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Chapter 5

ORBITAL-FREE KINETIC-ENERGY DENSITY FUNCTIONAL THEORY

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Abstract In the beginning of quantum mechanical Density-Functional Theory (DFT), there was the Thomas-Fermi (TF) model, which uses the electron density $\rho(\mathbf{r})$ (a function of only 3 coordinates) as the only physical variable. Calculations with this model were inexpensive but yielded poor numerical results due to a lack of understanding of exchange-correlation effects and the kinetic-energy density functional. Many years later, Hohenberg and Kohn (HK) established the formal foundation for DFT; Kohn and Sham (KS) devised a practical implementation and brought DFT into mainstream calculations of electronic structure. Although the KS formulation allows exact evaluation of the KS kinetic energy ($T_s[\rho]$), the one-electron orbitals introduced by the KS scheme inevitably encumber the formulation in three ways: (i) $3N$ (vs. 3) degrees of freedom, (ii) orbital orthonormalization, and (iii) Brillouin-zone (**k**-point) sampling in condensed phases. Given the accuracy of DFT with present exchange-correlation density functionals, it is logical to conclude that the last frontier in DFT is a better representation of the kinetic energy solely in terms of the density. If this is true, KS orbitals will be completely eliminated from DFT formulation, and the density can be solved directly from the TF-HK equation. This is certainly superior to the KS scheme because all energy terms can be computed in momentum space with an effectively linear scaling, $\mathcal{O}(M \ln M)$, where M is the integration grid size. This work reviews major ideas in the design of such optimal orbital-free kinetic-energy density functionals and their applications.

List of Abbreviations and Acronyms

ADA	Average-Density Approximation
AFWVA	Average Fermi Wave-Vector Approach
AWF	averaging weight function
CGE	Conventional Gradient Expansion
CLQL	correct large-q limit
DD	density-dependent
DFT	Density-Functional Theory
DI	density-independent
DM1	first-order reduced density matrix
EDF	energy density functional
EEDF	electronic energy density functional
FEG	free-electron gas
FFT	fast Fourier transformation
FWV	Fermi wave-vector
GGA	Generalized-Gradient Approximation
GS	ground state
HF	Hartree-Fock
HG	Hartree gas
HK	Hohenberg-Kohn
HKUEDF	HK universal energy density functional
HOMO	highest occupied molecular orbital
HREDF	Hartree repulsion energy density functional
KEDF	kinetic-energy density functional
KS	Kohn-Sham
LDA	Local-Density Approximation
LPS	local pseudopotential
LR	linear response
NLDA	Nonlocal Density Approximation
NLPS	nonlocal pseudopotential
OB	orbital-based
OF	orbital-free
PCF	pair-correlation function
QR	quadratic response
RPA	Random Phase Approximation
SADA	Semilocal Average-Density Approximation
SLDA	Semilocal-Density Approximation
SNDA	Simplified Nonlocal Density Approximation
TBFWV	two-body Fermi wave-vector
TF	Thomas-Fermi
TF-HK	Thomas-Fermi-Hohenberg-Kohn
TFλvW	Thomas-Fermi-λ-von Weizsäcker
WAD	weighted-average density
WADA	Weighted-Average-Density Approximation
WDA	Weighted-Density Approximation
XC	exchange-correlation
XCEDF	exchange-correlation energy density functional
XCH	exchange-correlation hole
XEDF	exchange energy density functional
vW	von Weizsäcker
vWλTF	von Weizsäcker-λ-Thomas-Fermi

I. INTRODUCTION

Calculations of ground state (GS) properties of fermionic systems have a long history. While many strategies focused on calculating a many-body wavefunction, other approaches sought to solve directly for the physical observable, namely, the electron density. Such are the techniques of Density-Functional Theory (DFT). Historically, DFT[1–28] began with the Thomas-Fermi (TF) model,[29–31] with considerable contributions from Dirac,[32] Wigner,[33] von Weizsäcker,[34] Slater[35,36] and Gáspár.[37] The Thomas-Fermi-Dirac-von Weizsäcker model[1,2,38–40] and the $X\alpha$ method[36,37,41] are the two major achievements before the "modern age." Not until some ten years later, Hohenberg and Kohn[42] laid the formal foundation for DFT; Kohn and Sham[43] then devised a practical implementation of DFT (in the similar spirit of the $X\alpha$ method). The theoretical foundation of DFT was further strengthened by Percus,[44] Levy,[45] Lieb,[46] Englisch and Englisch.[47,48]

For the GS, the two Hohenberg-Kohn (HK) theorems[42] legitimize the density $\rho(\mathbf{r})$ (a function of only 3 coordinates) as the basic variational variable; hence, all terms in the GS electronic energy of a quantum system are functionals of the density:

$$E_e[\rho] = T[\rho] + V_{ne}[\rho] + E_{ee}[\rho] \ , \tag{1}$$

where $E_e[\rho]$, $T[\rho]$, $V_{ne}[\rho]$, and $E_{ee}[\rho]$ are the total electronic, total kinetic, nuclear-electron attraction, and total inter-electron repulsion energy density functionals (EDF's), respectively. The sum $(T[\rho]+E_{ee}[\rho])$ is normally called the HK universal energy density functional (HKUEDF). However, the existence of the HK theorems does not provide much information about how to construct the electronic energy density functional (EEDF) solely in terms of the density explicitly, without relying on an orbital or wavefunction picture[*]. For an isolated many-electron quantum system, $V_{ne}[\rho]$ has a simple analytical OF expression,

$$V_{ne}[\rho] = \langle v_{ext}(\mathbf{r})\rho(\mathbf{r})\rangle \ , \tag{2}$$

where $v_{ext}(\mathbf{r})$ is the local nuclear-electron Coulomb attraction potential (one form of the so-called external potential). The other two terms in Eq. (1), however, do not have analytical OF expressions directly in terms of the density.

The Kohn-Sham (KS) scheme[43] introduces a single-determinant wavefunction in terms of the KS orbitals and partitions the HKUEDF into three main pieces:

$$T[\rho] + E_{ee}[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] \ , \tag{3}$$

where $T_s[\rho]$, $J[\rho]$, and $E_{xc}[\rho]$ are the KS kinetic, inter-electron Coulomb repulsion (also called the Hartree repulsion), and exchange-correlation (XC) EDF's,

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[*] Hereafter, we will use "orbital-free" (OF) to describe any physical entity that does not rely on an orbital or wavefunction picture and use "orbital-based" (OB) for the opposite.

respectively. The Hartree repulsion energy density functional (HREDF) has its classical OF appearance,

$$J[\rho] = \frac{1}{2}\left\langle \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right\rangle . \tag{4}$$

Because of different scaling properties, the exchange-correlation energy density functional (XCEDF) can be further decomposed into separate exchange and correlation components,[49–51]

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] , \tag{5}$$

where $E_x[\rho]$ and $E_c[\rho]$ are the exchange and correlation EDF's, respectively. Within the KS scheme, the KS kinetic-energy density functional (KEDF) can be evaluated exactly through the KS orbitals, but the exact OF expression of the XCEDF remains unknown. Fortunately, the absolute value of the XCEDF is much smaller than that of the KS KEDF or the HREDF, and even crude OF approximations of the XCEDF are generally fine in practice.[3–28] In contrast, the situation is not so fortunate for the KEDF because its value is nearly the same as the total energy (the electronic energy plus the nuclear-nuclear Coulomb repulsion energy); crude OF approximations of the KEDF do not bring satisfactory results.[1–28]

After more than seventy years of intense study,[1–28] a thorough understanding of the OF-KEDF remains as elusive as before. Of course, formally, one can easily write kinetic energy in the following well-known expression:

$$T = -\frac{1}{2}\left\langle \nabla_{\mathbf{r}}^2 \gamma(\mathbf{r},\mathbf{r}')\Big|_{\mathbf{r}=\mathbf{r}'} \right\rangle = \frac{1}{2}\left\langle \nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}'} \gamma(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \right\rangle , \tag{6}$$

for a given first-order reduced density matrix (DM1),[52–57] $\gamma(\mathbf{r},\mathbf{r}')$. In conventional OB methods,[58–60] the DM1 has a spectral resolution:

$$\gamma(\mathbf{r},\mathbf{r}') = \sum_i \gamma_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') , \tag{7}$$

where $\{\gamma_i\}$ are the occupation numbers of the orbitals $\{\phi_i(\mathbf{r})\}$, and $\{\phi_i(\mathbf{r})\}$ can be canonical KS orbitals,[43] canonical Hartree-Fock (HF) orbitals,[58–62] the more general Löwdin natural orbitals,[52–57, 63, 64] or even the Dyson orbitals.[65–70] If the orbitals are spin orbitals, the occupation numbers will lie between 0 and 1; otherwise, the occupation numbers range between 0 and 2.[52–57] The latter is usually called the spin-compensated case. When the occupation numbers are either 0 or 1 and the spin orbitals are mutually orthogonal, the DM1 has the useful idempotency property†,

$$\int \gamma(\mathbf{r},\mathbf{r}'')\gamma(\mathbf{r}'',\mathbf{r}')d\tau'' = \gamma(\mathbf{r},\mathbf{r}') \; . \tag{8}$$

The spin-compensated version of Eq. (8) has a prefactor of 2, due to the double occupancy of occupied orbitals,

$$\int \gamma(\mathbf{r},\mathbf{r}'')\gamma(\mathbf{r}'',\mathbf{r}')d\tau'' = 2\gamma(\mathbf{r},\mathbf{r}') \; . \tag{9}$$

Such orbitals are solutions of the following one-particle Schrödinger-like equations

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + \hat{v}_{eff}(\mathbf{r};[\rho])\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \; , \tag{10}$$

whose effective potential operator $\hat{v}_{eff}(\mathbf{r};[\rho])$ is generally a complicated functional of the density, which is the diagonal element of the DM1

$$\rho(\mathbf{r}) = \gamma(\mathbf{r},\mathbf{r}) \; . \tag{11}$$

For the GS, the HK theorems[42] guarantee that Eq. (10) of different *exact* theories all deliver the same GS density in spite of distinct mathematical structures of $\hat{v}_{eff}(\mathbf{r};[\rho])$ within different theoretical approaches[58–60] (i.e. local vs. nonlocal operators). The reason is simple: the density is one-to-one mapped on to the GS wavefunction, regardless of how the exact wavefunction and the exact density are calculated.

However, the major obstacle lies in the fundamental quest: how to express the DM1 in terms of a given density without solving Eq. (10) for orbitals. If this can be done, all terms in the HKUEDF will be accurately approximated. Consequently, the GS energy and density of a system with a fixed number of electrons can be obtained via solving a single Thomas-Fermi-Hohenberg-Kohn (TF-HK) equation:[42]

$$\frac{\delta E_e[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta V_{ne}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{ee}[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + v_{eff}^{KS}(\mathbf{r};[\rho]) = \mu \; , \tag{12}$$

where the density is the sole variational variable and μ is the Lagrange multiplier needed to keep the density normalized to the number of electrons in the system, N.

[†] It is clear that electrons are interacting with one another through the exchange hole or the exchange-correlation hole (see Section V), even within the quasi-independent-particle models, i.e., the HF method in the former and the KS method in the latter. We feel that the idempotency property cannot simply arise from a non-interacting or independent-particle nature. It is then more appropriate to use the term “idempotent” than “non-interacting” to characterize any entity that originates from the idempotency property.

The KS (local) effective potential has three components: the external potential, the Hartree potential, and the XC potential,

$$v_{eff}^{KS}(\mathbf{r};[\rho]) = v_{ext}(\mathbf{r}) + v_h(\mathbf{r}) + v_{xc}(\mathbf{r}) \ , \tag{13}$$

which are just functional derivatives of corresponding EDF's:

$$v_{ext}(\mathbf{r}) = \frac{\delta V_{ne}[\rho]}{\delta\rho(\mathbf{r})} \ , \tag{14}$$

$$v_h(\mathbf{r}) = \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\tau' \ , \tag{15}$$

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} \ . \tag{16}$$

Obviously, the OF-DFT approach based on Eq. (12) has many advantages over the OB approaches. First, the degrees of freedom is reduced from $3N$ to 3. Second, without any orbital dependence, the complication and cost associated with orbital manipulation, including orbital orthonormalization and orbital localization (for linear-scaling implementations), are avoided. Third, for metals, the need for Brillouin-zone (**k**-point) sampling of the wavefunction[71–80] is completely eliminated. Fourth, the utilization of the fast Fourier transformation (FFT)[81,82] in solving Eq. (12) is essentially linear-scaling with respect to system size[‡], while the cost in exactly solving Eq. (10) scales at least $\mathcal{O}(N^3)$, because of the matrix diagonalization step. Although OB linear-scaling $\mathcal{O}(N)$ density-functional methods[83–96] do exist, they are still much more complicated to implement and computationally more intensive than the OF-DFT approach.[97] In addition, these OB linear-scaling density-functional methods rely on orbital localization, which limits such techniques to non-metallic systems.[96]

All these positive features will be realized only if one knows all functionals in Eq. (1) solely in terms of the density. The accuracy of recent XCEDF's accounts for the popularity enjoyed by DFT via the KS scheme. Comparing to such high-quality XCEDF's, OF-KEDF's are still lacking accuracy and transferability for all kinds of systems in diverse scenarios, even after over seventy years of research. For this very reason, it has been widely recognized that the OF-KEDF is the most difficult component in the EEDF to be represented approximately.[3–5] Only very recently, better designed OF-KEDF's[98–111] have begun to appear, along with highly efficient numerical implementations[97,104–112] for large-scale condensed-phase simulations.[97,104–125] We set our task in this review to provide readers a

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[‡] The computational cost of an FFT scales essentially linearly $\mathcal{O}(M\ln M)$ with respect to the integration grid size M.

clear picture of past advances and possible routes to be taken in the future. It is our hope that more studies on OF-KEDF's along these lines will soon revive the OF scheme[97–141] based on Eq. (12) as the preferred method of implementation of DFT.

In this review, atomic units will be used throughout unless otherwise noted. The most relevant atomic units for this review are the Hartree unit for energy and the Bohr unit for length. One Hartree is about 27.211 electron volts and equals 2 Rydbergs; one Bohr is about 0.52918 Angströms. More details can be found in Ref. [58], p. 41−43, or Ref. [59], p. xiv−xv.

II. THE THOMAS-FERMI MODEL AND EXTENSIONS

The TF model marks the true origin of DFT, although its simplicity goes hand-in-hand with many defects. Most notably, it produces no binding for any system,[142–145] and is only exact for the free-electron gas (FEG). Numerical results based on this model are quite poor in general: the self-consistent density of Eq. (12) exhibits no shell structure for atomic species and falls off algebraically instead of exponentially. Although the Conventional Gradient Expansion (CGE) does improve the energy if a good density is used for the calculation, it does not remedy any defects of the original TF model, if Eq. (12) is solved self-consistently. Time has produced a vast number of papers on this subject; interested readers are advised to consult other review articles and books for details.[1–7, 38–40] Here, we only provide a brief summary to gain some physical understanding and lay the foundation for later sections.

II.1 THE THOMAS-FERMI MODEL

The TF model expresses the DM1 in terms of the plane wave basis of the FEG,

$$\gamma(\mathbf{r},\mathbf{r}') = \frac{2}{(2\pi)^3}\sum_{\mathbf{k}}^{\mathrm{occ.}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \,, \qquad (17)$$

where the prefactor of 2 comes from the Pauli exclusion principle[146, 147] that allows two electrons per plane wave. When the number of electrons becomes large, the summation in Eq. (17) can be replaced by an integration and an analytic expression can then be obtained for the DM1,

$$\gamma(\mathbf{r},\mathbf{r}') = \frac{1}{4\pi^3}\int^{\mathrm{occ.}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}d\tau_{\mathbf{k}} = \frac{\sin y_0 - y_0\cos y_0}{\pi^2\,|\mathbf{r}-\mathbf{r}'|^3} \,, \qquad (18)$$

where y_0 is a natural variable[50] for a FEG with a Fermi wave-vector (FWV) $k_F = (3\pi^2\rho_0)^{\frac{1}{3}}$ and an uniform density ρ_0,

$$y_0 = k_F\,|\mathbf{r}-\mathbf{r}'| \,. \qquad (19)$$

For later convenience, let us define a new variable $\beta(\mathbf{r}) = \rho^{\frac{1}{3}}(\mathbf{r})$, and $\beta_0 = \rho_0^{\frac{1}{3}}$.

Multiplying and dividing Eq. (18) by k_F^3, we can rewrite it in a simpler form:

$$\gamma(\mathbf{r}, \mathbf{r}') = \frac{k_F^3}{\pi^2} \frac{\sin y_0 - y_0 \cos y_0}{y_0^3} = 3\rho_0 \frac{j_1(y_0)}{y_0} \ , \tag{20}$$

where j_1 is the spherical Bessel function.[81] Direct insertion of Eq. (20) into Eq. (6) yields

$$T = \left\langle -\frac{1}{8} \nabla_{\mathbf{r}}^2 \rho_0 + C_{TF} \beta_0^5 \right\rangle = C_{TF} \left\langle \beta_0^5 \right\rangle \ , \tag{21}$$

where C_{TF} is the TF constant, $\frac{3}{10}(3\pi^2)^{\frac{2}{3}}$. Clearly, Eq. (21) is different from the TF functional for general systems,

$$T_{TF} = \langle t_{TF}(\mathbf{r}) \rangle = C_{TF} \left\langle \beta^5(\mathbf{r}) \right\rangle \ . \tag{22}$$

Going from Eq. (21) to Eq. (22), one has to replace ρ_0 with $\rho(\mathbf{r})$ in Eq. (20) for general systems,

$$\gamma(\mathbf{r}, \mathbf{r}') = 3\rho(\mathbf{r}) \frac{j_1(y)}{y} \ , \tag{23}$$

with a local FWV $k_F(\mathbf{r}) = \left(3\pi^2\right)^{\frac{1}{3}} \beta(\mathbf{r})$ and $y = k_F(\mathbf{r}) \left| \mathbf{r} - \mathbf{r}' \right|$. Then, the TF functional naturally follows.

However, one should ask whether the ansatz Eq. (23) is a valid one, and exactly how good is the TF approximation. It is certain that for systems other than the FEG, the idempotency property in Eq. (9) satisfied by any idempotent DM1 will no longer be true for Eq. (23). Hence, the TF functional is actually not an approximation for the T_s functional, the KS idempotent KEDF. Further, Eq. (23) has the wrong asymptotic behavior for isolated finite systems as both r and r' become large, where the exact DM1 goes like the product of the highest occupied molecular orbital (HOMO) of Eq. (10) at two different points $\mathbf{r}$ and $\mathbf{r}'$,[66, 148–153]

$$\lim_{r, r' \to \infty} \gamma(\mathbf{r}, \mathbf{r}') = \left[\gamma_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}') \right]_{i = HOMO} = \rho^{\frac{1}{2}}(\mathbf{r}) \rho^{\frac{1}{2}}(\mathbf{r}') \ . \tag{24}$$

Inserting Eq. (24) into Eq. (6) yields the von Weizsäcker (vW) functional:[34]

$$T_{vW}[\rho] = \langle t_{vW}(\mathbf{r}) \rangle = \frac{1}{8} \left\langle \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \right\rangle \ , \tag{25}$$

which is considerably different from the TF functional. In fact, at those regions where the density can be accurately described by a single orbital, the DM1 has the asymptotic form and the KEDF reduces to the vW functional. Therefore, the TF ansatz should actually be thought of as merely a simple extension that reduces to the exact form at the FEG limit.

