Innovations in Finite-Temperature Density Functionals

Valentin V. Karasiev, Travis Sjostrom, Debajit Chakraborty, James W. Dufty, Keith Runge, Frank E. Harris, and S.B. Trickey

Abstract Reliable, tractable computational characterization of warm dense matter is a challenging task because of the wide range of important aggregation states and effective interactions involved. Contemporary best practice is to do ab initio molecular dynamics on the ion constituents with the forces from the electronic population provided by density functional calculations. Issues with that approach include the lack of reliable approximate density functionals and the computational bottleneck intrinsic to Kohn-Sham calculations. Our research is aimed at both problems, via the so-called orbital-free approach to density functional theory. After a sketch of the relevant properties of warm dense matter to motivate our research, we give a survey of our results for constraint-based non-interacting free energy functionals and exchange-correlation free-energy functionals. That survey includes comparisons with novel finite-temperature Hartree-Fock calculations and also presents progress on both pertinent exact results and matters of computational technique.

V.V. Karasiev • T. Sjostrom • D. Chakraborty • K. Runge • F.E. Harris • S.B. Trickey (✉)
Quantum Theory Project, Departments of Physics and of Chemistry, University of Florida,
P.O. Box 118435, Gainesville, FL 32611-8435, USA
e-mail: trickey@qtp.ufl.edu; trickey@UFL.EDU
http://www.qtp.ufl.edu/ofdft

J.W. Dufty
Department of Physics, University of Florida, P.O. Box 118435, Gainesville, FL 32611-8435,
USA

F. Graziani et al. (eds.), *Frontiers and Challenges in Warm Dense Matter*,
Lecture Notes in Computational Science and Engineering 96,
DOI 10.1007/978-3-319-04912-0_3,

1 Setting and Perspective

Materials under extreme conditions have been a major and rewarding focus of condensed matter physics for well over a century. Low-temperature physics is a familiar example, with its modern form dating to the liquefaction of Hydrogen by Dewar in 1898 and of Helium by Kamerlingh Onnes in 1908 [1]. High energy-density physics (HEDP), the focus of the 2012 IPAM Long Program "Computational Methods in High Energy Density Plasmas", is less well-known, even in the scientific community. But from the perspective of shock and detonation phenomena at least, HEDP has as long and deep a scientific heritage as does low temperature physics. A history of early work on detonation waves [2], for example, notes the first detonation velocity measurements in condensed explosives by Abel in 1869, the beginnings of detonation theory (antecedent to the Chapman-Jouguet equation) by Michelson in 1890, and the Chapman-Jouguet relation itself by Chapman in 1899 and Jouguet in 1905 and 1906. Other examples could be given from plasma physics.

A sign of the richness of HEDP is that only much more recently has it been recognized that HEDP includes a complicated condensed matter regime now called warm dense matter (WDM). We discuss WDM traits briefly below. The challenge and opportunity to develop computationally tractable, predictive methods suitable for a comparatively unexplored condensed matter regime drew us together as a team. That same combination of challenge and opportunity led to Workshop IV "Computational Challenges in Warm Dense Matter" of the IPAM HEDP Long Program. The Workshop was a *de facto* review of theory, modeling, and simulation for WDM, with conversations among those already involved as well as with workers whose research clearly could be of relevance. In that context, we offer here a survey of our contributions, confident that we do not have to survey the entire area and, hence, the entire Workshop!

It is fitting to begin with a system perspective. WDM comprises a condensed matter regime characterized roughly by electron temperatures $\mathrm{T} \approx 1\text{–}15\,\mathrm{eV}$ and pressures to 1 Mbar or greater. (Aside: Theoretical and computational treatment of WDM involves diverse topics with many abbreviations. Most of the more common ones are listed in the Glossary; see the Appendix.) Recently WDM has attracted attention because of its importance in diverse physical systems, including exo-planet interiors, the path to inertial confinement fusion, and neutron stellar atmospheres [3–13]. The relationship between the WDM regime and other states of matter is illustrated schematically in Fig. 1. The regime is inherently challenging because its thermodynamics cannot be framed in terms of small perturbations from ideal, solvable models. WDM temperature and pressure ranges correspond to values of order unity in the two relevant expansion parameters: the Coulomb coupling parameter $\Gamma = Q^2/r_s k_B \mathrm{T}$ and the electron degeneracy parameter $\Theta = k_B \mathrm{T}/\epsilon_F$. (Here Q = the relevant charge, r_s = Wigner radius, ϵ_F = electron Fermi energy, T = temperature, k_B = Boltzmann constant.) WDM thus does not fall neatly within the parameter space typical of either ordinary condensed-matter physics or plasma physics. One result is that plasma physics methods which originate in the classical

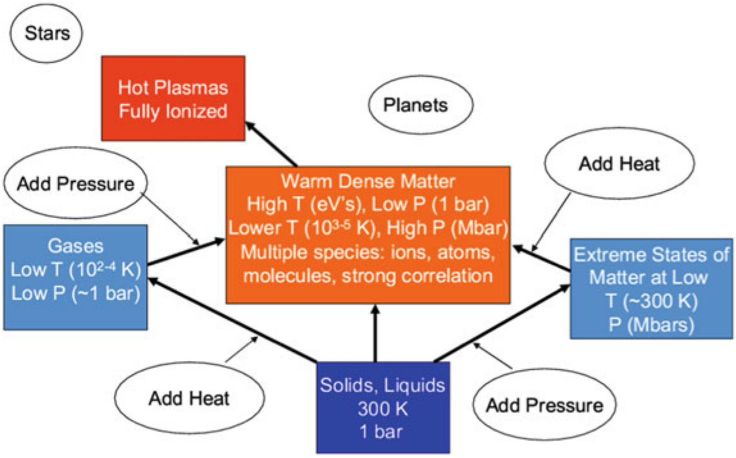


Fig. 1 Qualitative positioning of WDM relative to other physical states and systems

limit do not extend well into the WDM regime. At a fundamental level, such approaches cannot be entirely successful; the quantum limit cannot be recovered from classical physics.

Conversely, condensed-matter physics methods must be extended well beyond their normal realms of application. The logic is inexorable. A foundational element for understanding and manipulating material behavior is the equation of state (EOS). For materials under near-ambient conditions, best practice has evolved to be a combination of electronic structure calculations using density functional theory (DFT) and molecular dynamics (MD). In many cases, the zero-temperature EOS (or cold curve), including crystalline phase transitions, can be predicted quite accurately with DFT alone [14, 15]. For the nuclear (or ionic) contribution, so-called ab initio MD (AIMD; see Refs. [16–20]) is quite successful. In its simplest form (Born-Oppenheimer MD), AIMD gets the electronic forces on the nuclei (or ions) from a DFT calculation at each nuclear step. AIMD thereby combines chemical realism from explicit quantum mechanical treatment of the electrons with the more-or-less classical contributions of the nuclear species.

There are both conceptual and technical problems associated with this rosy picture, however, and they are worsened by extending into the WDM regime. A brief sketch of the customary DFT approach is needed for context. The variational minimization of the density functional customarily is via the well-known Kohn-Sham (KS) procedure [21]. It introduces a model (sometimes called "fictitious") non-interacting many-fermion system of the same density, n, as the physical system of interest. The density is expanded in the one-body states (orbitals) of the KS Hamiltonian

$$h_{\mathrm{KS}}[n]\varphi_i = \varepsilon_i \varphi_i \,, \tag{1}$$

$$n(\mathbf{r}) = \sum_i f_i |\varphi_i(\mathbf{r})|^2 \,, \tag{2}$$

with f_i the occupation numbers. For ambient T, it is appropriate to use $f_i = 0, 1$ (for the spin-polarized case); the T-dependence of the Fermi-Dirac distribution is negligible. The KS equation follows from decomposition of the fundamental Hohenberg-Kohn, Levy-Lieb functional [22–24] into non-interacting kinetic energy $\mathscr{T}_s$, Hartree, exchange, and correlation energies [25,26]. Observe that exchange and correlation are defined in terms of the KS decomposition, hence differ subtly from the quantities with the same names defined in other parts of many-electron theory. A free-energy (i.e., non-zero T) version of the theory exists; we give relevant details below. The essential point for now is that the KS equation continues to be valid but with full Fermi-Dirac occupation number T-dependence:

$$f_j \equiv f(\varepsilon_j - \mu) = [1 + \exp(\beta(\varepsilon_j - \mu))]^{-1} , \tag{3}$$

with $\beta = 1/k_B\mathrm{T}$ and μ the chemical potential. In the WDM regime, the many small, but non-negligible values of f_j for levels far above μ constrict drastically a computational bottleneck that already is evident at $\mathrm{T} = 0\,\mathrm{K}$. Simply, at $\mathrm{T} = 0\,\mathrm{K}$, diagonalization of the KS Hamiltonian means that the KS calculational cost scales as N_e^3 at best, with N_e = total number of electrons. If a conventional KS DFT calculation drives the AIMD, each MD step therefore also scales as N_e^3 or worse. Matters worsen as T increases. Then the computational burden increases proportionally to N_b^3, where N_b is the number of thermally occupied levels, with $N_b \gg N_e$ for WDM. This scaling of computational cost is a severe limitation for thorough exploration of WDM, as noted in recent practitioner remarks (Sept. 2012) [27,28]. Even with the massive computational power of the DOE labs, realistic KS-driven AIMD simulations of WDM remain at the level of heroic.

Our research program aims to eliminate the KS bottleneck in WDM simulations by making orbital-free DFT (OF-DFT) a viable alternative. Orbitals enter the KS procedure primarily as a device for computing the major part of the KE and, for nonzero T, also for computing the non-interacting entropy from the occupation numbers. Putting aside for now the present-day emphasis on developing explicitly orbital-dependent exchange-correlation functionals, the other free-energy contributions in conventional DFT are all explicit density functionals.

