Collective versus single-particle effects in the optical spectra of finite electronic quantum systems

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We study optical spectra of finite electronic quantum systems at frequencies smaller than the plasma frequency using a quasi-classical approach. This approach includes collective effects and enables us to analyse how the nature of the (single-particle) electron dynamics influences the optical spectra in finite electronic quantum systems. We derive an analytical expression for the low-frequency absorption coefficient of electro-magnetic radiation in a finite quantum system with ballistic electron dynamics and specular reflection at the boundaries: a two-dimensional electron gas confined to a strip of width $a$ (the approach can be applied to systems of any shape and electron dynamics - diffusive or ballistic, regular or irregular motion). By comparing with results of numerical computations using the random-phase approximation we show that our analytical approach provides a qualitative and quantitative understanding of the optical spectrum.

Optical spectra of finite metallic systems have been intensively investigated for almost a century. Early approaches such as Mie’s [1] are of classical nature. In [1] the absorption of electro-magnetic radiation by conducting spheres is determined. It is shown that the absorption spectrum exhibits a resonance at $\omega_p/\sqrt{3}$ (where $\omega_p$ is the bulk plasma frequency) due to collective motion of the charge carriers.

In the last decades there has been a substantial amount of work on the nature of such collective resonances in metallic clusters [2], nuclei [3], thin films [4-6], small metal particles [7], and dimensionally reduced quantum systems [8-10], investigating, in particular, quantum-mechanical effects. In most of these cases, the electron dynamics is ballistic (the mean free path $\ell$ is larger than the system size $a$). The majority of theoretical papers on the Mie resonance of finite metallic systems use the so-called random phase approximation (RPA), a self-consistent, quantum-mechanical approach incorporating collective effects. The nature of the Mie resonance in finite electronic quantum systems is well understood, both qualitatively and quantitatively (for a recent review see for instance [1]).

The emergence of the field of Mesoscopic Physics has fueled an increased interest in the electronic and optical properties of finite, disordered quantum systems (with diffusive electron dynamics, $\ell \ll a$) in external fields. In this context, attention has largely focussed on (quasi-)static properties, $\omega \approx \Delta/h$, where $\Delta$ is the mean level spacing of the system in question (which is generally smaller than $\omega_p$, by many orders of magnitude). Mesoscopic fluctuations of the static polarisability and the capacitance, for instance, were characterised in [11], and the electron density itself in [12]. In all of these cases, collective effects must be taken into account in order to adequately deal with the screening of the external field. In the static limit, a Thomas-Fermi (TF) ansatz is appropriate [11-13].

Much less is known about optical spectra in the low-frequency region $\Delta/h < \omega \ll \omega_p$, despite the fact that this regime is of particular interest: one expects that the spectra strongly depend on the nature of the (single-particle) electron dynamics: In ballistic systems, for example, it was argued [13] that optical spectra should exhibit resonances near multiples of $\omega_c = \pi v_F/a$ (see also [14]). Usually $\Delta/h \ll \omega_c \ll \omega_p$. According to [13], these resonances should overlap to give a linear frequency dependence of the absorption coefficient for $\omega \gg \omega_c$ in two-dimensional systems (classical and local electro-magnetic theories predict a quadratic dependence independent of dimension). These are striking and unexpected results. They were, however, obtained within a TF approximation which is valid in the static limit. It must be examined to which extent dynamic screening effects may modify the results [13].

Furthermore, in systems with ballistic chaotic dynamics, the optical spectra should, at least within a single-particle picture, reflect universal energy-level correlations found in classically chaotic quantum systems [16]. This issue was addressed in the seminal paper by Gorkov and Eliashberg [17], investigating the polarisability of metallic particles with disordered walls. However, the treatment neglects screening effects all together [18-20]. How does dynamical screening modify this picture?

Numerical calculations (based, for instance on the RPA) are ill-suited to answer these questions: They provide little qualitative insight in the low-frequency region and, more importantly, it is necessary to consider small systems or to make use of symmetries in order to make the numerical computations feasible. Disordered and (asymmetric) chaotic systems are very difficult to deal with. In order to understand how the classical single-particle dynamics is reflected in optical spectra of finite quantum systems, it is thus greatly desirable to have an analytical theory incorporating collective effects.