II.2 THE CONVENTIONAL GRADIENT EXPANSION AND GENERALIZED-GRADIENT APPROXIMATION

Dissatisfied with the TF model, researchers thought that including gradients of the density might allow the model to adjust to the local environment (i.e., deviations from the FEG limit) and might even remedy its defects. A great deal of effort was put into this strategy.[3–5, 154–188] The highest order gradient expansion with an analytic form is the sixth,[157]

$$T^{6}_{\mathrm{CGE}}[\rho] = \sum_{i=0}^{3} T_{2i}[\rho] = \sum_{i=0}^{3} \langle t_{2i} \rangle \ . \tag{26}$$

With the definition of natural variables,[50]

$$\xi_m = \frac{\boldsymbol{\nabla}^m \rho(\mathbf{r})}{\beta^{3+m}(\mathbf{r})} \ , \tag{27}$$

the integrands have a very compact form

$$t_{2i} = \beta^5(\mathbf{r}) f_{2i}(\xi_1, \xi_2, \xi_3, \ldots, \xi_{2i}) \ , \tag{28}$$

where $\{f_{2i}\}$ are analytic functions of the natural variables:

$$f_0 = C_{\mathrm{TF}} \ , \tag{29}$$

$$f_2 = \frac{(\xi_1)^2}{72} \ , \tag{30}$$

$$f_4 = \frac{(\xi_2)^2 - \frac{9}{8}\xi_2(\xi_1)^2 + \frac{1}{3}(\xi_1)^4}{1800 C_{\mathrm{TF}}} \ , \tag{31}$$

$$\begin{aligned} f_6 \ = \ & \frac{1}{504000 C^2_{\mathrm{TF}}} \Bigg[13(\xi_3)^2 + \frac{2575}{144}(\xi_2)^3 + \frac{249}{16}(\xi_1)^2 \xi_4 + \frac{1499}{18}(\xi_1)^2(\xi_2)^2 \\ & - \frac{1307}{36}\left[(\xi_1)^3 \cdot \xi_3\right] + \frac{343}{18}(\xi_1 \cdot \xi_2)^2 + \frac{8341}{72}\xi_2(\xi_1)^4 - \frac{1600495}{2592}(\xi_1)^6 \Bigg] \ . \end{aligned} \tag{32}$$

As one can see from above equations, the derivation quickly gets prohibitively involved that no analytic expression is available beyond sixth order. Nonetheless, a careful inspection of the detailed derivation reveals that f_{2i} has a more definite form[171]

$$f_{2i}(\xi_1, \xi_2, \xi_3, \ldots, \xi_{2i}) \ = \sum_{ac+bd=2i} C^{cd}_{ab} (\xi_a)^c (\xi_b)^d \ , \tag{33}$$

where $\{a, b, c, d\}$ are non-negative integers, $\{C_{ab}^{cd}\}$ are expansion coefficients, and ξ_0 is defined as 1. This immediately reveals that for any isolated, localized system whose density decays exponentially[§],[63,66,189–202] T_{2i} is divergent for all orders sixth and higher ($2i \geq 6$), because every term in Eq. (28) is unbounded asymptotically

$$\lim_{r \to \infty} \beta^5(\mathbf{r})(\xi_a)^c(\xi_b)^d \propto \beta^{5-2i}(\mathbf{r}) \to \infty \ . \tag{34}$$

One can further show that the corresponding potential, the functional derivative $\delta T_{2i}/\delta\rho$, is divergent for all orders fourth and higher ($2i \geq 4$) under the same condition. More generally, the same conclusion will hold for those regions where the density falls off exponentially (e.g., areas close to any nuclear centers). The consequence of such a property is that if the CGE is used for the OF-KEDF, the density from the self-consistent solution of Eq. (12) always decays algebraically,[4,172,173] where it should have exponential behavior.[63,66,189–202] Moreover, it will be shown in later sections that the CGE derivation has its flaws: the linear response (LR) of the CGE up to infinite order is wrong even at the FEG limit. As a result, the self-consistent solution based on the CGE will not produce any shell structure for atomic species,[4,172–174] regardless of the order of expansion.

Due to its simplicity, the second-order CGE[154–156,174]

$$T_{CGE}^2[\rho] = T_{TF}[\rho] + \frac{1}{9}T_{vW}[\rho] \tag{35}$$

has been the most used and has stimulated the development of the so-called TFλvW model,[3–5,40,173–188]

$$T_{TF\lambda vW}[\rho] = T_{TF}[\rho] + \lambda T_{vW}[\rho] \ , \tag{36}$$

where λ is some constant. After careful numerical fits, $\lambda = \frac{1}{5}$ has been found to be the optimal choice.[3–5,40,173–178] In general, aside from some intellectual value, the CGE is of little practical use for a full solution of the TF-HK equation, let alone the difficulty in accurately evaluating those high-order gradients of the density and complicated expressions of higher-order integrands.

Simultaneous with success of the Generalized-Gradient Approximation (GGA) for the XCEDF's,[203–242] similar efforts were being invested in analogous forms for the OF-KEDF's. Instead of going to higher and higher orders of gradients of the density, the GGA tries to capture most of those higher-order effects utilizing some proper functions of lower-order gradients, while retaining the form shown in Eq. (28),

$$T_{GGA}[\rho] = \left\langle \beta^5(\mathbf{r}) f_{GGA}(\xi_1, \xi_2) \right\rangle \ . \tag{37}$$

[§] As $r \to \infty$, both $\rho(\mathbf{r})$ and $\nabla^m\rho(\mathbf{r})$ decay exponentially. Therefore, $\lim_{r \to \infty} \xi_m \propto \beta^{-m}(\mathbf{r})$.

Such GGA OF-KEDF's are abundant in the literature,[243–249] but none of them delivers satisfactory results if Eq. (12) is solved variationally. The problem remains that they exhibit the wrong LR behavior (as discussed Section IV). On a deeper level, one recognizes that the XCEDF has a much smaller value compared with the total inter-electron repulsion energy or the total energy, while the value of the KEDF is of the same magnitude as the total energy, due to virial theorem. Therefore, a successful scheme for the XCEDF might not be expected to work for the KEDF, which needs a much higher accuracy. A corollary to this insight indicates that any successful treatment of the KEDF will most likely be more than sufficient for the XCEDF. We discuss this aspect more in Section V.

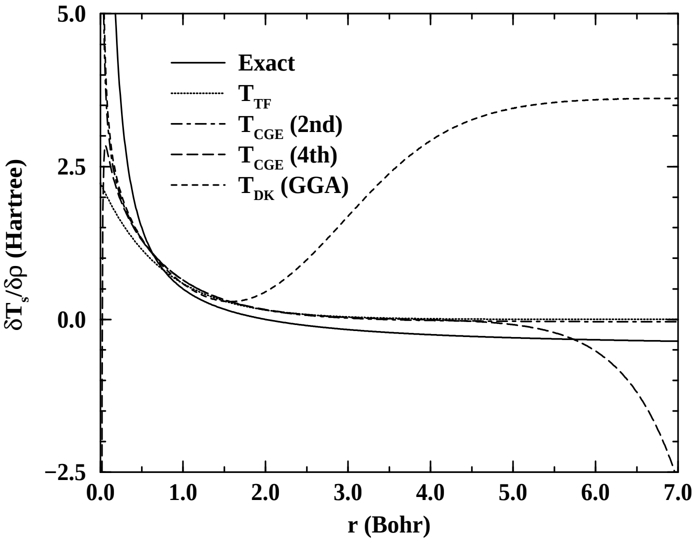

Figure 1 *Comparing the kinetic-energy potentials for H atom. The* T_{DK} *GGA OF-KEDF is from Ref. [244].*

We conclude this section by providing a comparison in Figures 1–5 of the kinetic-energy potentials of the CGE and several "better" GGA OF-KEDF's, using accurate densities for H, He, Be, Ne, and Ar atoms. For many-electron atoms, highly accurate densities (from atomic configuration interaction calculations)[250–253] are fed into the OF-KEDF's. Accurate potentials are obtained via a two-step procedure: the exact $\nu^{KS}_{eff}(\mathbf{r};[\rho])$ is obtained for a given accurate density,[253–272] and then the kinetic-energy potential is computed via Eq. (12)

$$\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} = \mu - \nu^{KS}_{eff}(\mathbf{r};[\rho]) \ , \tag{38}$$

where μ is taken to be the negative of the first ionization potential.[201, 202, 250–252] Figures 1–5 clearly shows that for general many-electron systems, the quality

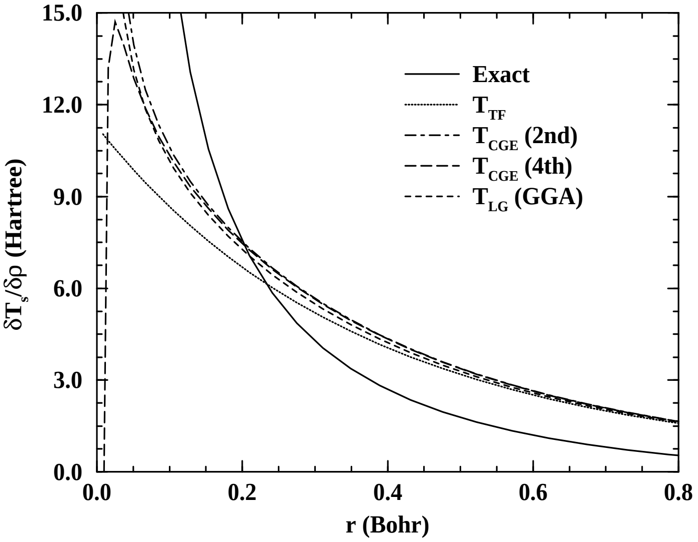

Figure 2 *Comparing the kinetic-energy potentials for He atom. The* T_{LG} *GGA OF-KEDF is from Ref. [245].*

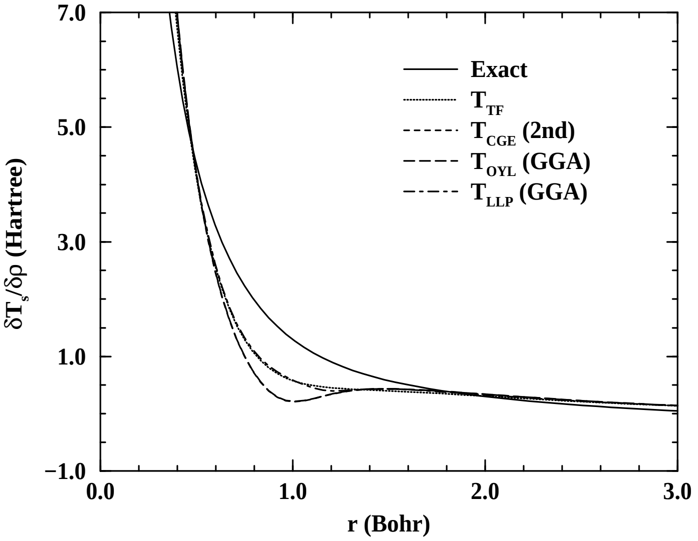

Figure 3 *Comparing the kinetic-energy potentials for Be atom. The* T_{OYL} *and* T_{LLP} *GGA OF-KEDF's are from Refs. [246] and [247], respectively. The* $T_{CGE}(2nd)$ *and* T_{OYL} *curves are almost on top of each other.*

of CGE and GGA OF-KEDF's potentials are rather poor, and sometimes the potential even exhibits unphysical asymptotic behavior (see Figure 1). As stated

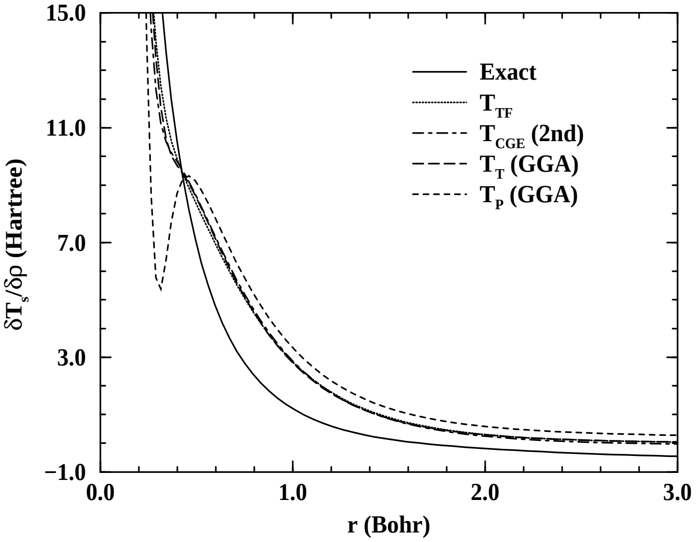

Figure 4 *Comparing the kinetic-energy potentials for Ne atom. The* T_T *and* T_P *GGA OF-KEDF's are from Refs. [248] and [249], respectively.*

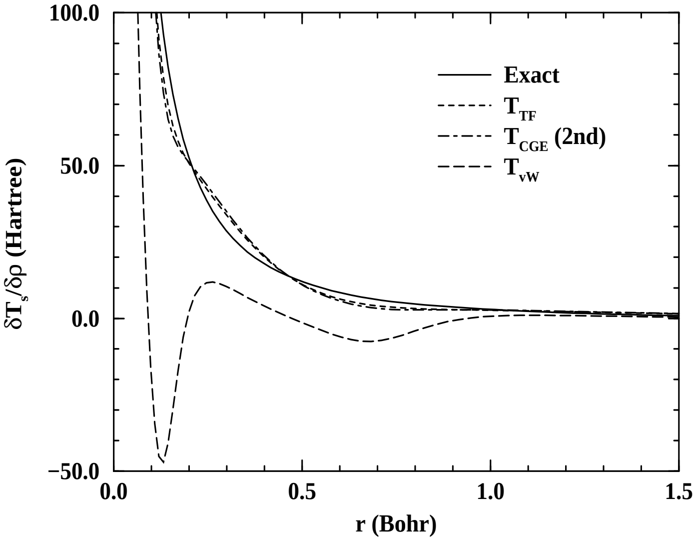

Figure 5 *Comparing the kinetic-energy potentials for Ar atom.*

above, the potential of the fourth-order CGE OF-KEDF diverges both near and far away from the nucleus (see Figures 1 and 2). Various GGA OF-KEDF's[243–249] do not improve the description of the potential, sometimes even worsening the agreement (see Figure 4). In fact, the potentials of various GGA OF-KEDF's are very similar to those of the second-order CGE and the TF functionals. It is also amazing to see very little difference between the second-order CGE and the TF functionals at the potential level. The potential of the vW functional, however, departs from the exact potential significantly, except for the regions very close to and far away from the nuclear core, where only one orbital dominates the contribution to the density (see Figure 5). These figures further suggest that the local truncation of the CGE[273,274] is not a significant improvement over the TF functional at the potential level because the CGE at various orders still cannot reproduce the exact kinetic-energy potential well. Such numerical comparisons demonstrate that the conventional wisdom in density functional design has its shortcomings: frequently only the energy value is fitted, while the physical content of the potential is seldom considered carefully.[236–239] Given the objective of the variational solution to the TF-HK equation, the importance of the accuracy of the kinetic-energy potential of any OF-KEDF cannot be overstated.

III. THE VON WEIZSÄCKER MODEL AND EXTENSIONS

The vW model looks at the OF-KEDF problem from a different angle. As already shown in Eqs. (24) and (25), the vW functional is the exact OF-KEDF for systems or regions of single orbital nature, such as the nuclear core and asymptotic regions of localized systems, one-electron systems, idempotent two-electron GS systems, and of course, all bosonic systems. However, it is completely wrong at the FEG limit, where the gradient of the density is zero everywhere and the TF functional is correct. Nonetheless, the vW functional offers a potentially good starting point for further approximation if the system is far away from the FEG limit (i.e. atoms, molecules, and realistic surfaces). Originally, the vW model was derived[34] after introducing modified plane waves of a certain form to account for inhomogeneity of the density, but we will present a general approach[5,98,275–280] that naturally unifies the TF and vW models together and plants the seed for further improvement in later sections.