Schematically, the OF-DFT simulation is compared with a conventional KS-DFT simulation in Fig. 2. The crucial difference is that the N_b-dimensional Kohn-Sham eigenvalue problem is replaced with a single 3-dimensional Euler-Lagrange equation. As already stated, the challenge addressed in this project is to generate the functionals which are ingredients of that equation. To illustrate the power of orbital-free methods, Fig. 3 shows our comparison for Hydrogen at $0.983\,\mathrm{g/cm^3}$, about a two-fold compression from ambient density. Discussion of these computations is below. Here, the essential point is that the OF-DFT simulation replaces the power-law scaling of the conventional KS-DFT-driven MD with a nearly invariant scaling.

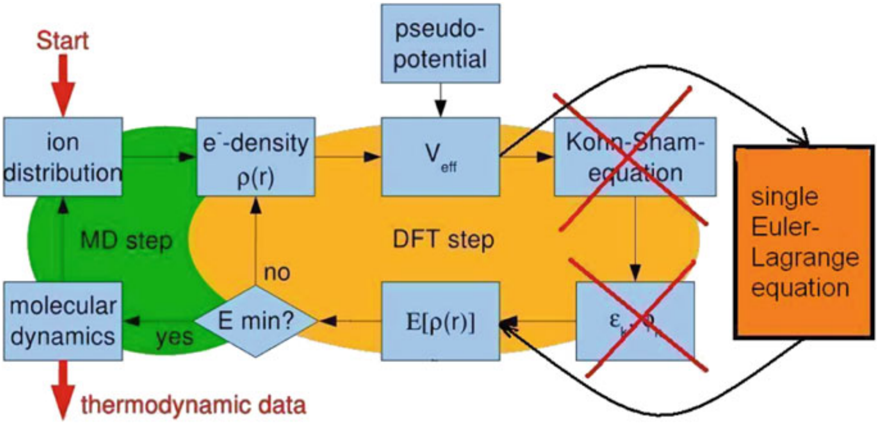


Fig. 2 Comparison of Kohn-Sham and orbital-free MD computational cycles (Credit for original: W. Lorenzen)

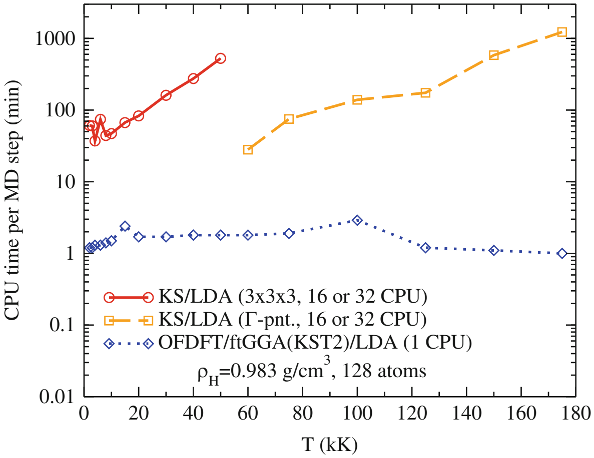


Fig. 3 Illustration of the dramatic advantage of OF-DFT: time per AIMD step as a function of T for KS-DFT vs. OF-DFT for Hydrogen

2 Primary Challenges

Identification of the primary challenges to use of OF-DFT for predictive WDM studies requires that we set out a few details of free-energy DFT (FE-DFT). At the level of the Born-Oppenheimer approximation, FE-DFT follows from a constrained search approach within the grand canonical ensemble [25, 29–32]. It should be stressed that this approach provides a firm theoretical foundation for FE-DFT, so the resulting equations cannot be dismissed as ad hoc or heuristic. The analysis yields the key result that, in parallel with ground-state DFT [22–24], there exists a universal functional $\mathscr{F}[n, \mathrm{T}]$ which gives the equilibrium free energy of a many-electron system with Coulomb interactions in terms of n and T. Once one has $\mathscr{F}$ for a given configuration of nuclei or ions $\{\mathbf{R}\}$, the electronic forces on those ions or nuclei can be computed from $\nabla_{\mathbf{R}}(\mathscr{F} + E_{\mathrm{ext}})$ with $E_{\mathrm{ext}} = \int d\mathbf{r} n(\mathbf{r}) \mathrm{v}_{\mathrm{ext}}(\mathbf{r})$ and $\mathrm{v}_{\mathrm{ext}}$ the external potential. (The ion-ion Coulomb repulsion term is omitted here for simplicity.).

To compute $\mathscr{F}$, one introduces, just as in zero-temperature DFT [21], a non-interacting system with the same density as the physical (interacting) system. The universal functional $\mathscr{F}[n, \mathrm{T}]$ thus partitions into a non-interacting part $\mathscr{F}_{\mathrm{s}}[n, \mathrm{T}]$ plus the classical Coulomb repulsion energy (Hartree energy) $\mathscr{F}_{\mathrm{H}}[n]$, and the exchange-correlation remainder $\mathscr{F}_{\mathrm{xc}}[n, \mathrm{T}]$

$$\mathscr{F}[n, \mathrm{T}] = \mathscr{F}_{\mathrm{s}}[n, \mathrm{T}] + \mathscr{F}_{\mathrm{H}}[n, \mathrm{T}] + \mathscr{F}_{\mathrm{xc}}[n, \mathrm{T}] , \tag{4}$$

where

$$\mathscr{F}_{\mathrm{s}}[n, \mathrm{T}] = \mathscr{T}_{\mathrm{s}}[n, \mathrm{T}] - \mathrm{T}\mathscr{S}_{\mathrm{s}}[n, \mathrm{T}] . \tag{5}$$

Here $\mathscr{T}_{\mathrm{s}}$ and $\mathscr{S}_{\mathrm{s}}$ are the non-interacting kinetic energy (KE) and entropy. The motivation is that $\mathscr{F}_{\mathrm{s}}$ and $\mathscr{F}_{\mathrm{H}}$ constitute the largest contributions to $\mathscr{F}$, yet can be calculated explicitly, while the smaller contribution $\mathscr{F}_{\mathrm{xc}}[n, \mathrm{T}]$ can be approximated. Analogously with the zero-T formulation, $\mathscr{F}_{\mathrm{xc}}$ contains not only Coulombic correlation and exchange effects, but also the difference between the kinetic energies and entropies of the actual and non-interacting systems.The expressions for the non-interacting KE and entropy are:

$$\mathscr{T}_{\mathrm{s}}[n, \mathrm{T}] := -\frac{1}{2} \sum_{j=1}^{\infty} \int d\mathbf{r}\, f_j\, \varphi_j^*(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r}) := \int d\mathbf{r}\, \tau_{\mathrm{orb}}(\mathbf{r}, \mathrm{T}) , \tag{6}$$

$$\mathscr{S}_{\mathrm{s}}[n, \mathrm{T}] = -k_{\mathrm{B}} \sum_j \{ f_j \ln f_j + (1 - f_j) \ln(1 - f_j) \} . \tag{7}$$

Variation with respect to the density then gives the KS Hamiltonian as

$$h_{\mathrm{KS}} = -\frac{1}{2}\nabla^2 + \mathrm{v}_{\mathrm{KS}}([n]; \mathbf{r}) \equiv -\frac{1}{2}\nabla^2 + \mathrm{v}_{\mathrm{ext}} + \mathrm{v}_{\mathrm{H}} + \mathrm{v}_{\mathrm{xc}} . \tag{8}$$

Here $\mathrm{v}_{\mathrm{H}} = \delta\mathscr{F}_{\mathrm{H}}/\delta n$, $\mathrm{v}_{\mathrm{xc}} = \delta\mathscr{F}_{\mathrm{xc}}/\delta n$, and the density is given in terms of the Fermi-Dirac occupation numbers f_j and the KS orbitals φ_j as in Eqs. (2) and (3).

The expressions for the non-interacting KE and entropy just given illustrate some of the challenges to OF-FE-DFT. In place of Eqs. (6) and (7), we must find adequately accurate, general, orbital-free representations for both, namely

$$\mathscr{T}_{\mathrm{s}}[n, \mathrm{T}] = \int d\mathbf{r}\, \tau_{\mathrm{s}}[n(\mathbf{r}), \mathrm{T}] \quad , \quad \mathscr{S}_{\mathrm{s}}[n, \mathrm{T}] = \int d\mathbf{r}\, \sigma_{\mathrm{s}}[n(\mathbf{r}), \mathrm{T}] . \tag{9}$$

Further, we must restrict consideration to XC functionals that are not explicitly orbital-dependent, i.e., functionals which correspond to rungs one or two on the Perdew-Schmidt Jacob's ladder [33] of complexity. This restriction motivates continued effort (including contributions from our group) to improve lower-rung zero-T XC functionals, despite their de-emphasis in the quantum chemistry community (which does not focus on orbital-free DFT). We therefore work with XC functionals of the form

$$\mathscr{F}_{\mathrm{xc}} = \int d\mathbf{r}\, f_{\mathrm{xc}}[n(\mathbf{r}), \mathrm{T}] \ . \tag{10}$$

For simplicity of notation we have omitted possible dependence on density gradients and higher derivatives of the density in several of the foregoing expressions. With all contributions in orbital-free form, the Euler equation becomes

$$\frac{\delta \mathscr{T}_{\mathrm{s}}}{\delta n} - \mathrm{T}\frac{\delta \mathscr{S}_{\mathrm{s}}}{\delta n} + \frac{\delta \mathscr{F}_{\mathrm{H}}}{\delta n} + \frac{\delta \mathscr{F}_{\mathrm{xc}}}{\delta n} = \mu - \mathrm{v}_{\mathrm{ext}} \ . \tag{11}$$

The primary challenges to the use of OF-DFT for WDM studies now can be identified succinctly. First, there is no constructive route from the exact DFT theorems [21–24] to viable approximations for the XC free energy [25, 29–32], an observation that is hardly surprising in view of the fact that no such route has been found for zero-temperature XC functionals. Secondly, the abandonment of an orbital description means that there also is no obvious constructive path for approximate functionals for either the non-interacting kinetic energy or entropy solely in terms of the density. Third, our work has shown that the functionals $\mathscr{T}_{\mathrm{s}}$, $\mathscr{S}_{\mathrm{s}}$, and $\mathscr{F}_{\mathrm{xc}}$ have a significant dependence on temperature that thus far has received insufficient attention.

