Time-Dependent Thomas-Fermi Approach for Electron Dynamics in Metal Clusters

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We propose a time-dependent Thomas-Fermi approach to the (nonlinear) dynamics of many-fermion systems. The approach relies on a hydrodynamical picture describing the system in terms of collective flow. We investigate in particular an application to electron dynamics in metal clusters. We make extensive comparisons with fully fledged quantal dynamical calculations and find overall good agreement. The approach thus provides a reliable and inexpensive scheme to study the electronic response of large metal clusters. [S0031-9007(98)06302-9]

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Time-dependent mean-field theories are a basic tool for describing the dynamics of many-fermion systems. They are widely used in many fields of physics and for a broad range of phenomena. The most detailed and advanced theory is the fully quantum mechanical mean-field approach, often called the time-dependent Hartree-Fock method, which was already proposed in the early days of quantum theory [1]. This requires, however, enormous technical efforts when the systems grow large. One thus often switches to semiclassical approaches from which the most widely used is probably the Vlasov equation; for a general introduction see [2], for a typical nuclear application [3], and for recent applications to the electron dynamics in metal clusters [4,5]. The Vlasov equation describes the dynamics of the one-body distribution function $f(\mathbf{r}, \mathbf{p}, t)$ in the full six-dimensional phase space and a reliable propagation is still a formidable task. Moreover, there can easily appear spurious side effects from an insufficient handling of the Pauli principle [6,7]. Simpler approaches are thus much more desirable. It is the aim of this Letter to present and to investigate such an approach, the time-dependent Thomas-Fermi (TDTF) method. It also offers a simple example of a time-dependent density functional theory based only on local density and current [8]. The validity of the approach depends, of course, on the particular physical circumstances. We discuss it here in the context of the electronic dynamics in metal clusters where we find that TDTF can provide a useful description of the gross features of the dynamics.

Electronic excitations in metal clusters, as connected with spectroscopic experiments, provide valuable insight into their structural and dynamical properties and have since long been studied in the framework of linear response theory [9]; for reviews, see [10,11]. Recently, new experimental techniques have accessed the regime of strong (nonlinear) electronic excitations, e.g., when probing the cluster with intense laser beams [12] or in collisions with fast, highly charged ions [13]. They require a fully fledged treatment of electron dynamics, i.e., a nonlinearized approach to the time-dependent many electron problem. In that context, Kohn-Sham equations solved in real time within the time-dependent local density approximation (TDLDA) are an appropriate formalism [14,15]. A TDTF description could possibly simplify those elaborate three-dimensional calculations for the purpose of exploratory studies. The static (extended) Thomas-Fermi approach was indeed successfully used to compute the structure of large clusters, for molecular dynamics simulations [16], and to calculate multipole spectra via RPA sum rules [17–20]. We investigate here an extension to nonlinear time-dependent phenomena.

The test cases employed here are modeled with a few further simplifying assumptions. During the short times of a few fs investigated here, ionic cores can be considered as frozen. The excitation mechanism is then simply described by an instantaneous initial shift of the whole electron cloud against the ionic background, which is a generic first guess for fast excitations [14]. This excitation provokes a collective dipole oscillation and fast electron emission. We shall hence consider these quantities in various kinematic regimes.

The TDTF model.—The essence and limitations of the TDTF approach can be best demonstrated in relation to the semiclassical, but more general, Vlasov approach. The stationary ground state in both cases is the Thomas-Fermi ground state, where the momenta are isotropically distributed inside a sphere around $\mathbf{p} = \mathbf{0}$ and with radius the local Fermi momentum. The p-space distribution can become much more complicated in a dynamical situation. Still, the leading feature may remain a simple collective flow with velocity field

$$\mathbf{u}(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \int \frac{\mathbf{p}}{m} f(\mathbf{r}, \mathbf{p}, t)\, d^3p\,. \tag{1}$$

But the local p distribution about the center $\mathbf{u}(\mathbf{r})$ can develop any curious deformation. The basic hypothesis of TDTF is that the dynamical distortions in p space are quickly relaxing back to a local Fermi sphere centered around the local hydrodynamic momentum $m\mathbf{u}(\mathbf{r})$. This

