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AN INTRODUCTION TO ORBITAL-FREE DENSITY FUNCTIONAL THEORY

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Given a quantum mechanical system of N electrons and an external potential (which typically consists of the potential due to a collection of nuclei), the traditional approach to determining its ground-state energy involves the optimization of the corresponding wavefunction, a function of $3N$ dimensions, without considering spin variables. As the number of particles increases, the computation quickly becomes prohibitively expensive. Nevertheless, electrons are indistinguishable so one could intuitively expect that the electron density – N times the probability of finding *any* electron in a given region of space – might be enough to obtain all properties of interest about the system. Using the electron density as the sole variable would reduce the dimensionality of the problem from $3N$ to 3, thus drastically simplifying quantum mechanical calculations. This is in fact possible, and it is the goal of orbital-free density functional theory (OF-DFT). For a system of N electrons in an external potential V_{ext} , the total energy E can be expressed as a functional of the density ρ [1], taking on the following form:

$$E[\rho] = F[\rho] + \int_{\Omega} V_{\text{ext}}(\vec{r})\rho(\vec{r}) d\vec{r} \quad (1)$$

Here, Ω denotes the system volume considered, while F is the universal functional that contains all the information about how the electrons behave and interact with one another. The actual form of F is currently unknown and one has to resort to approximations in order to evaluate it. Traditionally, it is split into kinetic and potential energy contributions, the exact forms of which are also unknown.

Kohn and Sham first proposed replacing the exact kinetic energy of an interacting electron system with an approximate, noninteracting, single

determinantal wavefunction that gives rise to the same density [2]. This approach is general and remarkably accurate but involves the introduction of one-electron orbitals.

$$E[\rho] = T_{\text{KS}}[\phi_1, \dots, \phi_N] + \int_{\Omega} V_{\text{ext}}(\vec{r})\rho(\vec{r})d\vec{r} + J[\rho] + E_{\text{xc}}[\rho] \quad (2)$$

T_{KS} denotes the Kohn–Sham (KS) kinetic energy for a system of N noninteracting electrons (i.e., for the case of noninteracting electrons, a single-determinantal wavefunction is the exact solution), the ϕ_i are the corresponding one-electron orbitals, J is the classical electron–electron repulsion, and E_{xc} is a correction term that should account for electron exchange, electron correlation, and the difference in kinetic energy between the interacting and noninteracting systems. If the ϕ_i are orthonormal, T_{KS} has the following explicit form:

$$T_{\text{KS}} = -\frac{1}{2} \int_{\Omega} \sum_{i=1}^N \phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) d\vec{r} \quad (3)$$

Unfortunately, the required orthogonalization of these orbitals makes the computational time scale cubically in the number of electrons. Although linear-scaling KS algorithms exist, they require some degree of localization in the orbitals and, for this reason, are not applicable to metallic systems [3]. For condensed matter systems, the KS method has another bottleneck: the need to sample the Brillouin zone for the wavefunction (also called “**k**-point sampling”) can add several orders of magnitude in cost to the computation. Thus, a further advantage of OF-DFT is that, without a wavefunction, this very expensive computational prefactor of the number of **k**-points is completely absent from the calculation.

At this point, many general, efficient and often accurate functionals are available to handle every term in Eq. (2) as functionals of the electron density alone, except for the kinetic energy. The development of a generally applicable, accurate, linear-scaling kinetic energy density functional (KEDF) would remove the last bottleneck in the DFT computations and enable researchers to study much larger systems than are currently accessible. In the following, we will focus our discussion on such functionals.

1. General Overview

Historically, the first attempt at approximating the kinetic energy assumes a uniform, noninteracting electron gas [4, 5] and is known as the Thomas–Fermi (TF) model for a slowly varying electron gas.

$$T_{\text{TF}} = \int_{\Omega} \frac{3}{10} (3\pi^2)^{2/3} \rho(\vec{r})^{5/3} d\vec{r} \quad (4)$$

The model, although crude, constitutes a reasonable first approximation to the kinetic energy of periodic systems. It fails for atoms and molecules, however, as it predicts no shell structure, no interatomic bonding, and the wrong behavior for ρ at the $r=0$ and $r=+\infty$ limits. We will discuss some ways to improve this model later.