The main result of this paper is an analytical expres-
sion for the absorption properties of a two-dimensional electron gas confined to a strip of width \( a \) [eqs. (14) and (13)]. This example exhibits all features of more complicated geometries. However, in the case discussed here, numerical RPA calculations are feasible and allow us to discuss the accuracy of the analytical approach.

In the following it is assumed that \( \Delta / \hbar < \omega < \omega_p \), \( E_F / \hbar \) where \( E_F \) is the Fermi energy. It is furthermore assumed that \( \lambda, \lambda_0 \gg a \gg \lambda_p \) where \( \lambda \) is the wavelength of the external radiation, \( \lambda_0 \) is the skin depth and \( \lambda_p \) is the Fermi wave-length.

We consider a closed metallic quantum system placed in an external electric field \( E_{\text{ext}} \) [with a time dependence \( \propto \exp(i \omega t) \)]. If the wave-length is much larger than the system size, the external field is approximately constant throughout the system and (neglecting retardation effects) can be written as the gradient of an electric potential \( \varphi_{\text{ext}}(r) = E_0 r \cdot \mathbf{e}_z \) \( r = (x, y, z) \) is a three-dimensional coordinate vector]. Within the RPA, the electronic response of the system to \( E_{\text{ext}} \) is calculated by solving a set of self-consistent equations for the effective electrical potential \( \varphi(r) = \varphi_{\text{ext}}(r) + \delta \varphi(r) \) \( \delta \varphi(r) \) is the potential due to the induced charge density \( \delta \varphi(r) \)

\[
\delta \varphi(r) = \int \mathrm{d}r' G(r, r') \delta \varphi(r'),
\]

(1)

with the boundary condition that \( \delta \varphi(r) \) vanishes as \( |r| \to \infty \). \( G(r, r') \) is the Green function of the Laplace equation \( \Delta G(r, r') = -\epsilon_0^{-1} \delta(r-r') \), \( \epsilon_0 \) is the dielectric constant. \( \Pi_0(r, r'; \omega) \) is the non-local polarisability

\[
\Pi_0(r, r'; \omega) = -2\varepsilon^2 \sum_{\alpha, \beta} \frac{f(\varepsilon_{\alpha}) - f(\varepsilon_{\beta})}{\varepsilon_{\alpha} - \varepsilon_{\beta} - i\hbar \omega + \gamma} \times \psi_{\alpha}^*(r') \psi_{\beta}(r') \psi_{\alpha}(r') \psi_{\beta}^*(r),
\]

(2)

\( \varepsilon \) is the electron charge, \( \varepsilon_{\alpha} \) and \( \psi_{\alpha}(r) \) are the single-particle eigenvalues and eigenfunctions of the undisrupted system, they are usually calculated with in a Hartree-Fock or a local-density approximation. \( f(\varepsilon) = \Theta(E_F - \varepsilon) \), and \( \gamma > 0 \) is smaller than \( \Delta \). Within the RPA, the absorption coefficient (proportional to the energy dissipation per unit time) may be written as

\[
\alpha(\omega) = \frac{\hbar \omega}{2E_0^2} \Im d(\omega)
\]

(3)

where

\[
d(\omega) = \int \mathrm{d}r \mathrm{d}r' \delta \varphi^*(r) \Pi_0(r, r'; \omega) \varphi(r')
\]

(4)

is the (complex) dipole moment and the asterisk denotes complex conjugation.