III.1 THE ORIGIN OF THE VON WEIZSÄCKER MODEL

Looking at Eqs. (20) and (23), one realizes that there are many other choices that reduce to the exact FEG limit. For example, taking Eq. (24) into account, one can introduce a much more general ansatz for the DM1,

$$\gamma(\mathbf{r},\mathbf{r}') = \rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}')g(y_2) \ , \tag{39}$$

$$y_2(\mathbf{r},\mathbf{r}') = \zeta_F(\mathbf{r},\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'| \ , \tag{40}$$

$$\zeta_F(\mathbf{r},\mathbf{r}') = \zeta_F(k_F(\mathbf{r}),k_F(\mathbf{r}')) \ , \tag{41}$$

where $g(y_2)$ is an analytic function of the two-body natural variable y_2,[50] and $\zeta_F(\mathbf{r},\mathbf{r}')$ is a two-body Fermi wave-vector (TBFWV). The specific functional forms of $g(y_2)$ and ζ_F are not important at present, as long as they both are symmetric analytic functions of $\mathbf{r}$ and $\mathbf{r}'$, and satisfy the following constraints:

$$\lim_{\mathbf{r}\to\mathbf{r}'} y_2(\mathbf{r},\mathbf{r}') = 0 \ , \tag{42}$$

$$\lim_{y_2\to 0} g(y_2) = 1 \ , \tag{43}$$

$$\lim_{\mathbf{r}'\to\mathbf{r}} \zeta_F(\mathbf{r},\mathbf{r}') = k_F(\mathbf{r}) \ , \tag{44}$$

$$\lim_{\rho\to\rho_0} g(y_2) = 3\frac{j_1(y_0)}{y_0} \ . \tag{45}$$

From Eqs. (40) and (41), one can further show that

$$\lim_{\mathbf{r}\to\mathbf{r}'} (\boldsymbol{\nabla}_{\mathbf{r}} + \boldsymbol{\nabla}_{\mathbf{r}'})\, g(y_2) = 0 \ . \tag{46}$$

Based on Eqs. (6) and (39)–(46), one can derive exactly

$$T = T_{vW}[\rho] + T_X[\rho] \ , \tag{47}$$

$$T_X[\rho] = \frac{1}{2}\left\langle \rho^{\frac{1}{2}}(\mathbf{r}) \middle| \delta(\mathbf{r}-\mathbf{r}')\,(\boldsymbol{\nabla}_{\mathbf{r}}\cdot\boldsymbol{\nabla}_{\mathbf{r}'})\, g(y_2) \middle| \rho^{\frac{1}{2}}(\mathbf{r}') \right\rangle \ , \tag{48}$$

where the vW functional appears naturally. Further manipulation yields

$$\begin{aligned}
T_X[\rho] &= -\frac{1}{2}\left\langle \rho^{\frac{1}{2}}(\mathbf{r}) \middle| \delta(\mathbf{r}-\mathbf{r}')\zeta_F^2(\mathbf{r},\mathbf{r}')\left(\frac{d^2 g(y_2)}{dy_2^2} + \frac{2}{y_2}\frac{dg(y_2)}{dy_2}\right) \middle| \rho^{\frac{1}{2}}(\mathbf{r}') \right\rangle && (49)\\
&= -\frac{5}{3}C_{TF}\left\langle \rho^{\frac{5}{6}+\alpha}(\mathbf{r}) \middle| \delta(\mathbf{r}-\mathbf{r}')\left(\frac{d^2 g(y_2)}{dy_2^2} + \frac{2}{y_2}\frac{dg(y_2)}{dy_2}\right) \middle| \rho^{\frac{5}{6}-\alpha}(\mathbf{r}') \right\rangle && (50)\\
&= G[g]T_{TF}[\rho] \ , && (51)
\end{aligned}$$

where α is some constant, and $G[g]$ is a functional of $g(y_2)$,

$$G[g] = -\frac{5}{3}\left(\frac{d^2 g(y_2)}{dy_2^2} + \frac{2}{y_2}\frac{dg(y_2)}{dy_2}\right)_{y_2\to 0} \ . \tag{52}$$

If $g(y_2)$ is chosen such that $G[g] = 1$, $T_X[\rho]$ will become the TF functional. It is straightforward to show that the simple choice $g(y_2) = 3j_1(y_2)/y_2$ satisfies this condition.[5,98,276–280] In general, however, the value of $G[g]$ depends on the specific form of $g(y_2)$. Nonetheless, it is desirable to enforce $G[g] = 1$, so that the general OF-KEDF model

$$T = T_{vW}[\rho] + G[g]T_{TF}[\rho] \tag{53}$$

exactly recovers the TF functional at the FEG limit and the vW functional at the asymptotic region of localized systems. Unfortunately, numerical tests show that this simple model greatly overestimates the kinetic energy.[3–5,148,179,281–283]

III.2 EXTENSIONS OF THE VON WEIZSÄCKER MODEL

Since the above simple derivation unifies the TF model and the vW model in a coherent approach, researchers were quite encouraged to try other extensions based on Eq. (53) to improve its accuracy.[3–5] There are two simple ways to accomplish this: replacing $G[g]$ by a function of electron number N and nuclear charge Z,[283–292]

$$T = T_{vW}[\rho] + G(N,Z)T_{TF}[\rho] \ , \tag{54}$$

or introducing a local prefactor for the TF functional,[280]

$$T = T_{vW}[\rho] + \langle G(\mathbf{r})t_{TF}(\mathbf{r})\rangle \ . \tag{55}$$

The first proposed form of $G(N,Z)$ was

$$G(N,Z) = 1 - \frac{A}{N^{1/3}} \ , \tag{56}$$

with the optimized empirical parameters $A = 1.412$ for neutral atoms only and $A = 1.332$ for atoms and ions.[283] A later version of $G(N,Z)$ was[290, 291]

$$G(N,Z) = \left(1 - \frac{2}{N}\right)\left(1 - \frac{A_1}{N^{1/3}} + \frac{A_2}{N^{2/3}}\right) \ , \tag{57}$$

with the optimized empirical parameters $A_1 = 1.314$ and $A_2 = 0.0021$.[291] The first factor in Eq. (57) allows Eq. (54) to recover the right limit (the vW functional) for one-electron systems (with the correct spin-polarization) and idempotent two-electron GS's. However, there are other ways to enforce the right limit, yet retain similarity to Eqs. (56). For example, one might replace the first factor in Eq. (57) by $(1-\delta_{1N}-\delta_{2N})$, where δ_{ij} is the Kronecker delta function.

Both Eqs. (54) and (55) can yield remarkably accurate results if G is fitted to the target systems, though nontransferability remains to be the key problem. For instance, highly accurate local behavior of the density, including the shell structure of atomic species, can be achieved for the local extension shown in Eq. (55), but the resulting system-dependent $G(\mathbf{r})$ is not transferable.[280] Similarly, Eq. (54) can give accurate results for the energy if good densities are used, but it again cannot reproduce the shell structure nor accurate energies if Eq. (12) is variationally solved.[292]

Imperfect though they are, the impact of these functionals on later, more refined developments cannot be overstated. To this end, some general observations can be made. Eq. (53) certainly lacks flexibility, since once $g(y_2)$ is chosen, $G[g]$ will have a fixed value for all systems. Eq. (54) is better due to the global dependence of $G(N,Z)$ on specific system parameters. Eq. (55) is the best among these three, since it accounts for the local behavior of the OF-KEDF.

IV. CORRECT RESPONSE BEHAVIOR

It has long been established in the molecular physics community that the atomic shell structure is the barometer to measure the quality of any OF-KEDF.[3–5] In solid state physics, the corresponding physical standard is the oscillations in the density, including both the short-range (near-neighbor) oscillations and the asymptotic Friedel oscillations for metals.[293–301] The Friedel oscillations are caused by the occupation of orbitals at the Fermi surface.[302, 303] It is also well understood that the correct LR behavior is the key to predicting such oscillations: the overall shape and the weak logarithmic singularity of the LR function are responsible for the short-range and asymptotic oscillations, respectively.[301, 304] In this section, we review the derivation of the LR function (for there are some mistakes with the derivation in Ref. [301]) and the strategy for incorporating it into the design of better OF-KEDF's.

IV.1 LINEAR-RESPONSE THEORY

In terms of LR theory,[293–301] a small change in the potential causes a first-order change in the density,

$$\delta\rho(\mathbf{r}) = \int \chi(\mathbf{r}-\mathbf{r}')\delta v(\mathbf{r}')d\tau' \ , \tag{58}$$

where $\chi(\mathbf{r}-\mathbf{r}')$ is the real-space LR function

$$\chi(\mathbf{r}-\mathbf{r}') = \frac{\delta\rho(\mathbf{r})}{\delta v(\mathbf{r}')} \ . \tag{59}$$

After Fourier transformation, Eq. (58) can be written in momentum space as[¶]

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}(\mathbf{q})\delta\tilde{v}(\mathbf{q}) \ , \tag{60}$$

where $\tilde{\chi}(\mathbf{q})$ is the momentum-space LR function. Moreover, from Eq. (59) and the chain rule for functional derivatives, one has

$$\delta(\mathbf{r}'-\mathbf{r}'') = \int \frac{\delta\rho(\mathbf{r}'')}{\delta v(\mathbf{r})}\frac{\delta v(\mathbf{r})}{\delta\rho(\mathbf{r}')}d\tau = \int \chi(\mathbf{r}-\mathbf{r}'')\frac{\delta v(\mathbf{r})}{\delta\rho(\mathbf{r}')}d\tau \ . \tag{61}$$

Taking the Fourier transform of the resulting equation yields

$$\hat{F}\left(\frac{\delta v(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) = \frac{1}{\tilde{\chi}(\mathbf{q})} \ , \tag{62}$$

where $\hat{F}$ denotes the Fourier transform.

[¶] Hereafter, the Fourier transform of a real-space function $f(\mathbf{r})$ will share the same symbol but with a tilde, $\tilde{f}(\mathbf{q})$.

Different pieces in Eq. (12) can be chosen to be the above perturbation potential, resulting in different LR functions,$^{293–301}$ which are closely related to the second functional derivatives of corresponding EDF's. For example, the (static) external LR function of only the nuclear-electron attraction potential is given by

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}_{\rm ext}(\mathbf{q})\delta\tilde{v}_{\rm ext}(\mathbf{q}) \ , \tag{63}$$

$$\frac{1}{\tilde{\chi}_{\rm ext}(\mathbf{q})} = \hat{F}\left(\frac{\delta v_{\rm ext}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) = \hat{F}\left(\frac{\delta^2 V_{ne}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right) \ . \tag{64}$$

The XC LR function of only the XC potential is given by

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}_{\rm xc}(\mathbf{q})\delta\tilde{v}_{\rm xc}(\mathbf{q}) \ , \tag{65}$$

$$\frac{1}{\tilde{\chi}_{\rm xc}(\mathbf{q})} = \hat{F}\left(\frac{\delta v_{\rm xc}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) = \hat{F}\left(\frac{\delta^2 E_{\rm xc}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right) \ . \tag{66}$$

The Hartree LR function of only the Hartree repulsion potential is given by

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}_{h}(\mathbf{q})\delta\tilde{v}_{h}(\mathbf{q}) \ , \tag{67}$$

$$\frac{1}{\tilde{\chi}_{h}(\mathbf{q})} = \hat{F}\left(\frac{\delta v_{h}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) = \frac{4\pi}{q^2} \ . \tag{68}$$

The LR function within the Random Phase Approximation (RPA) for a Hartree gas (HG) without XC is given by

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}_{\rm RPA}(\mathbf{q})\delta\tilde{v}_{\rm HG}(\mathbf{q}) \ , \tag{69}$$

$$\delta\tilde{v}_{\rm HG}(\mathbf{q}) = \delta\tilde{v}^{\rm KS}_{\rm eff}(\mathbf{q}) - \delta\tilde{v}_{\rm xc}(\mathbf{q}) = \delta\tilde{v}_{\rm ext}(\mathbf{q}) + \delta\tilde{v}_{h}(\mathbf{q}) \ , \tag{70}$$

$$\frac{1}{\tilde{\chi}_{\rm RPA}(\mathbf{q})} = \frac{1}{\tilde{\chi}_{\rm ext}(\mathbf{q})} + \frac{1}{\tilde{\chi}_{h}(\mathbf{q})} \ . \tag{71}$$

Then, the total LR function of the entire KS effective potential is given by

$$\delta\tilde{\rho}(\mathbf{q}) = \tilde{\chi}_{\rm tot}(\mathbf{q})\delta\tilde{v}^{\rm KS}_{\rm eff}(\mathbf{q}) \ , \tag{72}$$

$$\frac{1}{\tilde{\chi}_{\rm tot}(\mathbf{q})} = \hat{F}\left(\frac{\delta v^{\rm KS}_{\rm eff}(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right) = \hat{F}\left(\frac{\delta^2(E_e[\rho]-T_s[\rho])}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right) = -\hat{F}\left(\frac{\delta^2 T_s[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right) \ , \tag{73}$$

$$\frac{1}{\tilde{\chi}_{\rm tot}(\mathbf{q})} = \frac{1}{\tilde{\chi}_{\rm ext}(\mathbf{q})} + \frac{1}{\tilde{\chi}_{h}(\mathbf{q})} + \frac{1}{\tilde{\chi}_{\rm xc}(\mathbf{q})} = \frac{1}{\tilde{\chi}_{\rm RPA}(\mathbf{q})} + \frac{1}{\tilde{\chi}_{\rm xc}(\mathbf{q})} \ . \tag{74}$$

In Eq. (73), the second functional derivative of the EEDF is zero due to the TF-HK equation. Accurate numerical values of various LR functions for nearly FEG's can be found in Refs. [305] and [306].

IV.2 THE LINDHARD FUNCTION

For a nearly FEG, an analytic expression for the total LR function is already available, due to Lindhard.[307] For completeness, we provide a concise derivation below.

We start from the FEG limit, where the density ρ_0 is uniform, orbitals $\{\phi_{\mathbf{k}}(\mathbf{r})\}$ are simple plane waves,

$$\phi_{\mathbf{k}}(\mathbf{r}) = (2\pi)^{-\frac{3}{2}} e^{i\mathbf{k}\cdot\mathbf{r}} \ , \tag{75}$$

and the zeroth-order Hamiltonian is just the summation of all the kinetic-energy operators,

$$\hat{H}_0 = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \ , \tag{76}$$

where index i runs over all electrons in the system. Now, let us introduce a weak perturbation potential $\nu(\mathbf{r})$ into this system, so that to first order the orbitals can be written accurately as

$$\phi_{\mathbf{k}}^{(1)}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \sum_{\mathbf{k}'\neq\mathbf{k}} \frac{V_{\mathbf{k}'\mathbf{k}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}} \phi_{\mathbf{k}'}(\mathbf{r}) \ , \tag{77}$$

where the coupling element $V_{\mathbf{k}'\mathbf{k}}$ is given by first-order perturbation theory as

$$V_{\mathbf{k}'\mathbf{k}} = \langle \phi_{\mathbf{k}'}(\mathbf{r}) | \, \nu(\mathbf{r}) \, | \phi_{\mathbf{k}}(\mathbf{r}) \rangle = (2\pi)^{-3} \tilde{\nu}(\mathbf{k} - \mathbf{k}') \ . \tag{78}$$

Introducing a new variable $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and replacing the summation by an integration, one rewrites Eq. (77) as

$$\phi_{\mathbf{k}}^{(1)}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \frac{2}{(2\pi)^3} \int_{\mathbf{q}\neq 0} \frac{\tilde{\nu}(\mathbf{q})\phi_{\mathbf{k}-\mathbf{q}}(\mathbf{r})}{\mathbf{k}^2 - (\mathbf{k}-\mathbf{q})^2} d\tau_{\mathbf{q}} \ . \tag{79}$$

Then, the first-order change in the density due to the first-order change in the potential is

$$\begin{aligned} \delta\rho(\mathbf{r}) &= \sum_{\mathbf{k}}^{\text{occ.}} f_{\mathbf{k}} \left[\left| \phi_{\mathbf{k}}^{(1)}(\mathbf{r}) \right|^2 - |\phi_{\mathbf{k}}(\mathbf{r})|^2 \right] \\ &= \frac{4}{(2\pi)^6} \int_{\mathbf{q}\neq 0} \tilde{\nu}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{k}}^{\text{occ.}} \frac{f_{\mathbf{k}}}{\mathbf{k}^2 - (\mathbf{k}-\mathbf{q})^2} d\tau_{\mathbf{q}} \ , \end{aligned} \tag{80}$$

or in momentum space,

$$\delta\tilde{\rho}(\mathbf{q}) = \frac{1}{2\pi^3} \tilde{\nu}(\mathbf{q}) \sum_{\mathbf{k}}^{\text{occ.}} \frac{f_{\mathbf{k}}}{\mathbf{k}^2 - (\mathbf{k}-\mathbf{q})^2} \ , \tag{81}$$

where $f_{\mathbf{k}}$ is the occupancy of $\phi_{\mathbf{k}}(\mathbf{r})$. At zero Kelvin, $f_{\mathbf{k}}$ is a step function; otherwise, it is the Fermi-Dirac distribution function. Comparing Eqs. (60) and (81), one immediately has

$$\tilde{\chi}_{\mathrm{tot}}(\mathbf{q}) = \frac{1}{2\pi^3} \sum_{\mathbf{k}}^{\mathrm{occ.}} \frac{f_{\mathbf{k}}}{\mathbf{k}^2 - (\mathbf{k}-\mathbf{q})^2} \; . \tag{82}$$

In Eq. (82), setting $f_{\mathbf{k}} = 2$, replacing the summation by an integration, and doing some algebra, one finally obtains the Lindhard function[307]

$$\begin{aligned} \tilde{\chi}_{\mathrm{Lind}}(\mathbf{q}) &= \frac{1}{\pi^3} \int_0^{k_F} 2\pi k^2 \int_0^{\pi} \frac{\sin\theta}{2kq\cos\theta - q^2} d\theta dk \\ &= -\frac{1}{\pi^2 q} \int_0^{k_F} k \ln\left|\frac{q+2k}{q-2k}\right| dk \\ &= -\frac{k_F}{\pi^2}\left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|\right) \; , \end{aligned} \tag{83}$$

where $\eta = q/(2k_F)$ is a dimensionless momentum. This finishes the derivation of the LR function at the FEG limit[‖]. Therefore, the FEG limit of Eq. (73) is

$$\hat{F}\left(\left.\frac{\delta^2 T_s[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}\right) = -\frac{1}{\tilde{\chi}_{\mathrm{Lind}}(\mathbf{q})} = \frac{\pi^2}{k_F} F_{\mathrm{Lind}}(\eta) \; , \tag{84}$$

$$F_{\mathrm{Lind}}(\eta) = \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln\left|\frac{1+\eta}{1-\eta}\right|\right)^{-1} \; . \tag{85}$$

Extension to finite temperature T can be made by using the Fermi-Dirac distribution function for $f_{\mathbf{k}}$ in Eq. (82)

$$\tilde{\chi}^T_{\mathrm{tot}}(\mathbf{q}) = -\frac{1}{\pi^2 q} \int_0^{\infty} \frac{k}{1 + e^{(k^2 - k_F^2)/(2k_B T)}} \ln\left|\frac{q+2k}{q-2k}\right| dk \; , \tag{86}$$

where k_B is the Boltzmann constant. More generally, higher-order response functions can be obtained if the perturbation theory is carried out to higher orders, but the derivation quickly becomes tediously involved.[42,43,108–110,308–310]

A few comments need to be made here. First, it turns out that the restriction $\mathbf{q} \neq 0$ in the integration of Eq. (80) is not a problem at all because the Lindhard function is analytic for $\mathbf{q} = 0$. Second, there is a weak logarithmic singularity at $\eta = 1$ or $q = 2k_F$ where the slope of the Lindhard function is divergent. This singularity can be attributed to the pole of the denominator of Eq. (82), and is

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[‖] Careful readers might notice that in Ref. [301], there is a sign error in Eq. (6.38). Our derivation should be the correct version.

closely related to the step function behavior of $f_{\mathbf{k}}$ at the Fermi surface at zero Kelvin. In fact, the singularity persists even at finite temperature, as one can easily see this from Eq. (86). It can be further shown that from Eq. (86), the asymptotic Friedel oscillations in the density at a finite low temperature T are of the following form**[96, 311, 312]

$$\lim_{r\to\infty} \delta\rho(\mathbf{r}) \quad \propto \quad \frac{\cos(2k_F r)}{r^3} e^{-c k_B T r/k_F} \ , \tag{87}$$

where c is some positive constant. Moreover, the overall shape of the LR function is the key for a good description of the short-range oscillations in the density.[301, 304] Therefore, the fine details of the LR function are essential to reproduce any correct physics. Third, the utilization of the step-function form of $f_{\mathbf{k}}$ dictates that the Lindhard function is only valid for idempotent DM1's, because the occupancy is either 0 or 2. Fourth, for later reference, one can rewrite the Lindhard function in terms of a polynomial expansion[301, 304]

$$\frac{\tilde{\chi}_{\mathrm{Lind}}(\mathbf{q})}{-k_F/\pi^2} = \begin{cases} \sum\limits_{n=0}^{\infty} \eta^{2n}/(4n^2-1) & \text{for} \quad \eta < 1 \ , \\ \\ \sum\limits_{n=1}^{\infty} \eta^{-2n}/(4n^2-1) & \text{for} \quad \eta > 1 \ . \end{cases} \tag{88}$$

Taking the inverses of Eq. (88), one can also rewrite $F_{\mathrm{Lind}}(\eta)$ in terms of a polynomial expansion

$$F_{\mathrm{Lind}}(\eta) = \begin{cases} 1 + \sum\limits_{n=1}^{\infty} a_n \eta^{2n} & \text{for} \quad \eta < 1 \ , \\ \\ 3\eta^2 - \frac{3}{5} + 3\sum\limits_{n=1}^{\infty} b_{n+1}\eta^{-2n} & \text{for} \quad \eta > 1 \ . \end{cases} \tag{89}$$

Here the expansion coefficients $\{a_n\}$ and $\{b_n\}$ satisfy the same recurrence relation (c is either a or b)

$$c_n = \sum_{m=1}^{n} c_{n-m}\bar{c}_m \ , \ \ c_0 = 1 \ , \ \ \bar{a}_n = \frac{1}{4n^2-1} \ , \ \ \bar{b}_n = -3\bar{a}_{n+1} \ . \tag{90}$$

The first few coefficients are shown in Table I. Finally, it should be clear that none of those potential pieces in Eq. (12) are included in the zeroth-order Hamiltonian $\hat{H}_0$ in Eq. (76) and the entire KS effective potential is treated as the perturbation.

