is spherical,

$$\rho_R^0(r_R) = \frac{1}{4\pi}\sum_l (2l+1)N_{R,l}^0 \phi_{R,l}^2(r_R) = \sum_l N_{R,l}^{\text{total}}\rho_{R,l}(r_R),$$

where $\rho_{R,l}(r) = \frac{1}{4\pi}\phi_{R,l}^2(r)$. The different terms in the above Taylor expansion play different roles. In the following, we consider each term of Eq.(9) individually.

The first term $\tilde{T}_s^{\text{KEDF}}[\{N_{R,l}^0\}] = \tilde{T}_s^{\text{KEDF}}[\{N_{R,l}^{\text{total}}\}]$ determines the magnitude of the KE and the total occupation of each l channel inside the spheres. We can expand this term further according to different physical situations. Here, we consider transition metals, atoms with highly localized electrons around the cores. In transition metals, the electron density in the core region is dominated by the d channel contribution, i.e., $N_{R,d}^{\text{total}} \gg \{N_{R,s}^{\text{total}}, N_{R,p}^{\text{total}}\}$. Therefore, we make another Taylor expansion of $\tilde{T}_s^{\text{KEDF}}[\{N_{R,l}^0\}]$ at $N_{R,s}^0 = 0$ and $N_{R,p}^0 = 0$ because of their small occupations,

$$\tilde{T}_s^{\text{KEDF}}[N_{R,l}^0] = \tilde{T}_s^{\text{KEDF}}[N_{R,l}^0]\Big|_{N_{R,s/p}^0=0} + \sum_{l=s,p} \frac{\partial \tilde{T}_s^{\text{KEDF}}[N_{R,l}^0]}{\partial N_{R,l}^0}\Bigg|_{N_{R,s/p}^0=0} N_{R,l}^0 + \dots. \tag{10}$$

We only consider terms up to first order. It is clear that $\tilde{T}_s^{\text{KEDF}}[\{N_{R,l}^0\}]\Big|_{N_{R,s/p}^0=0}$ and $\frac{\partial \tilde{T}_s^{\text{KEDF}}[N_{R,l}^0]}{\partial N_{R,l}^0}\Big|_{N_{R,s/p}^0=0}$ only depend on $N_{R,d}^0$ of the localized electrons. For the Thomas-Fermi (TF) KEDF [1] contribution, we find

$$\tilde{T}_s^{\text{TF}}[N_{R,l}^0]\Big|_{N_{R,s/p}=0} = \alpha_{\text{TF}} \int_{\text{MT}} f(r)[N_{R,d}^{\text{total}}\rho_{R,d}(r)]^{\frac{5}{3}}d\vec{r}$$

$$= (N_{R,d}^{\text{total}})^{\frac{5}{3}}\alpha_{\text{TF}} \int_{\text{MT}} f(r)\rho_{R,d}^{\frac{5}{3}}(r)d\vec{r}$$

$$= (N_{R,d}^{\text{total}})^{\frac{5}{3}}V_{\text{TF}}, \tag{11}$$

where $V_{\text{TF}} = \alpha_{\text{TF}}\int f(r)\rho_{R,d}^{\frac{5}{3}}(r)d\vec{r}$ is a constant depending only on the fixed radial basis function $\phi_{R,d}$. Similarly, for the first order expansion coefficients for $l = s, p$, we find

$$\frac{\partial \tilde{T}_s^{\text{TF}}[N_{R,l}^0]}{\partial N_{R,l}^0}\Bigg|_{N_{R,s/p}^0=0} = \int_{\text{MT}} \frac{\delta \tilde{T}_s^{\text{TF}}}{\delta \rho}\frac{\partial \rho}{\partial N_{R,l}^0}\Bigg|_{N_{R,s/p}^0=0} d\vec{r}$$

$$= \frac{5}{3}(2l+1)\alpha_{\text{TF}} \int_{\text{MT}} f(r)[N_{R,d}^{\text{total}}\rho_{R,d}(r)]^{\frac{2}{3}}\rho_{R,l}(r)d\vec{r}$$

$$= \frac{5}{3}(2l+1)\alpha_{\text{TF}}(N_{R,d}^{\text{total}})^{\frac{2}{3}} \int_{\text{MT}} f(r)\rho_{R,d}^{\frac{2}{3}}(r)\rho_{R,l}(r)d\vec{r}$$

$$= (N_{R,d}^{\text{total}})^{\frac{2}{3}}C_{R,l}^{\text{TF}}. \tag{12}$$

Here $C_{R,l}^{\text{TF}}$ is a constant that is determined by the radial wavefunctions $\phi_{R,l=s,p}$ and $\phi_{R,d}$.