A deeper look at Eq. (3) reveals another approach to describing the kinetic energy as a functional of the density. Within the Hartree–Fock (HF) approximation [6], we have

$$\rho(\vec{r}) = \sum_{i=1}^N \phi_i^*(\vec{r})\phi_i(\vec{r}) \quad (5a)$$

$$\rho(\vec{r}) = \sum_{i=1}^N \rho_i(\vec{r}) \quad (5b)$$

so that, using the hermiticity of the gradient operator, and acting on Eq. (5) we obtain

$$\nabla^2 \rho(\vec{r}) = 2 \sum_{i=1}^N \left[\phi_i^*(\vec{r}) \nabla^2 \phi_i(\vec{r}) + \nabla \phi_i^*(\vec{r}) \nabla \phi_i(\vec{r}) \right] \quad (6)$$

Rearranging Eq. (6), integrating over Ω , and substituting Eq. (3) into Eq. (6) yields

$$T_{\text{KS}} = -\frac{1}{4} \int_{\Omega} \nabla^2 \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int_{\Omega} \sum_{i=1}^N \nabla \phi_i^*(\vec{r}) \nabla \phi_i(\vec{r}) d\vec{r} \quad (7)$$

Multiplying and dividing every term of the sum by ρ_i naturally introduces $\nabla \rho_i$

$$T_{\text{KS}} = -\frac{1}{4} \int_{\Omega} \nabla^2 \rho(\vec{r}) d\vec{r} + \frac{1}{8} \int_{\Omega} \sum_{i=1}^N \frac{|\nabla \rho_i(\vec{r})|^2}{\rho_i(\vec{r})} d\vec{r} \quad (8)$$

but does not provide a form for which the sum can be evaluated simply. Nevertheless, the first term can be rewritten as the integral of the gradient of the density around the edge of space.

$$\int_{\Omega} \nabla^2 \rho(\vec{r}) d\vec{r} = \oint_{\Omega} \nabla \rho(\vec{r}) d\vec{r} \quad (9)$$

For a finite system, the gradient of the density vanishes at large distances and for a periodic system the gradients on opposite sides of a periodic cell cancel each other out, so that this integral evaluates to zero in both cases. Finally, for a one-orbital system, we obtain the following exact expression for the kinetic energy [7].

$$T_{\text{VW}} = \frac{1}{8} \int_{\Omega} \frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})} d\vec{r} \quad (10)$$

Although only exact for up to two electrons, the von Weizsäcker (VW) functional is an essential component of the true kinetic energy and provides a good first approximation in the case of quickly varying densities such as those of atoms and molecules.

Unfortunately, the total energy corresponding to the ground-state electron density has the same magnitude as the exact kinetic energy. Consequently, errors made in approximating the kinetic energy have a dramatic impact on the total energy and, by extension, on the ground state electron density computed by minimization. Unlike the exchange-correlation energy functionals, which represent a much smaller component of the total energy, kinetic-energy functionals must be highly accurate in order to achieve consistently accurate energy predictions.

