Ab initio Computation of the Static Exchange–Correlation Kernel of Real Materials:
From Ambient Conditions to Warm Dense Matter

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The electronic exchange—correlation (XC) kernel constitutes a fundamental input for the estimation of a gamut of material properties such as the dielectric characteristics, the thermal and electrical conductivity, the construction of effective potentials, or the response to an external perturbation. In practice, no reliable method has been known that allows to compute the kernel of real materials. In this work, we overcome this long-standing limitation by introducing a new, formally exact methodology for the computation of the static XC kernel of arbitrary materials exclusively within the framework of density functional theory (DFT)—no external input apart from the usual XC-functional is required. As a first practical demonstration of the utility and flexibility of our methodology, we compare our new results with exact quantum Monte Carlo (QMC) data for the archetypical uniform electron gas model at both ambient and warm dense matter conditions. This gives us unprecedented insights into the performance of different XC-functionals, and has important implications for the development of new functionals that are designed for the application at extreme temperatures. In addition, we obtain new DFT results for the XC kernel of warm dense hydrogen as it occurs in fusion applications and astrophysical objects such as planetary interiors. The observed excellent agreement to the recent QMC results by Böhme et al. [Phys. Rev. Lett. 129, 066402 (2022)] clearly demonstrates that our framework is capable to even capture nontrivial effects such as XC-induced isotropy breaking in the density response of hydrogen at large wave numbers. Our method can easily be applied using standard DFT codes and will open up new avenues for the computation of the properties of real materials.

I. INTRODUCTION

The density functional theory (DFT) approach [1, 2] is arguably the most successful simulation tool in many-body physics, quantum chemistry, material science, and several related disciplines. Its main advantage is the evened out balance between reasonable accuracy and manageable computation cost, which allows for the ab initio description of real materials. While formally exact [3], DFT requires as external input the a-priori unknown exchange–correlation (XC) functional, which, in practice, has to be approximated. At ambient conditions, when the electrons can usually be assumed to be in their respective ground state, Jacob’s ladder of functionals [4, 5] serves as a useful categorization of different approximations. Furthermore, there exists an extensive body of literature on the empirical benchmark of a gamut of functionals for various applications [6–9]. Indeed, the number of publications that utilize the DFT approach has been exponentially increasing over the last years [10].

At the same time, we note that the drastic reduction of computation cost that often renders DFT simulations feasible in the first place is achieved by mapping the original many-electron problem of interest onto an effective single-electron problem. While, in theory, being exact [3], the bulk of information about electron–electron correlations is lost in the process. In practice, DFT gives straightforward access to the single-electron density \( n_e(r) \) and different contributions to the energy. In other words, two-body (and higher order) correlation functions cannot be readily computed. This is a highly unsatisfactory situation as many potentially profound insights into the system of interest are lost. In practice, advanced DFT applications such as linear-response time-dependent DFT (LR-TDDFT) require as an additional input the material specific XC-kernel \([11, 12] K_{xc}(q, \omega)\). Yet, very little is known about the actual XC-kernel of real materials [13, 14], and hitherto no feasible and universal way to compute it has been known.

In this work, we overcome this fundamental limitation by introducing a new, formally exact methodology for the ab initio calculation of the static XC-kernel within the framework of DFT for any material. The basic idea is schematically illustrated in Fig. 1. In principle, DFT is capable to give exact results for the single-particle density \( n_e(r) \) for any electronic Hamiltonian \( H_e \) (black curve, leftmost panel). As a second step, we propose to repeat such a DFT calculation for a modified Hamiltonian \( H_{q,A} = H_e + V_{ext}(q, A) \) that is subject to a monochromatic external perturbation of wave vector \( q \) and perturbation amplitude \( A \) [15–17]; this gives us the perturbed single-particle density \( n_{e,q,A}(r) \) (dashed blue curve, leftmost panel). In combination, we have thus gained direct access to the corresponding density modulation \( \Delta n_e(r)_{q,A} = n_{e,q,A}(r) - n_e(r) \) due to the external perturbation (second panel from left). In the limit of
provides access to electron–electron correlation functions such as the static structure factor $S$. Electron density

**FIG. 1.** Schematic illustration of our new methodology. First on the left: We use standard DFT to compute the single-electron density $n_e(r)$ with respect to the original electronic Hamiltonian of interest $\hat{H}$ (solid black) and b) with respect to a modified Hamiltonian subject to an external monochromatic perturbation $\hat{V}_{\text{ext}}$ (dashed blue). Second from left: We compute the corresponding density modulation $\Delta n_e(r)$ for different wave vectors $q$. Third from left: In the linear-response regime where $\langle \hat{V}_{\text{ext}} \rangle \ll \langle \hat{H} \rangle$, this gives us direct access to the static density response function $\chi(q)$ and the corresponding XC-kernel $K_{\text{xc}}(q)$ (blue crosses) for any material. First on the right: the XC-kernel can be used for the calculation of various electronic properties such as the dynamic structure factor $S_{\text{ee}}(q, \omega)$, dielectric properties $\epsilon(q, \omega)$, effective potentials $\phi_{\text{eff}}(r)$, transport properties like electrical conductivity $\sigma_{\text{el}}(q, \omega)$ and thermal conductivity $\sigma_{\text{th}}(q, \omega)$, and stopping power $\frac{\delta E}{\delta q}$. Furthermore, the XC-kernel provides access to electron-electron correlation functions such as the static structure factor $S_{\text{ee}}(q)$, which cannot be readily computed within standard DFT, via the fluctuation–dissipation theorem (FDT).