For the von Weizsäcker (vW) KEDF [2] contribution, we have

$$\tilde{T}_s^{\text{vW}}[N_{R,l}^0]\Big|_{N_{R,s/p}=0} = N_{R,d}^{\text{total}}\alpha_{\text{vW}} \int_{\text{MT}} f(r)\frac{\nabla\sqrt{\rho_{R,d}}\,\nabla\sqrt{\rho_{R,d}}}{2}d\vec{r}$$

$$= N_{R,d}^{\text{total}}E_{R,d}^{\text{vW}}. \tag{13}$$

Here $E_{R,d}^{\text{vW}} = \alpha_{\text{vW}}\int_{\text{MT}} \frac{\nabla\sqrt{\rho_{R,d}}\nabla\sqrt{\rho_{R,d}}}{2}d\vec{r}$ depends only on the radial wavefunction $\phi_{R,d}$, and

$$\frac{\partial \tilde{T}_s^{\text{vW}}[N_{R,l}^0]}{\partial N_{R,l}^0}\Bigg|_{N_{R,s/p}^0=0} = (2l+1)\alpha_{\text{vW}} \int_{\text{MT}}[-f(r)\frac{\nabla\rho_{R,d}\nabla\rho_{R,d}}{\rho_{R,d}} - 2\nabla(f(r)\frac{\nabla\rho_{R,d}}{\rho_{R,d}})]d\vec{r}$$

$$= C_{R,l}^{\text{vW}}. \tag{14}$$

$C_{R,l}^{\mathrm{vW}}$ obviously also only depends on the radial wavefunction of the $\phi_{R,l}$ and $\phi_{R,d}$ channels.

For the case of a nonlocal KEDF (e.g., WGC99 [3]), we obtain

$$\left. \tilde{T}_s^{\mathrm{NL}}[N_{R,l}^0] \right|_{N_{R,s/p}=0} = (N_{R,d}^{\mathrm{total}})^{\alpha+\beta} \int_{\mathrm{MT}}\!\!\int_{\mathrm{MT}} f(r)\rho_{R,d}^{\alpha}(r)W\left(|\vec{r}-\vec{r}\,'|\right)\rho_{R,d}^{\beta}(r')d\vec{r}d\vec{r}\,'$$

$$= (N_{R,d}^{\mathrm{total}})^{\frac{5}{3}} V_{R,d}^{\mathrm{NL}}, \tag{15}$$

since $\alpha + \beta = 5/3$, and

$$\left. \frac{\partial \tilde{T}_s^{\mathrm{NL}}[N_{R,l}^0]}{\partial N_{R,l}^0} \right|_{N_{R,s/p}^0=0} = (N_{R,d}^{\mathrm{total}})^{\alpha+\beta-1}(2l+1)\int_{\mathrm{MT}}\!\!\int_{\mathrm{MT}} f(r)[\alpha\rho_{R,d}^{\alpha-1}(r)\rho_{R,l}(r)W(|\vec{r}-\vec{r}\,'|)$$

$$\cdot \rho_{R,d}^{\beta}(r') + \beta\rho_{R,d}^{\alpha}(r)W(|\vec{r}-\vec{r}\,'|)\rho_{R,d}^{\beta-1}(r')\rho_{R,l}(r')]d\vec{r}d\vec{r}\,'$$

$$= (N_{R,d}^{\mathrm{total}})^{\frac{2}{3}} C_{R,l}^{\mathrm{NL}}. \tag{16}$$

Again, the constants $V_{R,d}^{\mathrm{NL}}$ and $C_{R,l}^{\mathrm{NL}}$ depend only on the fixed radial basis functions.