2. KEDFs for Finite Systems

In the case of a finite system such as a single atom, a few molecules in the gas phase, or a cluster, the electron density varies extremely rapidly near the nuclei, making the TF functional inadequate. Although many corrections have been suggested to improve upon the TF results for atoms, these modifications only yield acceptable results when densities obtained from a different method are used, usually HF. Left to determine their own densities self-consistently, these corrections still predict no shell structure for atoms. Nevertheless, the TF functional, or some fraction of it, may still be useful as a corrective term, as we will see later. Going back to the KS expression from Eq. (8), we introduce

$$n_i(\vec{r}) = \frac{\rho_i(\vec{r})}{\rho(\vec{r})} \quad (11)$$

which, when multiplying both sides by $\rho(\vec{r})$ and taking the gradient, yields

$$\nabla \rho_i(\vec{r}) = n_i(\vec{r}) \nabla \rho(\vec{r}) + \rho(\vec{r}) \nabla n_i(\vec{r}) \quad (12)$$

Substituting Eq. (12) into Eq. (8) gives the following expression:

$$T_{\text{KS}} = \frac{1}{8} \int_{\Omega} \sum_{i=1}^N \frac{(n_i(\vec{r}) \nabla \rho(\vec{r}) + \rho(\vec{r}) \nabla n_i(\vec{r}))^2}{n_i(\vec{r}) \rho(\vec{r})} d\vec{r} \quad (13)$$

The product is expanded into three sums and reorganized as

$$\begin{aligned} T_{\text{KS}} = \frac{1}{8} \int_{\Omega} & \left[\frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})} \sum_{i=1}^N n_i(\vec{r}) + 2 \nabla \rho(\vec{r}) \sum_{i=1}^N \nabla n_i(\vec{r}) \right. \\ & \left. + \rho(\vec{r}) \sum_{i=1}^N \frac{|\nabla n_i(\vec{r})|^2}{n_i(\vec{r})} \right] d\vec{r} \quad (14) \end{aligned}$$

From Eq. (11), it follows immediately that

$$\sum_{i=1}^N n_i(\vec{r}) = 1 \quad (15)$$

and so, making use of the linearity of the gradient operator in the second term of Eq. (14)

$$\sum_{i=1}^N \nabla n_i(\vec{r}) = \nabla \sum_{i=1}^N n_i(\vec{r}) = \nabla(1) = 0 \quad (16)$$

the expression further simplifies to

$$T_{\text{KS}} = \int_{\Omega} \frac{|\nabla \rho(\vec{r})|^2}{8\rho(\vec{r})} d\vec{r} + \int_{\Omega} \rho(\vec{r}) \sum_{i=1}^N \frac{|\nabla n_i(\vec{r})|^2}{8n_i(\vec{r})} d\vec{r} \quad (17)$$

As every quantity in the second integral is positive, we can conclude that the VW functional (the first term in Eq. 17) constitutes a lower bound on the noninteracting kinetic energy. This makes physical sense anyway, as we know that the VW kinetic energy is exact for any one-orbital system (one or two electrons, or any number of bosons). Any other orbital introduced will have to be orthogonal to the first. This introduces nodes in the wavefunction, which raises the kinetic energy of the entire system. Therefore, further improvements upon the VW model involve adding an extra term to take into account the larger kinetic energy in the regions of space in which more than one orbital is significant. Far away from the molecule, only one orbital tends to dominate the picture and the VW functional is accurate enough to account for the relatively small contribution of these regions to the total kinetic energy. Most of the deviation from the exact, noninteracting kinetic energy is located close to the nuclei, in the core region of atoms.

Corrections based on adding some fraction of the TF functional to the VW have been proposed (see, for instance, Ref. [8]), but only when nonlocal functionals (those depending on more than one point in space, e.g., r and r') are introduced is a convincing shell structure observed for atomic densities [9].

Even without such correction terms, the TF and VW functionals may still be enough to obtain an accurate description of the system in some limited cases. For instance, Wesolowski and Warshel used a simple, orbital-free KEDF to describe water molecules as a solvent for a quantum-chemically treated water molecule solute [10]. They were able to reproduce the solvation free energy of water accurately using this method.