small $A$, when linear response theory [18] becomes valid, we get straightforward access to the static linear density response function $\chi(q) = \chi(q, 0)$ [cf. Eq. (11)] and, in this way, the static XC-kernel $K_{\text{xc}}(q) = K_{\text{xc}}(q, 0)$ (second panel from right). The latter constitutes the key ingredient to a number of applications such as the interpretation of XRTS experiments [19–23], the incorporation of electronic XC-effects into quantum hydrodynamics [24–26], the construction of effective electronically screened potentials [18, 27, 28], the conductivity [29], and ionization potential depression [30]. Moreover, the fluctuation–dissipation theorem (FDT) [cf. Eq. (18) below] gives a direct relation between the thus obtained density response and a correlation function of two density operators, which provides the basis for LR-TDDFT calculations of the dynamic structure factor $S_{\text{ee}}(q, \omega)$. Consequently, our new framework for the XC-kernel opens up the enticing possibility to obtain the static structure factor $S_{\text{ee}}(q)$—the Fourier transform of the pair correlation function $g_{\text{ee}}(r)$—of two electrons exclusively within DFT and without any additional external input apart from the usual XC-functional of standard DFT. To rigorously demonstrate the correctness and utility of our new approach, we consider two representative systems. The first example is given by the uniform electron gas (UEG) [18, 31, 32], the archetypical electronic system that constitutes the basis for a gamut of applications such as the BCS theory of superconductivity [33] and Fermi liquid theory [18]. In the context of the present work, the UEG has the considerable advantage that reliable benchmark data for a number of properties are available based on highly accurate quantum Monte Carlo (QMC) calculations [34, 35]. As a second, even more challenging example, we consider hydrogen, the most abundant element in our universe, which is the subject of active investigation [13, 36–39]. Indeed, many fundamental questions about hydrogen such as the precise nature and location of the insulator-to-metal phase transition [37] remain unanswered. Here, we use our new methodology to obtain the static XC-kernel of hydrogen and find very good agreement to the recent exact QMC results by Böhme et al. [13]. In addition, we consider both the electronic ground state (i.e., the zero-temperature limit, $T = 0$) and highly excited states at the electronic Fermi temperature, $\Theta = k_B T / E_F = 1$ (with $E_F$ being the usual Fermi energy [18]). In fact, such extreme states are ubiquitous in nature [40], and occur in astrophysical objects such as giant planet interiors [41] and brown dwarfs [42]. Moreover, they are highly relevant for cutting-edge technological applications such as inertial confinement fusion [43] and the discovery of novel materials [44–46]. This *warm dense matter* regime is notoriously hard to describe [47, 48]; from the perspective of DFT, one requires a density functional of the XC-free energy $F_{\text{xc}}$ that explicitly depends on the electronic temperature $T$ [49–51]. While first promising developments [52–55] have become available over the last years, the field of finite-$T$ XC-functional still remains in its infancy, and the performance of various approximations [56, 57] is substantially less understood compared to the case of $T = 0$. Indeed, the bulk of DFT calculations for WDM is carried out on the basis of the zero-temperature approximation (ZTA) and the discovery of novel materials [44–46]. This *warm dense matter* regime is notoriously hard to describe [47, 48]; from the perspective of DFT, one requires a density functional of the XC-free energy $F_{\text{xc}}$ that explicitly depends on the electronic temperature $T$ [49–51]. While first promising developments [52–55] have become available over the last years, the field of finite-$T$ XC-functional still remains in its infancy, and the performance of various approximations [56, 57] is substantially less understood compared to the case of $T = 0$. Indeed, the bulk of DFT calculations for WDM is carried out on the basis of the zero-temperature approximation (ZTA) and the discovery of novel materials [44–46]. In this work, we compute the static XC-kernel $K_{\text{xc}}(q)$ of both the UEG and hydrogen using a number of different $T = 0$ and finite-$T$ XC-functional. This gives us unprecedented insights into the performance of different widespread approximations. In practice, we find...
that ground-state functionals are often more accurate than supposedly more consistent finite-T functionals in the WDM regime; this has profound consequences for the future construction of a new generation of XC-functional extensions that are specifically designed for the application in the WDM regime. Moreover, we show that our new framework is capable of giving highly accurate results for the XC-kernel even for the complicated case of partially ionized hydrogen, whereas the commonly used adiabatic local density approximation (ALDA) breaks down in this regime. Therefore, we are convinced that our new methodology will open up a gamut of avenues for future research, and facilitate unprecedented insights into the electronic structure of elements and materials for any combination of pressure and temperature.

The paper is organized as follows. In Sec. II, we introduce the relevant theoretical background, starting with brief discussions of the DFT method (II A) and linear-response theory (II B). In addition, we introduce the conceptual basis of our work, including the XC-kernel (II C) and its self-consistent estimation within the framework of DFT (II D), the static approximation [58] of the dynamic density response function and the computation of electron–electron correlation functions via the FDT (II E). Sec. III is devoted to the presentation of our new DFT results for the static density response and XC-kernel of both the UEG (III A) and warm dense hydrogen (III B), which, among other things, give us important new insights into the construction of XC-functional extensions for the application in the WDM regime. The paper is concluded by a summary of our main finding, and a discussion of their numerous implications for future works in Sec. IV.

II. THEORY AND SIMULATION METHODS

A. Density functional theory

Throughout this work, we consider an electronic Hamiltonian of the form

\[ \hat{H}_e = \hat{K} + \hat{W} + \hat{V} , \]

with \( \hat{K} \) being the kinetic (ideal) part, \( \hat{W} \) containing all electron–electron interaction terms, and \( \hat{V} \) being an external single-particle perturbation. In particular, \( \hat{V} \) takes into account the electron–ion interaction in case of a hydrogen snapshot, and also the monochromatic external perturbation that is used to obtain the electronic density response; more details on the last point are given in Sec. II B below.

In the ground state (i.e., in the limit of \( T = 0 \)), the basic idea of DFT is to express the total energy of the electrons as a functional of the electronic single-particle density \( n_e = n_e(\mathbf{r}) \) [59],

\[ E[n_e] = K_0[n_e] + E_{\text{Ha}}[n_e] + E_{\text{xc}}[n_e] + V[n_e] , \tag{2} \]

with the kinetic energy of a hypothetical noninteracting system at the same density \( K_0[n_e] \), the Hartree (i.e., mean-field) interaction energy \( E_{\text{Ha}}[n_e] \), the exchange–correlation energy \( E_{\text{xc}}[n_e] \), and the external potential energy \( V[n_e] \). The task at hand is then to find the ground-state density that minimizes Eq. (2). The final ingredient is given by the celebrated Hohenberg-Kohn theorem [60], which states that, in theory, all observables of the systems are fully determined by \( n_e(\mathbf{r}) \). In this way, the intractable original quantum many-body problem of interest has been mapped onto an effective single-electron problem, leading to a great reduction in the computational complexity. In practice, however, the functional dependence of many electron–electron correlation properties on \( n_e(\mathbf{r}) \) is unknown, and they cannot be computed. Overcoming this crucial limitation of DFT in the case of the static XC-kernel is the central task of the present work.

The minimization of \( E[n_e] \) within DFT requires us to evaluate all contributions to Eq. (2) with respect to different trial densities. Yet, this is only straightforward for \( E_{\text{Ha}}[n_e] \) and \( V[n_e] \). In particular, the XC contribution \( E_{\text{xc}}[n_e] \) contains the full information about many-body correlations and, therefore, would require the exact solution of the original \( N \)-electron problem, which is not feasible. In practice, \( E_{\text{xc}}[n_e] \), therefore, has to be approximated. Specifically, the particular choice of the XC-functional substantially influences the accuracy of a DFT simulation, which makes both the benchmarking of existing functionals and the construction of novel, more sophisticated approximations to the true \( E_{\text{xc}}[n_e] \) indispensible. The second problematic contribution to Eq. (2) is given by the noninteracting energy \( K_0[n_e] \), which, too, is generally unknown. This problem has been solved within the KS-DFT approach [59], where one employs an auxiliary system defined by the noninteracting single-particle Schrödinger equation

\[ \left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}}[n_e](\mathbf{r}) \right] \phi_\alpha(\mathbf{r}) = \epsilon_\alpha \phi_\alpha(\mathbf{r}) , \tag{3} \]

with \( \phi_\alpha(\mathbf{r}) \) and \( \epsilon_\alpha \) being the KS-orbitals and corresponding eigenvalues. In addition, the effective KS-potential \( v_{\text{KS}}[n_e](\mathbf{r}) \) is a functional of the electronic density

\[ n_e(\mathbf{r}) = \sum_{\alpha=1}^{N} |\phi_\alpha(\mathbf{r})|^2 , \tag{4} \]

and has to be determined self consistently (i.e., iteratively) within the KS-DFT formalism. The noninteracting kinetic energy can then straightforwardly be evaluated as