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is the typical assumption underlying any hydrodynamical model, namely, that the dynamics proceeds close to local equilibrium. The relevance of this assumption can be analyzed at the Vlasov level, in terms of the local stress tensor

$$\Pi_{ij}(\mathbf{r},t) = \int \frac{d^3p}{m} f(\mathbf{r},\mathbf{p},t) p_i' p_j' , \tag{2}$$

where $\mathbf{p}' = \mathbf{p} - m\mathbf{u}(\mathbf{r})$, which we disentangle into isotropic $I_{ij}(\mathbf{r},t) = 1/3\,\mathrm{Tr}[\Pi(\mathbf{r},t)]\delta_{ij}$ and anisotropic part $A_{ij}(\mathbf{r}) = \Pi_{ij}(\mathbf{r}) - I_{ij}(\mathbf{r})$. The relative local anisotropy is measured by the ratio

$$x(\mathbf{r},t) = \sqrt{\sum_{i\le j} A_{ij}^2} \Big/ 6I_{11} . \tag{3}$$

Its density weighted average

$$X(t) = \frac{\int \rho(\mathbf{r}) x(\mathbf{r})\, d^3r}{\int \rho(\mathbf{r})\, d^3r} \tag{4}$$

[where $\rho(\mathbf{r}) = \int f(\mathbf{r},\mathbf{p})\, d^3p$] then provides a global estimate for the deformation of the Fermi sphere. We can thus test the validity of the Thomas-Fermi approximation by analyzing results from realistic Vlasov computations.

We consider the typical case of an electron cloud excited by an initial shift with respect to the ionic background and indulge in using the jellium approximation for the background [14]. Figure 1 shows the global anisotropy $X(t)$ for three amplitudes from linear ($E^* = 1.2$ eV) to nonlinear ($E^* = 7.4$ eV) excitations. We observe a finite initial value of $X \sim 0.05$, although the system has been initialized in the Thomas-Fermi ground state with isotropic momentum distribution. This offset is due to the finite representation of $f(\mathbf{r},\mathbf{p},t)$ by means of test particles; it thus provides a measure of the numerical noise in $X(t)$ and is sufficiently small for our purpose. In much less than 1 fs, X drifts towards its maximum value $\sim 0.1-0.3$, and continues to oscillate. These oscillations reflect the dominant plasmon dynamics, show up with double plasmon frequency, and are slightly damped. Altogether the stress tensor hence typically exhibits 10%–20% of anisotropy. The assumption of spherically distributed momenta therefore appears reasonable, which suggests to use a (hydrodynamic) TDTF description for the gross features of electron dynamics in metal clusters.

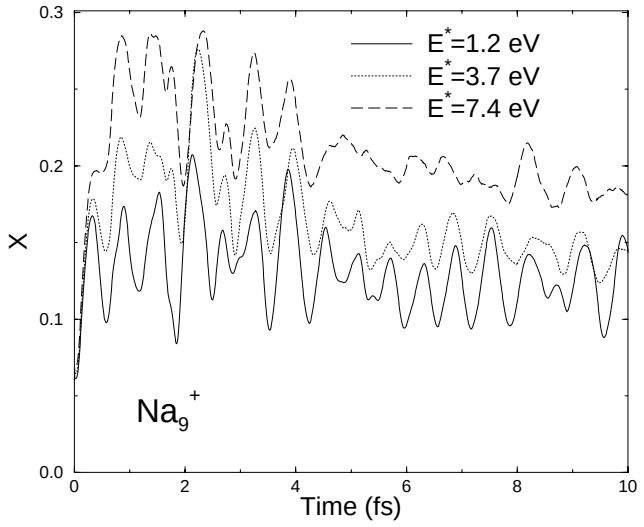

FIG. 1. Plot of the reduced parameter X [see Eq. (3)] as a function of time, for three different excitation energies in Na_9^+.