**Apparently, the correct decay prefactor is proportional to r^{-3}, rather than to r^{-2} as "proved" in Refs. [311] and [313]. The r^{-2} decay prefactor is obtained without taking into account the correct LR behavior.

Table I *First few coefficients of the polynomial expansion of* $F_{\mathrm{Lind}}(\eta)$. *Here* $a_n = p_n^a/q_n^a$ *and* $b_n = -p_n^b/q_n^b$.

n	p_n^a	q_n^a	p_n^b	q_n^b
1	1	3	1	5
2	8	45	8	175
3	104	945	8	375
4	1048	14175	12728	1010625
5	24536	467775	551416	65690625
6	24735544	638512875	41587384	6897515625
7	2262184	76621545	2671830232	586288828125
8	1024971464	44405668125	15330117543304	4288702777734375
9	3592514217256	194896477400625	185527734659128	64330541666015625
10	481989460497736	32157918771103125	1601650275310046776	6732191185348535156 25

Therefore, it is not relevant to talk about the XC effects on the Lindhard function unless, of course, one starts from some Hamiltonian that includes exchange and/or correlation, like the HF Hamiltonian or the KS Hamiltonian. If the latter step is taken, simple plane waves cannot be used as the zeroth-order orbitals any more. Nonetheless, the Lindhard function is ideal for our purpose because it is a "pure" kinetic model [see Eq. (84)].

IV.3 COMPARISON OF VARIOUS KINETIC-ENERGY DENSITY FUNCTIONALS

With Eq. (84) in hand, we can easily assess the quality of various OF-KEDF's mentioned in previous sections, by comparing their momentum-space LR functions with the Lindhard function. For instance, the momentum-space LR function of the TF functional is just the constant prefactor in Eq. (83),

$$\tilde{\chi}_{\mathrm{TF}} = -\frac{k_F}{\pi^2}\,, \tag{91}$$

which is only correct at $\mathbf{q} = 0$, the FEG limit. For convenience, the TF LR function is usually used to renormalize the momentum-space LR function of a given model K for the OF-KEDF,

$$\bar{\chi}_{K} = \frac{\tilde{\chi}_{K}}{\tilde{\chi}_{\mathrm{TF}}} = \left(\frac{\pi^2}{k_F}\right) \Bigg/ \hat{F}\left(\left.\frac{\delta^2 T_s^K[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}\right) = \frac{1}{F_K(\eta)}\,. \tag{92}$$

It is straightforward to work out the momentum-space LR functions for any given model OF-KEDF's. Table II shows some of the results.

Table II *The momentum-space LR functions of some model OF-KEDF's at the FEG limit, in terms of* $F_K(\eta)$ *via Eq. (92), where* $\eta = q/(2k_F)$. *The recurrence relation for expansion coefficients* $\{a_n\}$ *is given in Eq. (90), and the first ten coefficients are shown in Table I.*

Model $T_s[\rho]$	$F_K(\eta)$
Exact	$F_{Lind}(\eta)$
$T_{TF}[\rho]$	1
$T_{vW}[\rho]$	$3\eta^2$
$T_{TF}[\rho] + \lambda T_{vW}[\rho]$	$1 + 3\lambda\eta^2$
$T_{vW}[\rho] + \lambda T_{TF}[\rho]$	$3\eta^2 + \lambda$
$T^m_{CGE}[\rho]$	$\sum_{n=0}^{m} a_n \eta^{2n}$

Table II clearly indicates that none of the previously mentioned OF-KEDF's has the correct LR behavior at the FEG limit. Even more interestingly, the TF functional is supposed to be exact at the FEG limit, but its LR function has no momentum dependence. At first glance, one would think that there is some inconsistency involved. In fact, there is no conflict because the TF functional is only the zeroth-order perturbation result, while the Lindhard function is the first-order result. A similar "paradox" exists for the asymptotic Friedel oscillations in Eq. (87).

More specifically, the weak logarithmic singularity at $\eta = 1$ divides the Lindhard function [see Eqs. (88) and (89)] into two branches: the low-momentum ($\eta < 1$) branch with the TF LR function as the leading term, and the high-momentum ($\eta > 1$) branch with the vW LR function as the leading term. By itself, the vW LR function is completely wrong at low momentum: becoming divergent at $\eta = 0$. Combinations of the TF and vW functionals, either the TFλvW model [see Eq. (36)] or the vWλTF model [see Eq. (54)], cannot reproduce the overall shape of the Lindhard function. As a side note, it is desirable to keep λ positive so that the resulting LR function will not have a singularity. However, it is clear that both Eqs. (56) and (57) are not always semipositive definite for all positive real N, and thus should be used with caution. To aid our understanding, we plots the renormalized LR functions at the FEG limit in Figures 6 and 7.

It is also intriguing to notice that the complicated CGE (or the GGA) is not doing much better either. In fact, if one carries out the CGE derivation to infinite order, one only gets the low-momentum branch of the Lindhard function right, because the weak logarithmic singularity of the exact LR function was never taken into account properly in the CGE derivation. Moreover, the LR function of the higher-order CGE converges to the Lindhard function very slowly and decays to zero very quickly, as clearly shown in Figure 7. It should be understood that the CGE is correct up to all orders in perturbation theory, not like any finite

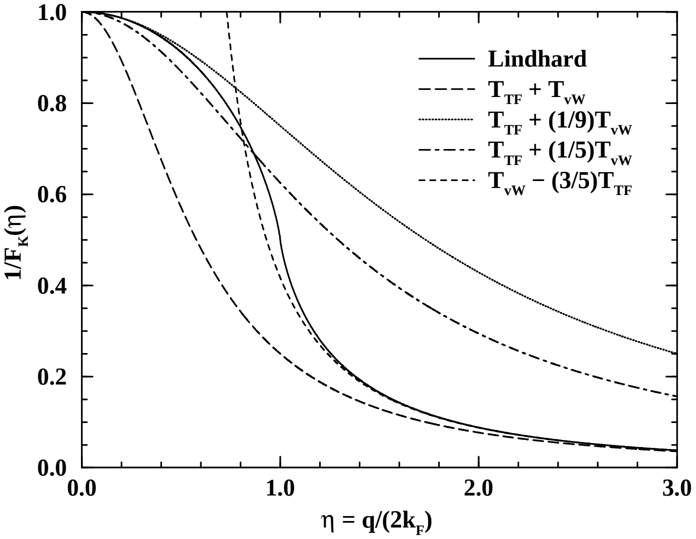

Figure 6 *Comparing the Lindhard function with the momentum-space LR functions of various model OF-KEDF's at the FEG limit.*

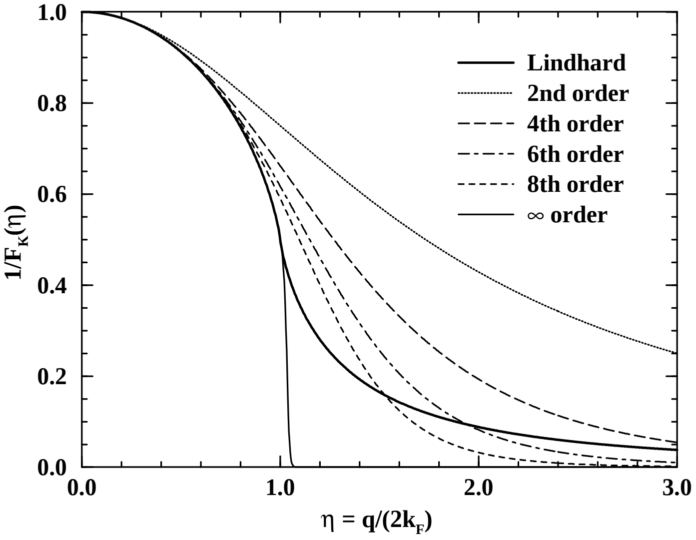

Figure 7 *Comparing the Lindhard function with the momentum-space LR functions of the CGE OF-KEDF's (up to infinite order) at the FEG limit.*

response theory, but its mishandling of the weak logarithmic singularity and the complexity in its derivation lend to its highly impractical nature. Similar to the second-order, low-momentum CGE, one can easily see from Eq. (89) and Table

II that the second-order, high-momentum CGE, which will be referred as the correct large-q limit (CLQL)[107] in later sections, is given by

$$T_{\mathrm{CLQL}} = T_{vW}[\rho] - \frac{3}{5} T_{\mathrm{TF}}[\rho] \;. \tag{93}$$

We believe that the CLQL is the right OF-KEDF for rapidly varying density regions. However, one should not attempt to use the CLQL generally, because its LR function $1/\left(3\eta^2 - \frac{3}{5}\right)$ has a pole at $\eta = 1/\sqrt{5}$.

In summary, all exercises so far seem to lead nowhere: simple-minded extensions based on the TF and vW functionals hit a dead end. A more innovative path has to be taken. Fortunately, there are such paths, mainly fueled by the advances in the design of the XCEDF's, namely the Average-Density Approximation (ADA)[314–316] and the Weighted-Density Approximation (WDA).[98, 260, 315–318]

Before we go any further, it is instructive to point out that almost all schemes (except for the CGE) discussed in this review, as well as by others, are unanimously based upon Eq. (20). In retrospect, this is not surprising, once one knows that Eq. (20) is just the zeroth-order term in the semiclassical expansion (in orders of $\hbar$, the Planck constant divided by 2π) of the DM1[168]

$$\gamma(\mathbf{r}, \mathbf{r}') = \gamma^{(0)}(\mathbf{r}, \mathbf{r}') + \gamma^{(2)}(\mathbf{r}, \mathbf{r}') \;, \tag{94}$$

$$\gamma^{(0)}(\mathbf{r}, \mathbf{r}') = \frac{k_F^3(\mathbf{r})}{\pi^2} \frac{j_1(y)}{y} \;, \tag{95}$$

$$\begin{aligned}
\gamma^{(2)}(\mathbf{r}, \mathbf{r}') = \frac{1}{96\pi^2} \Bigg\{ & 4\,[j_0(y) - y j_1(y)]\, \frac{\boldsymbol{\nabla}^2 k_F^2(\mathbf{r})}{k_F(\mathbf{r})} - 24\,[y j_0(y)]\, \frac{(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\nabla} k_F^2(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\
& - \left[(1 + y^2) j_0(y) - y j_1(y)\right] \frac{\left|\boldsymbol{\nabla} k_F^2(\mathbf{r})\right|^2}{k_F^3(\mathbf{r})} + 3\,[j_0(y) - y j_1(y)] \frac{\left|(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\nabla} k_F^2(\mathbf{r})\right|^2}{k_F(\mathbf{r})} \\
& + 8\,[y j_0(y)]\,(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\nabla} \left(\frac{(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\nabla} k_F^2(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right) \Bigg\} \;,
\end{aligned} \tag{96}$$

where j_0 and j_1 are the spherical Bessel functions.[81] Clearly, the overwhelming complexity of Eq. (96) precludes any efforts to more general OF-KEDF's based upon Eq. (94). Therefore, in the following, we will only concentrate on ideas that manipulate Eq. (95) to more general approximations.

V. NONLOCAL DENSITY APPROXIMATIONS

Before introducing the Nonlocal Density Approximations (NLDA's) for the OF-KEDF,[98–111] we would like to briefly outline the essence of the ADA and the WDA for the XCEDF[98, 260, 314–318] to aid our understanding later.

V.1 THE ESSENCE OF THE AVERAGE- AND WEIGHTED-DENSITY APPROXIMATIONS

In the language of the adiabatic connection formulation,[319–323] the XCEDF can be exactly written as

$$E_{xc}[\rho] = \frac{1}{2}\left\langle \rho(\mathbf{r}) \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \bar{\rho}_{xc}(\mathbf{r},\mathbf{r}') \right\rangle , \tag{97}$$

$$\bar{\rho}_{xc}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')\bar{h}_{xc}(\mathbf{r},\mathbf{r}') , \tag{98}$$

$$\bar{h}_{xc}(\mathbf{r},\mathbf{r}') = \int_0^1 h_\lambda(\mathbf{r},\mathbf{r}')d\lambda , \tag{99}$$

where $\bar{\rho}_{xc}(\mathbf{r},\mathbf{r}')$ and $\bar{h}_{xc}(\mathbf{r},\mathbf{r}')$ are the coupling-constant-(λ)-averaged exchange-correlation hole (XCH) and pair-correlation function (PCF), respectively. The PCF is symmetric in its variables

$$h_\lambda(\mathbf{r},\mathbf{r}') = h_\lambda(\mathbf{r}',\mathbf{r}) ; \tag{100}$$

the averaged XCH satisfies the sum rule

$$\int \bar{\rho}_{xc}(\mathbf{r},\mathbf{r}')d\tau' = \int \rho(\mathbf{r}')\bar{h}_{xc}(\mathbf{r},\mathbf{r}')d\tau' = -1 . \tag{101}$$

One can further split the XC effects into separate exchange and correlation contributions:

$$\bar{\rho}_{xc}(\mathbf{r},\mathbf{r}') = \rho_x(\mathbf{r},\mathbf{r}') + \rho_c(\mathbf{r},\mathbf{r}') , \tag{102}$$

$$\bar{h}_{xc}(\mathbf{r},\mathbf{r}') = h_x(\mathbf{r},\mathbf{r}') + h_c(\mathbf{r},\mathbf{r}') , \tag{103}$$

which satisfy different sum rules

$$\int \rho_x(\mathbf{r},\mathbf{r}')d\tau' = \int \rho(\mathbf{r}')h_x(\mathbf{r},\mathbf{r}')d\tau' = -1 , \tag{104}$$

$$\int \rho_c(\mathbf{r},\mathbf{r}')d\tau' = \int \rho(\mathbf{r}')h_c(\mathbf{r},\mathbf{r}')d\tau' = 0 . \tag{105}$$

(Interested readers should consult Refs. [50] and [51] for a concise, yet full description about the details of the adiabatic connection formulation. For brevity, we will not repeat them here.) The benefits of such a formulation are clear: the XCEDF has a quasi-Coulombic interaction form, where the pseudocharge $\bar{\rho}_{xc}(\mathbf{r},\mathbf{r}')$ and the PCF $h_\lambda(\mathbf{r},\mathbf{r}')$ carry all the information about XC effects.

Various approximations are built around the XCH and the PCF. For example, the well-known, widely-used Local-Density Approximation (LDA)[3–10, 42, 43, 324–326] assumes

$$\bar{\rho}_{xc}^{LDA}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})\bar{h}^{LDA}(\rho(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|) = \rho(\mathbf{r})\int_0^1 h_\lambda^{LDA}(\rho(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|)\,d\lambda\ , \tag{106}$$

which satisfies the sum rule required by Eq. (101)

$$\int \bar{\rho}_{xc}^{LDA}(\mathbf{r},\mathbf{r}')\,d\tau' = -1\ . \tag{107}$$

Similar to the generalization of the DM1 from Eqs. (20) to (23), one can think of the LDA is a generalization again of the FEG formula, i.e., replacing ρ_0 with $\rho(\mathbf{r})$ in $\bar{\rho}_{xc}^{FEG}(\mathbf{r},\mathbf{r}')$,[324–326]

$$\bar{\rho}_{xc}^{FEG}(\mathbf{r},\mathbf{r}') = \rho_0\bar{h}^{FEG}(\rho_0,|\mathbf{r}-\mathbf{r}'|) \to \rho(\mathbf{r})\bar{h}^{LDA}(\rho(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|)\ . \tag{108}$$

Unlike the poor performance of the LDA counterpart for the OF-KEDF, the LDA for the XCEDF actually does quite well most of the time, despite that Eq. (106) has the wrong density prefactor: $\rho(\mathbf{r})$ should be $\rho(\mathbf{r}')$ as in Eq. (98). Its success is attributable to Eq. (107) (which allows a systematic cancellation of errors) and the recipe shown in Eq. (108) (which provides a reasonable approximation for the spherically averaged XCH).[316]

In light of the success of the LDA, the ADA[314–316] closely follows the LDA and proposes

$$\bar{\rho}_{xc}^{ADA}(\mathbf{r},\mathbf{r}') = \bar{\rho}^{ADA}(\mathbf{r})\bar{h}^{LDA}\left(\bar{\rho}^{ADA}(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|\right)\ , \tag{109}$$

where the weighted-average density (WAD) is given by

$$\bar{\rho}^{ADA}(\mathbf{r}) = \int w\left(\bar{\rho}^{ADA}(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|\right)\rho(\mathbf{r}')\,d\tau'\ . \tag{110}$$

The peculiar recursion in Eq. (110) is mainly due to a lack of understanding of the TBFWV and due to the convenience of the automatic fulfillment of the sum rule for the XCH,

$$\int \bar{\rho}_{xc}^{ADA}(\mathbf{r},\mathbf{r}')\,d\tau' = -1\ . \tag{111}$$

The averaging weight function (AWF) $w\left(\bar{\rho}^{ADA}(\mathbf{r}),|\mathbf{r}-\mathbf{r}'|\right)$ is determined by enforcing the correct LR of the ADA XCEDF at the FEG limit,[305, 306]

$$\hat{F}\left(\left.\frac{\delta^2 E_{xc}^{ADA}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}\right) = \frac{1}{\tilde{\chi}_{xc}(\mathbf{q})} = \frac{1}{\tilde{\chi}_{Lind}(\mathbf{q})} - \frac{1}{\tilde{\chi}_{ext}(\mathbf{q})} - \frac{1}{\tilde{\chi}_{h}(\mathbf{q})}\ , \tag{112}$$

where Eqs. (66) and (74) are employed. In comparison, the LR function of the LDA XCEDF is only exact at $\mathbf{q}=0$ and has no momentum dependence,[306,327,328] while the LR functions of the GGA XCDEF's are also exact at $\mathbf{q}=0$ and have momentum dependence.[327,328] More interestingly, the LDA does a better job in reproducing the correct LR behavior than the GGA does, especially for the region of $q \leq 2k_F$.[306,327,328] This is the third reason for the success of the LDA XCEDF. Unfortunately, the LDA OF-KEDF does not enjoy similar success, because its LR function resembles the Lindhard function poorly (see Figure 6).