\[ K_0[n_e] = K_0[\{\phi_\alpha\}] = \sum_{\alpha=1}^{N} \int d\mathbf{r} \phi_\alpha^* (\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 \right] \phi_\alpha(\mathbf{r}) ; \tag{5} \]

all nonideal contributions to the full kinetic energy \( K \) are, by definition, contained in the XC-functional \( E_{\text{xc}}[n_e] \).
Let us conclude this overview of the KS-DFT approach by briefly touching upon its generalization to nonzero temperatures \[49\]. In that case, the minimization is carried out with respect to the free energy \(F[n_e]\), which leads to an additional entropic contribution to the corresponding XC-functional \(F_{xc}[n_e]\), with the latter explicitly depending on the temperature. In addition, the respective KS-orbitals are populated according to the Fermi distribution

\[ f(\alpha, T) = \left( 1 + e^{\beta(\epsilon_{\alpha} - \mu)} \right)^{-1}, \tag{6} \]

with \(\beta = 1/k_B T\) and \(\mu\) the chemical potential \[18\]. This leads to straightforward modifications of Eqs. (4) and (5).

A detailed overview of all relevant DFT simulation parameters is given in Appendix A.

### B. Linear-response theory

Let us consider the modified electronic Hamiltonian \[15–17\]

\[ \hat{H}_{q,\omega,A} = \hat{H}_e + 2A \sum_{j=1}^{N} \cos (q \cdot r_j - \omega t), \tag{7} \]

where the unperturbed system governed by \(\hat{H}_e\) is subject to a monochromatic external potential of wave vector \(q\), frequency \(\omega\), and amplitude \(A\). Clearly, the latter induces a change in the single-electron density, which is given by

\[ \Delta n_e(r)_{q,\omega,A} = \langle n_e(r) \rangle_{q,\omega,A} - \langle n_e(r) \rangle_0. \tag{8} \]

In the limit of small perturbation amplitudes \(A\), the induced density modulation is accurately described by linear-response theory, which gives the relation \[61\]

\[ \Delta n_e(r)_{q,\omega,A} = 2A \cos (q \cdot r - \omega t) \chi(q, \omega), \tag{9} \]

with \(\chi(q, \omega)\) being the dynamic linear response function.

In the static limit of \(\omega \to 0\), it is straightforward to use the standard DFT method to evaluate Eq. (8), and we denote the corresponding density modulation as

\[ \Delta n_e(r)_{q,A} = \Delta n_e(r)_{q,0,A}. \tag{10} \]

This leads to the relation

\[ \Delta n_e(r)_{q,A} = 2A \cos (q \cdot r) \chi(q), \tag{11} \]

where the static density response function is defined as \(\chi(q) = \chi(q, 0)\).

### C. Exchange–correlation kernel and Kohn-Sham response function

In practice, it is often convenient to express the full dynamic density response function as \[18, 62\]

\[ \chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - [v(q) + K_{xc}(q, \omega)] \chi_0(q, \omega)}, \tag{12} \]

where \(\chi_0(q, \omega)\) is a known reference function, \(v(q) = 4\pi/q^2\) the Coulomb interaction, and \(K_{xc}(q, \omega)\) the a-priori unknown exchange–correlation kernel. For completeness, we mention that Eq. (12) can be further extended for the description of inhomogeneous systems to the microscopic form \(\chi_{G,G'}(q, \omega)\), with \(G\) and \(G'\) being the reciprocal lattice vectors \[63\]; the generalization of our approach to this problem is conceptually straightforward, but not discussed in the present work. In general, only the LHS. of Eq. (12) has a well-defined physical meaning as the XC-kernel strongly depends on the particular choice of \(\chi_0(q, \omega)\) \[13\]. In the case of a uniform electron gas, it is common practice to use the Lindhard function as \(\chi_0(q, \omega)\), which describes the (physical) density response of an ideal Fermi gas at the same parameters. In this case, the XC-kernel, too, has a well-defined physical meaning and contains the full wave-vector- and frequency-resolved information about electronic XC-effects in the system. Moreover, it is then directly related to the local field correction \(G(q, \omega)\) that is the central property within dielectric theories \[64–69\],

\[ G(q, \omega) = -\frac{1}{v(q)} K_{xc}(q, \omega). \tag{13} \]

Hence, setting \(K_{xc} = 0\) in Eq. (12) leads to a description of the electronic density response on the mean-field level, which is commonly known as the random phase approximation \[18\],

\[ \chi_{RPA}(q, \omega) = \frac{\chi_0(q, \omega)}{1 - v(q) \chi_0(q, \omega)}. \tag{14} \]

Unfortunately, the situation is considerably less clear in the case of an inhomogeneous electron gas, for example in the potential of a fixed ion configuration. In this situation, it is common practice to compute the KS response function \[63, 70\] given by

\[ \chi_{KS}(q, \omega) = \frac{1}{\Omega} \sum_{\kappa,\alpha,i} \frac{f_{\alpha k} - f_{\alpha k+q}}{\omega + \epsilon_{\alpha k} - \epsilon_{\alpha k+q} + i\eta} \times \langle \phi_{\alpha k} | e^{-i\mathbf{q} \cdot \mathbf{r}} | \phi_{\alpha k+q} \rangle \langle \phi_{\alpha k+q} | e^{i\mathbf{q} \cdot \mathbf{r}} | \phi_{\alpha k} \rangle, \tag{15} \]

with \(\phi_{nk}\) and \(\epsilon_{nk}\) being the KS-orbitals and corresponding energy eigenvalues.

In the limit of a UEG, the KS-orbitals become plain waves, and Eq. (15) reverts to the Lindhard function. For nonuniform systems, the KS-orbitals by themselves have no clear physical meaning, but are needed via Eq. (12) for the description of real physical density response of a real system. Setting \(\chi_0(q, \omega) = \chi_{KS}(q, \omega)\) in Eqs. (12) and (14) means that the XC-kernel describes deviation measure between the true density response \(\chi(q, \omega)\) and the RPA version of the auxiliary quantity \(\chi_{KS}(q, \omega)\), cf. Eq. (16). Obviously, the true \(K_{xc}(q, \omega)\) depends on the XC-functional. For example, Böhm et al. \[13\] have recently shown that combining the ubiquitous adiabatic local density approximation (ALDA) \[63, 70\] kernel with the KS-response function computed from a standard
LDA DFT simulation leads to a double-counting of XC-effects in the density response of warm dense hydrogen, and an actual deterioration of the accuracy compared to \(K_{\text{xc}} = 0\). These empirical findings are further substantiated by our present analysis.

D. *Ab initio* exchange–correlation kernels from density functional theory

In the present work, we overcome the problematic combination of material-specific, XC-functional dependent KS orbitals with model kernels from other theories. Specifically, we present a universal and formally exact strategy to compute the appropriate static XC-kernel \(K_{\text{xc}}(\mathbf{q})\) for any material; no external input apart from the usual XC-functional is required.