Our research can be conceptualized in terms of these three challenges. The discussion which follows surveys the main points of our work to

- Uncover the T-dependence of $\mathscr{T}_{\mathrm{s}}$, $\mathscr{S}_{\mathrm{s}}$ for ranges of material densities and pressures appropriate to WDM by finite-T KS calculations
- Develop new, T-dependent generalized gradient approximations for $\mathscr{T}_{\mathrm{s}}$ and $\mathscr{S}_{\mathrm{s}}$
- Characterize the T-dependence of the exchange functional $\mathscr{F}_{\mathrm{x}}$ by comparison of both T-dependent local density approximation (LDA) [34] and ordinary T-independent LDA with thermal (finite-T) Hartree-Fock (tHF) calculations [35–37]
- Derive exact constraints and properties of the various contributions to the free energy density functional
- Improve $\mathrm{T} = 0\,\mathrm{K}$ orbital-free $\mathscr{T}_{\mathrm{s}}$ and $\mathscr{F}_{\mathrm{xc}}$ functionals (the obvious low-T limits of our target functionals)
- Develop the requisite technical means (algorithms, local pseudopotentials, projector augmented wave data sets, etc.).

A brief discussion of the context of our work is useful. Zero-temperature OF-KE functional development today has two streams. One uses two-point functionals, of the generic form

$$\mathscr{T}_s[n] = \int d\mathbf{r}_1 d\mathbf{r}_2 n^{\lambda}(\mathbf{r}_1) K[n(\mathbf{r}_1), n(\mathbf{r}_2), \mathbf{r}_1, \mathbf{r}_2] n^{\gamma}(\mathbf{r}_2) \tag{12}$$

with $\lambda + \gamma = 8/3$ and the kernel K referenced to the response of the homogeneous electron gas (HEG). See Ref. [38] for a didactic discussion. The motivation is to describe Friedel oscillations in solids and corresponding atomic and molecular electronic shell structure. While progress continues, the inherent non-locality of this approach causes computational burden (for example, see remarks in Ref. [39]). The two-point strategy also has conceptual limitations. The linear response formulation implicitly requires a reference density (think of the homogeneous electron gas). But a reference density is ill-defined for a truly unenclosed system, e.g., an atom or molecule, a problematic limitation for proper low-density limits such as in WDM (including the $\mathrm{T} = 0\,\mathrm{K}$ gas phase). So-called density-independent two-point kernels also are intrinsically unstable [40]. More complicated, density-dependent kernels thus are inescapable.

Another form of two-point functional development starts with modeling of the first-order reduced density matrix [41]. Recently, one of us worked on algorithms for two-point optimization of density matrices with respect to various idempotency constraints [42] (D. Chakraborty, R. Cuevas-Saavedra, P.W. Ayers, J. Chem. Phys., Unpublished) for atoms and molecules. Though this approach requires ingenuity in accurate modeling of a density matrix, it could be an alternative route to a more accurate two-point OFKE functional. With emphasis on computational speed, however, our main focus for $\mathscr{T}_\mathrm{s}$ approximations is on one-point functionals. We return to that emphasis at various points below.

One other matter of context also is important, namely that we are not working on the embedding form of OF-DFT [43, 44]. The distinction is important because the requirements on OF-KE embedding functionals differ substantially from those on approximations for $\mathscr{T}_\mathrm{s}$.

3 Advances

3.1 **T**-*Dependence of $\mathscr{T}_\mathrm{s}$, $\mathscr{S}_\mathrm{s}$, and New GGA Non-interacting Functionals*

Despite skepticism about obtaining adequate approximations for τ_s and σ_s, in fact recent times have seen significant progress. Suffice it to say here that in roughly the last decade a modest-sized but growing community of researchers is making headway on effective zero-temperature OF-DFT functionals. Several of us were involved [45–48]. A bibliographic list we keep lists 115 papers in that decade (and a total of 340). Though thorough, the list surely is not complete.

To have predictive capability, the approximate functionals should not be parameterized to voluminous data. That requirement leads to what are called constraint-based functionals. For the non-interacting functionals, our constraint-based development starts with a rigorous decomposition of $\mathscr{T}_\mathrm{s}$ that yields important positivity constraints. Rearrange Eq. (6) into the form with a positive-definite integrand,

$$\mathscr{T}_\mathrm{s} = \frac{1}{2}\sum_j f_j \int d\mathbf{r} \mid \nabla\varphi_j \mid^2 \ . \tag{13}$$

It follows that

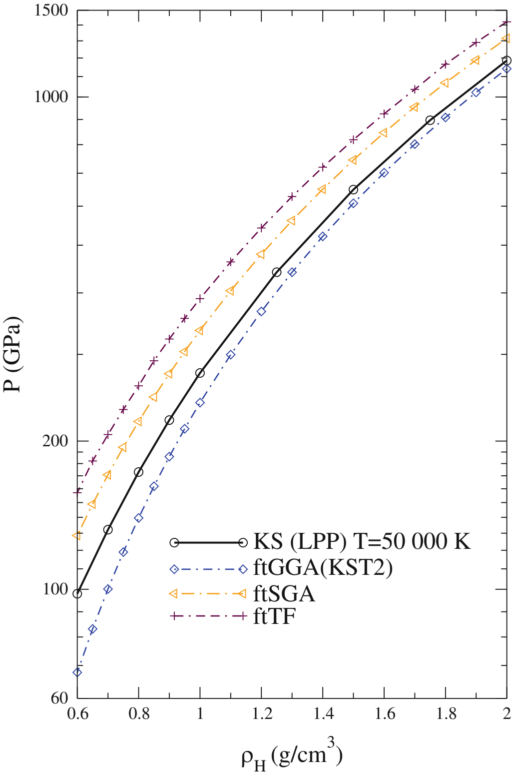
$$\begin{aligned} &\mathscr{T}_\mathrm{s}[n] := \mathscr{T}_\mathrm{W}[n] + \mathscr{T}_\theta[n], \\ &\text{with} \qquad \mathscr{T}_\mathrm{W}[n] = \frac{1}{8}\int \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}\, d\mathbf{r} \ \text{ and } \ \mathscr{T}_\theta[n] \ \geq 0\,. \end{aligned} \tag{14}$$

Note the absence of a Thomas-Fermi term and the importance of $\mathscr{T}_W$, the von Weizsäcker functional (vW) [49]. At T $=$ 0 K, the non-negativity of $\mathscr{T}_\theta$ ("Pauli term") is a rigorous requirement [50–53]. (Related discussions are in Refs. [48] and [54].) Recently, two of us proved that the non-negativity requirement also holds at T $>$ 0 K [55]. In consequence, the "Pauli potential", $\mathrm{v}_\theta \equiv \delta\mathscr{T}_\theta[n]/\delta n(\mathbf{r})$, also must be non-negative for all $\mathbf{r}$. This constraint is extremely strict; see our earlier work at zero temperature for examples [47]. (As occasionally happened during the IPAM Long Program, the vocabulary "Pauli potential" can cause confusion. Clearly the quantity discussed here is not the same as the effective potential used to mimic quantum effects in classical potential models.)

The only nonzero-T non-interacting free-energy functionals known prior to the work we are about to discuss are the Thomas-Fermi (ftTF) [56] and the gradient expansion. It usually is truncated at second order, leading to the nonzero-T second-order gradient approximation functional (ftSGA) [57–59]. Both functionals are exact in the high-T limit, but are inadequate to serve as a $\mathscr{T}_\mathrm{s}$ approximation in the WDM temperature range.

To address this lack of an adequate nonzero-T non-interacting free-energy functional, we have developed a generalized gradient approximation (GGA) framework [60]. Analysis of the gradient expansion shows clearly that the non-interacting kinetic energy and entropy contributions to the free energy differ in their dependence on T. From this, we were able to define appropriate, T-dependent reduced density gradients for parameterizing the kinetic and entropic contributions separately. By analogy with zero-T GGA, the nonzero-T GGAs are formed as the LDA energy density multiplied by a kinetic or entropic enhancement factor. Those factors are

Fig. 4 Pressure vs. material density of simple cubic H at T = 50,000 K for various non-interacting free-energy functionals $\mathscr{F}_s = \mathscr{T}_s - T\mathscr{S}_s$ compared to Kohn-Sham calculation. Note that the pressure axis is logarithmic



functions of the corresponding kinetic and entropic reduced density gradients. By construction, these nonzero-T GGA functionals satisfy exact scaling properties [55].

A simple, straightforward choice for the form of the nonzero-T GGA KE enhancement factor is a zero-T GGA enhancement factor (at least that choice provides a correct zero-T limit) but with the new kinetic reduced density variable instead of the zero-T reduced density gradient $s(\mathbf{r}) = (24\pi^2)^{-1/3}|\nabla n|/n^{4/3}$. There is no analogous choice for the entropic contribution. Instead, from a basic thermodynamic identity, we derived a differential equation which relates the two enhancement factors such that, once the KE enhancement factor is specified, its entropic counterpart can be calculated [60]. As a first example, we proposed a simple approximate solution to that rather complicated relationship and used it and a kinetic energy enhancement factor based on the zero-T “modified conjoint GGA” kinetic energy of Ref. [47]. Compared to either ftTF or ftSGA, the new Karasiev-Sjostrom-Trickey (KST2) functional is substantially superior, though still in need of improvement. An example of the effects on the EOS is in Fig. 4.