To derive TDTF, we come back to the variational formulation of Kohn-Sham equations

$$\delta \int dt \langle \psi | i\hbar\partial_t - H | \psi \rangle = 0 , \tag{5}$$

where $|\psi\rangle$ is a Slater determinant built on the Kohn-Sham orbitals ϕ_i and $H = T + U$ the LDA Hamiltonian. Hydrodynamical equations for the density alone can be derived from (5) in the general time-dependent density-functional theory formalism [8], but their practical use requires an approximate kinetic energy functional. It can be obtained through the local transform $\phi_i(\mathbf{r},t) = \phi_i^0(\mathbf{r},t)\exp[i\frac{\hbar}{m}\chi(\mathbf{r},t)]$, where both ϕ_i^0 and χ are real. The crucial approximation that one and the same velocity generator χ is used for all wave functions ϕ_i [21] compels each of them to follow the collective flow with irrotational velocity $\mathbf{u} = \nabla\chi$ [22]. This probably underestimates dissipation in collective modes, as discussed below. The kinetic energy, in turn, decouples as

$$\langle \psi | T | \psi \rangle = \langle \psi^0 | T | \psi^0 \rangle + \frac{m\rho u^2}{2} , \tag{6}$$

where ψ^0 is the Slater determinant built on the ϕ_i^0's alone.

Because of the weak deformation of the Fermi sphere, the local kinetic energy $\langle \psi^0 | \hat{T} | \psi^0 \rangle$ can be approximated at the Thomas-Fermi level as

$$T[\rho] = (3\pi^2)^{2/3} \int \frac{3\hbar^2}{10m} \rho(\mathbf{r},t)^{5/3} d^3r . \tag{7}$$

This semiclassical expression relies on a continuous level density and neglects the discrete nature of one-body levels. As analyzed in the next section, the relevance of such an approximation depends on the dynamical regime.

Equation (5) then leads to the set of coupled TDTF (hydrodynamic) equations:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{u}) = 0 , \tag{8}$$

$$m\frac{\partial\chi}{\partial t} + \frac{m}{2}(\nabla\chi)^2 + \frac{\delta U}{\delta\rho} + \frac{\delta T}{\delta\rho} = 0 . \tag{9}$$

For reasons of efficiency, we solve the coupled equations (8) and (9) via an effective Schrödinger equation, using the Madelung transform [23]. This is achieved

by packing the basic fields ρ and χ into one auxiliary wave function $\Phi(\mathbf{r},t) = \sqrt{\rho(\mathbf{r},t)}\exp[i\frac{\hbar}{m}\chi(\mathbf{r},t)]$, which follows the nonlinear Schrödinger equation

$$i\hbar\,\frac{\partial\Phi}{\partial t} = -\frac{\hbar^2}{2m}\,\Delta\Phi + \left(\frac{\delta U}{\delta\rho} + \frac{\delta T^0}{\delta\rho} + \frac{\hbar^2}{2m}\,\frac{\Delta\sqrt{\rho}}{\sqrt{\rho}}\right)\Phi \tag{10}$$

equivalent to Eqs. (8) and (9). This nonlinear Schrödinger equation is solved in three dimensions using the powerful techniques developed for solving the electronic TDLDA problem [24].

First results.—We are now going to compare the well established TDLDA results to those obtained within the TDTF approximation.

The spectrum of dipole oscillations is evaluated by recording the dipole moment $D(t)$ during time evolution and Fourier transforming the total sampled signal to $D(\omega)$. The dipole power spectrum is then obtained as $|D(\omega)|^2$. The number of emitted electrons $N_{\rm esc}$ is defined as the number of electrons outside a spherical box of radius $R_J + 2r_s$ (R_J being jellium radius and r_s Wigner-Seitz radius), centered around the ionic center of mass.