In particular, we carry out DFT simulations to compute the density modulation due to an external monochromatic modulation, cf. Eq. (10), using an XC-functional of our choice. This gives us results for the static density response function \(\chi(\mathbf{q})\) [Eq. (11)] that are exact on the level of DFT. Having both the physical response \(\chi(\mathbf{q})\) and a reference function such as \(\chi_0(\mathbf{q}) = \chi_{\text{KS}}(\mathbf{q}, 0)\), it is straightforward to invert Eq. (12) for the corresponding static XC-kernel,

\[
K_{\text{xc}}(\mathbf{q}) = - \left\{ v(q) + \left( \frac{1}{\chi(\mathbf{q})} - \frac{1}{\chi_0(\mathbf{q})} \right) \right\}, \quad (16)
\]

\[
= \frac{1}{\chi_{\text{RPA}}(\mathbf{q})} - \frac{1}{\chi(\mathbf{q})},
\]

E. Static approximation and fluctuation–dissipation theorem

The main present limitation of our new approach is given by its restriction to compute the XC-kernel in the limit of \(\omega = 0\). Still, it is possible to compute the dynamic density response function within the static approximation [58],

\[
\chi_{\text{stat}}(\mathbf{q}, \omega) = \frac{\chi_0(\mathbf{q}, \omega)}{1 - v(q) + K_{\text{xc}}(\mathbf{q}) \chi_0(\mathbf{q}, \omega)}, \quad (17)
\]

where the dynamic XC-kernel \(K_{\text{xc}}(\mathbf{q}, \omega)\) is approximated by its exact static limit. Eq. (17) thus combines a dynamic description on the level of the RPA with exact static correlations. This approximation has been shown to be highly accurate in the case of the UEG for weak to moderate coupling strengths, including the particularly relevant regime of metallic densities \(r_s = \tau/a_B \lesssim 5\) (with \(\tau\) being the Wigner-Seitz radius and \(a_B\) the first Bohr radius [71]). In fact, Eq. (17) constitutes the most accurate and consistent implementation of any static XC-kernel, and has considerable practical and conceptual advantages over widespread model kernels such as ALDA.

The fluctuation–dissipation theorem [18] then gives a straightforward relation between the dynamic density response function \(\chi(\mathbf{q}, \omega)\), and the dynamic structure factor \(S_{\text{ee}}(\mathbf{q}, \omega)\),

\[
S_{\text{ee}}(\mathbf{q}, \omega) = - \frac{\text{Im} \chi(\mathbf{q}, \omega)}{\pi \hbar (1 - e^{-\beta \omega})}. \quad (18)
\]

Specifically, the DSF is defined as the Fourier transform of the intermediate scattering function [72]

\[
F_{\text{ee}}(\mathbf{q}, t) = \langle \hat{n}_{\text{ee}}(\mathbf{q}, t)\hat{n}_{\text{ee}}(-\mathbf{q}, 0) \rangle , \quad (19)
\]

and constitutes the key property in state-of-the-art XRTS experiments. Therefore, Eqs. (17) and (18) open up the possibility to compare DFT simulation results that have been obtained via \(K_{\text{xc}}(\mathbf{q})\) and \(\chi_0(\mathbf{q}, \omega)\) to an experimental measurement.

In addition, Eq. (18) provides straightforward access to the static structure factor

\[
S_{\text{ee}}(\mathbf{q}) = \int_{-\infty}^{\infty} d\omega \, S_{\text{ee}}(\mathbf{q}, \omega), \quad (20)
\]

i.e., the Fourier transform of the usual pair correlation function \(g_{\text{ee}}(r)\). In combination, Eqs. (17), (18), and (20) imply that one can use KS-DFT to compute electron–electron correlation functions for any material, and without any additional external input. The interaction energy \(W\) then follows from an additional integration over the wave vector \(\mathbf{q}\). Finally, one might utilize the well-known adiabatic connection formula [18] (resulting in an integration over an effective coupling parameter \(\lambda \in [0, 1]\)) to obtain the free energy, which contains the full thermodynamic information about the system of interest.

III. RESULTS: STATIC DENSITY RESPONSE AND XC-KERNEL

A. Uniform electron gas

Let us begin our investigation of electron–electron correlation functions based on DFT and the fluctuation–dissipation theorem with an analysis of the static density response function \(\chi(\mathbf{q})\) of the UEG at ambient conditions (i.e., at \(T = 0\)) shown in Fig. 2. In particular, we have carried out DFT calculations governed by the perturbed Hamiltonian \(H_{q, A} = H_{q, 0, A}\) [cf. Eq. (7)] for multiple wave vectors \(\mathbf{q}\) and a sufficiently small perturbation amplitude \(A\); the different symbols show results for a selection of widely used XC-functional. As a reference, we also include the exact response of the UEG as the solid black lines, which are based on QMC results by Moroni et al. [16] (black squares) and taken from the neural-net representation from Ref. [73].

Panel a) has been obtained for \(r_s = 2\), which is a metallic density that can be probed in experiments for example with aluminum [74]. Evidently, all curves exhibit the
FIG. 2. Electronic static density response function $\chi(q)$ [left column] and XC-kernel $K_{xc}(q)$ [right column] of the UEG at ambient conditions ($\Theta = 0.01$) for $r_s = 2$ (top row) and $r_s = 5$ (bottom row). Solid (dashed) black line: exact UEG results based on the neural-net representation of Ref. [73] (analytical RPA). Black squares: exact QMC results by Moroni et al. [16]. The other symbols distinguish DFT calculations for the density modulation Eq. (10) using different XC-functionals; see panel a) and the main text.

same qualitative trends, i.e., the exact limit of perfect screening [75]

$$\lim_{q \to 0} \chi(q) = -\frac{q^2}{4\pi}$$

and the noninteracting limit

$$\lim_{q \to \infty} \chi(q) = \chi_0(q)$$

for small and large wave numbers $q = |q|$, respectively. For $q \lesssim q_F$ (with $q_F = (3\pi^2n)^{1/3}$ being the Fermi wave number [18]), all DFT curves using a non-zero XC-functional are in excellent agreement to the exact results. This can be seen particularly well in panel b) showing the corresponding deviations to the mean-field curve [Eq. (16)], see the discussion below. The good agreement is a direct consequence of the well-known compressibility sum-rule, see Eq. (23) and the corresponding discussion below. The most pronounced differences between the different functionals occur for intermediate wave numbers $1.5q_F \lesssim q \lesssim 2.5q_F$, where $\chi(q)$ exhibits a negative peak. From a physical perspective, this feature can be explained by the spontaneous alignment of electron pairs [76], which leads to a reduction in the free energy landscape and, therefore, an increased density response. This pair alignment is highly sensitive to electronic XC-effects, which leads to the observed impact of the XC-functional. For larger $q$, the impact of the XC-kernel again decreases, although some deviations remain over the entire depicted $q$-range.