3.2 T-*Dependence of* $\mathscr{F}_{\mathbf{xc}}$

Contemporary nonzero-T DFT calculations for AIMD typically use [61, 62] an XC functional derived for zero temperature, i.e.,

$$\mathscr{F}_{\mathrm{xc}}[n(\mathbf{r},\mathrm{T}),\mathrm{T}] \approx E_{\mathrm{xc}}[n(\mathbf{r},\mathrm{T})]\,. \tag{15}$$

A few workers have used nonzero-T LDA functionals that are based on interpolation between high and low-T limits, or on calculations in the intermediate temperature region obtained via approximate methods such as RPA or local-field corrections [34,63–65]. Beyond LDA, only the gradient expansion term for nonzero-T exchange has been given [66–68]. In short, there is not a well-established set of XC functionals suitable for DFT computations at nonzero temperature, in sharp contrast with the enormous diversity of approximate ground-state functionals.

This situation makes it a priority item to generate XC free-energy functionals of documented reliability at WDM temperatures. An important component of this task is the establishment of reference data for calibration and/or validation of candidate functionals. Somewhat surprisingly (and contrary to a referee comment we once received), there is little reference data for nonzero temperature of anywhere near the quality of the QMC data on which zero-T XC LDA is based [69]. This state of affairs is in contrast to that for zero temperature, for which there are QMC data, jellium surface data, and more-or-less standard test sets of molecular data and well-established solid-state data for lattice constants and bulk moduli that can be used to assess the quality of a new functional. Such benchmark data are not easy to generate from first-principles calculations for $\mathrm{T} > 0\,\mathrm{K}$.

In response, we have studied the effects of explicit T-dependence in the exchange free energy functional $\mathscr{F}_{\mathrm{x}}$, by comparing nonzero-T Hartree-Fock (thermal HF) calculations with nonzero-T DFT KS calculations for both extended (periodically bounded) and confined systems. The DFT calculations used exchange-only functionals, of both the nonzero-T [34] and ordinary zero-T types. Remark: Thermal HF is rigorously established in the grand ensemble; see Refs. [35–37]. In particular, the full T-dependence of the exchange free energy is obtained through thermally occupied orbitals which appear in the familiar HF exchange term.

The periodically bounded case that we studied [70] was bcc Li, compressed at one to three times ambient density and at $0 \leq \mathrm{T} \leq 100{,}000\,\mathrm{K}$. A careful study (see below) eliminated any pseudopotential effects. The resulting tHF and T-dependent LDA-exchange free energies agree semi-quantitatively. Both increase (decrease in magnitude) with increasing T. In marked contrast, the zero-T E_{x} functional with T-dependent density, $n(\mathbf{r},\mathrm{T})$, is essentially constant with increasing T. The electronic pressure for the nonzero-T exchange functional tracks the thermal HF results much more closely than the pressure from the zero-T functional. The pressure difference from either of the former two with respect to the zero-T functional is roughly 10 % at 100,000 K. See Fig. 5 for an example.

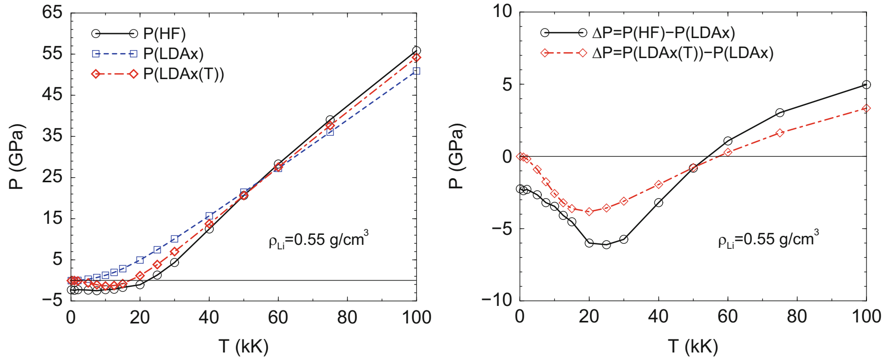


Fig. 5 Total pressure (*left*) and pressure difference (*right*) between two T-dependent $\mathscr{F}_x$ and a T-independent E_x used in a T-dependent calculation; bcc Li, $\rho = 0.55\,\mathrm{g/cm^3}$

Secondly, we devised and programmed an entirely new all-electron methodology (discussed below) for treatment of multi-atom systems confined in a hard-walled box [71]. For eight H atoms in a cubically symmetric array and $0 \le \mathrm{T} \le 300{,}000\,\mathrm{K}$, we find semi-quantitative agreement between the exchange free energy from tHF and that from the nonzero-T LDA X-functional F_{x}. As before, there is virtually no T-dependence from the zero-T $E_{\mathrm{xc}}[n(\mathbf{r}, \mathrm{T})]$. The energy difference between the N_e and $N_e + 1$ levels (the highest occupied and lowest unoccupied or virtual levels at $\mathrm{T} = 0\,\mathrm{K}$) decreases with increasing T for tHF but increases for DFT (for both zero-T and T-dependent functionals). This differing shift of initial virtuals as they become populated comes from their different self-interaction behavior. For DFT with an approximate XC functional, the initially occupied KS orbitals suffer spurious self-repulsion, whereas the original virtuals do not. In tHF, however, the virtuals arise from a full N_e-electron potential. Thus, as T increases, the initially occupied KS orbitals are partially depopulated and their self-interaction error decreases. In tHF, the initial virtuals become fractionally populated and thereby fractionally corrected (lowered).

For the correlation free energy, we compared several proposed nonzero-T XC functionals [34, 64, 65] with zero-T functionals for warm dense Li and H [72]. We find a non-trivial reduction in the total pressure. For simple cubic H (scH) with densities 1–4 $\mathrm{g/cm^3}$ and temperatures 100–300 kK, we find a pressure lowering of 2–4 %, relative to values predicted using zero-T XC functionals.

By use of the Quantum Espresso @ Profess code capacity discussed below (see Methodological and Technical Advances) , we have done orbital-free AIMD simulations for Hydrogen and Deuterium at material densities from near-equilibrium at $\mathrm{T} = 0\,\mathrm{K}$ to about a four-fold compression in the range $2{,}000\,\mathrm{K} \le \mathrm{T} \le 4{,}000{,}000\,\mathrm{K}$. We compared our newly developed KST2 non-interacting GGA functional (discussed above) to the reference KS AIMD for $\mathrm{T} < 200{,}000\,\mathrm{K}$ and to

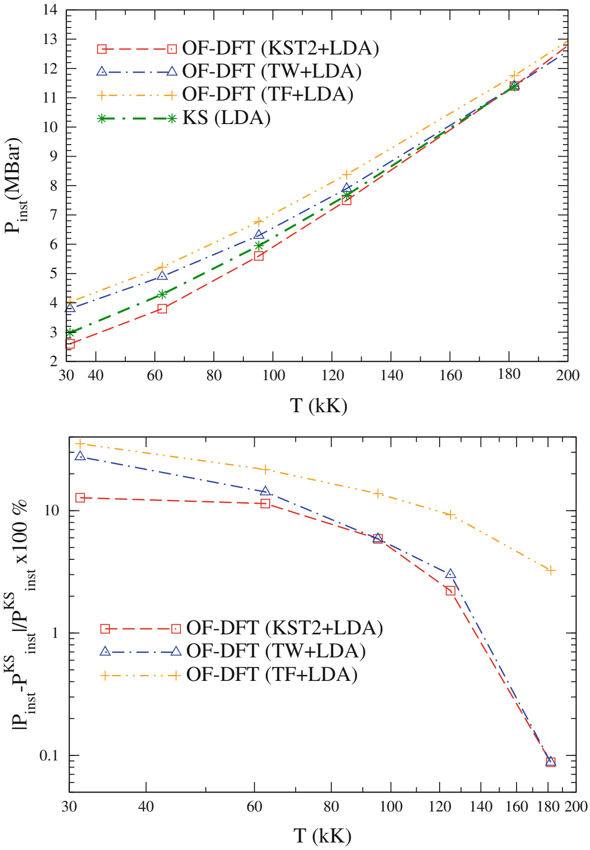


Fig. 6 *Top*: Instantaneous pressures for OF-DFT-AIMD compared to KS-AIMD for three OF-DFT non-interacting functionals: tTF, TW, and KST2. All with ground-state LDA XC. The system is Deuterium at material density $\rho = 1.9636\,\mathrm{g/cm^3}$. *Bottom*: percentage differences relative to KS-AIMD. Note the logarithmic temperature scale for both panels

both tTF and our finite-T generalization of the Tran-Wesołowski KE functional [73] and the corresponding approximate entropy functional obtained by the procedure in Ref. [60]. That functional is labeled ftTW. (We remark, in fairness to Tran and Wesołowski, that their functional never was intended for this purpose. We simply use it as an example of a zero-T functional from the literature which might, naïvely perhaps, be generalized to non-zero T.) To isolate the effects of the non-interacting functionals, all the simulations were done with simple ground-state LDA XC. Note that for $T > 200\,\mathrm{kK}$, the KS procedure becomes an intractable task. Figure 6 shows both the actual EOSs (with "instantaneous pressure", that is, without the ideal gas kinetic contribution) and the percentage error relative to the KS calculation for Deuterium at $\rho_{\mathrm{D}} = 1.96361\,\mathrm{g/cm^3}$ ($r_{\mathrm{s}} = 1.40\,\mathrm{bohr}$). The EOS from the KST2 functional clearly is in better agreement with the reference KS results than the EOS from either the ftTF or ftTW (which actually behaves rather like ftSGA) functionals, particularly in the lower part of the temperature range. Note added in proof: Subsequent development of the non-empirical VT84F functional provides essentially the same improvement [74].