Although this result is encouraging, the ultimate goal of OF-DFT is to determine a KEDF that would be accurate even without the backup provided by the traditional quantum-mechanical method. One key to judging of the

quality of a given functional is to express it in terms of its kinetic-energy density.

$$T[\rho] = \int_{\Omega} t(\rho(\vec{r})) d\vec{r} \quad (18)$$

The KS functional as it is expressed in Eq. (3) uniquely defines its kinetic-energy density. Certainly, if a given functional can reproduce the KS kinetic-energy density faithfully it must reproduce the total energy also. Any functional that differs from that one by a function that integrates to 0 over the entire system – like, for instance, the Laplacian of the density – will match the KS energy just as well but not the KS kinetic-energy density. For the VW functional, for instance, the corresponding kinetic-energy density should include a Laplacian contribution:

$$T_{\text{VW}} = \int_{\Omega} t_{\text{VW}}(\rho) d\vec{r} \quad (19)$$

$$t_{\text{VW}}(\rho) = -\frac{1}{4}\nabla^2\rho(\vec{r}) + \frac{|\nabla\rho(\vec{r})|^2}{8\rho(\vec{r})} \quad (20)$$

OF-DFT has experienced its most encouraging successes for periodic systems using a different class of kinetic energy functionals described below. These achievements led to attempts to use this alternative class of functionals for nonperiodic systems as well. Choly and Kaxiras recently proposed a method to approximate such functionals and adapt them for nonperiodic systems [11]. If successful, their method may further enlarge the range of applications where currently available functionals yield physically reasonable results.

3. KEDFs for Periodic Systems

If the system exhibits translational invariance, or can be approximated using a system that does, it becomes advantageous to introduce periodic boundary conditions and thus reduce the size of the infinite system to a small number of atoms in a finite volume. A plane-wave basis set expansion most naturally describes the electron density under these conditions. As an additional advantage, quantities can be computed either in real or reciprocal space, by performing fast Fourier transforms (FFTs) on the density represented on a uniform grid. The number of functions necessary to describe the electron density in a given system is highly dependent upon the rate of fluctuation of said density. Quickly varying densities need more plane waves in real space which translate into larger reciprocal-space grids and, consequently, into finer real-space meshes. Unfortunately, in real systems, electrons tend to stay mostly

around atomic nuclei and only occasionally venture in the interatomic regions of space. This makes the total electron density vary extremely rapidly close to the nuclei, in the core region of space. Consequently, an extremely large number of plane waves would be necessary to describe the total electron density.

One can get around this problem by realizing that the core region density is often practically invariant upon physical and chemical change. This observation is similar to the realization that only valence shell electrons are involved in chemical bonding. The valence electron density varies a lot less rapidly than the total density, so that if the core electrons could be removed, one could drastically reduce the total number of plane waves required in the basis set. Of course, the influence of the core electrons on the geometry and energy of the system must still be accounted for. This is done by introducing pseudopotentials that mimic the presence of core electrons and the nuclei. Obviously, if one is interested in any properties that require an accurate description of the electron density near the nuclei of a system, such pseudopotential-based methods will be inappropriate.

Each chemical element present in the system must be represented by its own unique pseudopotential, which is typically constructed as follows. First, an all-electron calculation on an atom is performed to obtain the valence eigenvalues and wavefunctions that one seeks to reproduce within a pseudopotential calculation. Then, the oscillations of the valence wavefunction in the core region are smoothed out to create a “pseudowavefunction,” which is then used to invert the KS equations for the atom to obtain the pseudopotential that corresponds to the pseudowavefunction, subject to the constraint that the all-electron eigenvalues are reproduced. Typically, this is done for each angular momentum channel, so that one obtains a pseudopotential that has an angular dependence, usually expressed as projection operators involving the atomic pseudowavefunctions. Such a pseudopotential is referred to as “nonlocal,” because it is not simply a function of the distance from the nucleus, but also depends on the angular nature of the wavefunction it acts upon. In other words, when a nonlocal pseudopotential acts on a wavefunction, s-symmetry orbitals will be subject to a different potential than p-symmetry orbitals, etc. (as in the exact solution to the Schroedinger equation for a one-electron atom or ion). This affords a nonlocal pseudopotential enough flexibility so that it is quite accurate and transferable to a diverse set of environments.

