On dissipative effects in volume plasmon response

P.-G. Reinhard\textsuperscript{a}, E. Krötscheck\textsuperscript{b}, E. Suraud\textsuperscript{b,c,d}

\textsuperscript{a}Institut für Theoretische Physik, Universität Erlangen, D-91058 Erlangen, Germany
\textsuperscript{b}Physics Department, University at Buffalo, The State University New York, Buffalo, NY 14260, USA and
\textsuperscript{c}Institute for Theoretical Physics, JKU Linz, Linz, Austria
\textsuperscript{d}Université de Toulouse, UPS; Laboratoire de Physique Théorique (IRSAMC), F-31062 Toulouse Cedex, France
\textsuperscript{e}CNRS; LPT (IRSAMC), Université de Toulouse, F-31062 Toulouse Cedex, France
E-mail: suraud@irsamc.ups-tlse.fr

Abstract. We study the importance of dissipation on the volume plasmon response in moderate size Sodium clusters. Volume plasmon response has been tentatively identified experimentally in Sodium clusters. An open question is whether the standard mean-field approach, based on Density Functional Theory (DFT), is sufficient to provide a proper description of such modes in a possibly non-linear regime of excitations. A conceptually simple approximation, based on a recently proposed quantum Relaxation Time Ansatz (RTA), is used to evaluate these effects. It turns out that the response is, in the explored cases, clearly dominated by the mean field, which allows the use of simplified theories that give access to larger systems.

1. Introduction
Finite fermions systems have for a long time been investigated by studying collective excitations [1]. In metal clusters, the optical response provides a key to understanding dynamical scenarios in a wide range of excitation energies [2, 3]. It has been studied especially in the low-energy/long-wavelength domain where the Mie surface plasmon plays a dominant role [4, 5]. Still, traces of volume plasmon excitations (associated with local density oscillations) have also been tentatively observed experimentally [6], along the lines of earlier theoretical investigations [7]. These results in metals complement similar investigations on volume plasmon modes in C\textsubscript{60} [8, 9].

A standard way to analyze collective modes is to study the dynamic structure function $S(k, \omega)$ of the system. Many investigations of $S(k, \omega)$ have been carried out in the long-wavelength limit ($k \rightarrow 0$), providing a good description of the low energy surface plasmon ($\omega$ around 2-3 eV) in simple metal clusters [10, 4]. “Volume” modes are expected to appear in the UV regime around 5-6 eV [7] and $S(k, \omega)$ should as well describe these excitations finite systems.

Time Dependent Density Functional Theory (TDDFT) in real time offers a complementary way to address such questions [11]. The theory has proven robust and flexible for the analysis of cluster dynamics [12, 2], especially at the Local Density Approximation level (TDLDA). Unlike linear response theory, TDLDA is not restricted to the linear domain and allows to address a large variety of dynamical scenarios [12, 3]. It remains, of course, a mean field theory ans is, therefore, limited to moderate excitation amplitudes. In the realm of larger excitations, TDDFT should in principle be complemented by a dissipative component built on top of TDLDA. The rigorous inclusion of dissipation in finite quantum systems is still an open problem, but there
exist pragmatic approaches which allow to estimate the potential impact of such effects [13]. Among others aspects it was shown that the surface plasmon response can be affected by dissipative effects. The case of volume plasmons has not yet been addressed in this way. It would nevertheless be interesting to explore that aspect in order to see to what extent a TDLDA approach, as used in [14], is validated at pure TDLDA level, which in turn would further justify other approaches as explored in [14]. This is the purpose of this short paper to explore that case.

The theoretical issues are addressed in section 2. A few illustrative results are presented in section 3, conclusions are drawn in section 4.

2. Theoretical approach

2.1. Mean field basics

Our starting point is a mean-field description of electron dynamics. We treat the systems by time-dependent density functional theory at the level of the Time-Dependent Local-Density Approximation (TDLDA). We formulate TDLDA within the usual Kohn-Sham picture on the basis of occupied single-particle (s.p.) wavefunctions \{|\varphi_i\rangle, i = 1 \ldots N\} determined by the time-dependent Kohn-Sham equation

\[
i \partial_t |\varphi_i\rangle = \hat{h}[\varrho]|\varphi_i\rangle
\]  

(1)

At the TDLDA level, the Kohn-Sham mean-field Hamiltonian \(\hat{h}[\varrho]\) is a functional of the instantaneous local density \(\varrho(r, t) = \sum_i |\varphi_i(r, t)|^2\) [15].