Since both the LDA and the ADA ignore the strict form of Eq. (98), the WDA[98,260,315–318] offers an alternative to obey it exactly,

$$\bar{\rho}_{xc}^{WDA}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')\bar{h}^{LDA}\left(\bar{\rho}^{WDA}(\mathbf{r}), |\mathbf{r}-\mathbf{r}'|\right) \ , \tag{113}$$

where the effective density $\bar{\rho}^{WDA}(\mathbf{r})$ is determined pointwise by enforcing the sum rule

$$\int \bar{\rho}_{xc}^{WDA}(\mathbf{r},\mathbf{r}')d\tau' = -1 \ . \tag{114}$$

Interestingly, numerical tests show that both the WDA and the ADA are generally superior to the LDA, but the ADA is the best[98,136–141,260,314–318,329–345] among the three. These results come with no surprise because all three approximations honor the sum rule of the XCH, but only the ADA complies with the right LR behavior at the FEG limit. It has been shown that the WDA XCEDF generally does not have the correct LR behavior,[328] which might be the cause of its poor performance, especially for the correlation energy. Nonetheless, by preserving the exact form of the XCH, the WDA should capture more of the anisotropic nature of the exact XCH, while the LDA and the ADA are spherically symmetric around $\mathbf{r}$. Furthermore, since the PCF's of both the ADA and the WDA have the same form as that of the LDA, they inevitably fail the symmetric requirement of Eq. (100). A simple symmetrization can fix this problem,[50]

$$\bar{h}_{sym}^{LDA}(\mathbf{r},\mathbf{r}') = \frac{\bar{h}^{LDA}(\bar{\rho}(\mathbf{r}), |\mathbf{r}-\mathbf{r}'|) + \bar{h}^{LDA}(\bar{\rho}(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|)}{2} \ , \tag{115}$$

but it destroys the automatic fulfillment of the sum rules in Eqs. (107) and (111) for the LDA and the ADA, and puts a heavier burden for the WDA to satisfy its own sum rule in Eq. (114).

It is also important to discuss the effect of the symmetrization on the XC potential, $\delta E_{xc}^{WDA}/\delta\rho$. For the exact XCEDF, the symmetric nature of the PCF directly leads to a two-term summation for the XC potential,

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} = v_1(\mathbf{r}) + 2v_2(\mathbf{r}) \ , \tag{116}$$

$$v_1(\mathbf{r}) = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}\frac{\delta\bar{h}_{xc}(\mathbf{r}',\mathbf{r}'')}{\delta\rho(\mathbf{r})}d\tau' d\tau'' \ , \tag{117}$$

$$v_2(\mathbf{r}) = \frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\bar{h}_{xc}(\mathbf{r},\mathbf{r}')d\tau' \, . \tag{118}$$

At large distance from a neutral atom, $v_2(\mathbf{r})$ goes to $-\frac{1}{2r}$ and $v_1(\mathbf{r})$ decays exponentially.[315,316,341,342] If a symmetric ansatz for the PCF is employed, the WDA XC potential will be symmetric automatically, just like the exact case above. Additionally, a symmetric XC potential has the exact asymptotic behavior ($-\frac{1}{r}$) and the spurious self-interaction effect in the HREDF $J[\rho]$ is mostly removed.[315,316,342] Unfortunately, because of the nonsymmetric nature of the ansatz for the PCF in Eq. (113), the XC potential within the present WDA framework has three terms instead,

$$v_{xc}^{WDA}(\mathbf{r}) = v_1^{WDA}(\mathbf{r}) + v_2^{WDA}(\mathbf{r}) + v_3^{WDA}(\mathbf{r}) \, , \tag{119}$$

$$v_1^{WDA}(\mathbf{r}) = \frac{1}{2}\int\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}\frac{\delta\bar{h}^{LDA}\left(\bar{\rho}^{WDA}(\mathbf{r}'), |\mathbf{r}'-\mathbf{r}''|\right)}{\delta\rho(\mathbf{r})}d\tau' d\tau'' \, , \tag{120}$$

$$v_2^{WDA}(\mathbf{r}) = \frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\bar{h}^{LDA}\left(\bar{\rho}^{WDA}(\mathbf{r}), |\mathbf{r}-\mathbf{r}'|\right) d\tau' \, , \tag{121}$$

$$v_3^{WDA}(\mathbf{r}) = \frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\bar{h}^{LDA}\left(\bar{\rho}^{WDA}(\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|\right) d\tau' \, . \tag{122}$$

Asymptotically, both $v_1^{WDA}(\mathbf{r})$ and $v_3^{WDA}(\mathbf{r})$ decay exponentially and $v_2^{WDA}(\mathbf{r})$ goes to $-\frac{1}{2r}$.[315,316,341,342] The inequality between $v_2^{WDA}(\mathbf{r})$ and $v_3^{WDA}(\mathbf{r})$ makes Eq. (119) differ from the exact form in Eq. (116). Although an *ad hoc* symmetrization can restore the exact form for the XC potential[331–333]

$$v_{xc}^{WDA}(\mathbf{r}) = v_1^{WDA}(\mathbf{r}) + 2v_2^{WDA}(\mathbf{r}) \, , \tag{123}$$

the corresponding XCEDF is unknown. For the sake of the internal self-consistency between the XCEDF and the XC potential, introducing a symmetric TBFWV [see Eq. (41)] seems to be the more elegant approach.

On the practical side, neither the ADA nor the WDA was widely applied in general to many-electron, realistic systems, due to their complicated functional forms.[98,136–141,260,314–318,329–345] Only very recently did efficient implementations of the WDA become available.[338–342] Even today, the ADA is still a "museum artifact," which has been applied only to spherical atomic species and the spherical jellium model.[314–316,346] The main obstacle lies in Eq. (110), where in addition to the recursion problem, one needs to do the integration over all space of $\mathbf{r}'$ for every point $\mathbf{r}$, yielding a numerical cost scaling quadratically, $\mathcal{O}(M^2)$, with respect to the integration grid size M. A straightforward application of the

FFT cannot be used to finesse this integration, because of the density dependence of the AWF, $w\big(\bar{\rho}^{ADA}(\mathbf{r}), |\mathbf{r}-\mathbf{r}'|\big)$.

What does all of the above analysis teach us? First and above all, the correct LR behavior at the FEG limit is vital for design of a good EDF. Second, proper sum rules should be satisfied to build in systematic error cancellation. Third, the introduction of a weight function releases the constraints on the original formulas at the FEG limit, allows any nonlocal effects to be modeled, and somewhat more importantly, provides a new degree of freedom so that other restrictions can be simultaneously satisfied. Fourth, any recursion should be avoided to permit more efficient implementation.[99, 346] This in turn calls for a better understanding of the TBFWV. Finally, the $\mathcal{O}(M^2)$ numerical barrier must be overcome so that any general application will be possible.[338–342]

V.2 THE CLASSICAL WEIGHTED-DENSITY APPROXIMATION

In the lineage of the methodology developed above, the ADA and the WDA are nonlocal extensions of the LDA formulation. In this sense, the TF model discussed in Section II.1 is the LDA counterpart for the OF-KEDF. However, the vW model discussed in Section III.1 is somewhat different, because the ansatz in Eq. (39) departs from the LDA ansatz in Eq. (23). For later convenience, we name the strategy in Section III.1 the Semilocal-Density Approximation (SLDA). In the following, through a detailed analysis of the exchange energy density functional (XEDF) and the OF-KEDF,[98] we shall see the classical WDA is actually closely related to the SLDA.

Right from the birth of the WDA, a joint approach to the XEDF and the OF-KEDF was presented.[98] It is not surprising because both are related to the DM1. For closed-shell systems, the XEDF has a simple analytic form[58–60]

$$E_x[\rho] = -\frac{1}{4}\left\langle \frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \right\rangle . \tag{124}$$

After an inspection of Eqs. (97), (98), and (124), one can then readily write the exchange hole and the exchange PCF as

$$\rho_x(\mathbf{r},\mathbf{r}') = -\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{2\rho(\mathbf{r})} , \tag{125}$$

$$h_x(\mathbf{r},\mathbf{r}') = -\frac{|\gamma(\mathbf{r},\mathbf{r}')|^2}{2\rho(\mathbf{r})\rho(\mathbf{r}')} . \tag{126}$$

The fulfillment of the sum rule in Eq. (104) is simply given by

$$\int |\gamma(\mathbf{r},\mathbf{r}')|^2 \, d\tau' = 2\gamma(\mathbf{r},\mathbf{r}) = 2\rho(\mathbf{r}) . \tag{127}$$

It is clear that Eq. (127) is less restrictive than the enforcement of the idempotency property in Eq. (9), because the right-hand side of Eq. (127) is the density, not the full DM1. Now, following the general LDA scheme and employing Eqs. (20) and (23), one has the LDA exchange PCF,

$$h_x^{LDA}(\mathbf{r},\mathbf{r}') = -\frac{9}{2}\left(\frac{j_1(y)}{y}\right)^2 \;, \tag{128}$$

and the celebrated Dirac LDA XEDF,[32]

$$E_D[\rho] = -\frac{9}{4}\left\langle \frac{\rho^2(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\left(\frac{j_1(y)}{y}\right)^2 \right\rangle = -C_D\left\langle \beta^4(\mathbf{r})\right\rangle \;, \tag{129}$$

where C_D is the Dirac constant, $\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}$. Invoking the WDA yields

$$h_x^{WDA}(\mathbf{r},\mathbf{r}') = -\frac{9}{2}\left(\frac{j_1(\bar{y}^{WDA})}{\bar{y}^{WDA}}\right)^2 \;, \tag{130}$$

$$E_x^{WDA}[\rho] = -\frac{9}{4}\left\langle \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\left(\frac{j_1(\bar{y}^{WDA})}{\bar{y}^{WDA}}\right)^2 \right\rangle \;, \tag{131}$$

where the effective variables are given by

$$\bar{y}^{WDA} = \bar{k}_F^{WDA}(\mathbf{r})\,|\mathbf{r}-\mathbf{r}'| \;, \tag{132}$$

$$\bar{k}_F^{WDA}(\mathbf{r}) = \left(3\pi^2\right)^{\frac{1}{3}}\,\bar{\beta}^{WDA}(\mathbf{r}) \;, \tag{133}$$

$$\bar{\beta}^{WDA}(\mathbf{r}) = \left[\bar{\rho}^{WDA}(\mathbf{r})\right]^{\frac{1}{3}} \;. \tag{134}$$

Comparing Eqs. (126) and (130) immediately reveals the WDA ansatz for the DM1:

$$\gamma^{WDA}(\mathbf{r},\mathbf{r}') = \rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}')g^{LDA}(\bar{y}^{WDA}) \;, \tag{135}$$

$$g^{LDA}(\bar{y}^{WDA}) = 3\frac{j_1(\bar{y}^{WDA})}{\bar{y}^{WDA}} \;. \tag{136}$$

It is striking that Eq. (135) closely resembles Eq. (39); hence, the classical WDA is actually a generalized SLDA [of course, the element of the TBFWV of Eqs. (40) and (41) is missing]. Similar to the derivation shown in Eqs. (46)–(53), the WDA OF-KEDF can be easily derived from Eq. (135),[98]

$$T_s^{WDA}[\rho] = T_{vW}[\rho] + C_{TF}\left\langle \rho(\mathbf{r})\left[\bar{\beta}^{WDA}(\mathbf{r})\right]^2\right\rangle \;. \tag{137}$$

It is important to note that the effective density $\bar{\rho}^{WDA}(\mathbf{r})$ must be everywhere semipositive definite so that all effective quantities are then properly defined. Within the WDA, the explicit enforcement of the sum rule [see Eq. (127)]

$$\int \rho(\mathbf{r}') \left[g^{LDA}(\bar{y}^{WDA})\right]^2 d\tau' = 2 \ , \tag{138}$$

might just ensure this because all papers on the WDA have not reported a single violation so far.[98, 136–141, 260, 315–318, 329–345] Nonetheless, more thorough studies should definitely clarify this issue.

Ignoring the correlation component in Eq. (12), one can solve the exchange-only TF-HK equation within the WDA. Numerical results are in favor of this approach in terms of energy, but the density still exhibits no shell structure for lighter atomic species ($Z \leq 30$).[136–140] In addition, because the WDA ansatz of Eq. (135) is a generalization of the single-orbital form in Eq. (24), the WDA greatly improves the description of the density both near and far away from nuclear centers, as the nuclear cusp condition[57, 347–349] and asymptotic decay[63, 66, 189–202] are better modeled over the LDA.[136–140] Specifically for idempotent two-electron GS systems, the fulfillment of the sum rule for the exchange hole [see Eq. (138)] yields a null effective density $\bar{\rho}^{WDA}(\mathbf{r})$ and hence exactly cancels the self-interacting effects from the HREDF and reduces the WDA OF-KEDF to the correct limit: the vW functional.[98]

However, studies on the WDA are far from finished yet; many important questions can be asked. For example, we still do not know whether it is the WDA XEDF or the WDA OF-KEDF that causes the appearance of the shell structure in heavier atoms ($Z > 30$). Nor do we know the reason why the shell structure is not evident for lighter atomic species. How does the *ad hoc* symmetrization scheme[331–333] [see Eq. (123)] effect the LR behavior? How does the individual WDA XEDF compare with the exact HF exchange if the KS and the HF equations are solved? Similarly, how good is the WDA OF-KEDF by itself if the TF-HK equation is solved with the LDA XCEDF instead of the WDA XCEDF?

On the other hand, the WDA has two quite severe defects. First, the correct LR behavior has not been taken into account. Second, a consistent, efficient symmetrization scheme for the exchange PCF at both the energy and potential levels is still lacking. In fact, one can symmetrize the exchange PCF in Eq. (130) by introducing a symmetric TBFWV in Eq. (132),

$$\bar{y}^{WDA}_{sym} = \bar{\zeta}^{WDA}_F(\mathbf{r}, \mathbf{r}') \, |\mathbf{r} - \mathbf{r}'| \ , \tag{139}$$

$$\bar{\zeta}^{WDA}_F(\mathbf{r}, \mathbf{r}') = \bar{\zeta}^{WDA}_F\left(\bar{k}^{WDA}_F(\mathbf{r}), \bar{k}^{WDA}_F(\mathbf{r}')\right) \ , \tag{140}$$

which still delivers the same expression as Eq. (137) for the OF-KEDF. Strangely, there has yet to appear a study on this coherent symmetrization scheme.

V.3 THE SEMILOCAL AVERAGE-DENSITY APPROXIMATIONS

As all numerical results indicate that the WDA is heading into the right direction, incorporating the correct LR behavior[99–104, 314, 346] becomes the next logical step. The ADA immediately comes into mind, but proper modifications have to be made. The Semilocal Average-Density Approximation (SADA)[99–104] constitutes the first step towards this goal.

If a joint approach is taken for both the XEDF and the OF-KEDF, the ADA ansatz for the DM1 has the LDA form:

$$\gamma^{ADA}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r})g^{LDA}(\bar{y}^{ADA}) = 3\rho(\mathbf{r})\frac{j_1(\bar{y}^{ADA})}{\bar{y}^{ADA}} \ , \tag{141}$$

which inherits all the weak points of the LDA, outlined in Section II. To overcome this dilemma, one can simply preserve the WDA ansatz shown in Eq. (135), but replace all WDA effective entities by its SADA counterparts,

$$\gamma^{SADA}(\mathbf{r},\mathbf{r}') = \rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}')g^{LDA}(\bar{y}^{SADA}) = 3\rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}')\frac{j_1(\bar{y}^{SADA})}{\bar{y}^{SADA}} \ . \tag{142}$$

To avoid the recursion problem in Eq. (110), the SADA further simplifies the definition for the WAD,[99–104, 346]

$$\bar{\rho}^{SADA}(\mathbf{r}) = \int w\left(\zeta_F(\mathbf{r},\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|\right)\rho(\mathbf{r}')d\tau' \ , \tag{143}$$

where the TBFWV symmetrizes the AWF[††] and consequently the kinetic-energy potential, $\delta T_s^{SADA}/\delta\rho$. Analogous to the TBFWV symmetrization scheme in Eqs. (139) and (140), one obtains all the corresponding SADA entities,

$$\gamma_{sym}^{SADA}(\mathbf{r},\mathbf{r}') = \rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}')g^{LDA}(\bar{y}_{sym}^{SADA}) \ , \tag{144}$$

$$h_x^{SADA}(\mathbf{r},\mathbf{r}') = -\frac{1}{2}\left[g^{LDA}(\bar{y}_{sym}^{SADA})\right]^2 \ , \tag{145}$$

$$E_x^{SADA}[\rho] = -\frac{1}{4}\left\langle \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\left[g^{LDA}(\bar{y}_{sym}^{SADA})\right]^2 \right\rangle \ , \tag{146}$$

$$T_s^{SADA}[\rho] = T_{vW}[\rho] + C_{TF}\left\langle \rho(\mathbf{r})\left[\bar{\beta}^{SADA}(\mathbf{r})\right]^2 \right\rangle \ , \tag{147}$$

[††] Earlier papers on the SADA[99, 100, 346] did not introduce the TBFWV in the AWF, but instead used $\rho(\mathbf{r})$, very much similar to the nonsymmetric ADA AWF in Eq. (110).

where the averaged variables are given by

$$\bar{y}^{SADA}_{sym} = \bar{\zeta}^{SADA}_{F}(\mathbf{r},\mathbf{r}')\,|\mathbf{r}-\mathbf{r}'| \ , \tag{148}$$

$$\bar{\zeta}^{SADA}_{F}(\mathbf{r},\mathbf{r}') = \bar{\zeta}^{SADA}_{F}\left(\bar{k}^{SADA}_{F}(\mathbf{r}), \bar{k}^{SADA}_{F}(\mathbf{r}')\right) \ , \tag{149}$$

$$\bar{k}^{SADA}_{F}(\mathbf{r}) = \left(3\pi^2\right)^{\frac{1}{3}} \bar{\beta}^{SADA}(\mathbf{r}) \ , \tag{150}$$

$$\bar{\beta}^{SADA}(\mathbf{r}) = \left[\bar{\rho}^{SADA}(\mathbf{r})\right]^{\frac{1}{3}} \ . \tag{151}$$

The kinetic-energy potential of Eq. (147) is then readily given by

$$\frac{\delta T^{SADA}_{s}[\rho]}{\delta\rho(\mathbf{r})} = \frac{\delta T_{vW}[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta T^{SADA}_{X}[\rho]}{\delta\rho(\mathbf{r})} \ , \tag{152}$$

$$\frac{\delta T_{vW}[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\frac{\boldsymbol{\nabla}^2\sqrt{\rho(\mathbf{r})}}{\sqrt{\rho(\mathbf{r})}} = \frac{1}{8}\frac{|\boldsymbol{\nabla}\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} - \frac{1}{4}\frac{\boldsymbol{\nabla}^2\rho(\mathbf{r})}{\rho(\mathbf{r})} \ , \tag{153}$$

$$\begin{aligned}\frac{\delta T^{SADA}_{X}[\rho]}{\delta\rho(\mathbf{r})} &= \frac{2C_{TF}}{3}\left\{\int \frac{\rho(\mathbf{r}')}{\bar{\beta}^{SADA}(\mathbf{r}')}\left[w(\mathbf{r},\mathbf{r}') + \rho(\mathbf{r})\frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\rho(\mathbf{r})}\right] d\tau'\right.\\ &\quad \left. + \frac{\rho(\mathbf{r})}{\bar{\beta}^{SADA}(\mathbf{r})}\int \rho(\mathbf{r}')\frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\rho(\mathbf{r})} d\tau'\right\} + C_{TF}\left[\bar{\beta}^{SADA}(\mathbf{r})\right]^2 \ ,\end{aligned} \tag{154}$$

where $w(\mathbf{r},\mathbf{r}')$ is the AWF shown in Eq. (143).