Let us next analyze the respective accuracy of the various XC-functionals. Firstly, we note that the KS-response function [cf. Eq. (15)], when being inserted into the RPA expression Eq. (14), reproduces the analytical RPA (dashed black curve) for all functionals, as the respective KS-orbitals of the unperturbed UEG are always plane waves. Similarly, evaluating the density modulation Eq. (10) based on a harmonically perturbed DFT simulation and setting $E_{xc}[n_e] = 0$ (grey circles) gives the same mean-field description. Regarding the different approximations for $E_{xc}[n_e]$, we find that both the LDA functional by Perdew and Wang [77] (light blue circles) and the generalized gradient approximation (GGA)
by Perdew, Burke and Ernzerhof (PBE [78], orange diamonds) give indistinguishable results. This is expected as all gradient terms vanish in the case of a UEG. The comparison to the exact QMC data gives good qualitative agreement for \( q \lesssim 2q_F \), and deterioration in the quality for larger wave numbers \( q \). Let us next consider the AM05 functional by Armiento and Mattsson [79] (purple up-triangles), which is a semi-local GGA, and has been shown to give comparable quality to hybrid functionals in the description of solids [80]. Moreover, it has been applied to the calculation of electronic structures at WDM parameters [81–83]. Here, we find that AM05 is the least accurate functional and substantially underestimates the true depth of the minimum in the static density response. The semi-empirical PBEsol [84] (blue plusses) constitutes a significant improvement over PBE for \( q \gtrsim 2q_F \). Finally, the meta-GGA SCAN [85] (green diamonds) exhibit the best performance, as it is expected.

To get a more rigorous insight into the performance of the different functionals, we show the corresponding XC-kernel \( K_{\text{xc}}(q) \) that we have obtained by evaluating Eq. (16) in Fig. 2 b). Throughout this work, we follow the usual convention [73, 86, 87] and divide \( K_{\text{xc}} \) by the Coulomb interaction \( v(q) \), resulting in the commonly analyzed local field correction, cf. Eq. (13). In the limit of small \( q \), the LFC is known to satisfy the exact compressibility sum-rule [86],

\[
\lim_{q \to 0} G(q) = \frac{q^2}{4\pi} \frac{\partial^2}{\partial n^2} (nF_{\text{xc}}) \, ,
\]

with \( n = N/V \) being the average number density. It is depicted as the dashed blue parabola in Fig. 2; we note that it holds \( \lim_{T \to 0} F_{\text{xc}} = E_{\text{xc}} \) in the ground-state limit. Evidently, Eq. (23) is accurately reproduced both by the exact neural-net representation and by all depicted XC-functionals in the limit of small \( q \). Moreover, both the LDA and PBE functionals have been constructed to reproduce Eq. (23) for all \( q \) [88] in the case of the UEG, which is substantiated by the presented empirical analysis. Remarkably, the parabolic small-\( q \) expansion remains reasonably accurate for \( q \lesssim 2q_F \); this is a highly nontrivial observation and explains the success of both the simple LDA and the somewhat more sophisticated PBE in the description of bulk materials that has been reported in previous investigations [16].

In contrast, the AM05 functional only reproduces Eq. (23) for \( q \lesssim 1.2q_F \). For large \( q \), it has been designed to reproduce the Airy gas model [80], resulting in a substantial, unphysical drop towards negative values in this regime. The semi-empirical PBEsol, on the other hand, is virtually indistinguishable from PBE for \( q \lesssim 2.5q_F \), and exhibits a somewhat higher accuracy at large wavenumbers. Finally, SCAN constitutes by far the most accurate functional and gives basically exact results over the entire depicted \( q \)-range since it was designed to reproduce the exact ground state QMC results in this range of wave-numbers [85].

In the bottom row of Fig. 2, we show the same analysis for a lower density, \( r_s = 5 \). Physically, this is located near densities of the conduction electrons in Potassium and Rubidium, and can also be probed in evaporation experiments such as hydrogen jets [89]. Due to the role of \( r_s \) as the quantum coupling parameter [18, 32], the electrons are more strongly correlated at these conditions, which results in a sharper minimum in \( \chi(q) \). Consequently, the impact of the different XC-functionals is more pronounced. Overall, we find the same qualitative trends as for \( r_s = 2 \): AM05 is, by far, the least accurate functional, whereas SCAN is virtually exact for all depicted \( q \); Eq. (23) is accurate for \( q \lesssim 2q_F \), which explains the high accuracy of LDA, PBE, and PBEsol; the latter constitutes a substantial improvement over PBE for \( q \gtrsim 3q_F \).

Let us next repeat this analysis for the UEG in the WDM regime, i.e., at the electronic Fermi temperature \( \Theta = 1 \) shown in Fig. 3. Firstly, we note that, due to the increased temperature, the impact of Coulomb correlation effects is decreased. Consequently, the negative minimum in \( \chi(q) \) is less pronounced compared to \( T = 0 \) for both values of \( r_s \). At the same time, we find substantially more pronounced differences between the various depicted XC-functionals. In particular, the finite-\( T \) LDA functional by Groth et al. [53] (red circles) is even somewhat less accurate compared to the ground-state LDA and PBE.

To understand these counterintuitive observations, we have to consider the XC-kernel shown in the right column of Fig. 3. In particular, the dashed red and blue lines show the exact small-\( q \) expansion Eq. (23) evaluated at \( \Theta = 1 \) and \( \Theta = 0 \), respectively. Evidently, the ground-state LDA (and PBE) follows the latter curve, as it is expected. Similarly, the finite-\( T \) LDA follows the red curve and, therefore, reproduces the correct impact of the temperature on the small-\( q \) limit. This can be seen particularly well in the inset where we show a magnified segment. It can be expected that even the recent finite-\( T \) extension of PBE by Karasiev et al. [54] shows this behavior as it has been constructed to reproduce the finite-\( T \) LDA. In practice, however, the impact of \( K_{\text{xc}}(q) \) on the density response function vanishes for \( q \to 0 \), and even the RPA [Eq. (14)] becomes exact. For \( q \gtrsim q_F \), where the impact of the XC-kernel is most pronounced, the ground-state evaluation of Eq. (23) constitutes a superior approximation to the true curve (solid black). Therefore, the ground-state LDA exhibits a superior accuracy compared to the theoretically more consistent temperature-dependent functional.

This is a highly important point that deserves a more detailed investigation. To this end, we define a relative agreement measure (RAM) between the LFCs evaluated from the ground-state and finite-\( T \) LDA functionals towards the true LFC of the UEG as

\[
\text{RAM} = \frac{\int_0^{2q_F} |G_{\text{LDA}}(q) - G_{\text{ML}}(q)| \, dq}{\int_0^{2q_F} |G_{\text{T-LDA}}(q) - G_{\text{ML}}(q)| \, dq} = \frac{\Delta_{\text{LDA}}}{\Delta_{\text{T-LDA}}} \, ;
\]

here \( G(q) \) corresponds to the local field correction de-


fig. 3. Electronic static density response function $\chi(q)$ [left column] and XC-kernel $K_{xc}(q)$ [right column] of the UEG at WDM [47, 48] conditions ($\Theta = 1$) for $r_s = 2$ (top row) and $r_s = 5$ (bottom row). Solid (dashed) black line: exact UEG results based on the neural-net representation of Ref. [73] (analytical RPA). The other symbols distinguish DFT calculations for the density modulation Eq. (10) using different XC-functionals; see panel a) and the main text.