In the following we derive an explicit analytical expression for the absorption coefficient \( \alpha(\omega) \) of a finite electronic quantum system in an external electric field, valid in the frequency range \( \Delta / \hbar < \omega \ll \omega_p \). We make use of the approximations suggested in [21]. First, according to Fermi’s golden rule, the absorption coefficient is

\[
\alpha(\omega) \simeq \frac{\pi \hbar^2 \omega^2}{2 \Delta^2 E_0^2} \left| \langle \psi_{\alpha} | \varphi | \psi_{\beta} \rangle \right|^2 \frac{\epsilon_{\alpha} \simeq E_F}{\epsilon_{\alpha} - \epsilon_{\beta} - i\omega}. \tag{5}
\]

Second, the matrix elements of \( \varphi \) are evaluated within a semi-classical approximation [14,22,23]. Third, \( \delta \varphi \) itself is determined within a quasi-classical approximation: according to [11], the effective electric potential is given by (in symbolic notation)

\[
\varphi = -\Pi_0^{-1} \delta \varphi.
\]

(6)

In order to determine \( \delta \varphi \), eqs. (1) are usually solved numerically, using a real-space discretisation [29] or by expanding in a suitable basis set. An approximate analytical solution may be obtained by noting that for \( \omega \ll \omega_p \), \( ||\langle G \Pi_0 || \gg 1 \). In other words, \( \delta \varphi \) is well approximated by the classical charge density \( \delta \varphi_{\text{cl}} \) of the metallic system subjected to an external potential \( \varphi_{\text{ext}} \),

\[
\Delta \varphi_{\text{cl}} = -\delta \varphi_{\text{cl}} / \epsilon_0
\]

(7)

with \( \varphi_{\text{cl}}(r) \to \varphi_{\text{ext}}(r) \) as \( |r| \to \infty \) and \( \varphi_{\text{cl}} = 0 \) within the system (in the classical limit, the external field is thus screened out completely). Eq. (7) may be solved for \( \delta \varphi_{\text{cl}} \) using standard methods [27].

Fourth, \( \Pi_0 \) is determined within a quasi-classical approximation [28,21]

\[
\Pi_0(r, r'; \omega) = e^2 \nu_d \left[ \delta(r-r') + i \omega P^{(d)}(r, r'; \omega) \right]
\]

(8)

where \( \nu_d \) is the density of states per unit volume in \( d \) dimensions and \( P^{(d)}(r, r'; \omega) \) is the Fourier transform of the classical propagator \( P^{(d)}(r, r'; t) \). In ballistic systems it is written as a sum over classical paths \( p \) from \( r \) to \( r' \)

\[
P^{(d)}(r, r'; \omega) = \sum_{\text{cl. paths } p} \left| \det \left[ \frac{\partial (r')}{{\partial (r, n_p)}} \right] \right|^{-1} \exp(i \omega \tau_p). \tag{9}
\]

Here \( \tau_p \) is the time taken from \( r \) to \( r' \) along the path \( p \), and \( n_p \) is a unit vector describing the direction of the initial velocity. For diffusive systems see e.g. [29].

In the following we show by comparison with quantum-mechanical RPA calculations that [11,14] provide a qualitative and quantitative description of absorption in the frequency range \( \Delta / \hbar < \omega \ll \omega_p \).

**Two-dimensional strip.** We consider a two-dimensional electron gas confined to a strip in the \( x-y \)-plane surrounded by vacuum [20], subject to a time-dependent electric field \( E_{\text{ext}} \) directed along the negative \( x \)-axis [compare fig. 1(a)]. The width of the strip (along the \( x \)-axis) is \( a \), its length \( L \) (along the \( y \)-axis), with \( L \gg a \). Within the system, the electrons move ballistically, and they are specularly reflected at the boundaries at \( x = \pm a/2 \).
We write \( \delta g(r) = \delta \sigma(x, y) \delta(z) \). For \( L \gg a \), the surface-charge density \( \delta \sigma \) depends on \( x \) only and the resolvent \( G \) is written as

\[
G = \frac{1}{\epsilon_0} \int \frac{dq}{2\pi i} \frac{1}{q} e^{i q(x-x')} e^{-|q||z-z'|}. \tag{10}
\]

With

\[
\frac{1}{L} \int dy dy' \Pi_0(r; r'; \omega) = \Lambda_0(x, x'; \omega) \delta(z) \delta(z'), \tag{11}
\]

the RPA-equations \([1]\) are reduced to a set of one-dimensional equations for \( \varphi(x, z = 0) \) with the kernel \( \Lambda_0(x, x'; \omega) \). We model the confinement in the \( x \)-direction by introducing hard-wall boundary conditions. This is adequate in the range of parameters considered below and simplifies the quasi-classical analysis. We solve the resulting self-consistent equations numerically using a real-space discretisation and obtain the absorption coefficient from \([2]\).