Combining Eqs. (11)-(16), we can approximate

$$\tilde{T}_s^{\mathrm{TF+vW+NL}}[N_{R,l}^0] \approx (V_{R,d}^{\mathrm{TF}} + V_{R,d}^{\mathrm{NL}}) \cdot (N_{R,d}^{\mathrm{total}})^{\frac{5}{3}} + N_{R,d}^{\mathrm{total}} E_{R,d}^{\mathrm{vW}}$$

$$+ \sum_{l=s,p} \frac{[(C_{R,l}^{\mathrm{TF}} + C_{R,l}^{\mathrm{NL}})(N_{R,d}^{\mathrm{total}})^{\frac{2}{3}} + C_{R,l}^{\mathrm{vW}}]}{2l+1} N_{R,l}^{\mathrm{total}}. \tag{17}$$

Here we want to emphasize that all the parameters defined above, such as C, V and E, are determined by the fixed radial basis functions, and thus are system independent. This system independence promises that the approximation to E^{NL} using the above form features good transferability as long as the basis functions are transferable. A more accurate approximation can be obtained by including higher order terms in the expansion of the functional $T_s^{\mathrm{TF+vW+NL}}[N_{R,l}^0]$ in Eq. (10). Eq. (10) applies if $N_{R,d}^{\mathrm{total}} \gg N_{R,s/p}^{\mathrm{total}}$ in the core region, e.g., for transition metals. According to the above ideas, one can also derive a similar formula for, e.g., oxygen, where the p channel is localized and dominates in the core region. Because the d channel in transition metals is localized, $N_{R,d}^{\mathrm{total}}$ only weakly responds to system changes. Therefore, as a good approximation for the present case of transition metals, we can rewrite Eq. (17),

$$\tilde{T}_s^{\mathrm{TF+vW+NL}}[N_{R,l}^0] = V_R^{d,\mathrm{KEDF}}(N_{R,d}^{\mathrm{total}})^{\frac{5}{3}} + \sum_{R,l=s,p,d} N_{R,l}^{\mathrm{total}} E_R^{l,\mathrm{KEDF}}. \tag{18}$$

Combination of Eq. (7), Eq. (8) and Eq. (18) gives the first two leading terms in E^{NL} used in the main manuscript

$$E^{\mathrm{NLPS}} + \tilde{T}_s - \tilde{T}_s^{\mathrm{KEDF}}[N_{R,l}^0] = \sum_{R,l} N_{R,l}^{\mathrm{total}} E_R^{l,\mathrm{NLPS}} + \sum_{R,l} N_{R,l}^{\mathrm{total}} E_R^{l,T_s} - V_R^{d,\mathrm{KEDF}}(N_{R,d}^{\mathrm{total}})^{\frac{5}{3}} - \sum_{R,l} N_{R,l}^{\mathrm{total}} E_R^{l,\mathrm{KEDF}}$$

$$= \sum_{R,l} N_{R,l}^{\mathrm{total}} E_R^l - V_R^{d,\mathrm{KEDF}}(N_{R,d}^{\mathrm{total}})^{\frac{5}{3}}. \tag{19}$$

The first term contains all the linear contributions of NLPS and $\tilde{T}_s$ and $-\tilde{T}_s^{KEDF}$ and the second term corrects the leading nonlinear contributions in the KEDF. In a more general form, we can rewrite the second term in Eq. (19) to obtain

$$E^{\mathrm{NL}} = \sum_{R,l} N_{R,l}^{\mathrm{total}} E_R^l - \sum_{R,l} V_R^{l,\mathrm{KEDF}}(N_{R,l}^{\mathrm{total}})^{\frac{5}{3}}. \tag{20}$$

For transition metals, $V_R^{l=s/p,\mathrm{KEDF}} = 0$ and only $V_R^{d,\mathrm{KEDF}}$ remains. The discussions above suggest good transferability of the parameters in the above equation.