It should be clear that the three TBFWV's introduced in Eqs. (139), (143), and (148) need not to be identical; proper functional forms have to be chosen individually. It is also curious to note that the final forms of the OF-KEDF within the WDA and the SADA, Eqs. (137) and (147), are indifferent to the symmetrization of the exchange PCF or the DM1 and only depend on the relevant average or effective density. In fact, the functional form for $g(y_2)$ in Eq. (39) has little influence over the final form of the OF-KEDF. Hence, other functional forms can also be considered.[260, 318, 350–352] Yet, there is currently no systematic, coherent, and consistent scheme to fix the functional forms for the TBFWV and $g(y_2)$ in conjunction with the simultaneous enforcement of the idempotency property for the DM1 and the correct LR behavior.

Unlike the WDA that enforces the idempotency property for its DM1 ansatz, the SADA trades the idempotency requirement for the correct LR behavior of the OF-KEDF:[99–104]

$$\hat{F}\left(\left.\frac{\delta^2 T^{SADA}_{s}[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right|_{\rho_0}\right) = -\frac{1}{\tilde{\chi}_{Lind}(\mathbf{q})} \ , \tag{155}$$

for a given form of the TBFWV in Eq. (143),[50, 101–103, 111]

$$\zeta_{\mathrm{F}}^{\nu}(\mathbf{r},\mathbf{r}') = \left(\frac{k_{\mathrm{F}}^{\nu}(\mathbf{r}) + k_{\mathrm{F}}^{\nu}(\mathbf{r}')}{2}\right)^{\frac{1}{\nu}} . \tag{156}$$

Eq. (155) yields a universal second-order differential equation for the AWF for every fixed value of q,[101]

$$\begin{aligned} &6\eta^2\tilde{w}''(\eta) - [\eta\tilde{w}'(\eta)]^2 + 6\eta\tilde{w}'(\eta)\,[2\tilde{w}(\eta) - 11 + \nu] + 36\tilde{w}(\eta)\,[6 - \tilde{w}(\eta)] \\ &= 180\left[F_{\mathtt{Lind}}(\eta) - 3\eta^2\right] , \end{aligned} \tag{157}$$

where $\tilde{w}'(\eta)$ and $\tilde{w}''(\eta)$ are the first and the second derivatives of $\tilde{w}(\eta)$ with respect to η, respectively. Note that ν is explicitly involved in the determination of the AWF. If Eq. (156) is replaced by the FEG FWV k_{F}, all terms involving derivatives in the left-hand side of Eq. (157) will be removed, yielding the density-independent (DI) AWF. This universal differential equation can be numerically solved via standard techniques.[82] Figure 8 compares one such density-dependent (DD) AWF in momentum space for $\nu = \frac{1}{2}$[102, 103] with its DI counterpart; there is a sizable effect of the density dependence on the AWF. (The discussion and comparison of the SNDA results in Figure 8 are provided in Section V.4.)

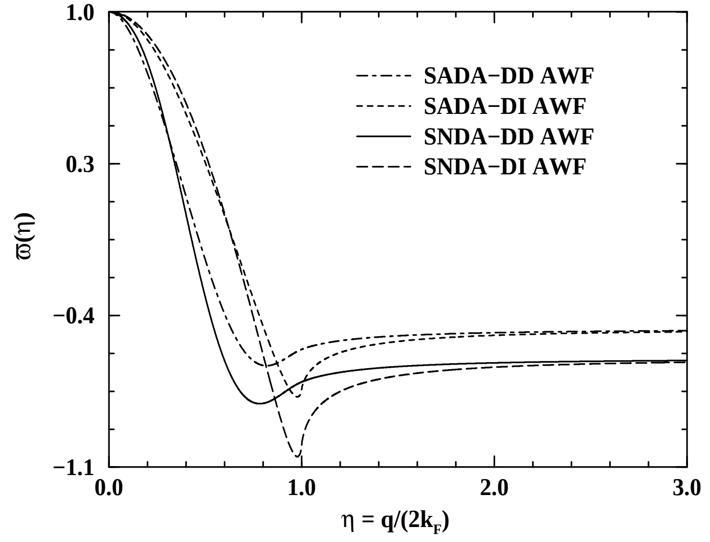

Figure 8 *The DD and DI AWF's in momentum space for the FEG. The parameter* ν *of the SADA OF-KEDF with the DD AWF is 1/2, while the three parameters* $\{\vartheta, \kappa, \nu\}$ *of the SNDA OF-KEDF with the DD AWF are* $\{5/6 \pm \sqrt{5}/6, 2.7\}$. *See Ref. [111] for details.*

Unfortunately, no direct numerical comparison is available for us to assess the quality of this trade-off from the WDA to the SADA. Nonetheless, we believe that by itself, the SADA OF-KEDF should be better than the WDA one because of the correct LR behavior, but this might only be true for a nearly FEG, which should approximately satisfy the idempotency property of the FEG DM1. For other highly inhomogeneous systems, the WDA OF-KEDF might eventually win over the SADA one.

It is also fascinating to discuss the origin of the atomic shell structure within the WDA and the SADA. Recall from Section V.2, shell structure appears for heavier atomic species ($Z > 30$) within the exchange-only WDA treatment.[136–140] The SADA without the proper symmetrization of the AWF in Eq. (143) behaves very much the same[101] (even only with the LDA XCEDF). This implies that the WDA effectively captures most of the overall shape of the correct LR function even without any explicit enforcement, and that enforcing the correct LR behavior for the OF-KEDF alone, the SADA is able to remedy the defects of the LDA XCEDF. This is certainly encouraging for both the WDA and the SADA. On the other hand, the SADA with a proper symmetrization of the AWF in Eq. (143) is able to produce shell structure for all atomic species,[101] because the kinetic-energy potential is properly symmetrized this time. This further emphasizes the importance of the symmetrization on the potential level.

At this point, one might wonder whether there is a better scheme that concurrently enforces the exact idempotency property for the DM1 and the correct LR behavior. The answer is yes; we have started to look into this possibility. Two driving forces are behind this idea. First, numerical results show that the empirically optimal ν value $-\frac{1}{2}$[101, 102] is good for the energy but bad for the density; a universal ν value for all systems seems to be unphysical. Second, the specific form of the TBFWV in Eq. (156) can be justified, but the natural variable argument[50] actually allows more general forms for the TBFWV as long as they satisfy[‡‡]

$$k_F(\mathbf{r})\frac{\partial \zeta_F(\mathbf{r},\mathbf{r}')}{\partial k_F(\mathbf{r})} + k_F(\mathbf{r}')\frac{\partial \zeta_F(\mathbf{r},\mathbf{r}')}{\partial k_F(\mathbf{r}')} = \zeta_F(\mathbf{r},\mathbf{r}') \; . \tag{158}$$

Introduction of the AWF within the ADA and the SADA allows for an extra degree of freedom so that the correct LR behavior can be exactly obeyed. Then, the explicit enforcement of the idempotency property on the DM1 should in principle determine an unique functional form for the TBFWV of the AWF. We have started to work on this idea; numerical results will be published elsewhere. For later reference, we call this scheme the Weighted-Average-Density Approximation (WADA).

Similar to the requirement of the semipositivity on the WDA effective density $\bar{\rho}^{WDA}(\mathbf{r})$, the WAD $\bar{\rho}^{SADA}(\mathbf{r})$ must be everywhere semipositive definite as well

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[‡‡] The rather complicated Feynman-path-integral-like local averaging scheme due to Wang and Teter[108] is consistent with the natural variable argument.

so that all average quantities are properly defined. Unfortunately, this condition is not generally satisfied in Eq. (143).[99] It is unclear to us how Eq. (151) can be evaluated for a negative $\bar{\rho}^{SADA}(\mathbf{r})$. Some measures must be taken by the authors who developed the SADA for the OF-KEDF to rescue the situation, but no details have been given on this matter.[99–103] If by any chance, the absolute value of $\bar{\rho}^{SADA}(\mathbf{r})$ is always used in Eq. (151), then the kinetic-energy potential and pertinent quantities should be adjusted to this change accordingly; otherwise, the entire SADA formulation lacks internal self-consistency.

However, there have been some attempts to deal with this problem in general.[100,101,104] Inspection of Eqs. (134) and (151) immediately reveals that the problem is due to the fractional power ($\frac{1}{3}$) raised on the effective density $\bar{\rho}^{WDA}(\mathbf{r})$ and the WAD $\bar{\rho}^{SADA}(\mathbf{r})$. To preserve the integrity of the formulation, one can directly use $\bar{\beta}^{WDA}(\mathbf{r})$ and $\bar{\beta}^{SADA}(\mathbf{r})$ instead, making no reference to their density counterparts. Of course, this is subject to suitable TBFWV's $\bar{\zeta}_F^{WDA}(\mathbf{r},\mathbf{r}')$ and $\bar{\zeta}_F^{SADA}(\mathbf{r},\mathbf{r}')$. For simple symmetrization purposes, the arithmetic mean [i.e., setting ν=1 in Eq. (156)] might be both physically and numerically meaningful. Consequently, the core equation of the SADA, Eq. (143), should be changed to[100,104]

$$\overline{\beta^{SADA}}(\mathbf{r}) = \int w(\zeta_F(\mathbf{r},\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|)\, \beta(\mathbf{r}')d\tau' \,, \tag{159}$$

and consequently, the second term of Eq. (147) becomes[100,104]

$$T_X^{SADA}[\rho] = C_{TF}\left\langle \rho(\mathbf{r}) \left[\overline{\beta^{SADA}}(\mathbf{r})\right]^2 \right\rangle \,. \tag{160}$$

One can then straightforwardly derive the potential of Eq. (160):

$$\begin{aligned} \frac{\delta T_X^{SADA}[\rho]}{\delta\rho(\mathbf{r})} = \frac{2C_{TF}}{3} & \left\{ \int \frac{\rho(\mathbf{r}')\overline{\beta^{SADA}}(\mathbf{r}')}{\beta(\mathbf{r})} \left[\frac{w(\mathbf{r},\mathbf{r}')}{\beta(\mathbf{r})} + \frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\beta(\mathbf{r})} \right] d\tau' \right. \\ & \left. + \beta(\mathbf{r})\overline{\beta^{SADA}}(\mathbf{r}) \int \beta(\mathbf{r}') \frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\beta(\mathbf{r})} d\tau' \right\} + C_{TF}\left[\overline{\beta^{SADA}}(\mathbf{r})\right]^2 \,, \end{aligned} \tag{161}$$

where $w(\mathbf{r},\mathbf{r}')$ is the AWF in Eq. (159). This idea goes beyond the conventional sense of averaging: from averaging the density to averaging the local FWV, which differs from $\beta(\mathbf{r})$ by a constant prefactor of $(3\pi^2)^{\frac{1}{3}}$. For later reference, we call this idea the Average Fermi Wave-Vector Approach (AFWVA). Some primary studies on such an idea have been reported,[100,101,104] but the AFWVA is not totally free of potential problems. For an asymptotically decaying density, the first integral in Eq. (161) might be divergent because the denominator has the decaying density.[101] More studies should be carried out to see whether a suitable choice of the TBFWV can overcome this problem.

V.4 SIMPLIFIED NONLOCAL DENSITY APPROXIMATIONS

So far, we have been mainly following the most logical route: from an ansatz for the DM1 to its resulting OF-KEDF. However, if the DM1 and the XEDF or more general XCEDF are not our major interests, is there any simpler way to approximate the OF-KEDF? This is indeed a legitimate question. First, numerous numerical tests show that the WDA and the ADA only improve the description of the XCEDF marginally; it is very hard to further refine the systematic error cancellation built in the LDA for the XCEDF.[3, 4, 98, 136–141, 260, 315–318, 329–342] For a large number of practical applications, the LDA for the XCEDF is more or less sufficient.[3–10] Second, the SADA OF-KEDF with the DD AWF is able to reproduce shell structure for all atomic species; this is achieved just with the LDA XCEDF and without explicit enforcement of the idempotency property.[101] Especially for nearly FEG systems, such as extended metallic materials, where the SLDA OF-DM1 formula for the FEG [see Eq. (39)] will approximately satisfy the exact idempotency property, the SADA OF-KEDF alone will be a highly accurate model. Additionally, due to the nature of the metallic band structure, a very fine mesh for the Brillouin-zone (**k**-point) sampling[71–80] is needed to converge the KS calculations. Numerically, this is quite expensive because one needs to calculate the wavefunction for all symmetrically unique **k** points, increasing the computational cost greatly. Therefore, the OF-DFT approach based on the TF-HK equation with a highly accurate approximation for the OF-KEDF alone might be sufficient for general practical purposes, and is certainly better for metallic systems.

To accomplish this, let us go back to Section III.1 and pay close attention to Eqs. (49) and (50). Both Eqs. (137) and (147) are generalizations of Eq. (53) along the SLDA path,

$$T_s^{SLDA}[\rho] = T_{vW}[\rho] + C_{TF}\left\langle \rho(\mathbf{r})\beta^2(\mathbf{r})\right\rangle \ . \tag{162}$$

On the other hand, the double integration form in Eqs. (48)–(50) suggests the following Simplified Nonlocal Density Approximation (SNDA),[105–111]

$$T_s^{SNDA}[\rho] = T_{vW}[\rho] + T_X^{SNDA}[\rho] \ , \tag{163}$$

$$T_X^{SNDA}[\rho] = C_{TF}\left\langle \rho^{\vartheta}(\mathbf{r})\middle|\, w\left(\zeta_F(\mathbf{r},\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|\right) \middle|\rho^{\kappa}(\mathbf{r}')\right\rangle \ , \tag{164}$$

where $\{\vartheta, \kappa\}$ are positive parameters, and the TBFWV can take the form shown in Eq. (156). The potential of $T_X^{SNDA}[\rho]$ takes a much simpler form than Eq. (154),

$$\begin{aligned}\frac{\delta T_X^{SNDA}[\rho]}{\delta\rho(\mathbf{r})} = C_{TF}\Bigg\{&\vartheta\rho^{\vartheta-1}(\mathbf{r})\int\rho^{\kappa}(\mathbf{r}')w(\mathbf{r},\mathbf{r}')d\tau' + \rho^{\vartheta}(\mathbf{r})\int\rho^{\kappa}(\mathbf{r}')\frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\rho(\mathbf{r})}d\tau' \\ &+ \kappa\rho^{\kappa-1}(\mathbf{r})\int\rho^{\vartheta}(\mathbf{r}')w(\mathbf{r},\mathbf{r}')d\tau' + \rho^{\kappa}(\mathbf{r})\int\rho^{\vartheta}(\mathbf{r}')\frac{\partial w(\mathbf{r},\mathbf{r}')}{\partial\rho(\mathbf{r})}d\tau'\Bigg\} \ ,\end{aligned} \tag{165}$$

where $w(\mathbf{r},\mathbf{r}')$ is the AWF shown in Eq. (164). Again, this kinetic-energy potential has a possible divergence problem if one of the two positive parameters $\{\vartheta,\kappa\}$ is smaller than 1.

A direct comparison between Eqs. (162) and (163) immediately suggests that the SNDA effectively takes the whole piece $\beta^2(\mathbf{r})$ to a weighted average

$$\overline{\beta^2(\mathbf{r})}^{\mathrm{SNDA}} = \rho^{\vartheta-1}(\mathbf{r}) \int w\left(\zeta_{\mathrm{F}}(\mathbf{r},\mathbf{r}'), |\mathbf{r}-\mathbf{r}'|\right) \rho^{\kappa}(\mathbf{r}')d\tau' \,. \tag{166}$$

This averaging is considerably different from those of the WDA, the SADA, and even the AFWVA. It has been said before that the averaging employed by the WDA and the SADA still preserves or requires the semipositivity of the final average density [see Eqs. (134) and (151)]. The AFWVA goes one step further [see Eq. (159)] and allows negative average FWV's in the formulation, but still maintains the semipositivity of the square of the average FWV as used in Eqs. (137) and (147). The SNDA is much more drastic and permits even a negative average square of the FWV. In doing so, the link between the DM1 and the OF-KEDF is obscured, because the effective local FWV from any negative average square of the FWV is imaginary, if a simple square root operation is taken. Nonetheless, if the DM1 is not our concern, the SNDA should be an efficient solution to the OF-KEDF problem.