The above discussion presents a second significant challenge for OF-DFT beyond kinetic energy density functionals, since nonlocal pseudopotentials cannot be employed in OF-DFT, because no wavefunction exists to be acted upon by the orbital-based projection operators intrinsic to nonlocal pseudopotentials. In the case of an orbital-free description of the density, the pseudopotentials must be local (depending only on one point in space) and spherically symmetrical around the atomic nucleus. Thus, in OF-DFT, the challenge is to

construct accurate and transferable local pseudopotentials for each element. An attempt in this direction specifically for OF-DFT was made by Madden and coworkers, where the OF-DFT equation

$$\frac{\delta T_{\text{KS}}}{\delta \rho} + V_{\text{ext}} + \frac{\delta J}{\delta \rho} + \frac{\delta E_{\text{xc}}}{\delta \rho} = \mu \quad (21)$$

is inverted to find a local pseudopotential (the second term on the left-hand side of Eq. (21)) that reproduces a crystalline density derived from a KS calculation using a nonlocal pseudopotential [12]. Here the terms on the left-hand side of Eq. (21) are the density functional variations of the same terms given in Eq. (2), except that in OF-DFT, T_{KS} will be a functional of the density only and not of the orbitals. On the right-hand side is μ , the chemical potential. This method yielded promising results for alkali and alkaline earth metals, but was not extended beyond such elements because inherent to the method was the assumption and use of a given approximate kinetic energy density functional. Hence the pseudopotential had built into it the success and/or failure associated with any given choice of kinetic energy functional. A related approach for constructing local pseudopotentials based on embedding an ion in an electron gas was proposed by Anta and Madden; this method yielded improved results for liquid Li, for example [13]. More recently, Zhou *et al.* proposed that improved local pseudopotentials for condensed matter could be obtained by inverting not the OF-DFT equations but instead the KS equations so that the exact kinetic energy could be used in the inversion procedure. This was done subject to the constraint of reproducing accurate crystalline electron densities, using a modified version of the method developed by Wang and Parr for the inversion procedure [14]. Zhou *et al.* showed that a local pseudopotential could be constructed in this way that, e.g., for silicon, yielded bulk properties for both semiconducting and metallic phases in excellent agreement with predictions by a nonlocal pseudopotential within the KS theory. This bulk-derived local pseudopotential also exhibited improved transferability over those derived from a single atomic density. In principle, Zhou *et al.*'s approach is a general scheme applicable to all elements, since the exact kinetic energy is utilized [15].

With local pseudopotentials now in hand, we turn our attention back to calculating accurate valence electron densities via kinetic-energy density functionals within OF-DFT. The valence electron density in condensed matter can be viewed as fluctuating around an average value that corresponds to the total number of electrons spread homogeneously over the system. If this were exactly the case, we would have a uniform electron gas for which the kinetic energy is described exactly by the TF functional in Eq. (4) with a constant density. For an inhomogeneous density, the TF functional still constitutes an

appropriate starting point and is the zeroth order term of the conventional gradient expansion (CGE) [16].

$$T_{\text{KS}}[\rho] = T_{\text{TF}}[\rho] + T^2[\rho] + T^4[\rho] + T^6[\rho] + \dots \quad (22)$$

Here, T^2 , T^4 , and T^6 correspond to the second-, fourth-, and sixth-order corrections, respectively. All odd-order corrections are zero. The second-order correction is found to be one ninth of the VW kinetic energy, while the fourth-order term is [17]:

$$T^4[\rho] = \frac{1}{540(3\pi^2)^{2/3}} \int_{\Omega} \rho^{1/3} \left[\frac{(\nabla^2 \rho)^2}{\rho^2} - \frac{9\nabla^2 \rho (\nabla \rho)^2}{8\rho^3} + \frac{(\nabla \rho)^4}{3\rho^4} \right] d\vec{r} \quad (23)$$