We next consider the first order term in Eq. (9): one can easily confirm that $\left. \frac{\partial \tilde{T}_s^{\mathrm{TF/vW}}}{\partial N_R^{lm}} \right|_{\{N_{R,l}^0\}}$ is independent of the magnetic quantum number m,

$$\left. \frac{\partial \tilde{T}_s^{\mathrm{TF/vW}}}{\partial N_R^{lm}} \right|_{N_{R,l}^0} = \int_{\mathrm{MT}} \frac{\delta \tilde{T}_s^{\mathrm{TF/vW}}}{\delta\rho} \left. \frac{\partial\rho}{\partial N_R^{lm}} \right|_{\{N_{R,l}^0\}} d\vec{r}$$

$$= \int_{\text{MT}} \left. \frac{\delta \tilde{T}_s^{\text{TF/vW}}}{\delta \rho} \right|_{\{N_{R,l}^0\}} \phi_{R,l}^2(r)|Y_{lm}|^2 r^2 dr d\Omega$$

$$= \int_0^{Ws} \left. \frac{\delta \tilde{T}_s^{\text{TF/vW}}}{\delta \rho} \right|_{\{N_{R,l}^0\}} \phi_{R,l}^2(r) r^2 dr$$

$$= A_R^l, \tag{21}$$

since $\left. \frac{\delta \tilde{T}_s^{\text{KEDF}}}{\delta \rho} \right|_{\{N_{R,l}^0\}}$ is a spherical potential because of the spherical electron density when $N_R^{lm} = N_{R,l}^0$. This leads to

$$\sum_{lm} \left. \frac{\partial \tilde{T}_s^{\text{TF/vW}}}{\partial N_R^{lm}} \right|_{\{N_{R,l}^0\}} \Delta N_R^{lm} = \sum_l A_R^l \sum_{m=-l}^l \Delta N_R^{lm} = 0.$$

However, for the WGC99 KEDF [3], the NL part $\left. \frac{\partial T_s^{\text{NL}}}{\partial N_R^{lm}} \right|_{\{N_{R,l}^0\}}$ explicitly depends on the quantum number m, due to its nonlocal nature and the non-spherical density distribution in the given crystal structure. Therefore, this NL KEDF part contributes to the first order term, which consequently depends on the symmetry of the structure. This symmetry dependence results in a first order error in Eq. (9). However, contributions of the NL KEDF term are small and can be further reduced by introducing a weighting function for the KEDF [4]. We thus neglect this first order term for E^{NL}.

In the following, we focus next on the second and third order terms for different KEDFs in Eq. (9). Since the s channel features only a single m value, $N_{R,s} - N_{R,s}^0 = 0$, i.e., it does not contribute. We neglect contributions from the largely unoccupied p channel since they are very small for transition metals. Thus, the second and third terms in Eq.(9) are simplified as,

$$\frac{1}{2} \sum_{R,l=d,m,m'} \left. \frac{\partial^2 \tilde{T}_s^{\text{KEDF}}}{\partial N_R^{lm} \partial N_R^{lm'}} \right|_{\{N_{R,l}^0\}} \Delta N_R^{lm} \Delta N_R^{lm'} +$$

$$\frac{1}{6} \sum_{R,l=d,m,m',m''} \left. \frac{\partial^3 \tilde{T}_s^{\text{KEDF}}}{\partial N_R^{lm} \partial N_R^{lm'} \partial N_R^{lm''}} \right|_{\{N_{R,l}^0\}} \Delta N_R^{lm} \Delta N_R^{lm'} \Delta N_R^{lm''} + \ldots. \tag{22}$$

From now on, we only consider the TF and vW KEDFs for the coefficients of second and third order terms because of their dominant contributions (as compared to the NL part of the KEDF). For the second order coefficients, we have

$$\frac{1}{2} \left. \frac{\partial^2 \tilde{T}_s^{\text{TF/vW}}}{\partial N_R^{dm} \partial N_R^{dm'}} \right|_{\{N_{R,l}^0\}} = \frac{1}{2} \int_{\text{MT}} \left. \frac{\delta^2 \tilde{T}_s^{\text{TF/vW}}}{\delta \rho^2} \right|_{\{N_{R,l}^0\}} |\psi_{R,dm} \psi_{R,dm'}|^2 d\vec{r}$$