Figure 2 shows $|D(\omega)|^2$ and $N_{\rm esc}(t)$ predicted by TDTF, TDLDA, and Vlasov simulations for Na_9^+ with jellium background and initialized with an excitation energy of 4.7 eV, namely, slightly beyond linear regime. For both plotted quantities, we see a reasonable agreement between TDTF and TDLDA, which hints at the relevance of the TDTF approximation in that case. Note, however, that the TDTF spectrum is slightly narrower. This reflects an underestimated dissipation, as argued in the previous section. The Vlasov computation, on the other hand, overestimates the width of the peak due to spurious dissipation in the Vlasov dynamics [6,7]. The numbers of emitted electrons $N_{\rm esc}$ also compare fairly well, although TDTF somewhat overestimates $N_{\rm esc}$. This is probably due to the fact that the Fermi level obtained in the TF approximation lies higher in energy than the corresponding LDA highest occupied molecular orbital. The Vlasov result for $N_{\rm esc}$ also appears reasonable, but strongly depends on the numerical parameters used to represent the phase-space distribution $f(\mathbf{r},\mathbf{p},t)$ [6,7]. Altogether, systematic comparisons at various excitation energies show that the TDTF model provides a fair approximation to the exact TDDLA result. We thus conclude that among the two semiclassical models considered here, TDTF performs the best.

The Na_9^+ cluster is a particular case where the optical spectrum shows a well isolated plasmon peak with little Landau fragmentation. In order to have an essentially different case, we consider electron excitation in Na_{20} where the interplay between collective and individual motions is stronger [25]. This time, the ionic background is treated by local pseudopotentials, the ground state geometry being obtained in the cylindrically averaged pseudopotential scheme model [26]. Figure 3 shows the power spectra corresponding to a shift along the longest cluster's axis, both in the linear ($E^* = 2.6$ eV) and in the nonlinear ($E^* = 9.7$ eV) regimes. In the linear case, the TDLDA

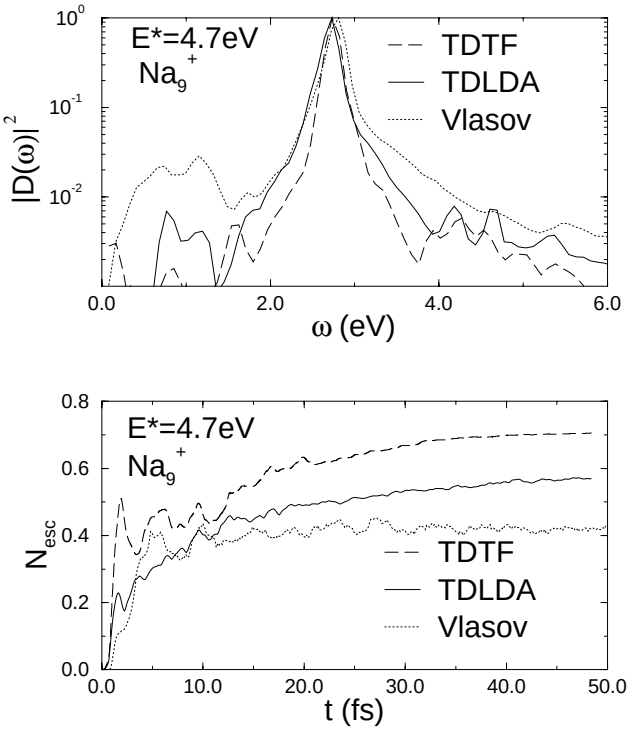

FIG. 2. Dipole power spectrum (upper part) and number of emitted electrons (lower part) in Na_9^+ as obtained by TDLDA, TDTF, and Vlasov simulations for $E^* = 4.7$ eV.