fined in Eq. (13) above. We note that the upper limit of $2q_F$ has been chosen based on the empirical approximate validity range of the small-$q$ expansion Eq. (23); using larger upper limits always favours the ground-state LDA, which tends to have a smaller pre-factor in the parabolic expansion. The results for Eq. (24) are shown as the heat-map in Fig. 4 in the $r_s$-$\Theta$-plane covering the entire range of metallic densities and the temperatures that are most relevant for WDM research [32, 47, 48]. In particular, a RAM below one signifies that the ground-state LDA provides an overall more accurate kernel compared to the finite-$T$ functional. At $\Theta = 0$, both LDA representations are, by construction [53], identical. Remarkably, the ground-state LDA becomes substantially more accurate around $\Theta \gtrsim 0.3$, and the RAM attains its lowest values between the two dashed green lines, i.e., around $\Theta = 1$. This is precisely the regime where the impact of the temperature on the XC-functional has the most influence on the total free energy $F[n_e]$ [50, 51] and, therefore, on the outcome of a DFT simulation. Yet, as we have seen above, this leads to a larger pre-factor in Eq. (23) and, therefore, a less accurate XC-kernel for $q \gtrsim 0.5q_F$ on the level of the LDA. For completeness, we note that the RAM only exceeds unity for $r_s \sim 1$ and $\Theta \sim 4$ in the presented overview; the impact of $K_{xc}$, however, is negligible due to the high temperature and density.

We stress that these findings have profound consequences for the construction of the next generation of XC-functionals that are specifically designed for the application at WDM conditions. Evidently, translating Jacob’s ladder of functional approximations [4] from the ground-state to finite temperatures does not necessarily improve the quality of DFT simulations in the WDM regime. Making the lowest rung—i.e., the LDA—explicitly $T$-dependent might actually lead to a deterioration of the attained accuracy. Moreover, this deficiency is, by design, not removed on the GGA-level, which is based on the same $q \to 0$ expansion. Returning to Fig. 3, we further find that the ground-state SCAN functional performs similarly poorly as AM05, which is in stark contrast to its impressive accuracy at $T = 0$, cf. Fig. 2. We thus conclude that the meta-GGA corrections on which
of the density response and XC-kernel of the UEG leads to a recommendation for the construction of novel XC-functionals that fulfill the demanding requirements of WDM theory. As we have seen, it is important to construct a functional that combines the correct $T$-dependence of Eq. (23) with an accurate description of XC-effects over the entire relevant $q$-range. This is particularly important for WDM applications, where large $q$ play a more important role in practical applications compared to ambient conditions [47]. In this regard, a promising candidate is given by a new class of nonlocal functionals based on the adiabatic connection formula and the fluctuation–dissipation theorem [91, 92].

### B. Warm dense hydrogen

To demonstrate the broad utility of our new approach, we next consider hydrogen at extreme conditions—a state of matter that plays a central role in the description of the implosion path of a fuel capsule towards nuclear fusion [43] and naturally occurs within a gamut of astrophysical objects such as giant planet interiors [41]. In Fig. 5, we show our new DFT results for the static density response of hydrogen that has been computed for a single fixed configuration of proton coordinates, i.e., a single ion snapshot from a corresponding DFT-MD simulation. We note that, while the averaging over many snapshots is straightforward, benchmarking DFT for a single proton configuration constitutes an even more rigorous test of our methodology as, in this way, error cancellation between different snapshots is ruled out. The left column of Fig. 5 shows results for $\chi(q)$ at $\Theta = 1$, and the top and bottom rows have been obtained for $r_s = 2$ and $r_s = 4$. For these parameters, we are able to compare our new DFT results to exact QMC data by Böhme et al. [13] (black squares) that have been obtained for the same ion configuration. In addition, we also include both the exact (solid black) and RPA results (dashed black) for the UEG model at the same conditions [73]. At the higher density, where hydrogen is known to be mostly ionized, the bulk of the electrons can be categorized as unbound, meaning that they are not primarily localized around the protons. Therefore, the density response of hydrogen closely resembles the UEG model at these conditions. In addition, we find that our DFT evaluation of the perturbed density Eq. (10) is in good agreement with the QMC reference data for all $q$, and only weakly depends on the employed functional. In particular, the difference between ground-state (light blue circles) and finite-$T$ (red circles) LDA is small, with the former being a trifle more accurate. The corresponding results for the static XC-kernel are shown in the right column of Fig. 5 and, overall, closely resemble our earlier findings for the UEG model, cf. Fig. 3 above.

From a physical perspective, the case of $r_s = 4$ shown in Fig. 5 c) is even more interesting. In addition to the more pronounced impact of Coulomb correlations (and, therefore, electronic XC-effects), hydrogen is partly ionized at these conditions, with an approximate fraction of free electrons of $\alpha = 0.54 - 0.6$ [13, 93]. Consequently, the numerical results for $\chi(q)$ exhibit a substantially reduced density response compared to the UEG model, as the bound electrons cannot react to the external potential. Overall, we find good qualitative agreement between DFT and the QMC data over the entire depicted $q$-range, even though the true reduction of the density response due to the localization around the protons is somewhat underestimated around the vicinity of the negative minimum, i.e., $q_F \lesssim q \lesssim 3q_F$. Remarkably, we find that all XC-functionals reproduce the nontrivial increase in the magnitude of $\chi(q)$ compared to the UEG model around $q \approx 4q_F$, which has very recently been explained as a consequence of isotropy breaking in the presence of the proton configuration in Ref. [13].

In Fig. 5 b) and d), we show the corresponding XC-kernels, that we have extracted from the different $\chi(q)$ data sets (both QMC and DFT evaluations of Eq. (10) using different XC-functionals) via Eq. (16), but using the same data for the reference function $\chi^0(q)$ that we have obtained from a separate DFT simulation with the XC-functional being set to zero. This has the advantage that XC-kernels from different theories are directly comparable to each other. For completeness, we note that extracting the actual XC-functional dependent kernel by inserting the respective $\chi_{KS}(q, 0)$ into Eq. (16) is straightforward, but would make the direct comparison less meaningful. The resulting data for $K_{xc}(q)$ of hydrogen at $r_s = 4$ and $\Theta = 1$ qualitatively agree with each other, but starkly disagree from the UEG model at these conditions. In particular, we do not find the simple parabolic behaviour Eq. (23) for LDA/PBE. In addition,
FIG. 5. Electronic static density response function $\chi(q)$ [left column] and XC-kernel $K_{xc}(q)$ [right column] computed from the same mean-field reference function (see the main text) $\chi_0(q)$ of hydrogen at WDM [47, 48] conditions ($\Theta = 1$) for $r_s = 2$ (top row) and $r_s = 4$ (bottom row). Solid (dashed) black line: exact results for the UEG model at the same conditions based on the neural-net representation of Ref. [73] (analytical RPA). Black squares: exact QMC results for hydrogen by Böhm et al. [13]. The other symbols distinguish DFT calculations for the density modulation Eq. (10) using different XC-functionals; see panel a) and the main text.

The kernel attains remarkably small values for $q \lesssim 2.5q_F$, followed by a pronounced increase for $q \gtrsim 3q_F$. Clearly, our new methodology is capable to accurately capture the complex interplay of the ion structure with electronic XC-effects as they manifest in $K_{xc}(q)$.