$$= \frac{1}{2} \int_0^{Ws} \left. \frac{\delta^2 \tilde{T}_s^{\text{TF/vW}}}{\delta \rho^2} \right|_{\{N_{R,l}^0\}} \phi_{R,d}^2 \phi_{R,d}^2 r^2 dr \cdot \int |Y_{dm} Y_{dm'}|^2 d\Omega$$

$$= \frac{1}{2} (4\pi)^2 \int_0^{Ws} \left. \frac{\delta^2 \tilde{T}_s^{\text{TF/vW}}}{\delta \rho^2} \right|_{\{N_{R,l}^0\}} \rho_{R,d}^2 r^2 dr \int |Y_{dm} Y_{dm'}|^2 d\Omega$$

$$= U_R^{\text{TF/vW,d}} A_{dm,dm'}, \tag{23}$$

since $\left. \frac{\delta^2 \tilde{T}_s^{\text{TF/vW}}}{\delta \rho^2} \right|_{\{N_{R,l}^0\}}$ is spherical inside the MT spheres. Here the quantity $U_R^{\text{TF/vW,d}} = 2\pi \int_0^{Ws} \frac{\delta^2 T_s^{\text{TF/vW}}}{\delta \rho^2} |_{N_{R,l}^0}$ $\rho_{R,d}^2 r^2 dr$, and $A_{lm,lm'} = 4\pi \int |Y_{lm} Y_{lm'}|^2 d\Omega$ which measures the overlap of the different spherical harmonics and is system independent. Therefore, the second order term can be rewritten as

$$\frac{1}{2} \sum_{R,l=d,m,m} \left. \frac{\partial^2 \tilde{T}_s^{\text{TF/vW}}}{\partial N_R^{lm} \partial N_R^{lm'}} \right|_{\{N_{R,l}^0\}} \Delta N_R^{dm} \Delta N_R^{dm'} \approx \sum_{R,l=d} U_R^{\text{TF/vW,d}} \sum_{m,m'=-2}^2 A_{dm,dm'} \Delta N_R^{dm} \Delta N_R^{dm'}$$

$$= \sum_{R,l=d} \tilde{U}_R^{\text{TF/vW,d}} \sum_{m=-2}^2 (\Delta N_R^{dm})^2, \tag{24}$$

since we numerically find the relations: $A_{dm,dm',m\neq m'} = \frac{1}{3}A_{dm,dm}$, $A_{dm,dm} = A_{dm',dm'}$ for $m \neq m'$. Here $\widetilde{U}_R^d = \frac{2}{3}U_R^{TF/vW,d}A_{dm,dm}$. It is obvious that $\widetilde{U}_R^{TF/vW}$ depends on the $N_{R,l}^0$ because of the dependence in $U_R^{TF/vW,d}$ as defined after Eq. (23) as a functional of ρ. To obtain system independent parameters for expressing the $U_R^{TF/vW,d}$, one can proceed further by Taylor expansion for $U_R^{TF/vW,d}$ around $N_{R,s/p}^0 = 0$. Since the localized d electrons dominate the MT spheres in transition metals, we adopt the above form for the present Letter as a proof of principle. Future work will include a more transferable model for $U_R^{TF/vW,d}$ [4]. Finally, we consider the third order expansion coefficients in Eq. (22),

$$
\begin{aligned}
\frac{1}{6}\left.\frac{\partial^3 \tilde{T}_s^{\mathrm{TF/vW}}}{\partial N_R^{lm}\partial N_R^{lm'}\partial N_R^{lm''}}\right|_{\{N_{R,l}^0\}} &= \frac{1}{6}\int_{\mathrm{MT}}\left.\frac{\delta^3\tilde{T}_s^{\mathrm{TF/vW}}}{\delta\rho^3}\right|_{\{N_{R,l}^0\}}|\psi_{R,dm}\psi_{R,dm'}\psi_{R,dm''}|^2 d\vec{r} \\
&= \frac{1}{6}\int_{\mathrm{MT}}\left.\frac{\delta^3\tilde{T}_s^{\mathrm{TF/vW}}}{\delta\rho^3}\right|_{\{N_{R,l}^0\}}(\phi_{R,d}^2)^3|Y_{dm}Y_{dm'}Y_{dm''}|^2 d\vec{r} \\
&= \frac{1}{6}\int_0^{Ws}\left.\frac{\delta^3\tilde{T}_s^{\mathrm{TF/vW}}}{\delta\rho^3}\right|_{\{N_{R,l}^0\}}(\phi_{R,d}^2)^3 r^2 dr\int|Y_{dm}Y_{dm'}Y_{dm''}|^2 d\Omega \\
&= \frac{1}{6}(4\pi)^3\int_0^{Ws}\left.\frac{\delta^3\tilde{T}_s^{\mathrm{TF/vW}}}{\delta\rho^3}\right|_{\{N_{R,l}^0\}}\rho_{R,d}^3 r^2 dr\int|Y_{dm}Y_{dm'}Y_{dm''}|^2 d\Omega \\
&= K_R^{\mathrm{TF/vW},d}\Lambda_{d,m,m',m''},
\end{aligned}
\tag{25}
$$