The time propagation can be expressed in a simple matrix form in terms of the one-body density matrix \(\hat{\varrho}\):

\[
i \partial_t \hat{\varrho} = \left[\hat{h}[\varrho], \hat{\varrho}\right].
\]  

(2)

In general, \(\hat{\varrho}\) and \(\hat{h}\) are not simultaneously diagonal during time evolution. One often prefers the basis of natural orbitals in which \(\hat{\varrho}\) is diagonal (and \(\hat{h}\) is not). The one-body density matrix is then expressed as

\[
\hat{\varrho} = \sum_{\alpha=1}^{\infty} |\phi_\alpha\rangle W_\alpha \langle \phi_\alpha |.
\]  

(3)

where the weights \(W_\alpha\) are the probability with which a state \(|\phi_\alpha\rangle\) is occupied. The local density is then expressed as \(\varrho(r, t) = \sum_\alpha W_\alpha |\phi_\alpha(r, t)|^2\). In a pure TDLDA evolution, the weights \(W_\alpha\) do not depend on time and the time propagation is fully accommodated by the time evolution of the \(|\phi_\alpha(t)\rangle\). Changes in \(W_\alpha\) and fractional \(W_\alpha\) can only be generated by dissipation which is an effect beyond TDLDA.

2.2. A quantum Relaxation Time Ansatz (RTA)

A formally simple way to include a dissipative component into mean-field evolution by is to add a collision term \(i\partial_t \hat{\varrho} - [\hat{h}, \hat{\varrho}] = \hat{I}[\hat{\varrho}]\) [16, 17] to the time evolution of the density matrix Eq. (2). Following experience gained in classical and semi-classical cases [18], we approximate the quantum collision term by a Relaxation Time Approximation (RTA) which leads to the dynamical equation

\[
\partial_t \hat{\varrho} = -i[\hat{h}, \hat{\varrho}] - \frac{1}{\tau_{\text{relax}}} (\hat{\varrho} - \hat{\varrho}_{\text{eq}}[\varrho, j, E]),
\]  

(4)

Two key quantities enter this expression: \(\hat{\varrho}_{\text{eq}}\) represents the density operator of the thermally equilibrated state, “constrained by” the local density \(\varrho(r, t)\), current distribution \(j(r, t)\) and total energy \(E(t)\) at the given instant \(t\) where the collision term is applied; \(\tau_{\text{relax}}\) is the relaxation time.
starting point: \( \dot{\rho}(t) = \sum_{\alpha} |\phi_{\alpha}(t)\rangle W_{\alpha}(t) \langle \phi_{\alpha}(t)| \)

1. mean-field propagation: 
   \( |\phi_{\alpha}^{\text{mf}}(t)\rangle = \hat{U}(t + \Delta t, t)|\phi_{\alpha}(t)\rangle \)
   
   \( W_{\alpha}(t) = W_{\alpha}^{\text{mf}} = \text{const.} \)

   \( \dot{\rho}_{\text{mf}}(t + \Delta t) = \sum_{\alpha} |\phi_{\alpha}^{\text{mf}}(t)\rangle \langle \phi_{\alpha}^{\text{mf}}(t)| \)

   \( g_{\text{mf}}(r, t + \Delta t), \dot{J}_{\text{mf}}(r, t + \Delta t), E_{\text{mf}} \)

2. density-constrained mean field (DCMF)

\[ \dot{\rho}_{\text{eq}} = \dot{\rho}_{\text{eq}}[g_{\text{mf}}(r), \dot{J}_{\text{mf}}(r), E_{\text{mf}}] \]

\[ \dot{\rho}_{\text{eq}} = \sum_{\alpha} |\phi_{\alpha}'\rangle W'_{\alpha} \langle \phi_{\alpha}'| \]

3. intrinsic excitation energy \( E_{\text{intr}}^{\ast} \)

\[ h\tau_{\text{relax}}^{-1} = 0.40 \frac{\sigma_{ee} r_s^2}{N} E_{\text{intr}}^{\ast} \]

\[ \dot{\rho}(t + \Delta t) = \rho_{\text{mf}}(t + \Delta t) - \frac{\Delta t}{\tau_{\text{relax}}} [\dot{\rho}_{\text{mf}} - \dot{\rho}_{\text{eq}}] \]

4. diagonalize to natural orbitals:

\[ \dot{\rho}(t + \Delta t) = \sum_{\alpha} |\phi_{\alpha}(t + \Delta t)\rangle W_{\alpha}(t + \Delta t) \langle \phi_{\alpha}(t + \Delta t)| \]

5. final fine-tuning of \( W_{\alpha} \) to reproduce \( E_{\text{mf}} \)

\[ \dot{\rho}(t + \Delta t) = \sum_{\alpha} |\phi_{\alpha}(t + \Delta t)\rangle W_{\alpha}(t + \Delta t) \langle \phi_{\alpha}(t + \Delta t)| \]

Figure 1. Sketch of the scheme for performing RTA time step \( t \rightarrow t + \Delta t \). Taken from [13].

which is estimated by semi-classical Fermi liquid theory [13]. In the Sodium clusters examined here, \( \tau_{\text{relax}} \) is

\[ \frac{\hbar}{\tau_{\text{relax}}} = 0.40 \frac{\sigma_{ee}}{r_s^2} E_{\text{intr}}^{\ast} \]

Above, we have introduced the intrinsic (thermal) energy \( E_{\text{intr}}^{\ast} \) of the system and the in-medium electron-electron cross section \( \sigma_{ee} \) (\( r_s \) is the effective Wigner-Seitz radius of the electron cloud). See [13] for technical details.

