Non-empirical Generalized Gradient Approximation Free Energy Functional for Orbital-free Simulations

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We report the first wholly non-empirical general gradient approximation, non-interacting free energy functional for orbital-free density functional theory and use that new functional to provide forces for finite-temperature molecular dynamics simulations in the warm dense matter (WDM) regime. The new functional provides good-to-excellent agreement with reference Kohn-Sham calculations under WDM conditions at a minuscule fraction of the computational cost of corresponding orbital-based simulations.

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where $v_\theta([n];r) := \frac{\delta T_\theta}{\delta n} \equiv \frac{\delta (T_s[n] - T_{vW}[n])}{\delta n(r)} \geq 0$, $\forall r$, (3)

with $T_{vW}[n] = \int dx_0 \tau_{vW}^{TF}(n)(5s^2/3)$ the von Weizsäcker (vW) functional [17]; and (iii) recovery of vW behavior in the large-$s$ limit.

Constraint (i) guarantees a correct description for uniform and slow-varying densities. As shown in Refs. [18, 19], positivity of $v_\theta$ is required to achieve molecular and solid binding. Constraint (iii) follows from the Kato nuclear-cusp condition [23], so we adopt a suitably modified form [24]. Thus, the non-empirical APBEK [21] $T = 0$ K functional uses the PBE X enhancement factor [22]. Manifestly it violates constraint (iii). As to (i), the GE coefficient for APBEK is 0.23889, which corresponds to the modified gradient expansion [21]. But $v_\theta$ from APBEK violates constraint (ii) in that $v_\theta^{APBEK}$ has negative singularities at nuclear positions. The behavior of $v_\theta$ near a nucleus, $r \approx 0$, follows from the Kato nuclear-cusp condition [22]

$$n(r) \sim e^{-2kr} = (1 - 2Zr) + O(r^2).$$

Thus $v_\theta^{APBEK}(r) \sim a/r$ with $a < 0$ for $r \approx 0$.

To satisfy constraints (i) and (ii) simultaneously and incorporate (iii) therefore requires a more flexible form. Constraint (iii) also occurs in the VT{84} X enhancement factor [24], so we adopt a suitably modified form for $F_r$,

$$F_{vT84F}^r(s) = 1 + \frac{\mu s^2 e^{-\alpha s^2}}{1 + \mu s^2} + (1 - e^{-\alpha s^2/2})(s - n/2 - 1) + \frac{5s^2}{3},$$

with $m = 8$, $n = 4$. (“F” in “VT84F” denotes this free-energy adaptation.) The last term in Eq. (5) provides the correct large-$s$ limit, constraint (iii). The parameters $\mu$ and $\alpha$ then must be determined from constraints (i) and (ii). Expansion of Eq. (5) at small-$s$ gives $F_{vT84F}^r(s) = 1 + (5/3 - \alpha + \mu)s^2 + O(s^4)$. Constraint (i) imposes a relation between the two parameters, $\alpha = \mu - 5/3 + 5/27$. Evaluation of the Pauli potential for small-$r$ from the density Eq. (1), shows that the singular term $a/r$ becomes marginally positive for $\mu = 2.778$. That gives $\alpha = 1.2965$. Eq. (5) then fixes the kinetic and entropic enhancement factors in the free-energy functional Eq. (1), $F_{vT84F}^s(s)$ and $F_{vT84F}^s(s) = 2 - F_{vT84F}^s(s_\sigma)$. For comparison, we also built the non-interacting free-energy functional APBEF from the zero-$T$ APBEK KE [21] by use of the same prescription, that is $F_{vAPBEF}^s(s) = 1 + \mu s^2/(1 + s^2 \mu / \kappa)$ and $F_{vAPBEF}^s(s_\sigma) = 2 - F_{vAPBEF}^s(s_\sigma)$ with $\mu = 0.23889$, $\kappa = 0.804$.