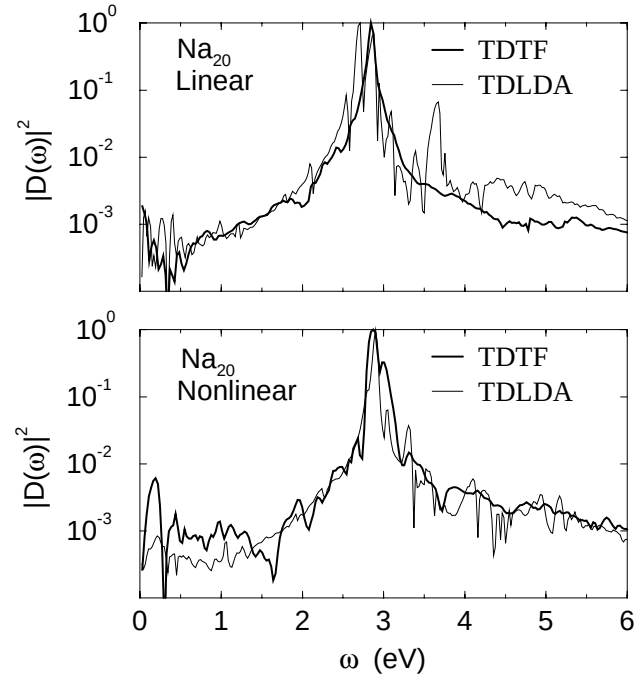

FIG. 3. Dipole power spectra in Na_{20} in the linear (upper part) or nonlinear (lower part) regimes. The oscillatory motion is performed along the longest axis of the cluster.

spectrum shows a fragmented, double peak structure. The TF approach, averaging out single particles levels, smooths down the power distribution with respect to the TDLDA result and yields only one average plasmon peak. Notice, also, that it fails to reproduce the particle-hole transition at 3.6 eV. The nonlinear TDLDA spectrum, at the opposite, hardly shows any structure. In this regime, the intrinsic deficiencies of TDTF to reproduce Landau fragmentation are of little importance and the spectra obtained in the two methods become very similar. From these computations in Na_{20} we conclude that TDTF can be reasonably trusted where the high energy electron dynamics is concerned, as could be expected for the semiclassical methods at high energy.

The above tests of the TDTF method have been carried out for relatively small clusters as these represent the most critical test conditions and as TDLDA calculations are readily available. Semiclassical approaches usually become more justified and efficient with increasing system size [11]. To demonstrate the performance for a larger cluster, we consider Na_{93}^{+} with jellium background as a test case and plot in Fig. 4 the dipole strength $S(\omega) = \mathrm{Im}[D(\omega)]$ for small amplitude excitations [14] in comparison with the experimental absorption cross section [27] and with quantal RPA results [28]. As in [28], the spectrum has been convoluted with a Lorentzian profile with width $0.1\omega_{\mathrm{plasmon}}$, which simulates the inhomogeneous line broadening by ionic vibrations. We see again that TDTF provides the appropriate average peak position but misses, of course, the substantial Landau fragmentation. The deficiency to miss Landau fragmentation thus naturally persists also for large clusters. The full TDLDA results converge, nonetheless, towards the TDTF picture with increasing system size because the fragmentation structure will be more and more washed out such that the spectra resemble more to one pronounced peak. The width of the peak, however, remains always underestimated by TDTF. But this feature can be corrected in a further step by complementing TDTF with a friction term.

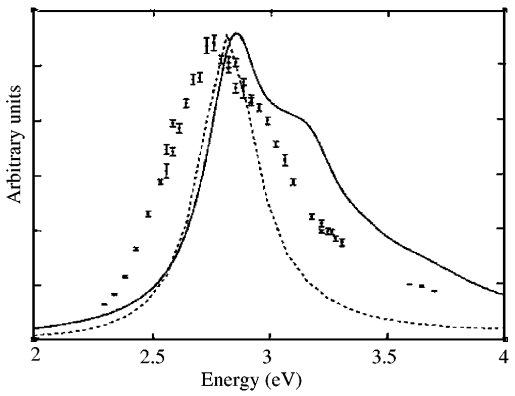

FIG. 4. TDTF strength function in Na_{93}^{+} (dashed line) as compared to experiment ([27], error bars) and RPA ([28], full line).

In this paper, we have demonstrated the capabilities of TDTF for studying the fs dynamics of the electron cloud in metal clusters as one typical example for many-fermion dynamics. The TDTF is a hydrodynamical approach which describes the system solely in terms of collective flow. It manages to describe properly the gross features of a cluster's electronic dynamics which is dominated by the collective plasmon oscillations. Moreover, TDTF gives also a pertinent picture of electron emission. By construction, the TDTF method neglects any detailed particle-hole excitations with the consequence that dissipation (from Landau fragmentation) is underestimated. This disease will be cured in future versions of TDTF by adding a viscosity component into the underlying hydrodynamics. But already the present result is very encouraging showing that TDTF can be used with confidence to describe the gross features of electron dynamics. This will be particularly useful for very large clusters where fully time-dependent LDA calculations are not yet feasible.

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