To understand the observed differences of the actual kernel of hydrogen to the UEG model, we have to go back to Fig. 5 c), where we show the mean-field results [corresponding to $\chi_{RPA}(q)$] as the grey circles. Interestingly, these data are in excellent agreement to the other data sets. In fact, the very small values of $K_{xc}(q)$ that have been obtained by inserting the QMC data into Eq. (16) directly indicate that the results that have been obtained without an XC-functional are more accurate than the other DFT data. This is, however, likely coincidental and comes as a result of the crossover from the UEG-like behaviour of hydrogen at $\Theta = 1$ for $r_s \lesssim 2$ to the case of atomic/molecular hydrogen at large $r_s$, where the electrons are predominantly localized around the protons. In the former limit, it is well known that the RPA underestimates the true density response [32] whereas, in the latter case, it underestimates the true degree of localization around the ions, resulting in an effective overestimation of the magnitude of $\chi(q)$. The present case of $r_s = 4$ is located between these two limits, and the apparent accurate description of $\chi(q)$ by the mean-field calculation is a direct consequence of the cancellation of RPA-errors, which have a positive (negative) sign for small (large) $r_s$; other observables such as the single-electron density $n_e(r)$ are less accurately reproduced by the mean-field calculations compared to the other depicted XC-functionals.

The observed stark increase in $K_{xc}(q)$ for large wave numbers, too, can be directly traced back to the behaviour of $\chi_0(q)$ and the depicted mean-field response $\chi_{RPA}(q)$, which does not reproduce the increase in magnitude of the density response compared to the UEG model at these conditions. Consequently, the latter pre-
dominantly constitutes an XC-effect that is determined by the XC-kernel, and, therefore, is accurately captured by our new methodology.

Let us conclude this analysis of the static density response of warm dense hydrogen by comparing our new approach to the current state-of-the-art. In Fig. 6, we again consider hydrogen at \( r_s = 4 \) and \( \Theta = 1 \); the black squares, blue circles, and orange triangles show the QMC, LDA, and PBE results from Fig. 5. Green crosses: Static (\( \omega \to 0 \)) limit of LR-TDDFT results within RPA [Eq. (14)] based on \( \chi_{KS}(q,\omega) \) using KS-orbitals from a ground-state LDA calculation. Red crosses: corresponding ALDA results. Top panel: relative error with respect to exact QMC benchmark data. The inconsistent incorporation of the ALDA model kernel leads to a deterioration compared to RPA for all depicted wave numbers \( q \).

![Image](image.png)

FIG. 6. Illustration of the inconsistent combination of \( \chi_{KS}(q,\omega) \) with the ALDA kernel. Bottom: Static density response of warm dense hydrogen with \( r_s = 4 \) and \( \Theta = 1 \); the light blue circles, orange diamonds, and black squares are taken from Fig. 5. Green crosses: Static (\( \omega \to 0 \)) limit of LR-TDDFT results within RPA [Eq. (14)] based on \( \chi_{KS}(q,\omega) \) using KS-orbitals from a ground-state LDA calculation. Red crosses: corresponding ALDA results. Top panel: relative error with respect to exact QMC benchmark data. The inconsistent incorporation of the ALDA model kernel leads to a deterioration compared to RPA for all depicted wave numbers \( q \).

seen particularly well in the top panel showing a the relative deviation to the exact QMC reference data. Even worse, including the widely used ALDA model as the XC-kernel (red crosses)—a standard practice within LR-TDDFT [63, 70]—actually increases the systematic errors for all \( q \). This constitutes an unambiguous demonstration of the practical impact of the inconsistent combination of a KS-response function with an XC-kernel from a different model, which is overcome by our new approach.

IV. CONCLUSIONS AND OUTLOOK

A. Summary

In this work, we have presented a new, formally exact approach to compute the electronic static XC-kernel \( K_{xc}(q) \) of any given material within the framework of DFT, and without any additional external input apart from the usual XC-functional. In particular, we propose to carry out KS-DFT simulations of a harmonically perturbed system, which gives us straightforward access to linear-response properties and, in this way, the sought-after electron–electron XC-kernel.

As the first application, we have studied the UEG model, which is the archetypical system of interacting electrons and plays a central role in the context of DFT. At ambient conditions (i.e., \( T = 0 \)), DFT simulations of the harmonically perturbed electron gas accurately reproduce the static linear density response function \( \chi(q) \) over the entire \( q \)-range. This is a direct consequence of the small-\( q \) limit of the XC-kernel [Eq. (23)], which, remarkably, reproduces the exact static kernel for \( q \lesssim 2q_F \) [16]. Regarding \( K_{xc}(q) \) itself, we have found that SCAN constitutes by far the most accurate functional at \( T = 0 \) and is basically exact for all \( q \).

An additional interesting research question is the performance of different XC-functionals in the WDM regime, i.e., \( \Theta = 1 \). Interestingly, we have found that the ground-state LDA/PBE functionals perform better than their consistently temperature-dependent counterparts. Our analysis has revealed that this is a nontrivial consequence of the compressibility sum-rule Eq. (23): the \( T \)-dependent LDA is indeed superior in the limit of \( q \to 0 \), but here the impact of \( K_{xc}(q) \) on the actual density response and related properties is negligible. For \( q \sim q_F \), the ground-state expansion more accurately reproduces the true XC-kernel, which results in a superior accuracy of \( T = 0 \) LDA and GGA functionals at \( \Theta = 1 \). This insight has profound consequences for the development of the next generation of XC-functionals that are specifically designed for the application at WDM conditions.

As the next step, we have carried out a similar analysis for warm dense hydrogen, which is of prime importance for technological applications such as nuclear fusion and a host of astrophysical applications. Overall, we have found that the DFT evaluation of the density modulation
due to an external perturbation [Eq. (10)] is indeed capable to very accurately, though not exactly, describe the density response of hydrogen both for $r_s = 2$ and $r_s = 4$. In particular, our method captures the nontrivial increase in magnitude of the density response for $q \gtrsim 3q_F$ due to the isotropy breaking of the proton configuration [13]; we stress that this feature is decisively shaped by electronic XC-effects and, therefore, not reproduced on the level of the RPA. In other words, the accurate, material-specific XC-kernel is indispensable. For $r_s = 2$, hydrogen is predominantly ionized and $K_{xc}(q)$ exhibits an UEG-like behaviour. Yet, the UEG model breaks completely down at $r_s = 4$ as the physical behaviour of the system is substantially shaped by the localization of a substantial fraction of the electrons around the protons. Our new approach, on the other hand, accurately captures the actual behaviour of the XC-kernel known from exact QMC simulations [13] over the entire $q$-range, with both the ground-state and finite-$T$ LDA functionals being the most accurate. An additional practical insight from this investigation is given by the inconsistent double counting of Coulomb correlation effects when a KS-response function $\chi_{KS}(q, \omega)$ that has been computed on the basis of a non-zero XC-functional is combined with the ALDA model, which, by itself, contains the full wave-number resolved information about electronic XC-effects of the UEG based on Eq. (23). In that case, the inclusion of the ALDA kernel in Eq. (12) actually leads to a deterioration of the quality compared to the corresponding RPA expression with $K_{xc} \equiv 0$.