Starting with the sixth-order term, all further corrections diverge for quickly varying or exponentially decaying densities [18]. Moreover, the fourth-order correction constitutes only a minor improvement over the second-order term and its potential $\delta T^4[\rho]/\delta\rho$ also diverges for quickly varying or exponentially decaying densities. Usually then, the CGE expansion is truncated at second order as

$$T_{\text{CGE}}[\rho] = T_{\text{TF}}[\rho] + \frac{1}{9}T_{\text{VW}}[\rho] \quad (24)$$

For slowly varying densities, this truncation is reasonable.

For the nearly-free electron gas, linear response theory can provide an additional constraint on the kinetic-energy functional [19].

$$\hat{F} \left(\left. \frac{\delta^2 T[\rho]}{\delta\rho^2} \right|_{\rho_0} \right) = -\frac{1}{\chi_{\text{Lind}}} = \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right)^{-1} \quad (25)$$

Here \hat{F} denotes the Fourier transform, δ the functional derivative evaluated at a reference density ρ_0 , and χ_{Lind} is the Lindhard susceptibility function, the expression for which is detailed on the right-hand side, where $\eta = q/2k_{\text{F}}$, q is the reciprocal space wave vector and $k_{\text{F}} = (3\pi^2\rho_0)^{1/3}$. Although the exact susceptibility is known in this case, the actual kinetic-energy functional is not. Its behavior at the small and large q limits can be evaluated, however. The exact linear response matches the CGE only for very slowly varying densities, which correspond to small values of q .

$$\text{Lim}_{\eta \rightarrow 0} \hat{F} \left(\left. \frac{\delta^2 T[\rho]}{\delta\rho^2} \right|_{\rho_0} \right) = \text{Lim}_{\eta \rightarrow 0} \hat{F} \left(\left. \frac{\delta^2 (T_{\text{TF}}[\rho] + \frac{1}{9}T_{\text{VW}}[\rho])}{\delta\rho^2} \right|_{\rho_0} \right) \quad (26)$$

In the limit of infinitely quickly varying densities or the large q limit (LQL), the linear response behavior is very different.

$$\text{Lim}_{\eta \rightarrow +\infty} \hat{F} \left(\left. \frac{\delta^2 T[\rho]}{\delta\rho^2} \right|_{\rho_0} \right) = \text{Lim}_{\eta \rightarrow +\infty} \hat{F} \left(\left. \frac{\delta^2 (-\frac{3}{5}T_{\text{TF}}[\rho] + T_{\text{VW}}[\rho])}{\delta\rho^2} \right|_{\rho_0} \right) \quad (27)$$

As we saw before though, the VW kinetic energy constitutes a lower bound to the kinetic energy. Therefore, here the linear response behavior cannot be correct (we are far from the small perturbations away from the uniform gas limit required in linear response theory) and we can conclude that linear response theory inadequately describes quickly varying densities. Nevertheless, a lot of effort has been made to determine the corresponding kinetic-energy functional.

Bridging the gap between the small and large q to obtain the linear response kinetic-energy functional involves explicitly enforcing the correct linear response behavior. Pioneering work in this direction by Wang and Teter [20], Perrot [21], and Smargiassi and Madden [22] produced impressive results for many main group metals. A correction term is added to the TF and VW functionals to enforce the linear response.

$$T[\rho] = T_{\text{TF}}[\rho] + T_{\text{VW}}[\rho] + T_{\text{X}}[\rho] \quad (28)$$