where $K_R^{\mathrm{TF/vW},d} = \frac{2\pi}{3}\int_0^{Ws}\left.\frac{\delta^3 T_s^{\mathrm{TF/vW}}}{\delta\rho^3}\right|_{\{N_{R,l}^0\}}\rho_{R,d}^3 r^2 dr$, and $\Lambda_{d,m,m',m''} = \int(4\pi)^2|Y_{dm}Y_{dm'}Y_{dm''}|^2$. Similar to $U_R^{\mathrm{TF/vW},d}$, $K_R^{\mathrm{TF/vW},d}$ depends on $N_{R,l}^0$, as we show in Ref. [4]. However, the MT region is, for transition metals, again dominated by the localized d electrons. For the applications in this Letter, we do not consider this $N_{R,l}^0$ dependence . We will apply the more accurate model [4] for $K_R^{\mathrm{TF/vW},d}$ in our future work.

The quantities $\Lambda_{d,m,m',m''}$ and $A_{d,m,m'}$ are evaluated numerically by using a Lebedev quadrature grid [5].
Summarizing, by combining Eqs. 6, 20, 22, 23, and 25, we obtain a form of E^{NL} as follows,

$$
\begin{aligned}
E^{\mathrm{NL}}[\{N_R\}] = &\sum_{R,l}E_R^l N_{R,l}^{\mathrm{total}} - \sum_{R,l}V_R^l(N_{R,l}^{\mathrm{total}})^{5/3} - \sum_{R,l,mm'}U_R^l A_{l,mm'}\Delta N_R^{lm}\Delta N_R^{lm'} \\
&- \sum_{R,l,mm'm''}K_R^l\Lambda_{l,mm'm''}\Delta N_R^{lm}\Delta N_R^{lm'}\Delta N_R^{lm''},
\end{aligned}
\tag{26}
$$

Although we derive this form based on transition metals in which the ionic core region is dominated by the d channel, it can be easily generalized to elements with s or p channel dominating the core region.

COMPUTATIONAL DETAILS

In all our calculations at different levels of theory, the Perdew-Burke-Ernzerhof (PBE)[6] form of the generalized gradient approximation is used as the exchange-correlation functional, and a nonlinear core correction [7] is applied for Ti.

Our KSDFT-NLPS calculations are carried out using the ABINIT [8] software package. The Troullier-Martins (TM) form [9] of the nonlocal pseudopotential (NLPS) with a nonlinear core correction is used and generated by the FHI98 code [10] with $r_{\mathrm{cutoff}} = 2.2$ bohr and $r_{nlc} = 1.2$ bohr as the cutoff radius for the core electron density. The kinetic energy cutoff for the plane wave basis is 1600 eV (equivalent to 6400 eV in our OFDFT code PROFESS 2.0 [11]) for the different Ti bulk phases. We use the following Monkhorst-Pack grids for k-point sampling: 30x30x20 for HCP, 30x30x30 for FCC, 30x30x30 for BCC, and 26x26x26 for SC within cells containing 2, 1, 2, and 1, respectively. In the calculations of surface formation energies, we use the following k-point sampling: 26x26x1 for all the surfaces (FCC (100), BCC (100), and HCP (0001)) within the periodic cells containing 17, 15, and 15 atomic layers, respectively, with 1 atom in each atomic layer. The vacuum thickness that separates the surfaces in all calculations is 22 Angstroms. For the vacancy formation energy calculation, we use k-point sampling of 8x8x10 for the supercell

containing 63 atoms and 1 vacancy site.