3.3 Exact Properties

Success for the constraint-based strategy obviously depends on having a sufficient number of meaningful constraints. The many formal relationships known for zero-temperature DFT have played that role in the development of constraint-based ground state XC functionals. Corresponding relationships at nonzero temperature would be useful, hence it is important to determine the extent to which the zero-T results remain valid or can be generalized for non-zero T. We have established a number of formal results for free energy DFT.

Homogeneous scaling [75–78] has been particularly important in developing zero-T XC functionals. We have extended this scaling to finite-T non-interacting functionals with a thorough analysis [55] and showed that (i) exact representation in terms of the one-particle Fermi density matrix is extremal among all single-particle density matrices; (ii) the von Weizsäcker functional is a lower bound to the non-interacting kinetic energy for all T; (iii) a single-particle density matrix corresponding to the TF approximation can be identified, thus giving an upper bound for the free energy; and (iv) exact scaling and associated upper and lower bounds can be established for the free energy, energy, and entropy functionals. Similar scaling results for the interacting system were published shortly thereafter by Pittalis et al. [79] via an analysis analogous with ground-state DFT scaling. Our scaling uses dimensional analysis and a demonstration of the relationship of DFT functionals to those of inhomogeneous-system thermodynamics. We have extended the treatment to the interacting case [80]. For it, both T and charge scaling are involved.

We also have investigated the phenomenological nonzero-T Thomas-Fermi functional (ftTF) for the non-interacting free energy [81–83]. From a functional expansion of the local free-energy density about its value at an arbitrary point, the LDA emerges as the leading term. This is the TF approximation for very large N_e, but not for finite N_e, as demonstrated by an exact evaluation for $N_e = 4$ in three dimensions at $\mathrm{T} = 0\,\mathrm{K}$. The non-interacting HEG free energy was calculated at finite T for arbitrary N_e, which gives the basis for a generalized TF approximation. Carried out to second order at nonzero T, the procedure generalizes the Perrot result [59] to arbitrary gradients. The expansion coefficients are non-linear response functions for the ideal Fermi gas as functions of the local density. The result is an exact limit for a class of non-local, linear response functionals introduced phenomenologically by others, for example, Refs. [38, 84–86].

Further, we have addressed the failure of the TF approximation for singular external potentials (e.g., Coulomb potentials) by a formal map of the exact functional for a given external potential onto a fictitious TF functional for an effective external potential [87], which we find to be a thermal TF approximation without the singularity.

The classical-map procedure [88] is an alternative route to functionals. It represents an equilibrium non-uniform quantum system by a corresponding classical system chosen to reproduce thermodynamic and structural properties. The connection allows application of classical strong-coupling methods. To obtain a better formal basis, we analyzed the grand canonical ensemble correspondence for the two systems [89] and showed that it enables definition of the classical-system effective T, local chemical potential, and pair potential. Approximate inversion of these definitions follows from the integral equations of classical liquid state theory. The structure and thermodynamics of the HEG (jellium) were calculated this way across a wide range of T and densities, including various high-T, weak-coupling, and low-density limits. We find good agreement with zero-T diffusion Monte Carlo results. The shell structure of harmonically confined charges (nonzero-T "harmonium") also was studied, with the result that both diffraction and exchange degeneracy can produce shell structure even in the absence of Coulomb correlations.

WDM transport properties are beyond the scope of strict DFT (which describes thermodynamic properties). Nevertheless, the KS orbitals and eigenvalues often are assumed to provide an effective medium, or mean field theory for the dynamical properties as well (e.g., transport properties, opacities, scattering cross sections). These uncontrolled approximations appear to have some empirical basis for validity. To clarify this context and provide improved approximations, the following initial results [90] have been obtained: (i) The exact Green-Kubo expression for the frequency-dependent conductivity has been evaluated in an arbitrary single-particle basis which is assumed to approximately diagonalize the Hamiltonian. The Kubo-Greenwood form follows, providing the basis for a variational formulation and associated improvements. (ii) A formal quantum kinetic theory for the Green-Kubo time-correlation functions provides a second approach to the context for the Kubo-Greenwood approximation. In particular, a natural mean-field approximation based on exact initial correlations goes beyond Hartree-Fock and is closely connected to the choice of a Kohn-Sham basis.

3.4 Better Zero-T Limit Functionals

To have at least reasonable levels of chemical realism in AIMD simulations of WDM, the zero-T KE functional $\mathcal{T}_s[n, \mathrm{T} = 0]$ is an important limit. In Ref. [91], we showed that an intriguing and novel information-theoretic orbital-free form for the zero-T KE functional is seriously flawed by violation of various positivity constraints. The analysis led us to propose a modified form which is positive definite. It remains to explore and develop that concept.

The zero-T XC functional $E_{\mathrm{xc}}[n]$ is a similarly important limiting case for WDM simulations. In Refs. [92–95], one of us, with colleagues in Mexico, showed ways to make significant improvements in GGA E_{x} energetics. In addition, we gave both an improved (relative to B3LYP [96] and revTPSS [97]) meta-GGA and an improved hybrid functional. If a proposed rung-reduction procedure (analogous with the construction of the LYP functional [98]) works, these will give us better GGA X functionals, hence also contribute to the OF-DFT agenda.

3.5 Methodological and Technical Advances

With Eq. (14) and the substitution $\delta\mathscr{T}_{\mathrm{W}}/\delta n = -n^{-1/2}\nabla^2(n^{1/2})/2$, the Euler equation, Eq. (11), takes the form of a one-orbital eigenvalue equation,

$$\left\{-\frac{1}{2}\nabla^2 + \frac{\delta\mathscr{T}_\theta}{\delta n} - \mathrm{T}\frac{\delta\mathscr{S}_{\mathrm{s}}}{\delta n} + \mathrm{v}_{\mathrm{KS}}\right\} n^{1/2} = \mu\, n^{1/2}\,. \tag{16}$$

The form of this equation led to the seemingly obvious notion that numerical solution would be straightforward with a standard KS code. However, one of our studies [99] confirmed the contradictory prior claim [100] that, in general, such codes cannot handle the peculiar potential which appears in Eq. (16). The difficulty is the repulsive nature of any KE functional. The problem is worsened by the singular nature of approximate GGA KE functionals. Direct minimization algorithms are essential.

Most KS codes used to study WDM employ non-local pseudopotentials (PPs). The PPs are fitted to free ground-state atoms, hence their transferability to WDM conditions is not guaranteed but must be verified. We developed a new procedure to test PP transferability to high compression [70] by comparison to all-electron results for clusters of the same local symmetry and near-neighbor distances. For Li, we found that standard norm-conserving PPs and projector-augmented wave (PAW) data sets used in packages such as ABINIT [101, 102], QUANTUM ESPRESSO [103] and VASP [104–107] have relatively small transferability compression ranges, typically up to 1.5-, 4.5- or 7-fold compression depending on details. The compensation charge density (CCD) sometimes included in PAW data sets was found to cause problems at high compressions. Without CCD and with cutoff radius reduced by about a factor of two, we were able to build all-electron PAW LDA and GGA data sets for Li which are transferable to at least 140-fold compression.

Though OF-DFT in principle does not need PPs to exclude chemically inactive core states, regularization of the nuclear-electron interaction singularity is required for efficient implementation, e.g., in a plane-wave basis. PPs developed for KS calculations generally are non-local, i.e., orbital-dependent, thus are inapplicable in OF-DFT calculations. Local pseudopotentials (LPP) must be developed for OF-DFT. But there is no standard or even dominant method to do that. We developed a new method [99] aimed specifically at OF-DFT calculations. The LPP is constructed as a normalized linear combination of l-components of a norm-conserving non-local PP (NLPP). The coefficients are constrained to reproduce some bulk property. The method was tested for bcc Li. An alternative procedure, used for scH, is to fit the parameters of the simple Heine-Abarenkov model [108, 109] such that a bulk property (in our case, the lattice parameter) from a more sophisticated PP is reproduced. We showed that bulk properties are reproduced for material densities to at least $15\ \mathrm{g/cm^3}$ and for $\mathrm{T} \leq 100{,}000\ \mathrm{K}$.

Most of our OF-DFT calculations were done with a locally modified version of the PROFESS code [110, 111]. Originally set up with two-point KE functionals, it performs periodic OF-DFT calculations. Our modifications included adding four nonzero-T non-interacting free-energy functionals: (i) standard Thomas-Fermi (ftTF); (ii) gradient-corrected ftTF, i.e., the nonzero-T second-order gradient approximation (ftSGA)); and (iii) our new two-parameter Karasiev-Sjostrom-Trickey (KST2) form and the nonzero-T extension of the Tran-Wesołowksi zero-T KE (see details in Ref. [60]). For orbital-free AIMD, we coded an interface between PROFESS and QUANTUM-ESPRESSO [103] to replace KS forces with those from OF-DFT. This modified package enables comparison between KS AIMD and OF-DFT AIMD on the same footing [112].

The thermal Hartree-Fock, hard-walled rectangular box calculations mentioned in Sect. 3.2 [71] obviously require a basis set which is compatible with the box boundary conditions and also yields a computationally tractable problem. Sine functions, our original choice, turned out to have drawbacks for rapid matrix-element evaluation. Thus, we exploited familiarity with Gaussian type orbitals (GTOs) to provide efficient four-center integral calculation. The new basis is Cartesian GTOs truncated to match the boundary conditions and scaled to retain continuity at the atomic sites.