Fig. 1 shows the two main differences between the VT84F and APBEF Pauli enhancement factors, $F_r(s) - (5s^2/3)$ for VT84F, $F_r(s) - (5s^2/3)$ is non-negative and vanishes at large-$s$ and has positive slope near $s \approx 0.39$ to provide the correct sign of the corresponding $v_\theta^{VT84F}$ near nuclear sites. APBEF has neither feature. At small-$s$, both functions have similar behavior defined by the gradient expansion with similar coefficients.

We have implemented these functionals in a modified version of the PROFESS [22] code which we have interfaced to the QUANTUM ESPRESSO code [26] to support KS and OFDFT AIMD calculations on the same footing [27]. The data in Table I illustrate the critical importance of satisfying constraint Eq. (3). (Both these calculations used Perdew-Zunger local density approximation (LDA) exchange-correlation (XC) [28].) At $T = 0$ K, the VT84F KE functional gives binding in sc-H and fcc-Al with lattice constants underestimated by about 6% for sc-H and about 2% for fcc-Al. The APBEK functional has typical ordinary GGA KE functional behavior. It fails to yield binding because of violation of constraint Eq. (3) [18]. The bulk moduli from VT84F, however, are higher than the reference KS values.

To test the OF functionals at finite $T$, we started from static calculations with cold nuclei and hot electrons. Such a situation arises, for example, when a target is

| System/Method               | $a$ (Å) | $B$ (GPa) |
|-----------------------------|---------|-----------|
| sc-H                        |         |           |
| OFDFT (VT84F+LDA)           | 1.353   | 175.3     |
| KS (LDA) [11]               | 1.446   | 108.4     |
| fcc-Al                      |         |           |
| OFDFT (VT84F+LDA)           | 4.095   | 120.4     |
| KS (LDA) [24]               | 4.020   | 79.66     |

FIG. 1: VT84F and APBEF Pauli term enhancement factors $F_r(s) - (5s^2/3)$ as a function of $s$ ($T = 0$ K).
irradiated by a femtosecond laser pulse. Calculations were done for sc-H at material density $\rho_H=0.60$ and 2.0 g/cm$^3$. Owing to machine-time limitations, we were able to complete KS calculations only up to $T=4 \times 10^5$ K for $\rho_H=0.60$ g/cm$^3$ and to 10$^6$ K for $\rho_H=2.0$ g/cm$^3$.

Fig. 2 compares the electronic heat capacity, $C^e_V$, as a function of electronic $T$ for sc-H at material density $\rho_H=0.60$ and 2.0 g/cm$^3$.

FIG. 2: Electronic heat capacity, $C^e_V$, as a function of electronic $T$ for sc-H at material density $\rho_H=0.60$ and 2.0 g/cm$^3$.

FIG. 3: Upper panel: pressures for OFDFT and KS AIMD, both with explicitly $T$-dependent XC [34] compared with PIMC [12] results for Deuterium at $\rho_D=1.964$ g/cm$^3$ ($r_s=1.40$ bohr). Lower panel: relative differences of OFDFT and PIMC pressures with respect to KS values.

tactical point is that the second derivative discontinuity of fits used in the OFDFT calculations (see Ref. [11]) affects the OFDFT results for $C^e_V$ at $T \approx T_F/2$.

The second finite-$T$ test of our new functional was to calculate the deuterium equation of state (EOS) in the WDM regime [33]. All the AIMD simulations were performed with 64-512 atoms in the simulation cell (depending on material density) using the NVT ensemble regulated by the Andersen thermostat. For KS calculations at $T \leq 31, 250$ K, we used a $3 \times 3 \times 3$ Monkhorst-Pack k-grid [31], while for higher $T$ a single $\Gamma$-point was used. All the calculations used an explicitly $T$-dependent LDA (TLD) XC functional [34]; see Ref. [32] for justification.