Here T_{X} is the correction, usually a nonlocal functional of the density that can be expressed as a double integral

$$T_{\text{X}}[\rho] = \int_{\Omega} \rho^{\alpha}(\vec{r}) \int_{\Omega} w(\vec{r} - \vec{r}') \rho^{\beta}(\vec{r}') d\vec{r}' d\vec{r} \quad (29)$$

where w is called the response kernel and is adjusted to produce the global linear response behavior, while α and β are functional-dependent parameters. More complex functionals, based either on higher-order response theories [23], for instance) or on density-dependent kernels (like those of Chacón and coworkers [24] or Wang *et al.* [25] can produce more general and transferable results. However, their excellent performance comes with increased computational costs and, in the case of the Chacón functional, with quadratic scaling of the computational time with system size. Nevertheless, computations using these functionals are several orders of magnitude faster than those using the KS kinetic energy. For example, Jesson and Madden performed DFT molecular dynamics simulations of solid and liquid aluminum using the Foley and Madden KEDF, on systems four times larger and for simulation times twice as long [26] as previous KS molecular dynamics studies [27] could consider. Although the melting temperature they predicted was much lower than the experimental value and previous predictions, it appears that their pseudopotential, not their KEDF, was the main source of error.

It is important to emphasize that even the best of today's functionals do not exactly match the accuracy of the KS method, exhibiting non-negligible deviations from the KS densities and energies in many cases. This should spur further developments of kinetic-energy density functionals.

4. Conclusions and Outlook

Despite more than seventy years of research in this field and some tremendous progress, kinetic-energy density functionals have not yet reached a degree of sophistication that allow their use reliably and transferably for all elements in the periodic table and for all phases of matter. One could easily view the development of accurate descriptions of the kinetic energy in terms of the density alone as the last great frontier of density functional theory. Currently, OF-DFT research is moving from the development of new, approximate functionals to attempting to determine the properties of the exact one [28]. Also, it is becoming clearer that reproducing the KS energy for a given system is not a guarantee of functional accuracy. More efforts have been devoted to trying to reproduce the kinetic energy density predicted by the KS method at every point in space [29]; one can expect this type of effort to intensify in the future. If highly accurate and general forms for the kinetic-energy density functional are discovered, which retain the linear scaling efficiency of current functionals, OF-DFT will undoubtedly become the quantum-based method of choice for investigating wavefunction-independent properties of large numbers of atoms. Aside from spectroscopic quantities, most properties of interest (e.g., vibrations, forces, dynamical evolution, structure, etc.) do not depend on knowledge of the electronic wavefunction and hence OF-DFT can be employed. For further reading about advanced technical details in kinetic-energy density functional theory, see Wang and Carter [30].

References

- [1] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Phys. Rev.*, 136, B864–B871, 1964.
- [2] W. Kohn and L.J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, 140, A1133–A1138, 1965.
- [3] S. Goedecker, "Linear scaling electronic structure models," *Rev. Mod. Phys.*, 71(4), 1085–1123, 1999.
- [4] E. Fermi, "Un metodo statistico per la determinazione di alcune proprietà dell'atomo," *Rend. Accad., Lincei* 6, 602–607, 1927.
- [5] L.H. Thomas, "The calculation of atomic fields," *Proc. Camb. Phil. Soc.*, 23, 542–548, 1927.
- [6] C.C.J. Roothaan, "New developments in molecular orbital theory," *Rev. Mod. Phys.*, 23, 69–89, 1951.
- [7] C.F. von Weizsäcker, "Zur Theorie der Kernmassen," *Z. Phys.*, 96, 431–458, 1935.
- [8] P.K. Acharya, L.J. Bartolotti, S.B. Sears, and R.G. Parr, "An atomic kinetic energy functional with full Weizsäcker correction," *Proc. Natl. Acad. Sci. USA*, 77, 6978–6982, 1980.
- [9] P. García-González, J.E. Alvarellos, and E. Chacón, "Kinetic-energy density functional: atoms and shell structure," *Phys. Rev. A*, 54, 1897–1905, 1996.