A Cartesian GTO of order ν has factors of the form

$$g^{\nu}(x) = (x - x_c)^{\nu} e^{-\alpha(x-x_c)^2} \tag{17}$$

The function can be made into one which is zero at the box boundaries $x = 0$ and $x = L_x$ by subtracting a shift equal to the original function value at each end. When x_c is not at the box center, that shift differs for the two ends. Thus, we split the original function into two pieces, then shift by the two end-values, and scale the two shifted pieces such that the resulting function is continuous. The outcome is an un-normalized Cartesian factor

$$\begin{aligned} g^{\nu}_{box}(x) &= a_0\left(g^{\nu}(x) - \Delta_0\right) \quad 0 \le x \le x_c \\ &= a_L\left(g^{\nu}(x) - \Delta_{L_x}\right) \quad x_c \le x \le L_x \end{aligned} \tag{18}$$

with $\Delta_0 = g^{\nu}(0)$, $\Delta_{L_x} = g^{\nu}(L_x)$. These are the Cartesian factors of our truncated GTO (tGTO) basis. Because the tGTOs may not have continuous derivatives, kinetic energy matrix elements require attention. In fact, nothing unusual happens. The kinetic energy is the expected sum of piecewise contributions, except for the case of p-type functions, which have a simple correction term. Appropriate matrix element expressions were rederived to take account of these modifications from normal molecular GTO-basis techniques. The procedure was implemented in an entirely new code which supports both thermal HF and KS DFT calculations for any ion arrangement and T. So far we have used 1–32 H atoms and T up to 300 kK. The highly optimized code is written in C++ utilizing MPI. Future development includes nonzero-T post-tHF calculations for correlation and AIMD with analytically calculated forces.

Faced with a dearth of nonzero-T HEG data for calibrating and validating new OF-DFT functionals, we have undertaken a focused study using the restricted path-integral MD (PIMD) technique [113, 114]. This choice is deliberately complementary to the PIMC work underway elsewhere [69]. The original PIMD code had been applied to a rather low density HEG ($r_s = 5$ bohr) and T $< 2{,}500$ K, which is low for WDM. We have modified the code to extend the density and temperature ranges as well as remedy some instabilities. Initial results at $r_s = 4$ and 5 bohr and T $< 7{,}000$ K are encouraging. For example, the average KE of these HEGs can be fit with a Sommerfeld expansion

$$\begin{aligned} \bar{\mathscr{T}}(\mathrm{T}) &= \mathscr{T}_0[1 + ax^2 + bx^4 + \cdots]\,, \\ x &:= \frac{1}{\beta \mathscr{T}_0}\,, \end{aligned} \tag{19}$$

where $\mathscr{T}_0 := \mathscr{T}(\mathrm{T} = 0)$. Through fourth order, the data are fit well by $a = 5.48$, $b = 78.0$ for both densities. Additional useful data for functional development is being calculated (V. Kapila, K. Runge, P.A. Deymier, unpublished).

4 Outlook and Challenges

While authors' perspectives on their own work may merit some skepticism, we think the spirit of the IPAM Long Program is exemplified by the word "Challenges" in the program name. So we venture comment on three questions.

1. What does this all mean, especially for application to the WDM problem?
2. What do we recommend as preferred practice at this point?
3. What are the shortcomings of the approaches and approximations we have used thus far?

About all these, prudence requires keeping clearly in mind that there is much still to be learned about free-energy DFT, about its orbital-free form, and about dynamics. That in mind, we plunge ahead.

The finding relative to question (1) that is perhaps most intriguing is that there is significant temperature-dependence in the XC free energy. Equation (15) does not hold in general. But how, then, are the apparent successes, e.g. Ref. [115], in using Eq. (15) to be understood? We suspect that the underlying distinction is between calculating the EOS or the Hugoniot for a system versus calculating a Kubo-Greenwood conductivity. Such a conductivity is given by

$$\sigma(\omega) = \frac{1}{N_{\text{config}}} \sum_{I=1}^{N_{\text{config}}} \sum_{\mathbf{k}} w_{\mathbf{k}} \sigma_{\mathbf{k}}(\omega; \{\mathbf{R}\}_I),$$

$$\sigma_{\mathbf{k}}(\omega; \{\mathbf{R}\}_I) = \frac{2\pi}{3\omega\Omega} \sum_{i,j}^{N_b} \sum_{\nu=1}^{3} (f_{i,\mathbf{k},I} - f_{j,\mathbf{k},I}) |\langle \varphi_{j,\mathbf{k},I} | \nabla_\nu | \varphi_{i,\mathbf{k},I} \rangle|^2$$
$$\times \delta(\epsilon_{j,\mathbf{k},I} - \epsilon_{i,\mathbf{k},I} - \omega) \ . \qquad (20)$$

Here Ω is the system volume, $w_{\mathbf{k}}$ is the weight of point $\mathbf{k}$ in the Brillouin zone and the KS quantities have multiple indices in consequence of configurational sampling ("snapshotting") over the AIMD trajectories. The obvious distinction with an EOS or Hugoniot calculation is that transport coefficients depend on matrix elements with respect to KS orbitals and upon the associated KS eigenvalues. It has been known since the earliest days of ground-state DFT that one can have an E_{xc} functional that gives good bulk properties (e.g. lattice parameters) but a poor band structure. However, another simple functional, call it $\tilde{E}_{\text{xc}}$, usually can be found such that $\tilde{\text{v}}_{\text{xc}} = \delta \tilde{E}_{\text{xc}}/\delta n$ gives a good band structure (but poor bulk properties) [116]. We suspect that a similar distinction may be relevant to the T-dependent case. What we have found is that the T-dependence of $\mathscr{F}_{\text{xc}}$ is important for the EOS. It does not necessarily follow that the T-dependence of the associated v_{xc} is important. If the T-dependence is important in principle, it is not necessarily true that an approximate v_{xc} has the *correct* T-dependence for Eq. (20) even if its precursor $\mathscr{F}_{\text{xc}}$ does well for the EOS or Hugoniot.

For OF-DFT, question (1) invites a discussion of the obviously related issue of the T-dependence of the non-interacting functionals $\mathscr{T}_{\text{s}}$ and $\mathscr{S}_{\text{s}}$. For these, we think the evidence is clear. The only functionals that come reasonably close to reproducing the KS results are our KST2 and the combination of full vW with full TF, i.e., ftVWTF. We have not discussed ftVWTF here, but refer to Ref. [60]. What is relevant here is that the two functionals behave quite similarly. They also share a drawback, in that both have empirical elements. But ftVWTF is, we think, irretrievably empirical in the sense that it is an ad hoc combination of two functionals, one for the high-T, high density limit, the other for the 1- and 2-electron localized limit. Our KST2 is empirical only in the sense of having two constants chosen to match KS calculations on a few reference silicate systems. (Silicates were chosen for historical reasons having nothing to do with WDM.) We have formulated a procedure by which we believe we can eliminate that empirical dependence. That procedure is under study at this writing.

Question (1) also implicates the issue of approximate $\mathscr{F}_{\text{xc}}$ functionals that are orbital free. Were we to have the exact $\mathscr{T}_{\text{s}}$ and $\mathscr{S}_{\text{s}}$, we still would be stuck with XC approximations which, in the T → 0 K limit would be no better than today's XC GGAs. The problem is that no current $E_{\text{xc}}^{\text{GGA}}$ does equally well on molecular and extended systems. For a given GGA functional form, constraint-based arguments can be used (and have been) to give parameterizations that are well-suited to molecules, but do poorly on solids. A different choice of constraints leads to the opposite result. (Discussion and references are in Ref. [94].) Since WDM can comprise both extended phase and localized regimes concurrently, this is a problem.

So what do we recommend? For now, use KST2 for $\mathcal{T}_s$ and $\mathcal{S}_s$, but be aware that better functionals will be forthcoming from our group as well as from others. For $\mathcal{F}_x$, what we have designated above as LDAx(T) is the choice for the moment if one wants to include T-dependence at least semi-quantitatively. We do not know what to say about $\mathcal{F}_c$ at the moment. Whatever the choice of OF-functionals, for those computing transport coefficients, the need to do KS calculations at snapshotted ion configurations provides an internal consistency test on the OF calculation. For a given ion configuration $\{\mathbf{R}\}$, simply compare the KS and OF-DFT densities and energies. This also leads to recommending, once again, the graded-sequence-of-approximations (GSA) procedure [117]. In the present context, the simplest GSA simulation is to run a few AIMD-MD steps with approximate OF-DFT functionals, then do a single KS step to get force corrections, then do another set of OF-DFT steps, etc.

Some of the shortcomings of the present state of affairs already have been mentioned, e.g. the lack of uniformly good predictive behavior from any E_{xc}^{GGA} available today. It is worth emphasizing that the problem is more tangled (and may be worse) in WDM than in ordinary materials because of the thermal occupation of KS levels which, at $T = 0$ K, are virtuals (unoccupied). Self-interaction error, which is known in E_{xc}^{GGA} and $\mathcal{F}_{xc}^{GGA}$, may also play an unexpected role in $\mathcal{T}_s$ and $\mathcal{S}_s$. This problem is easy to state. Improper self-repulsion allowed by approximate E_{xc} and $\mathcal{F}_{xc}$ functionals (zero T, non-zero T respectively) delocalizes the density n incorrectly. Presumably that delocalization has the effect of reducing the numerical values of $\mathcal{T}_s[n]$ (zero-T) or $\mathcal{T}_s[n, T]$ (non-zero T) from what they would be were one to use the exact (non-self-interacting) XC functionals. We do not know what such delocalization does to $\mathcal{S}_s$. A second shortcoming of all current OF-DFT functionals at $T = 0$ K is that none of them is built to satisfy the differential virial relationship between the KE and XC functional [75]. Presumably this problem carries over to non-zero temperature.

Acknowledgements We acknowledge, with thanks, many informative conversations with participants in the IPAM Long Program, including Kieron Burke, Jerome Daligault, Mike Desjarlais, Andreas Görling, Frank Graziani, Leslie Greengard, Hardy Gross, Stephanie Hansen, Walter Johnson, David Levermore, Winfried Lorenzen, Patrick Ludwig, Andreas Markmann, Michael Murillo, Aurora Pribram-Jones, Ronald Redmer, Luke Shulenberger, and Brian Wilson. We thank Russell Caflisch, Christian Ratsch, and Roland McFarland for the arrangements for those of us who visited IPAM. This work was supported under U.S. Dept. of Energy BES (TCMP, TMS) grant DE-SC 0002139.