The upper panel of Fig. 3 compares pressures for deuterium at $\rho_D=1.964$ g/cm$^3$ ($r_s=1.40$ bohr) from OFDFT and KS AIMD simulations, along with PIMC results. Our VT84F functional tends to underestimate the pressure while both TF and APBEF overestimate it. However, our new functional reduces the error at $T=200$ kK to 15% compared to the TF error of 24%. Note that APBEF, which fails to predict an equilibrium ground state, nevertheless gives about the same relative pressure error as VT84F, hence provides an inconsistent description. The error in the OFDFT values decreases with increasing $T$, such that at $T=95, 250$ K that error is about 3% for the two GGAs versus 6% for TF. At $T=181, 825$ K (the highest $T$ for which we were able to complete the KS AIMD simulation), that error is 1.5% for TF compared to tenths of a percent for VT84F (and for APBEF as well). Comparison of PIMC to KS gives
relative differences of essentially the same magnitude as the OFDFT calculations which use the new functionals. At the lowest temperature, $T = 31,250$ K, PIMC overestimates the pressure by 15%, with the error decreasing rapidly with increasing $T$.

In the high-$T$ TF limit, the system goes over to a fully ionized electron-ion plasma. Fig. 4 shows the excess pressure relative to the TF model for $125,000 \leq T \leq 4,000,000$ K. For $T = 125,000$ and $181,825$ K, where KS data are available, both VT84F and APBEF provide excellent agreement (within about 2%). Our OFDFT results also are in reasonably good agreement with the PIMC data (almost within the margin of numerical error).

Fig. 5 compares KS and OFDFT pressures for deuterium as a function of $\rho_D$ for three temperatures. The small deviations of the values from the VT84F functional with respect to the KS values at lowest density, $\rho_D = 0.674$ g/cm$^3$, $T=31,250$ K, diminish quickly with increasing $\rho_D$ or increasing $T$.

Fig. 6 compares KS and OFDFT ion pair-correlation functions (PCF) for two temperatures. The upper panel ($T = 31,250$ K) demonstrates that all the OFDFT calculations predict structural properties at this temperature in reasonable agreement with the KS results, except for some discrepancies (peaks) near $r = 1.0\text{Å}$. We suspect, but have not been able to confirm, that those peaks are related to nuclear site singularities in the GGA Pauli potential, Eq. (3). Those singularities could lead to peaks such as seen in hard- or soft-sphere liquid PCFs [35]. Note also that the peaks are consistent with the overly large bulk moduli via the compressibility sum rule [36]. In any event, for $T = 62,500$ K and above, the agreement between OFDFT and KS PCFs becomes satisfactory.

Comparison of computational times per AIMD step for OFDFT and KS is in Fig. 4. The calculations were done on a single CPU to provide the most favorable case for KS (no parallel overhead). The OFDFT timings are essentially independent of $T$ and faster than corresponding KS AIMD runs by from one to two orders of magnitude for the range of $T$ shown. In practice, the KS calculations typically need 8 to 64 CPUs for reasonable turn-around. In that case, the OFDFT advantage is substantially greater.

In summary, we have presented a new, wholly non-empirical parameterization of a ground-state orbital-free KE functional and used it to generate new kinetic and entropic non-interacting free-energy functionals. These new functionals have several virtues. First, the ground state part gives a reasonable description of the ground-state solid for $\text{sc-H}$ and $\text{fcc-Al}$, something not achieved by any other non-empirical KE GGA. Second, the consequent free-energy functionals give good WDM properties for $\text{sc-H}$ in the static lattice case (e.g. electronic heat capacity) and provide a competitive-quality AIMD simulation of the deuterium EOS. All of this is with the long-promised computational speed advantage of OFDFT.
FIG. 7: CPU time per AIMD step as a function of $T$ for OFDFT-MD calculations compared to the KS-MD data. Deuterium at $\rho_D = 1.964$ g/cm$^3$ ($r_s = 1.40$ bohr), 128 atoms in simulation cell.

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