The corresponding quasi-classical approximation for \( \alpha(\omega) \) is obtained as described above: the classical surface-charge density is determined by solving \([1]\) in elliptic cylinder coordinates: \( \delta \sigma_{cl}(x) = 2\epsilon_0 E_0(\alpha^2 - x^2)^{-1/2} \Theta(|x| - a/2) \). The corresponding classical field lines are shown in fig. 2(a). According to eqs. \([3,4]\) the one-dimensional kernel \( \Lambda_0(x, x'; \omega) \) is given by a sum over classical paths as shown in fig. 2(b) which may be summed by Poisson summation. Using \([4]\) one obtains for the effective electric potential

\[
\varphi(x) = \sum_{\mu > 0} \varphi_\mu \cos \left[ \frac{\mu \pi (x/a + 1/2)}{2} \right], \tag{12}
\]

\[
\varphi_\mu = 2\pi \epsilon_0 E_0 \frac{\sqrt{\omega^2 - \omega_0^2}}{\omega^2 - \omega_0^2} \sin \left( \frac{\mu \pi}{2} \right) J_1 \left( \frac{\mu \pi}{2} \right). \tag{13}
\]

Eq. \([13]\) has an intuitive interpretation: neglecting a correction term \( \varphi_{bdy}(x) \) which is small except for \( x \) in a boundary layer of width \( \delta x \propto v_F/\omega \), eq. \([12]\) can be written as a sum over two terms

\[
\varphi \simeq \varphi_{stat} + \varphi_{dyn} \tag{13}
\]

where \( \varphi_{stat}(x, z = 0) = (\epsilon_0 q_s)^{-1} \delta \sigma(x) \) is the (linearised) TF potential \( (q_s = e^2 v_F/\epsilon_0) \) is the two-dimensional TF screening vector) and \( \varphi_{dyn} \) is a dynamical contribution corresponding to a current building up the screening charges. It obeys \( \partial^2 \varphi_{dyn}/\partial x^2 = -(m_e \omega^2/e^2) \delta \sigma/\epsilon_0 \) where \( m_e \) is the electron mass and \( \sigma_0 \) is the areal charge density of the electrons.

Fig. 2(a) shows \( \varphi(x) \) according to \([12]\) and \([13]\) compared with the results of a numerical RPA calculation. One observes excellent agreement (and \( \varphi_{bdy} \) is small except at the boundary). Our results show that for larger frequencies \( \omega > \omega_c \), the dynamical potential \( \varphi_{dyn} \) makes a significant contribution to \( \varphi \) and dynamical screening effects cannot be neglected. For the absorption coefficient we obtain using eqs. \([3]\) and \([4]\)

\[
\alpha(\omega) \simeq \frac{\pi^2 h^2}{e^2 v_F} \frac{\omega^2}{\omega_c^2} \sum_{\mu > |\omega|/\omega_c} \frac{\sqrt{\mu^2 \omega^2 - \omega^2}}{\mu^2} J_1^2(\mu \pi/2) \tag{14}
\]

with limiting forms

\[
\alpha(\omega) \simeq \begin{cases} 
\frac{\pi^2 \hbar^2}{e^2 v_F} \frac{\omega^2}{\omega_c^2} \sinh(\mu \pi) J_1^2(\mu \pi/2) & \text{for } \omega \ll \omega_c, \\
\pi \hbar^2 \omega_c/4e^2 v_F & \text{for } \omega \gg \omega_c \end{cases} \tag{15}
\]

and \( C \simeq 0.12 \). In fig. 2(b), we show quantum-mechanical RPA results in comparison with eqs. \([14]\) and \([15]\) and observe excellent agreement. We observe prominent resonances in the absorption coefficient near odd multiples of \( \omega_c \), due to single-particle cyclotron orbits (electrons moving in phase with the external field). This establishes that the single-particle resonances conjectured in \([3]\) exist within the RPA. Their positions, strengths and shapes are very well described by \([4]\). Eq. \([15]\) and the inset of fig. 2(b) show that in the limit of large frequencies (\( \omega \gg \omega_c \)), the absorption coefficient is linear in \( \omega \). In the opposite limit (\( \omega \ll \omega_c \)) where the TF approach is adequate, it is quadratic.