Note that the RTA equation (4) is very involved because many entries depend in various ways on the actual state \( \dot{\rho}(t) \) of the system. Equation (4) determines the mean field Hamiltonian \( \hat{h} = \hbar [\hat{g}] \) as well as the instantaneous equilibrium density \( \dot{\rho}_{\text{eq}} \), which is attained by calculations with with constraint on the actual \( g(r) \), \( j(r) \) and energy \( E \), which is obtained by calculations constrained by the actual \( g(r), j(r) \) and energy \( E \). In practice, the RTA evolution is performed every \( \Delta t \) time intervals on top of mean-field evolution performed at a finer \( \delta t \) time step. For the sake of clarity the actual RTA evolution is sketched in Figure 1.

2.3. TDLDA and RTA description of finite momentum response

The goal of this paper is to investigate the importance of dissipation for the response at finite momentum transfer. The response of the system can be rather simply examined within the real time TDLDA used here and similarly within RTA described above. This response has been widely studied in the long-wavelength limit. Real time TDLDA (or RTA) evolution is initialized by an initial boost \( \exp (i a z) \) acting on all single electron wavefunctions (\( \phi_i \) or \( \phi_{\alpha} \), which coincide at initial time). The boost amplitude controls the degree of linearity of the process. The response is analyzed via the dipole operator along the boost excitation axis \( z \) as \( D(t) = \int d^3r z \hat{g}(r) \). Its
An alternative procedure to calculate the response to an external field

2.4. The response approach: An alternative to real time TDLDA

where the asterisk and the inverse is understood as the convolution product. The

The above boost mechanism dominantly excites the surface plasmon. In order to access the
volume plasmon we use a finite momentum \( k \) excitation operator:

\[
\varphi_i(r, t) \rightarrow \exp(iaj_1(kr)z/r)\varphi_i(r, t)
\]

where \( r^2 = |r|^2 \), and \( j_1(x) \) is the spherical Bessel function of order 1. The amplitude
parameter \( a \) can again be chosen freely, for example to remain in the linear response regime
where it disappears from the final analysis. The response is analyzed as in case of the surface
plasmon but now considering the Bessel weighted dipole

\[
D_1(t) = \int d^3r \varrho(r, t)j_1(kr)z/r
\]

in time. Spectral information is then again obtained by Fourier transforming \( D_1(t) \rightarrow \tilde{D}_1(\omega) \).

As is obvious from the above definitions, the TDLDA and RTA frameworks are equally suited
to study the response at any finite momentum: the excitation mechanism is performed the same
way in both cases and the response is analyzed via observables directly attained though the
matter density \( \varrho(r) \).

2.4. The response approach: An alternative to real time TDLDA

An alternative procedure to calculate the response to an external field \( \delta U_{\text{ext}}(r, t) \) is to linearize
equations of motion and compute the induced density \( \delta \varrho(r, t) \) directly expressed from the density-
density response function \( \chi(r, r'; \omega) \):

\[
\delta n(r, t) = n(r) \int d^3r'\chi(r, r'; \omega)\delta U_{\text{ext}}(r, \omega).
\]

The response function can be computed starting from the stationary Kohn-Sham wave
functions \( \varphi_i(r) \) and restricting excited states to one-particle-one-hole excitations. This basically
leads to the RPA response function

\[
\chi(r, r'; \omega) = [(1 - \chi_0 * V_{p-h}^{-1} * \chi_0)](r, r'; \omega)
\]

where the asterisk and the inverse is understood as the convolution product. The \( \chi_0 \) is the non
interacting response function and the particle-hole interaction \( V_{p-h} \), LDA level, consists of the
Coulomb potential and a contact interaction associated to the exchange-correlation correction,

\[
V_{p-h}(r, r') = V_c(|r - r'|) + \frac{d^2\varepsilon_{xc}(\varrho)}{d\varrho^2}\delta(r - r')
\]

where \( \varepsilon_{xc}(\varrho) \) is the local exchange-correlation energy density.

Only the diagonal part of the density-density response function is probed in inclusive
scattering experiments

\[
\chi(k; \omega) = \frac{1}{N} \int d^3r d^3r' e^{i(k \cdot (r - r'))}\chi(r, r'; \omega).
\]

and the dynamic structure function \( S(k, \omega) \) is then

\[
S(k, \omega) = \frac{1}{\pi} Im\chi(k; \omega) \quad (\omega > 0).
\]