B. Outlook

The new framework that has been introduced in this work opens up the unprecedented possibility to compute the electronic XC-kernel of arbitrary materials; even complex atomic mixtures [94–96] do not pose a fundamental challenge to our approach. This will have a strong impact on a number of research fields within physics, chemistry, material science, and related disciplines. First and foremost, we note that the XC-kernel is the key ingredient to a host of practical applications, such as the construction of electronically screened effective potentials [18, 27, 28], the incorporation of correlation effects into quantum hydrodynamics [24–26], and the estimation of the energy loss characteristics of high-energy density plasmas [97–99]. A particularly important example is given by the interpretation of XRTS experiments within the widely used Chihara approximation [19, 100], which gives one direct access to a number of system parameters such as the electronic temperature.

The presented set-up can be easily extended to consistently address a number of issues, such as the combination with a DFT-MD run to average different properties over multiple ion configurations, or the microscopic density response $\chi_{G,G'}(q, \omega)$ that becomes important for strongly anisotropic systems [63]. Moreover, our idea is not limited to electronic pair correlations. A gradual increase in the amplitude $A$ of the external harmonic perturbation gives one straightforward access to the nonlinear electronic density response [17, 61, 101] of any given system, which, in turn, is directly connected to higher-order correlation functions between three and more electrons [102]. In other words, our approach gives one access to the full hierarchy of many-electron correlations within the framework of DFT, and without any additional external input.

On the one hand, our methodology will directly benefit from the availability of more sophisticated XC-functionals on higher rungs of Jacob’s ladder such as the promising hybrid functional by Heyd, Scuseria, and Ernzerhof (HSE) [103]. On the other hand, the analysis of the XC-kernel $K_{xc}(q)$ on the basis of a particular functional can give valuable insights to guide new developments, as we have demonstrated for the case of WDM in Sec. III above.

Let us conclude this work by outlining two particularly promising and potentially highly impactful routes for future research.

1) Linear-response TDDFT. We expect the proposed combination of the material-specific static XC-kernel $K_{xc}(q)$ with the consistent dynamic KS reference function $\chi_{KS}(q, \omega)$ [cf. Eq. (17)] to provide the basis for the systematic development of future LR-TDDFT calculations of a gamut of dynamic properties such as the dynamic structure factor $S_{ee}(q, \omega)$ of real materials. In particular, we note that this approach avoids the aforementioned inconsistency between the material-specific KS orbitals and model kernels from other theories, and, therefore, has considerable practical and conceptual advantages over previously employed approximations such as ALDA.

2) Electron–electron correlation functions. The second key future application of our method is given by the highly accurate estimation of electron–electron correlation functions such as the static structure factor $S_{ee}(q)$ and the corresponding pair correlation function $g_{ee}(r)$. In this regard, the only conceptual limitation of our current framework is given by the static approximation Eq. (17). While being highly accurate for the UEG at metallic densities [20, 58], a detailed and rigorous future investigation of its performance for more complex materials is indispensable. In any case, there is strong reason to believe that the static approximation will not be fundamentally insurmountable. In this regard, a highly promising route is provided by a Wick rotation, which allows one to transform the frequency integration in Eq. (20) into a summation over discrete, imaginary Matsubara frequencies [18]. In this way, one can re-cast the original quest for an explicitly dynamic XC-kernel $K_{xc}(q, \omega)$—a most formidable challenge that can only be met for a number of simplified model systems and limited parameters—into the estimation of electronic XC-effects within the imaginary-time domain.
more tractable in practice; indeed, various QMC methods give straightforward access to imaginary-time correlation functions [104] without the need for a subsequent analytic continuation. Taken together, we envision the future combination of our present framework that provides the formally exact and material-specific XC-kernel on the static level with the imaginary-time XC-structure based on cutting-edge QMC simulations.

DATA AVAILABILITY

The data supporting the findings of this study are available on the Rossendorf Data Repository (RODARE) [105].

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Appendix A: DFT simulation details

For the KS-DFT calculations of the presented XC kernels and dynamic response functions within LR-TDDFT, we used the GPAW code [106–109], which is a real-space implementation of the projector augmented-wave method.

For the calculation of the XC kernel presented in Figs. 2, 3, and 5, the following parameters have been used:

For the UEG at $\theta = 0.01$, $r_s = 2$ and $r_s = 5$, the calculations were performed with 38, 54, and 66 particles in the main cell. For the UEG at $\theta = 1$ and $r_s = 2$, the simulations were performed with 14 and 34 particles.

This is consistent with previous QMC investigations [17, 73, 110, 111], where it has been shown that finite-size errors are negligible at the present conditions. For the UEG at $\theta = 1$ and $r_s = 5$, the calculations were performed with 14 particles. For hydrogen at $\theta = 1$ and $r_s = 2$, the simulations were performed with 14, 20, and 30 particles in the main cell. For hydrogen at $\theta = 1$ and $r_s = 4$, the calculations were performed with 14 and 20 particles.

The main cubic cell size is computed as $L = r_s (\frac{2}{3} N)^{1/3}$. Accordingly, perturbation wave numbers (set along the $z$ axis) are defined by $q = \eta \times 2\pi/L$, with $\eta$ being a positive integer number. We used a Monkhorst-Pack [112] sampling of the Brillouin zone. For the UEG at $r_s = 2$ ($r_s = 5$), a $k$-point grid of $N_k \times N_k \times N_k$ total points with $N_k = 12$ ($N_k = 8$) was used. For hydrogen we used $N_k = 8$. The cutoff energy was set to $800$ eV at $\theta = 1$ and $r_s = 2$, and to $440$ eV at other $r_s$ and $\theta$ values. The number of bands in the case of the UEG at $r_s = 2$ and $\theta = 1$ was set to $N_b = 500$ (with the smallest occupation number $f_{\min} \lesssim 10^{-7}$). At $r_s = 5$ and $\theta = 1$ we used $N_b = 240$ bands with $f_{\min} \lesssim 10^{-6}$.

For hydrogen at $r_s = 2$ and $\theta = 1$, the number of bands was set to $N_b = 440$ (for 14 and 20 particles) and $N_b = 600$ (for 30 particles). For hydrogen at $r_s = 4$ and $\theta = 1$, the number of bands was set to $N_b = 300$ (for 14 particles) and $N_b = 400$ (for 20 particles).

For the UEG at $r_s = 2$ ($r_s = 5$), the perturbation amplitude was set to $A = 0.01$ ($A = 0.002$), with $A$ being in Hartree atomic units. For hydrogen at $r_s = 2$ and $r_s = 4$, the perturbation amplitude was set to $A = 0.01$.

The simulation results were cross-checked by performing UEG calculations using Abinit [113–116] for LDA, PBE, and PBEsol XC functionals at the same parameters.

For the calculation of the static KS density response function of hydrogen at $r_s = 4$ and $\theta = 1$, the main simulation cell size was set to $L = 8.224 \, \text{Å}$ (with 14 particles in the main simulation cell), the number of bands 1900, the $k$-point grid $4 \times 4 \times 4$, and the cut-off energy in the thermal equilibrium calculation was set to $E_{\text{cut}} = 400$ eV. For the computation of the static KS density response function a plane-wave cut-off of 90 eV was used and the wave numbers $q = j f_{\min}$, with $j = 1...5$ ($j = 1...4$), were considered.

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