Appendix

Acronyms

AIMD	Ab initio molecular dynamics
B3LYP	Empirical XC functional [96] which combines Becke 3-parameter X with Lee, Yang, Parr parameterization of Colle-Salvetti correlation [118]
BO; BOMD	Born-Oppenheimer; Born-Oppenheimer molecular dynamics
DFT	Density functional theory
ftSGA	Finite-T second-order gradient approximation
ftTF	Finite-T Thomas-Fermi
FE-DFT	Free-energy density functional theory, i.e. nonzero-T DFT
GGA	Generalized gradient approximation; most commonly an XC functional but also used here for KS (non-interacting) kinetic energy and entropy functionals
GTO	Gaussian-type orbital
HEDP	High energy-density physics
HEG	Homogeneous electron gas
meta-GGA	An approximate functional (most commonly XC) dependent on higher derivatives of the density than a GGA. Most use the KS KE orbital density τ_{orb}
KE	Kinetic energy
KS	Kohn-Sham
LDA; LSDA	Local-density approximation; local spin-density approximation
OF-DFT	Orbital-free density functional theory
OF-KE	Orbital-free kinetic energy (usually, orbital-free KS kinetic energy)
PAW	Projector Augmented Wave
PIMD	Restricted Path Integral Molecular Dynamics
PP	Pseudopotential
QMC	Quantum Monte-Carlo
RPA	Random phase approximation
tHF	thermal Hartree-Fock
TF	Thomas-Fermi
VASP	Vienna Ab-initio Simulation Program
vW	von Weizsäcker functional
WDM	Warm dense matter
X	Exchange
XC	Exchange-correlation

Symbols

Not infrequently the same symbol is used for different quantities in the $\mathrm{T} > 0\,\mathrm{K}$ and $\mathrm{T} = 0\,\mathrm{K}$ DFT literature. An example is temperature and kinetic energy. In our papers we have worked toward a simple standard, as close as reasonably possible to the $\mathrm{T} = 0\,\mathrm{K}$ DFT literature. In its present form, that usage is as follows.

$\beta = 1/k_{\mathrm{B}}\mathrm{T}$

$E_{\mathrm{x}},\ E_{\mathrm{xc}}$ = exchange, exchange-correlation functional

$\mathscr{F}$ = Helmholtz free energy

$\mathscr{F}_{\mathrm{xc}},\ \mathscr{F}_{\mathrm{s}}$ = XC and KS free energies

k_{B} = Boltzmann's constant

$\mathscr{S},\ \mathscr{S}_{\mathrm{s}}$ = total, KS entropy

$n(\mathbf{r})$ = electron density at point $\mathbf{r}$

T = temperature

$\mathscr{T},\ \mathscr{T}_{\mathrm{s}}$ = total, KS kinetic energy

References

1. K. Gavroglu, Eur. J. Phys. **15**, 9 (1994) and references therein
2. P.A. Bauer, E.K. Dabora, N. Manson, in *Dynamics of Detonations and Explosions: Detonations*, ed. by A.L. Kuhl, J.-C. Leyer, A.A. Borisov, W.A. Siriganano (American Institute of Aeronautics and Astronautics, Washington, DC, 1991), pp. 3ff and references therein
3. *Basic Research Needs for High Energy Density Laboratory Physics* (Report of the Workshop on Research Needs, Nov. 2009). U.S. Department of Energy, Office of Science and National Nuclear Security Administration (2010); see Chapter 6 and references therein
4. H.F. Wilson, B. Militzer, Phys. Rev. Lett. **108**, 111101 (2012)
5. R.P. Drake, Phys. Today **63**, 28 (2010) and references therein
6. B.A. Remington, R.P. Drake, D.D. Ryutov, Rev. Mod. Phys. **78**, 755 (2006) and references therein
7. R.P. Drake, *High-Energy-Density Physics* (Springer, Berlin, 2006) and references therein
8. J. Li, C.B. Agee, Nature **381**, 686 (1996)
9. M.J. Drake, K. Righter, Nature **416**, 39 (2002)
10. E. Jagoutz, H. Palme, H. Baddenhausen, K. Blum, M. Cendales, G. Dreibus, B. Spettel, V. Lorenz, H. Wanke, Proc. Lunar Planet. Sci. Conf. **10**, 2031 (1979)
11. H. Wanke, Phil. Trans. Roy. Soc. Lond. A **303**, 287 (1981)
12. C.J. Allegre, J.-P. Poirer, E. Humler, A.W. Hofmann, Earth Planet. Sci. Lett. **134**, 515 (1995)
13. K. Righter, M.J. Drake, Earth Planet. Sci. Lett. **146**, 541 (1997)
14. J.C. Boettger, S.B. Trickey, Phys. Rev. B **51**, R15623 (1995)
15. J.C. Boettger, S.B. Trickey, Phys. Rev. B **53**, 3007 (1996)
16. R.N. Barnett, U. Landman, Phys. Rev. B **48**, 2081 (1993)

17. D. Marx, J. Hutter, Ab initio molecular dynamics: theory and implementation, in *Modern Methods and Algorithms of Quantum Chemistry*, ed. by J. Grotendorst, NIC Series, vol. 1 (John von Neumann Institute for Computing, J ulich, 2000), pp. 301ff and references therein
18. J.S. Tse, Annu. Rev. Phys. Chem. **53**, 249 (2002)
19. D. Marx, J. Hutter, *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods* (Cambridge University Press, Cambridge, 2009) and references therein
20. T.D. Kühne, Ab-initio molecular dynamics arXiv:1201.5945 [physics.chem-ph]
21. W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965)
22. P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964)
23. M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979)
24. E.H. Lieb, Int. J. Quantum Chem. **24**, 243 (1983)
25. R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford, New York, 1989). For T-dependent theory see Sections 3.6 and 9.1
26. R.M. Dreizler, E.K.U. Gross, *Density Functional Theory* (Springer, Berlin, 1990)
27. L.A. Collins (Los Alamos National Lab), Equilibrium and non-equilibrium orbital-free molecular dynamics simulations at extreme conditions, CECAM Workshop, Paris, 05 Sept 2012
28. D.O. Gericke (Univ. Warwick), Effective interactions and ion dynamics in warm dense matter, Invited Talk I8, Physics of Non-ideal Plasmas 14, Rostock Germany, 11 Sept 2012
29. N.D. Mermin, Phys. Rev. **137**, A1441 (1965)
30. A.K. Rajagopal, A density functional formalism for condensed matter systems, in *Density Functional Methods in Physics*, ed. by J. da Providencia, R.M. Dreizler, NATO ASI B, vol. 123 (Plenum, New York, 1985), pp. 159ff
31. M.V. Stoitsov, I.Zh. Petkov, Ann. Phys. **184**, 121 (1988)
32. R.M. Dreizler, Density functional theory at finite temperatures, in *The Nuclear Equation of State, Part A*, ed by W. Greiner, H. Stöcker, NATO ASI B, vol. 216 (Plenum, NY, 1989), pp. 521ff
33. J.P. Perdew, K. Schmidt, A.I.P. Conf. Proc. **577**, 1 (2001)
34. F. Perrot, M.W.C. Dharma-wardana, Phys. Rev. A **30**, 2619 (1984)
35. N.D. Mermin, Ann. Phys. (NY) **21**, 99 (1963)
36. J. Sokoloff, Ann. Phys. (NY) **45**, 186 (1967)
37. J. Dolbeault, P. Felmer, M. Lewin, Math. Model. Methods Appl. Sci. **19**, 347 (2009)
38. Y.A. Wang, E.A. Carter, Orbital-free kinetic-energy density functional theory, Chap. 5 in *Theoretical Methods in Condensed Phase Chemistry*, ed. by S.D. Schwartz (Kluwer, New York, 2000), pp. 117ff and references therein
39. M. Hodak, W. Lu, J. Bernholc, J. Chem. Phys. **128**, 014101 (2008)
40. X. Blanc, E. Cances, J. Chem. Phys. **122**, 214106 (2005)
41. E.V. Ludeña, J. Chem. Phys. **79**, 6174 (1983)
42. R. Cuevas-Saavedra, D. Chakraborty, P.W. Ayers, Phys. Rev. A **85**, 042519 (2012)
43. T.A. Wesołowski, Phys. Rev. A **77**, 012504 (2008) and references therein
44. J.W. Kaminski, S. Gusarov, T.A. Wesołowski, A. Kovalenko, J. Phys. Chem. A, **114**, 6082 (2010) and references therein
45. V.V. Karasiev, S.B. Trickey, F.E. Harris, J. Comput. Aided Mat. Des. **13**, 111 (2006)
46. V.V. Karasiev, R.S. Jones, S.B. Trickey, F.E. Harris, Recent advances in developing orbital-free kinetic energy functionals, in *New Developments in Quantum Chemistry*, ed. by J.L. Paz, A.J. Hernández (Transworld Research Network, Kerala, 2009), pp. 25ff
47. V.V. Karasiev, R.S. Jones, S.B. Trickey, F.E. Harris, Phys. Rev. B **80**, 245120 (2009)
48. S.B. Trickey, V.V. Karasiev, R.S. Jones, Int. J. Quantum Chem. **109**, 2943 (2009)
49. C.F. von Weizsäcker, Z. Phys. **96**, 431 (1935)
50. Y. Tal, R.F.W. Bader, Int. J. Quantum Chem. **S12**, 153 (1978)
51. L.J. Bartolotti, P.K. Acharya, J. Chem. Phys. **77**, 4576 (1982)
52. J.E. Harriman, The interface between reduced density matrices and density functional theory, in *Density Matrices and Density Functionals*, ed. by R. Erdahl, V.H. Smith Jr. (D. Reidel, Dordrecht, 1987), pp. 359ff