The bulk local pseudopotential (BLPS) [12] used in KS-BLPS and conventional OF-BLPS calculations is obtained by inverting the Kohn-Sham equations according to the procedure outlined in [13]. We use the Ti BCC phase for this inversion, because we found that the HCP and FCC phases generate very scattered potential values in Fourier space. We also used the same nonlinear core correction in the construction of the BLPS, with the core density constructed with FHI98. The KS-BLPS calculation is done by ABINIT with the same kinetic energy cutoff and k-point sampling as KS-NLPS that excellently converges all results.

OFDFT calculations do not require k-point sampling. For the conventional OF-BLPS calculation, we use a kinetic energy cutoff of 6400 eV which well converges all results.

For the AMD OFDFT calculations, we use the s channel of the TM NLPS as the local pseudopotential with nonlinear core correction, with a kinetic energy cutoff of 11000 eV to converge the total energy to an error below 0.5 meV per titanium atom. The basis functions inside the MT sphere are derived from KS-NLPS calculation of the Ti FCC phase at its equilibrium lattice structure. We use 2.2 bohr for the MT inner sphere radius and 2.7 bohr for the outer sphere radius. (The required mapping from the spheres onto the Cartesian grid induces serious numerical instabilities that are avoided by the use of a double sphere technique combined with a double grid approach [4].)

We use the same formula as Ref. [14] to determine the bulk moduli of different phases and the elastic constants of the HCP structure. The vacancy formation energy is calculated by employing Eq.5 in Ref. [15] at fixed volume in the limit of an infinitely large system,

$$E_{vf} = E[63, 1, V] - \frac{63}{64} E[64, 0, V],\tag{27}$$

where $E[63, 1, V]$ is the total energy of a cell with 63 Ti atoms and one vacancy site, $E[64, 0, V] = 64 E_{\mathrm{HCP}}$, where E_{HCP} is the ground state energy of the bulk Ti HCP phase per atom, and $V = 64 V_{\mathrm{HCP}}$, where V_{HCP} is the ground state volume per atom of the bulk Ti HCP phase.

---

[1] L. H. Thomas, Proc. Cambridge Philos. Soc. **23**, 542 (1927); E. Fermi, Rend. Accad. Naz. Lincei **6**, 602 (1927); E. Fermi, Z. Phys. **48**, 73 (1928).
[2] C. F. v. Weizsäcker, Z. Phys. **96**, 431 (1935).
[3] Y. A. Wang, N. Govind, and E. A. Carter, Phys. Rev. B **60**, 16350 (1999).
[4] Youqi Ke, et. al. to be published (2013).
[5] V. I. Lebedev, Zh. V̄ȳchisl. Mat. Mat. Fiz. **16** (2): 293306 (1976).
[6] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[7] S.G.Louie, S.Froyen and M. Cohen, Phys. Rev. B **26**, 1738 (1982).
[8] X. Gonze,*et.al.*, Computer Phys. Comm. **180**, 2582-2615 (2009).
[9] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[10] M. Fuchs, M. Scheffler, Comput. Phys. Commun. **119**, 67-98 (1999).
[11] Linda Hung, Chen Huang, Ilgyou Shin, Gregory S. Ho, Vincent L. Lignres, Emily A. Carter, Comp. Phy. Commun. **181**, 2208 (2010).
[12] B. Zhou, Y. A. Wang, and E. A. Carter, Phys. Rev. B **69**, 125109 (2004); S. Watson, B. J. Jesson, E. A. Carter, and P. A. Madden, Europhys. Lett. **41**, 37 (1998).
[13] C. Huang and E. A. Carter, Phys. Chem. Chem. Phys. **10**, 7109 (2008).
[14] I. Shin and E. A. Carter, Modell. Simul. Mater. Sci. Eng. **20**, 015006 (2011).
[15] G. Ho, M. T. Ong, K. J. Caspersen, and E. A. Carter, Phys. Chem. Chem. Phys. **9**, 4951 (2007).