- [10] T. Wesolowski and A. Warshel, “*Ab initio* free-energy perturbation calculations of solvation free-energy using the frozen density-functional approach,” *J. Phys. Chem.*, 98, 5183–5187, 1994.
- [11] N. Choly and E. Kaxiras, “Kinetic energy density functionals for non-periodic systems,” *Solid State Commun.*, 121, 281–286, 2002.
- [12] S. Watson, B.J. Jesson, E.A. Carter, and P. A. Madden, “*Ab initio* pseudopotentials for orbital-free density functionals,” *Europhys. Lett.*, 41, 37–42, 1998.
- [13] J.A. Anta and P.A. Madden, “Structure and dynamics of liquid lithium: comparison of *ab initio* molecular dynamics predictions with scattering experiments,” *J. Phys. Condens. Matter*, 11, 6099–6111, 1999.
- [14] Y. Wang and R.G. Parr, “Construction of exact Kohn–Sham orbitals from a given electron density,” *Phys. Rev. A*, 47, R1591–R1593, 1993.
- [15] B. Zhou, Y.A. Wang, and E.A. Carter, “Transferable local pseudopotentials derived via inversion of the Kohn–Sham equations in a bulk environment,” *Phys. Rev. B*, 69, 125109, 2004.
- [16] D.A. Kirzhnits, “Quantum corrections to the Thomas–Fermi equation,” *Sov. Phys. – JETP*, 5, 64–71, 1957.
- [17] C.H. Hodges, “Quantum corrections to the Thomas–Fermi approximation – the Kirzhnits method,” *Can. J. Phys.*, 51, 1428–1437, 1973.
- [18] D.R. Murphy, “The sixth-order term of the gradient expansion of the kinetic energy density functional,” *Phys. Rev. A*, 24, 1682–1688, 1981.
- [19] J. Lindhard. *K. Dan. Vidensk. Selsk. Mat. Fys. Medd.*, 28, 8, 1954.
- [20] L.-W. Wang and M.P. Teter, “Kinetic-energy functional of the electron density,” *Phys. Rev. B*, 45, 13196–13220, 1992.
- [21] F. Perrot, “Hydrogen–hydrogen interaction in an electron gas,” *J. Phys. Condens. Matter*, 6, 431–446, 1994.
- [22] E. Smargiassi and P.A. Madden, “Orbital-free kinetic-energy functionals for first-principles molecular dynamics,” *Phys. Rev. B*, 49, 5220–5226, 1994.
- [23] M. Foley and P.A. Madden, “Further orbital-free kinetic-energy functionals for *ab initio* molecular dynamics,” *Phys. Rev. B*, 53, 10589–10598, 1996.
- [24] P. García-González, J.E. Alvarellos, and E. Chacón, “Nonlocal symmetrized kinetic-energy density functional: application to simple surfaces,” *Phys. Rev. B*, 57, 4857–4862, 1998.
- [25] Y.A. Wang, N. Govind, and E.A. Carter, “Orbital-free kinetic-energy density functionals with a density-dependent kernel,” *Phys. Rev. B*, 60, 16350–16358, 1999.
- [26] B.J. Jesson and P.A. Madden, “*Ab initio* determination of the melting point of aluminum by thermodynamic integration,” *J. Chem. Phys.*, 113, 5924–5934, 2000.
- [27] G.A. de Wijs, G. Kresse, and M.J. Gillan, “First-order phase transitions by first-principles free-energy calculations: the melting of Al,” *Phys. Rev. B*, 57, 8223–8234, 1998.
- [28] T. Gál and Á. Nagy, “A method to get an analytical expression for the non-interacting kinetic energy density functional,” *J. Mol. Struct.*, 501–502, 167–171, 2000.
- [29] E. Sim, J. Larkin, and K. Burke, “Testing the kinetic energy functional: kinetic energy density as a density functional,” *J. Chem. Phys.*, 118, 8140–8148, 2003.
- [30] Y.A. Wang and E.A. Carter, “Orbital-free kinetic energy density functional theory,” In: S.D. Schwartz (ed.), *Theoretical Methods in Condensed Phase Chemistry*, Kluwer, Dordrecht, pp. 117–184, 2000.