After enforcing the correct LR at the FEG limit as done in Eq. (155), one obtains the following universal second-order differential equation for every fixed value of q,[111]

$$\begin{aligned} &\eta^2\tilde{w}''(\eta,\rho_0) + [\nu + 1 - 6(\vartheta+\kappa)]\,\eta\tilde{w}'(\eta,\rho_0) + 36\vartheta\kappa\tilde{w}(\eta,\rho_0) \\ &= 20\left[F_{\mathrm{Lind}}(\eta) - 3\eta^2\right]\rho_0^{\frac{5}{3}-(\vartheta+\kappa)}\,, \end{aligned} \tag{167}$$

which is considerably simpler than Eq. (157). Moreover, the simple form of Eq. (167) allows a power series solution for the inhomogeneous part and an analytic solution for the homogeneous part so that the AWF can be calculated up to arbitrary accuracy. This in turn further permits us to do a careful analysis of the limits of the SNDA OF-KEDF for $q\to 0$ and $q\to\infty$ limits.[111] This involves Fourier transforming the exact solution of Eq. (167) and substituting the resultant expression into Eq. (164). The results are, at the $q\to 0$ limit (corresponding to slowly varying densities),

$$\begin{aligned} T_s^{\mathrm{SNDA}}[\rho] &\to T_{\mathrm{TF}}[\rho] + T_{vW}[\rho] + d_0\left\langle \left(\frac{\rho(\mathbf{r})}{\rho_0}\right)^{\vartheta+\kappa-1} \middle|\, t_{vW}(\mathbf{r})\right\rangle \\ &\to T_{\mathrm{TF}}[\rho] + (1+d_0)T_{vW}[\rho] + d_0(\vartheta+\kappa-1)\left\langle\delta\sigma | t_{vW}(\mathbf{r})\right\rangle + \mathcal{O}(\delta\sigma^2)\,, \end{aligned} \tag{168}$$

$$d_0 = \frac{32\vartheta\kappa}{9(\vartheta+\kappa-1)\left(\vartheta+\kappa+1-\frac{\nu}{3}\right) - 36\vartheta\kappa}\,, \tag{169}$$

and at the $q \to \infty$ limit (corresponding to rapidly varying densities),

$$T_s^{SNDA}[\rho] \to T_{vW}[\rho] + T_{TF}[\rho] + d_\infty \left\langle \left(\frac{\rho(\mathbf{r})}{\rho_0}\right)^{\vartheta+\kappa-\frac{5}{3}} \middle| t_{TF}(\mathbf{r}) \right\rangle$$
$$\to T_{vW}[\rho] + (1+d_\infty)T_{TF}[\rho] + d_\infty\left(\vartheta+\kappa-\frac{5}{3}\right)\langle\delta\sigma|t_{TF}(\mathbf{r})\rangle + \mathcal{O}(\delta\sigma^2)\ , \quad (170)$$

$$d_\infty = \frac{32}{9\left(\vartheta+\kappa-\frac{5}{3}\right)\left(\vartheta+\kappa+\frac{5}{3}-\frac{\nu}{3}\right)-36\vartheta\kappa}\ , \quad (171)$$

where $\delta\sigma = \rho(\mathbf{r})/\rho_0 - 1$. For a nearly FEG, $|\delta\sigma| \ll 1$. It is clear that the first two terms of Eqs. (168) and (170) closely resemble the second-order CGE [Eq. (35)] and the CLQL [Eq. (93)], respectively. However, there is no single set of $\{\vartheta, \kappa, \nu\}$ that simultaneously removes all spurious $\delta\sigma$ terms in Eqs. (168) and (170), and makes them reduce to the second-order CGE and the CLQL, respectively. Numerical tests strongly suggest that the fulfillment of the CLQL is more important than the correct behavior at the $q \to 0$ limit (the second-order CGE).[107] Therefore, the parameters $\{\vartheta, \kappa\}$ are chosen such that Eq. (170) is identical to the CLQL.[111] This leads to the following two equations:

$$\left\{\begin{array}{rcl} \vartheta+\kappa & = & \frac{5}{3} \\ 1+d_\infty & = & -\frac{3}{5} \end{array}\right. , \quad (172)$$

whose solution is symmetrically displaced around $\frac{5}{6}$

$$\vartheta, \kappa = \frac{5 \pm \sqrt{5}}{6}\ . \quad (173)$$

We can then use the remaining parameter ν to fine-tune the behavior around the $q \to 0$ limit so that the effect of the spurious $\delta\sigma$ terms and the leading terms in Eq. (168) can be well-balanced. We have found that $\nu = 2.7$ is the optimal value at least for Al metal surfaces and bulk phases.[111] Interestingly, without going through the above analysis, Eq. (50) already suggests that $\vartheta + \kappa = \frac{5}{3}$, because this particular choice leaves most of the density dependence out of the AWF. For comparison, we plot both the DD and DI AWF's of the SNDA in Figure 8. Again, we find a sizable effect of the density dependence on the AWF. It is also interesting to note that the AWF's of the SNDA and the SADA behave very similarly to each other.

VI. NUMERICAL IMPLEMENTATIONS

Having laid the theoretical foundation for the OF-KEDF's, we now face three technical issues in their numerical implementation: how to solve the TF-HK equation efficiently, how to generate suitable local pseudopotentials (LPS's), and most importantly, how to make the entire OF-DFT scheme linear-scaling with respect to the system size. We will address these topics in turn.

VI.1 VARIATIONAL OPTIMIZATION OF THE THOMAS-FERMI-HOHENBERG-KOHN EQUATION

Given the total electronic energy in Eq. (1), one can write down a general density functional $\Pi[\rho]$ for a system with a fixed number of electrons N,

$$\Pi[\rho] = E_e[\rho] - \mu\left[\langle\rho(\mathbf{r})\rangle - N\right] \ , \tag{174}$$

where μ is a Lagrange multiplier. $\Pi[\rho]$ will be minimized with respect to $\rho(\mathbf{r})$, to determine the GS of the system. However, it has been found[106,125,126] that the positivity of $\rho(\mathbf{r})$ is not guaranteed in general if $\rho(\mathbf{r})$ is used directly as the generalized coordinate in conventional optimization algorithms[82] like the steepest-descent or conjugate-gradient methods. To circumvent this problem, one can work with a new variational variable $\varphi(\mathbf{r})$

$$\rho(\mathbf{r}) = \varphi^2(\mathbf{r}) \ , \tag{175}$$

to ensure a positive $\rho(\mathbf{r})$ during the entire minimization process.[97,111,124–126] On the other hand, because $\varphi(\mathbf{r})$ has a richer structure than $\rho(\mathbf{r})$ in momentum space,[97] more plane waves and a finer Fourier grid are needed to represent $\varphi(\mathbf{r})$ well. This is an inevitable trade-off. If $\varphi(\mathbf{r})$ can be thought of as a quasi-orbital,[125,126] we can utilize the same numerical technique as in the implementations of the KS scheme: just using a Fourier grid twice as dense in each spatial direction as the grid required for $\rho(\mathbf{r})$.[353] In other words, the maximum integer multiple of the basic momentum vector along one particular direction is given by

$$n_i^{max} = 2\left(\frac{L_i\sqrt{E_{cut}}}{2\pi}\right) \ , \tag{176}$$

where E_{cut} is the plane-wave cutoff in Rydbergs, and L_i is the dimension of the simulation box along this direction.

Aside from the numerical stability consideration, one can actually rationalize the $\varphi(\mathbf{r})$-formulation. Starting from the following identity,

$$T_s[\rho] \equiv T_{vW}[\rho] + T_X[\rho] \ , \tag{177}$$

and utilizing Eq. (153),

$$\frac{\delta T_{vW}[\rho]}{\delta\rho(\mathbf{r})} = -\frac{1}{2}\frac{\boldsymbol{\nabla}^2\varphi(\mathbf{r})}{\varphi(\mathbf{r})} \ , \tag{178}$$

one can easily rewrite the TF-HK equation in a fully equivalent quasi-orbital form

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v_{eff}^{KS}(\mathbf{r};[\rho]) + \frac{\delta T_X[\rho]}{\delta\rho(\mathbf{r})}\right)\varphi(\mathbf{r}) = \mu\varphi(\mathbf{r}) \ , \tag{179}$$

closely resembling the equation of the conventional $\sqrt{\rho(\mathbf{r})}$-formulation,[202, 354–360]

$$\left(-\frac{1}{2}\boldsymbol{\nabla}^2 + v^{\mathrm{KS}}_{\mathrm{eff}}(\mathbf{r};[\rho]) + \frac{\delta T_X[\rho]}{\delta\rho(\mathbf{r})}\right)\sqrt{\rho(\mathbf{r})} = \mu\sqrt{\rho(\mathbf{r})}\ . \tag{180}$$

However, this $\varphi(\mathbf{r})$-formulation is more general than the $\sqrt{\rho(\mathbf{r})}$-formulation, because $\varphi(\mathbf{r})$ behaves truly like an orbital, with positive and negative regions, while $\sqrt{\rho(\mathbf{r})}$ is everywhere semipositive. It is also interesting to notice that Eq. (177) closely resembles Eqs. (47), (137), (147), (162), and (163).

Based on a first-order differential equation with a fictitious time τ

$$\frac{d\varphi(\mathbf{r})}{d\tau} + \frac{\delta\Pi[\rho]}{\delta\varphi(\mathbf{r})} = 0\ , \tag{181}$$

the steepest-descent approach is the simplest scheme[82, 353, 361, 362]

$$\varphi_{n+1}(\mathbf{r}) = \varphi_n(\mathbf{r}) - \Delta\frac{\delta\Pi[\rho]}{\delta\varphi_n(\mathbf{r})}\ , \tag{182}$$

$$\begin{aligned}\frac{\delta\Pi[\rho]}{\delta\varphi_n(\mathbf{r})} &= \frac{\delta\Pi[\rho]}{\delta\rho_n(\mathbf{r})}\frac{\delta\rho_n(\mathbf{r})}{\delta\varphi_n(\mathbf{r})} = 2\varphi_n(\mathbf{r})\left(\frac{\delta E_e[\rho]}{\delta\rho_n(\mathbf{r})} - \mu\right) \\ &= \frac{\delta E_e[\rho]}{\delta\varphi_n(\mathbf{r})} - \varphi_n(\mathbf{r})\mu_2\ ,\end{aligned} \tag{183}$$

where Δ is the step size, $\mu_2 = 2\mu$, and $\delta\Pi[\rho]/\delta\varphi_n(\mathbf{r})$ is the steepest-descent vector at the nth iteration. To obtain the value for μ_2, one takes the square of both sides of Eq. (182), integrates over all space, enforces the same normalization for the density at different iterations, and derives a quadratic equation for μ_2:[97]

$$\Delta(\mu_2)^2 + 2(1-\Delta I_1)\mu_2 + (\Delta I_2 - 2I_1) = 0\ , \tag{184}$$

$$N \equiv \left\langle \varphi^2_{n+1}(\mathbf{r})\right\rangle \equiv \left\langle \varphi^2_n(\mathbf{r})\right\rangle\ , \tag{185}$$

$$I_1 = \frac{1}{N}\left\langle \varphi_n(\mathbf{r})\left|\frac{\delta E_e[\rho]}{\delta\varphi_n(\mathbf{r})}\right.\right\rangle\ , \tag{186}$$

$$I_2 = \frac{1}{N}\left\langle\left(\frac{\delta E_e[\rho]}{\delta\varphi_n(\mathbf{r})}\right)^2\right\rangle\ . \tag{187}$$

Solving this equation yields[97]

$$\mu_2 = \frac{(\Delta I_1 - 1) \pm \sqrt{1 + \Delta^2[(I_1)^2 - I_2]}}{\Delta}\ . \tag{188}$$

At convergence, the density is stationary for the TF-HK equation; hence, from Eq. (183),

$$\lim_{n\to\infty} I_1 = \frac{1}{N} \langle \varphi_n(\mathbf{r}) \,|\varphi_n(\mathbf{r})\mu_2 \,\rangle = \mu_2 \; , \tag{189}$$

$$\lim_{n\to\infty} I_2 = \frac{1}{N} \left\langle \varphi_n^2(\mathbf{r})(\mu_2)^2 \right\rangle = (\mu_2)^2 \; . \tag{190}$$

Thus, the equality between both sides of Eq. (188) only permits the "+" solution,

$$\mu_2 = \left(I_1 - \frac{1}{\Delta} \right) + \sqrt{\frac{1}{\Delta^2} - [I_2 - (I_1)^2]} \; . \tag{191}$$

To keep μ_2 always real during the entire iteration process, the maximum step size is given by[97]

$$\Delta_1^{max} = \frac{1}{\sqrt{I_2 - (I_1)^2}} \; , \tag{192}$$

where the generalized Schwarz inequality[81] guarantees the right-hand side to be real.

This scheme is concurrent for both the density and μ_2: at every iteration step, one first tests whether Δ is less than the maximum value allowed according to Eq. (192), then calculates μ_2 according to Eq. (191), and propagates the density to the next step. It is important to know[97] that no extra density normalization effort is needed because the density is always normalized by choosing the value for μ_2 according to Eq. (191). Numerical tests show that the steepest-descent scheme still has an instability problem and the convergence radius for Δ is quite small.[111]

To overcome these problems, we have formulated the energy minimization in terms of a damped second-order equation of motion[361,362] for the generalized coordinate $\varphi(\mathbf{r})$ with a damping or friction coefficient Θ,

$$\frac{d^2\varphi(\mathbf{r})}{d\tau^2} + \Theta \frac{d\varphi(\mathbf{r})}{d\tau} + \frac{\delta\Pi[\rho]}{\delta\varphi(\mathbf{r})} = 0 \; , \tag{193}$$

which yields

$$\varphi_{n+1}(\mathbf{r}) = z_n(\mathbf{r}) + \left(\Omega\Delta^2\mu_2\right) \varphi_n(\mathbf{r}) \; , \tag{194}$$

$$z_n(\mathbf{r}) = (1+\Omega)\varphi_n(\mathbf{r}) - \Omega\varphi_{n-1}(\mathbf{r}) - \Omega\Delta^2 \frac{\delta E_e[\rho]}{\delta\varphi_n(\mathbf{r})} \; , \tag{195}$$

$$\Omega = \frac{1}{1+\Theta\Delta} \; . \tag{196}$$

Using similar procedures to those shown above, one can easily work out the formula for μ_2 that automatically ensures the normalization of the density at every iteration,

$$\mu_2 = \frac{\sqrt{(J_1)^2 - J_2 + 1} - J_1}{\Omega\Delta^2} , \tag{197}$$

$$J_1 = \frac{\langle z_n(\mathbf{r})\varphi_n(\mathbf{r})\rangle}{N} , \tag{198}$$

$$J_2 = \frac{\left\langle z_n^2(\mathbf{r})\right\rangle}{N} . \tag{199}$$

The maximum Δ can be computed by enforcing the real solution for μ_2:

$$(J_1)^2 - J_2 + 1 \geq 0 , \tag{200}$$

but it proves to be a very costly exercise because of the complicated structure of $z_n(\mathbf{r})$ in Eq. (195). One can, however, tackle this problem through a much simpler path outlined below.

We first observe that the damping factor Ω normally has a small value and after some iterations, two consecutive $\varphi(\mathbf{r})$ will not differ too much. Then, one has approximately

$$z_n(\mathbf{r}) \approx \varphi_n(\mathbf{r}) - \Omega\Delta^2 \frac{\delta E_e[\rho]}{\delta\varphi_n(\mathbf{r})} . \tag{201}$$

Substituting Eq. (201) into Eq. (200), one has something very similar to Eq. (192):

$$\frac{\Delta^2}{1 + \Theta\Delta} \leq \Delta_1^{max} , \tag{202}$$

which yields directly

$$\Delta_2^{max} = \frac{\sqrt{(\Theta\Delta_1^{max})^2 + 4\Delta_1^{max}} + \Theta\Delta_1^{max}}{2} , \tag{203}$$

where Δ_1^{max} is defined in Eq. (192). We have found that this scheme is not only easy to implement, but also offers greater stability even when Δ becomes much larger than that of the simple steepest-descent method. We have also found that minimization algorithms based on the conjugate-gradient method actually converge faster, but require very accurate line minimizations that can be difficult to implement.

VI.2 GENERATION OF LOCAL PSEUDOPOTENTIALS

Since the OF-DFT scheme is purely based on the density, only LPS's (pseudopotentials that depend only on $\mathbf{r}$)[363–369] can be used to calculate the V_{ne} term in Eq. (2). More general nonlocal pseudopotentials (NLPS's) that depend on both $\mathbf{r}$ and $\mathbf{r}'$ require either the DM1 or the full wavefunction for the calculation of V_{ne}. We therefore will concentrate on how to construct high-quality LPS's.[369] Before that, however, it is pedagogical to briefly outline the essence of the conventional OB NLPS theory.[370–372]

Let us start from any general set of one-particle Schrödinger-like equations like Eq. (10),

$$\hat{h}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \, , \tag{204}$$

where $\hat{h}$, $\{\phi_i(\mathbf{r})\}$, and $\{\epsilon_i\}$ are a one-particle Hamiltonian and its associated eigen-orbitals and eigen-orbital energies, respectively. For practical purposes, the orbitals are classified into two groups: valence orbitals $\{\phi_i^v(\mathbf{r})\}$ (those with high orbital energies) and core orbitals $\{\phi_i^c(\mathbf{r})\}$ (those with low orbital energies). Of course, the criterion on how high is "high" and how low is "low" depends on the nature of the system and problems under investigation; we just assume that such a partition is permissible and meaningful. Then, we introduce a set of valence pseudo-orbitals $\{\psi_i^v(\mathbf{r})\}$ such that the exact valence orbitals can be expressed as

$$\phi_i^v(\mathbf{r}) = \psi_i^v(\mathbf{r}) - \sum_j^{N_c} \left\langle \phi_j^c(\mathbf{r}) | \psi_i^v(\mathbf{r}) \right\rangle \phi_j^c(\mathbf{r}) \, , \tag{205}$$

where N_c is the number of the core orbitals. (This expansion projects the exact core orbitals out of the valence pseudo-orbitals, to make a meaningful partitioning.) Substituting Eq. (205) into Eq. (204) for the valence orbitals, we obtain

$$\hat{h}_i^{ps}\psi_i^v(\mathbf{r}) = \epsilon_i\psi_i^v(\mathbf{r}) \, , \tag{206}$$

where the orbital-dependent pseudo-Hamiltonian $\hat{h}_i^{ps}$ relates to the exact Hamiltonian $\hat{h}$ via an orbital-dependent nonlocal operator $\hat{v}_i^{nloc}$:

$$\hat{v}_i^{nloc} = \hat{h}_i^{ps} - \hat{h} = \sum_j^{N_c} (\epsilon_i - \epsilon_j^c) \left| \phi_j^c(\mathbf{r}) \right\rangle \left\langle \phi_j^c(\mathbf{r}) \right| \, . \tag{207}$$

The NLPS is simply the sum of $\hat{v}_i^{nloc}$ and the external potential $v_{ext}(\mathbf{r})$ in $\hat{h}$,

$$\hat{v}_{nloc}^{ps} = v_{ext}(\mathbf{r}) + \hat{v}_i^{nloc} \, . \tag{208}$$

It is clear from Eq. (207) that the pseudization only turns on for the valence orbitals and has a null effect on the core orbitals. More interestingly, the exact orbital energies are not altered. Similar to Eq. (7), one can define the valence pseudo-density in terms of the valence pseudo-orbitals:

$$\rho^{\nu}_{ps}(\mathbf{r}) = \sum_{i}^{N_\nu} \gamma^{\nu}_{i} \left|\psi^{\nu}_{i}(\mathbf{r})\right|^2 \ . \tag{209}$$

where N_ν and γ^{ν}_{i} are the number of the valence orbitals and the occupation numbers of the valence orbitals, respectively. It is important to notice that in this formal NLPS theory, the exact GS wavefunction is still one-to-one mapped on to the GS valence pseudo-density for a given valence-core partitioning, because the NLPS's are uniquely defined via Eqs. (207) and (208), in which all the exact entities are functionals of the exact GS density. Various numerical implementations are readily available to construct such NLPS's.[370–386]

Having read the above, one might wonder about the origin of the LPS. Historically, earlier LPS's were designed from empirical fitting of experimental data;[363–367] later, more refined, *ab initio* schemes required the reproduction of the valence orbital energies.[368] However, theoretically speaking, only NLPS's will be able to exactly reproduce the same orbital energies. Therefore, it is natural to conclude that the theoretical foundation for LPS's has to be built according to a very different blueprint from that of the NLPS's. On the other hand, the solution seems already to be self-evident if one thinks a little bit deeper. The conventional NLPS theory concentrates mostly on the reproduction of the exact orbital energies and further requires the atomic pseudo-orbitals and atomic pseudo-density to reproduce the exact ones in the valence region.[370–372] Since often only the valence density is of greatest concern to chemistry and condensed matter physics, one can just pay attention to the weakest condition for pseudopotentials: the pseudo-density should reproduce the exact density in the valence region. Furthermore, because there are already an abundant number of high-quality NLPS's,[370–386] one can just instead devise a LPS scheme to reproduce the same pseudo-density from a NLPS calculation. This proves to be a logically meaningful theoretical foundation for LPS's.