53. M. Levy, H. Ou-Yang, Phys. Rev. A **38**, 625 (1988)
54. R. Baltin, J. Chem. Phys. **86**, 947 (1987)
55. J.W. Dufty, S.B. Trickey, Phys. Rev. B **84**, 125118 (2011)
56. R.P. Feynman, N. Metropolis, E. Teller, Phys. Rev. **75**, 1561 (1949)
57. J. Bartel, M. Brack, M. Durand, Nucl. Phys. A **445**, 263 (1985)
58. M. Brack, C. Guet, H.-B. Hakansson, Phys. Rep. **123**, 275 (1985)
59. F. Perrot, Phys. Rev. A **20**, 586 (1979)
60. V.V. Karasiev, T. Sjostrom, S.B. Trickey, Phys. Rev. B **86**, 115101 (2012)
61. B. Holst, R. Redmer, M. Desjarlais, Phys. Rev. B **77**, 184201 (2008)
62. D.A. Horner, F. Lambert, J.D. Kress, L.A. Collins, Phys. Rev. B **80**, 024305 (2009)
63. W. Ebeling, W. Richert, W.D. Kraeft, W. Stolzmann, Phys. Stat. Solidi (b) **104**, 193 (1981)
64. S. Tanaka, S. Mitake, S. Ichimaru, Phys. Rev. A **32**, 1896 (1985)
65. F. Perrot, M.W.C. Dharma-wardana, Phys. Rev. B **62** 16536 (2000); Ibid. **67**, 079901(E) (2003)
66. D.J.W. Geldart, E. Dunlap, M.L. Glasser, M.R.A. Shegelski, Solid State Commun. **88**, 81 (1993)
67. E. Dunlap, D.J.W. Geldart, Can. J. Phys. **72**, 1 (1994)
68. M.L. Glasser, D.J.W. Geldart, E. Dunlap, Can. J. Phys. **72**, 7 (1994)
69. E. Brown. D. Ceperley, J. Dubois, Simulation of the warm, dense homogeneous electron gas. Paper X24-2, American Physical Society, March meeting, 1 Mar 2012
70. V.V. Karasiev, T. Sjostrom, S.B. Trickey, Phys. Rev. E **86**, 056704 (2012)
71. T. Sjostrom, F.E. Harris, S.B. Trickey, Phys. Rev. B **85**, 045125 (2012)
72. T. Sjostrom, Finite-temperature hartree-fock exchange and exchange-correlation free energy functionals, *IPAM Workshop IV, Computational Challenges in Warm Dense Matter*, UCLA, Los Angeles, May 2012, https://www.ipam.ucla.edu/publications/plws4/plws410624.pdf and to be published
73. F. Tran, T.A. Wesołowski, Int. J. Quantum Chem. **89**, 441 (2002)
74. V.V. Karasiev, D. Chakraborty, O.A. Shukruto, S.B. Trickey, Phys. Rev. B **88**, 161108(R) (2013)
75. M. Levy, J.P. Perdew, Phys. Rev. A **32**, 2010 (1985)
76. M. Levy, The coordinate scaling requirements in density functional theory, in *Single-Particle Density in Physics and Chemistry*, ed. by N.H. March (Academic, London/San Diego, 1987), pp. 45ff
77. M. Levy, Phys. Rev. A **43**, 4637 (1991)
78. M. Levy, Coordinate scaling requirements for approximating exchange and correlation, in *Density Functional Theory*, ed. by E.K.U. Gross, R.M. Dreizler, NATO ASI B, vol. 337 (Plenum, New York, 1995), pp. 11ff
79. S. Pittalis, C.R. Proetto, A. Floris, A. Sanna, C. Bersier, K. Burke, E.K.U. Gross, Phys. Rev. Lett. **107**, 163001 (2011)
80. J.W. Dufty, S.B. Trickey, Finite temperature scaling in density functional theory (in preparation)
81. T. Gál, J.W. Dufty, S.B. Trickey, Local density approximation to the kinetic energy functional for finite N_e, in preparation
82. J. Dufty, S. Dutta, Phys. Rev. E **87**, 032101 (2013)
83. J. Dufty, S. Dutta, Phys. Rev. E **87**, 032102 (2013)
84. L.W. Wang, M.P. Teter, Phys. Rev. B **45**, 13196 (1992)
85. B.J. Zhou, V.L. Ligneres, E.A. Carter, J. Chem. Phys. **122**, 044103 (2005)
86. C. Huang, E.A. Carter, Phys. Rev. B **81**, 045206 (2010)
87. J.W. Dufty, S.B. Trickey, Revised Thomas-Fermi functional for singular potentials, American Physical Society, March 2013 meeting abstract
88. F. Perrot, M.W.C. Dharma-wardana, Phys. Rev. B **62**, 16536 (2000)
89. J.W. Dufty, S. Dutta, Contrib. Plasma Phys. **52**, 100 (2012)
90. J.W. Dufty, Derivation and context of Kubo-Greenwood transport coefficients (in preparation)
91. S.B. Trickey, V.V. Karasiev, A. Vela, Phys. Rev. B **84**, 075146 (2011)

92. A. Vela, J.C. Pacheco-Kato, J.L. Gázquez, J.M. del Campo, S.B. Trickey, J. Chem. Phys. **136**, 144115 (2012)
93. J. Martín del Campo, J.L. Gázquez, R.J. Alvarez-Mendez, S.B. Trickey, A. Vela, Analysis of the generalized gradient approximation for the exchange energy, in *Concepts and Methods in Modern Theoretical Chemistry*, vol. 1, ed. by volume honoring Professor B.M. Deb, S.K. Ghosh and P.K. Chattaraj (Taylor and Francis/CRC, Boca Raton, 2012) in press
94. J.M. del Campo, J.L. Gázquez, S.B. Trickey, A. Vela, J. Chem. Phys. **136**, 104108 (2012)
95. J. Martín del Campo, A. Vela, J.L. Gázquez, S.B. Trickey, Chem. Phys. Lett. **543**, 179 (2012)
96. P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. **98**, 11623 (1994)
97. J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, J.W. Sun, Phys. Rev. Lett. **103**, 026403 (2009). Erratum, Ibid. **106**, 179902 (2011)
98. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B **37**, 785 (1984)
99. V.V. Karasiev, S.B. Trickey, Comput. Phys. Commun. **183**, 2519 (2012)
100. G.K-L. Chan, A.J. Cohen, N.C. Handy, J. Chem. Phys. **114**, 631 (2001)
101. X. Gonze, B. Amadon, P.-M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote, T. Deutsch, L. Genovese, Ph. Ghosez, M. Giantomassi, S.G̃oedecker, D.R. Hamann, P. Hermet, F. Jollet, G. Jomard, S. Leroux, M. Mancini, S.M̃azevet, M.J.T. Oliveira, G. Onida, Y. Pouillon, T. Rangel, G.-M. Rignanese, D. Sangalli, R. Shaltaf, M. Torrent, M.J. Verstraete, G. Zerah, J.W. Zwanziger, ABINIT: first-principles approach to material and nanosystem properties, Comput. Phys. Commun. **180**, 2582 (2009)
102. X. Gonze, G.-M. Rignanese, M. Verstraete, J.-M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, Ph. Ghosez, M. Veithen, J.-Y. Raty, V. Olevano, F.B̃runeval, L. Reining, R. Godby, G. Onida, D.R. Hamann, D.C. Allan, A brief introduction to the ABINIT software package, Zeit. Kristallogr. **220**, 558 (2005)
103. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L.C̃hiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, Quantum espresso: a modular and open-source software project for quantum simulations of materials, J. Phys. Condens. Matter **21**, 395502 (2009)
104. G. Kresse, J. Hafner, Phys. Rev. B **47**, 558 (1993)
105. G. Kresse, J. Hafner, Phys. Rev. B **49**, 14251 (1994)
106. G. Kresse, J. Furthmüller, Comput. Mat. Sci. **6**, 15 (1996)
107. G. Kresse, J. Furthmüller, Phys. Rev. B **54**, 11169 (1996)
108. V. Heine, I. Abarenkov, Phil. Mag. **9**, 451 (1964)
109. L. Goodwin, R.J. Needs, V. Heine, J. Phys. Condens. Matter **2**, 351 (1990)
110. G.S. Ho, V.L. Lignères, E.A. Carter, Comput. Phys. Commun. **179**, 839 (2008)
111. L. Hung, C. Huang, I. Shin, G.S. Ho, V.L. Lignères, E.A. Carter, Comput. Phys. Commun. **181**, 2208 (2010)
112. V.V. Karasiev, T. Sjostrom, S.B. Trickey, Finite-temperature orbital-free DFT molecular dynamics: coupling PROFESS and QUANTUM ESPRESSO (in preparation)
113. Ki-dong Oh, P.A. Deymier, Phys. Rev. B **58**, 7577 (1998) and references therein
114. Ki-dong Oh, P.A. Deymier, Phys. Rev. B **59**, 11276 (1999) and references therein
115. M.P. Desjarlais, J.D. Kress, L.A. Collins, Phys. Rev. E **66**, 025401 (2002)
116. D.A. Liberman, This distinction was recognized in the different values of α in the Xα exchange functional of the late 1960s and early 1970s, Phys. Rev. **171**, 1 (1968) as well as references in J.W.D. Connolly, in *Semiempirical Methods of Electronic Structure Calculation, Part A: Techniques*, ed. by G.A. Segal (Plenum, NY 1977), pp. 105ff
117. D.E. Taylor, V.V. Karasiev, K. Runge, S.B. Trickey, F.E. Harris, Computat. Mat. Sci. **39**, 705 (2007)
118. R. Colle, O. Salvetti, Theor. Chim. Acta **37**, 329 (1975)