We conclude that the quasi-classical approximation described above, for the parameters considered here, provides a quantitative description of the optical properties.

Three-dimensional thin film. To conclude we discuss \( \varphi \) for a thin film \([2]\) of width \( a \) in the \( y-z \)-plane subject to an external potential \( \varphi_{ext}(r) = E_0 x \hat{e}_x \). The classical charge density is concentrated at the boundary, \( \delta \sigma_{cl}(x) = \pm \delta \sigma \delta(x \pm a/2) \). The corresponding static and dynamical contributions to \( \varphi(x) \) are singular: we thus use the TF charge density \([1]\) instead of \( \delta \sigma_{cl} \) (appropriate in the limit of small \( k_\parallel \) corresponding to high electron densities): \( \delta \sigma_{TF}(x) = k_\parallel \epsilon_0 E_0 \sinh(k_\parallel x)/\cosh(k_\parallel a/2) \). Here \( k_\parallel^2 = e^2 v_F/\epsilon_0 \) is the three-dimensional TF screening vector. The RPA equations are easily solved within a real-space discretisation. Our results for \( \varphi(x) \) are shown in fig. 3 and compared to results of the analytical approach using eqs. \([3]\) and \([4]\).

We have also calculated the absorption coefficient for \( \Delta/\hbar < \omega \ll \omega_p \) within the RPA. The analytical approach must be used with caution in the case of the film since it requires that \( \varphi \) be smooth on the scale of \( \lambda_F \). It turns out that \( \alpha(\omega) \) is, to a good approximation, quadratic in \( \omega \) as opposed to the two-dimensional case. As in \( d = 2 \) dimensions we observe resonances near odd multiples of \( \omega_c \) (not shown).

[1] G. Mie, Ann. Phys. 25 (1908) 377.
[2] Metal clusters, W. Eckardt, ed., Wiley, Chichester (1999).
[3] Oscillations in finite quantum systems, G. F. Bertsch and R. A. Broglia, CUP, Cambridge (1994).
[4] R. A. Ferrell, Phys. Rev. 111 (1958) 1214.
Collective effects and the nature of the plasma resonances in thin films were discussed in \cite{8} and, within the RPA, in \cite{9,10}.

FIG. 1. (a) Electric field lines (in the x-z-plane) for an infinitely long metallic strip of width \( a \) (in the x-y-plane, oriented along the y-axis) placed in a constant external electric field \( E_{\text{ext}} = -E_0 \delta x \). (b) Classical paths from \( x \) to \( x' \) contributing to \( \Lambda_0(x,x';\omega) \).

FIG. 2. Left: \( \varphi(x) \) for a strip of width \( a = 10^3 \text{[a.u.]} \) with \( r_s = 1 \): quantum-mechanical results (●), analytical results according to eq. \cite{12} (—) and eq. \cite{13} (— —). The inset shows the correction term \( \varphi_{\text{bdy}}(x) \). Right: Shows \( \text{Im} \, d(\omega) \) (for \( a = 10^4 \text{[a.u.]} \) and \( r_s = 1 \)) as a function of \( \omega \): RPA result (— — —) and eq. \cite{14} (— — —). The inset shows \( \alpha(\omega) \) as a function of \( \omega \); RPA result (— — —) and eq. \cite{15} (— — —). As usual \( r_s = r_s/\lambda_0 \) where \( \lambda_0 \) is the Bohr radius and \( r_0 \) is the length scale defined in terms of area per electron.

FIG. 3. Shows \( \varphi(x) \) for a thin film of width \( a = 50 \text{[a.u.]} \) with \( r_s = 1 \): RPA results (●), analytical results according to eq. \cite{16} (—) and using \( \varphi \approx \varphi_{\text{stat}} + \varphi_{\text{dyn}} \) (— —).