The first level of sophistication[369] is quite simple: for a suitable LPS, the solution of the TF-HK equation should yield the same NLPS pseudo-density $\rho^{nloc}_{ps}(\mathbf{r})$ for a given model XCEDF,

$$\mu = \nu^{ps}_{loc}(\mathbf{r}) + \left(\frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta J[\rho]}{\delta\rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})} \right)_{\rho(\mathbf{r})=\rho^{nloc}_{ps}(\mathbf{r})} . \tag{210}$$

However, one has to additionally choose a model for the OF-KEDF to make this work. Consequently, the resulting LPS will have some contribution from the difference between the exact KEDF and the model OF-KEDF. This is less than optimal and can be avoided if and only if the OF-KEDF is not involved in any way. We therefore need a scheme that relates the pseudo-density directly to a LPS. In fact, there are already many mature schemes to obtain the effective local potential from a given input density.[253–272] We can just employ one such scheme and obtain the *exact* LPS for an input NLPS pseudo-density within a given model XCEDF. This scheme makes no reference to any approximation of the OF-KEDF or the response function, and one only needs to perform one KS-like calculation. More importantly, this scheme allows LPS's to be calculated within the same realistic environment of systems under investigation. Therefore, transferability will not be a problem, if NLPS's are chosen carefully for the target systems.

In the literature, there are some attempts[125–134] to directly use NLPS's with the OF-DFT scheme via Eq. (180), but the following argument proves such practice is not sound. First, NLPS's will introduce a phase to the quasi-orbital, hence it is Eq. (179), not Eq. (180), that should be used in the first place. Second, even if one accepts the utilization of NLPS's, Eq. (179) cannot be derived with NLPS's. In general, for a NLPS $\hat{v}^{ps}_{nloc}(\mathbf{r},\mathbf{r}')$, one needs the DM1 to calculate the V_{ne} term,

$$V_{ne}[\gamma] = \langle \hat{v}^{ps}_{nloc}(\mathbf{r},\mathbf{r}')\gamma(\mathbf{r},\mathbf{r}')\rangle \ , \tag{211}$$

which is very different from the LPS case,

$$V_{ne}[\rho] = \langle v^{ps}_{loc}(\mathbf{r})\rho(\mathbf{r})\rangle \ . \tag{212}$$

With Eq. (211), one cannot derive Eq. (180) [nor Eq. (179)] without the assumption

$$\gamma(\mathbf{r},\mathbf{r}') = \rho^{\frac{1}{2}}(\mathbf{r})\rho^{\frac{1}{2}}(\mathbf{r}') \ , \tag{213}$$

which is certainly not true in general. On the other hand, this calls for research into highly accurate OF approximations to the DM1 so that conventional NLPS's can be readily applied even in the OF-DFT scheme,[387] just like the OB KS scheme. More studies along the lines discussed in Section V ought to be done to pursue this goal.

VI.3 EVALUATION OF THE DENSITY-DEPENDENT AVERAGING WEIGHT FUNCTION

Having gone thus far with the OF-KEDF's, one ultimately faces the most difficult problem: how to make the entire OF-DFT scheme, especially the evaluation of the DD AWF, linear-scaling with respect to the system size. This is a general numerical bottleneck of all the NLDA's, as discussed in Section V: the presence of DD terms inside the AWF in Eq. (164) makes a straightforward application of the FFT impossible. However, one can use a Taylor series expansion[81] to factor out the density dependence in the AWF, because the DD AWF is not a functional, but some analytic function, of the density. For example, the DD AWF in real space can be written as (up to second order),[111]

$$\begin{aligned} w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|) &= w(k_F^*,|\mathbf{r}-\mathbf{r}'|) + \left.\frac{\partial w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho(\mathbf{r})}\right|_{\rho_*}\sigma(\mathbf{r}) \\ &+ \left.\frac{\partial w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho(\mathbf{r}')}\right|_{\rho_*}\sigma(\mathbf{r}') \\ &+ \left.\frac{\partial^2 w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho^2(\mathbf{r})}\right|_{\rho_*}\frac{\sigma^2(\mathbf{r})}{2} \\ &+ \left.\frac{\partial^2 w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho^2(\mathbf{r}')}\right|_{\rho_*}\frac{\sigma^2(\mathbf{r}')}{2} \\ &+ \left.\frac{\partial^2 w(\zeta_F(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho(\mathbf{r})\partial\rho(\mathbf{r}')}\right|_{\rho_*}\sigma(\mathbf{r})\sigma(\mathbf{r}') + \cdots , \end{aligned} \tag{214}$$

where $\sigma(\mathbf{r}) = \rho(\mathbf{r}) - \rho_*$, and $k_F^* = (3\pi^2\rho_*)^{\frac{1}{3}}$ are the deviation from, and the FWV magnitude of, a reference uniform density ρ_*. It is clear that the density dependence is absorbed into simple powers of $\sigma(\mathbf{r})$, and that all the partial differentials are functions of ρ_*, which can be evaluated via an FFT,[111]

$$\hat{F}\left(\left.\frac{\partial w(\zeta_F^\gamma(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho(\mathbf{r})}\right|_{\rho_*}\right) = -\frac{\eta_*\tilde{w}'(\eta_*,\rho_*)}{6\rho_*} , \tag{215}$$

$$\hat{F}\left(\left.\frac{\partial^2 w(\zeta_F^\gamma(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho^2(\mathbf{r})}\right|_{\rho_*}\right) = \frac{\eta_*^2\tilde{w}''(\eta_*,\rho_*) + (7-\nu)\eta_*\tilde{w}'(\eta_*,\rho_*)}{36\rho_*^2} , \tag{216}$$

$$\hat{F}\left(\left.\frac{\partial^2 w(\zeta_F^\gamma(\mathbf{r},\mathbf{r}'),|\mathbf{r}-\mathbf{r}'|)}{\partial\rho(\mathbf{r})\partial\rho(\mathbf{r}')}\right|_{\rho_*}\right) = \frac{\eta_*^2\tilde{w}''(\eta_*,\rho_*) + (1+\nu)\eta_*\tilde{w}'(\eta_*,\rho_*)}{36\rho_*^2} , \tag{217}$$

where $\eta_* = q/(2k_F^*)$, and $\tilde{w}'(\eta_*,\rho_*)$ and $\tilde{w}''(\eta_*,\rho_*)$ are the first and the second derivatives of $\tilde{w}(\eta_*,\rho_*)$ with respect to η_*, respectively. Figure 9 shows one such AWF and its derivatives in momentum space for $\{\vartheta,\kappa,\nu\} = \{\frac{5}{6} \pm \frac{\sqrt{5}}{6}, 2.7\}$.

For maximum numerical efficiency, all derivative terms of the AWF are kept in momentum space so that one FFT is saved for each of their evaluations. For example, during the evaluation of the following general double integral, the first FFT can be avoided:

$$\begin{aligned} \langle f_1(\mathbf{r})|w(\mathbf{r}-\mathbf{r}')|\, f_2(\mathbf{r}')\rangle &= \frac{1}{V}\sum_{\mathbf{q}} \tilde{w}(\mathbf{q}) \left\langle f_1(\mathbf{r}) \middle| e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \middle| f_2(\mathbf{r}') \right\rangle \\ = \frac{1}{V}\sum_{\mathbf{q}} \tilde{w}(\mathbf{q}) \left\langle f_1(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}} \right\rangle \left\langle f_2(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}} \right\rangle &= \frac{1}{V}\sum_{\mathbf{q}} \tilde{w}(\mathbf{q})\tilde{f}_1(-\mathbf{q})\tilde{f}_2(\mathbf{q}) , \end{aligned} \tag{218}$$

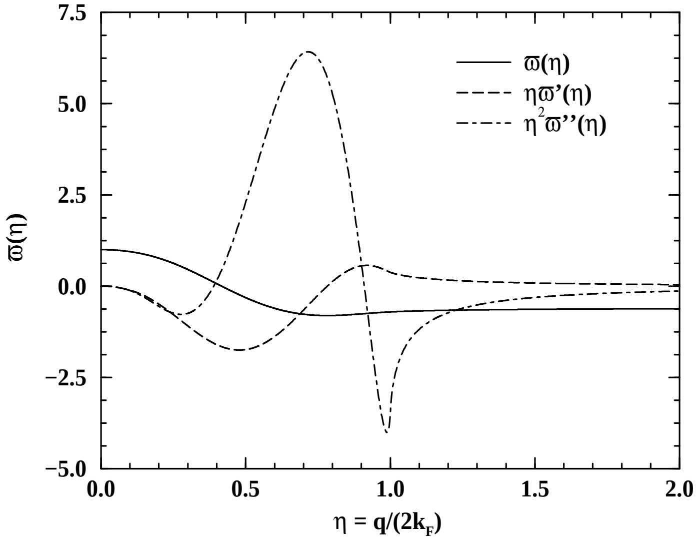

Figure 9 *The DD AWF and its derivatives in momentum space for the FEG. The three parameters* $\{\vartheta, \kappa, \nu\}$ *of the SNDA OF-KEDF are* $\{5/6 \pm \sqrt{5}/6, 2.7\}$.

where V is the volume of the simulation cell, and $f_1(\mathbf{r})$ and $f_2(\mathbf{r})$ are some functions of the density. Now, the computational cost has been reduced from scaling quadratically with grid size[99–103] to scaling essentially linearly with the system size, $\mathcal{O}(M\ln M)$. The current scheme is only three times as expensive as the conventional one based on the LR theory with the DI AWF.[105–108] By contrast, the OF-KEDF's based on quadratic response (QR) theory[108–110] are over ten times as expensive as the OF-KEDF's based on LR theory with the DI AWF.[105–108]

For bulk solids, the natural choice for ρ_* is obviously ρ_0. However, this scheme is only valid for a nearly FEG, where $\rho(\mathbf{r})$ does not differ too much from ρ_0. For other systems like atoms, molecules, and realistic surfaces, this scheme might suffer severely because ρ_0 is no longer well-defined and $\rho(\mathbf{r})$ can have large oscillations and decays to zero asymptotically. On the other hand, if ρ_* is carefully chosen to treat high-density regions satisfactorily, the breakdown in those regions where $\rho(\mathbf{r})$ is small and far below ρ_* might not be so severe because the error made in the second-order Taylor series expansion of Eq. (214) might be suppressed by the smallness of $\rho(\mathbf{r})$ in these regions. We have demonstrated the success of such an approach for realistic surfaces.[111] Ideally, one would like to eliminate the reference uniform density ρ_* from the construction of the DD AWF completely, yet still maintaining the $\mathcal{O}(M\ln M)$ scaling. We have successfully developed such a general $\mathcal{O}(M\ln M)$ scheme; the details of which will be reported later.[388]

There is a subtle point worth mentioning. There is a limitation for the SNDA OF-KEDF's with the TBFWV in the form of Eq. (156), because their potentials [Eq. (165)] are divergent for any asymptotically decaying density if one of the two positive parameters $\{\vartheta, \kappa\}$ is smaller than 1. Unfortunately, numerical tests show that those OF-KEDF's with $\{\vartheta, \kappa\}$ larger than 1 perform rather poorly.[107,111] Hence, the self-consistent density of the TF-HK equation with the SNDA OF-KEDF's will actually approach a finite small constant asymptotically, if one of $\{\vartheta, \kappa\}$ is smaller than 1.[97,388] In comparison, the SADA OF-KEDF does not have this problem as long as the ratio $\rho(\mathbf{r})/\bar{\beta}^{SADA}(\mathbf{r})$ in Eq. (154) does not diverge anywhere. Numerical tests[99–103] suggest that this conclusion might be true, but more thorough studies need to be done to further clarify this point. Certainly, it would be highly desirable to examine different choices for the form of the TBFWV. Nonetheless, the present SNDA can still be widely used for condensed-phase calculations so long as the vacuum size is not too big; otherwise, the much more complicated and costly SADA should be employed. In any case, the linear-scaling numerical procedure discussed above can be easily applied to all forms of NLDA OF-KEDF's.

Now, in the TF-HK equation, all the potential terms can be set up by conventional plane-wave-basis techniques[353,371,372,389] with essentially linear scaling. However, for very large systems with more than 5000 nuclei, the computational cost associated with the nuclear-nuclear Coulomb repulsion energy becomes the major bottleneck.[116] In this case, linear-scaling Ewald summation techniques should be utilized.[390–413]

VII. APPLICATIONS AND FUTURE PROSPECTS

Due to its favorable linear scaling, the OF-DFT scheme based on the TF-HK equation has been used somewhat,[1–7,38–40,172–174] but the poor quality of the OF-KEDF's had shunned away further interest, especially after the success of the KS formulation. As better, high-quality NLDA OF-KEDF's were invented, the OF-DFT scheme is gradually regaining its popularity.[97–141] However, the lack of linear-scaling implementations of the NLDA OF-KEDF's with the DD AWF had confined their applications only to spherical atomic species and spherical jellium models.[98–103,136–141] Nonetheless, the NLDA OF-KEDF's with the DI AWF permit linear-scaling implementations via direct use of the FFT [see Eq. (218)]; hence, bulk solids and liquids entered into the OF-DFT application realm.[97,104,106–123] Very recently, a linear-scaling implementation of the NLDA OF-KEDF's with the DD AWF emerged,[111] and a scheme to treat highly inhomogeneous systems like realistic surfaces was tested with semiquantitative success.[111] An immediate application to the study of the metal-insulator transition in a 2-dimensional array of metal nanocrystal quantum dots (with 498 Al atoms per simulation cell) further magnifies its promise.[97]

With present workstation computational resources, systems of thousands of atoms can be studied.[116–118] So far, the largest system studied dynamically by the OF-DFT scheme had 6714 Na atoms,[116] spanning 1.5 picoseconds. Such a size is inconceivable for the present OB *ab initio* and DFT methods. In fact, the OF-DFT scheme is purely restricted by the grid size, not by the number of electrons, and certainly has clear advantages over the OB methods. With the help of linear-scaling Ewald summation techniques,[390–413] even significantly larger systems can be modeled dynamically within the DFT description using current computational power.

Rather than repeating here the details of various applications, we feel that it would be more useful to pinpoint a few issues ("holy grails") of future significance.

First of all, the "golden holy grail" is a highly accurate OF procedure to approximate the DM1. If this can be done, not only will the KEDF and the XEDF be modeled accurately, but also the conventional NLPS's[370–386] could then be directly used in the OF-DFT calculations.[387]

Once the "golden holy grail" has been achieved, the "silver holy grail" would then be to use a *pure* OF-DFT scheme to predict every GS property other than those requiring detailed OB descriptions. In particular, non-HOMO orbital energies (or a band structure) and all orbitals of many-electron systems cannot be obtained from an OF-DFT calculation. For example, the OF-DFT study of the metal-insulator transition in a 2-dimensional array of metal nanocrystal quantum dots was aided by tight-binding calculations, using the self-consistent OF-DFT density as input, to estimate the band gap as a function of particle separation.[97] Is it possible, in principle, to access the information about at least the band gap directly from an OF description? The answer is actually yes! There is a long history of studying the asymptotic decay behavior of the DM1 in condensed phases[94–96, 311, 312, 414–428] and the latest results[312] show that for weak-binding insulating systems, the DM1 decays exponentially and the decay length is directly proportional to the band gap ϵ_{gap},

$$\lim_{|\mathbf{r}-\mathbf{r}'|\to\infty} \gamma(\mathbf{r},\mathbf{r}') \quad \propto \quad e^{-c\,\epsilon_{\mathrm{gap}}|\mathbf{r}-\mathbf{r}'|}\,, \tag{219}$$

where c is some positive constant. For tight-binding insulating systems, the results are mixed,[96, 312, 428] but are closely related to the strength of the external potentials or pseudopotentials used.[312] If the external potentials or pseudopotentials are chosen carefully, an exponential decay behavior can still be observed.[312] On the other hand, for metallic systems at zero Kelvin, the DM1 decays algebraically like the Friedel oscillations, as shown in Eq. (87).[96, 311, 312] Therefore, from the asymptotic decay behavior of a highly accurate OF approximation for the DM1, one can access the band gap information directly, distinguishing between insulators and metals.

Finally, the "bronze holy grail" is the WADA that concurrently enforces the correct LR behavior at the FEG limit and the exact idempotency property for any OF approximation of the DM1. Of course, the correct LR behavior is critical for any EDF to outperform its LDA counterpart. However, one should not push the limit too far with regard to higher-order response behaviors. Past numerical tests have shown that the SNDA OF-KEDF's with the DD AWF based on LR theory and the ones with the DI AWF based on QR theory perform indistinguishably from one another for bulk solids (metals and insulators alike).[108–111, 388] Hence, the requirement for EDF's to have correct higher-order response behaviors at the FEG limit can be waived. From another perspective, realistic systems are normally not *very* close to the FEG limit, and correct higher-order response behaviors at the FEG limit will not enhance the performance of EDF's much. Ideally, one should enforce the exact response behavior within a realistic environment of the systems under investigation, but it is very difficult to do, if not impossible. The NLDA with the DD AWF based on LR theory is the most logical compromise between theoretical rigor and numerical efficiency. Furthermore, for a nearly FEG (like any metallic system), the exact idempotency property of the SLDA OF-DM1 of the FEG [see Eq. (39)] should be approximately satisfied automatically, but for insulating systems, explicit enforcement of the exact idempotency property is required. This incidentally bestows us another way to distinguish metals from insulators: testing how well the exact idempotency property of the SLDA OF-DM1 is satisfied.[388] Such an approach is considerably simpler than the one just mentioned above, since the analysis of the asymptotic decay behavior of the DM1 is avoided, permitting a fast on-the-fly assessment of the metal-insulator transition during the course of an OF-DFT molecular dynamics simulation.

We believe that in the near future, all three "holy grails" listed above will be achieved, and the OF approach will become the preferred method of implementation of DFT. We hope this review draws the attention of the theoretical chemistry and physics communities to make this come to pass.

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