Quantum absorption in small metal particles

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We evaluate the electric dipole absorption in small metal particles in a longitudinal electric field taking into account the Fermi-Thomas screening. When either the level broadening or the frequency of the field are larger than the mean energy-level spacing, the main contribution to absorption is classical, with quantum corrections. When both the broadening and the frequency are smaller than the mean level spacing, the absorption is manifestly quantum and can be understood in terms of the two-level system.

I. INTRODUCTION

The classical absorption in small diffusive metal particles and narrow films has been evaluated in a companion paper [1], which hereafter is referred to as I. It was found that, aside from the corrections of the order $(\Lambda L)^{-1}$, where $\Lambda$ is the Thomas-Fermi wave-vector,

$$\Lambda^2 = 4\pi e^2 \frac{dn}{d\mu}$$

$dn/d\mu$ is the thermodynamic density of states and $L$ is the system size, the result coincides with that [2] obtained using the (complex) Drude dielectric constant,

$$\epsilon_D = 1 - \frac{4\pi i \sigma_D}{\omega}$$

for metal characterization. Here

$$\sigma_D = \frac{\sigma_0}{1 + i \omega \tau}$$

is the Drude conductivity, $\sigma_0 = D\Lambda^2/4\pi$ is the Boltzmann conductivity, and $D$ and $\tau$ are, respectively, the electron diffusion coefficient and scattering time.

Namely, for a spherical particle of radius $a$ such that $a\Lambda \gg 1$, the absorption in the oscillating electric field of amplitude $E_0$ and frequency $\omega \ll \tau^{-1}$ is given by [3]

$$Q_{\text{class}} = \frac{9}{2} \left(\frac{\omega E_0}{4\pi}\right)^2 \frac{V}{\sigma_0} \left(1 - \frac{11}{2a\Lambda}\right) = Q_{RD} \left(1 - \frac{11}{2a\Lambda}\right)$$

where $V = 4\pi a^3/3$ is the particle volume. In eq. [4], $Q_{RD}$ is the standard Rayleigh-Drude result for absorption where it is assumed that the applied field is screened due to the surface charge. The second term in parentheses describes the correction due to the fact that the Thomas-Fermi screening occurs, in reality, within the layer $\sim \Lambda^{-1}$ from the particle surface. In what follows, we will neglect such corrections.

The subject of this work is the quantum limit of the electric-dipole absorption. If the level broadening $\gamma$ or $\omega$ are much larger than the mean energy-level spacing $\Delta$ then, barring small quantum corrections, the absorption is classical and is given by eq. [4]. If, however, $\gamma, \omega \lesssim \Delta$, the absorption can be described in terms of the two-level system and is manifestly quantum. We evaluate the temperature dependence of quantum absorption using the ideas - developed in relation to the original work by Gor’kov and Eliashberg [3] - of Lushnikov, Simonov and Maksimenko [4] and Shklovskii [5]. Below, we will assume that $\gamma < \omega \ll D/a^2$ - the inverse time of the electron diffusion to the boundary, and neglect the difference between $Vdn/d\mu$ and $\nu = 2\Delta^{-1}$ - the mean level density at the Fermi level.

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12 accounts for spin degeneracy
II. CLASSICAL ABSORPTION

We refer to I for a detailed analysis of classical absorption. In summary, eq. (4) was obtained as a result of solving the Maxwell equation and the current continuity condition combined with the generalized Einstein transport (constitutive) equation and using the appropriate boundary condition. However, for the purposes which will be explained below, we concentrate on the alternative, yet equivalent, linear-response formulation (6) wherein eq. (4) can be also obtained from (see Appendix B in Ref. [1]).

\[ Q_{\text{class}} = \frac{\omega^2 \Lambda^4 D}{2 (4\pi)^2 \sigma_0} \int \int \phi_{st}(r) d(r, r'; 0) \phi_{st}(r') dr' dr \]

\[ = \frac{\omega^2 E_0^2 \Lambda^4 D}{2 (4\pi)^2 \sigma_0} \int \int f(r) (r \cdot r') d(r, r'; 0) f(r') dr' dr \]

where \( d(r, r'; 0) \) is the static limit of the diffusion propagator (diffusion) satisfying the equation

\[ D \nabla^2 d(r, r'; \omega) = -\delta(r - r') + \frac{1}{r^3} + i\omega d(r, r'; \omega) \]

\[ \nabla_n d(r, r'; \omega) |_{\theta} = \nabla_n d(r, r'; \omega) |_{\theta} = 0 \]

and \( \phi_{st} \) is the (quasi) static potential inside the particle,

\[ \phi_{st}(r) = (-E_0 \cdot r) f(r) \]

The latter falls off exponentially within the layer \( \sim \Lambda^{-1} \) from the particle surface according to

\[ f(r) = \frac{3a}{r^3} \cosh (a \Lambda) i_1 (r \Lambda) \]

\[ i_1(x) = \sqrt{\frac{\pi}{2x}} I_{\frac{1}{2}}(x) \]

where \( i_1(x) \) and \( I_{\frac{1}{2}}(x) \) are the spherical Bessel and Bessel function of imaginary argument respectively. As was already mentioned above, we neglect the corrections in orders of \((a\Lambda)^{-1}\) (the complete expressions can be found in I).

Solving eqs. (7) and (8), we find

\[ d(r, r'; 0) = \frac{1}{4\pi |r - r'|} + \frac{2r}{3V} + \sum_{i=1}^{\infty} \frac{(l + 1) (rr')^l}{4\pi la^{2l+1}} P_l (\cos \theta) \]

where \( P_l (\cos \theta) \) is the Lagrange polynomial and \( \theta \) is the angle between \( r \) and \( r' \). Due to the term \( r \cdot r' = rr' \cos \theta \), only the term \( \propto P_1 (\cos \theta) = \cos \theta \) in eq. (12),

\[ d_1(r, r'; 0) = \left( \frac{1}{4\pi r'^3} + \frac{rr'}{2\pi a^3} \right) \cos \theta \]

contributes to the integral of eq. (6), where \( r_\text{<} \) and \( r_\text{>}_\text{>}_{\text{>}} \) denote the lesser and greater, respectively, of \( r \) and \( r' \). Evaluating the integral, we find the standard Rayleigh-Drude result for absorption, \( Q_{RD} \) in eq. (4).

We emphasize that all above results are obtained, strictly speaking, for \( \ell \Lambda \ll 1 \) (see I). The opposite limit \( \ell \Lambda \gg 1 \) must be a subject of a separate analysis. In such a limit an analogy with the anomalous skin-effect in a transverse field can be drawn wherein the diffusive description of electrons is possible at a distance of order or larger than \( \ell \) from the boundary while the field penetration (skin) depth is smaller than \( \ell \) (3), (8). In the longitudinal field studied here, it is the Thomas-Fermi screening length that plays the role of the field penetration depth. While the depth in the anomalous skin effect is purely dynamical, the Thomas-Fermi depth is dominated by the static component \( \sim \Lambda^{-1} \).

III. QUANTUM ABSORPTION

Quantum absorption can be evaluated using the standard time-dependent perturbation theory (9) where one must distinguish between the transitions in the continuous and discrete spectra. The spectrum can be regarded as effectively continuous when \( \gamma \gg \Delta \) in which circumstance (as well as for \( \omega \gg \Delta \)) it is classical and is given by \( Q_{RD} \), up to quantum corrections. When, on the other hand, \( \gamma, \omega \lesssim \Delta \), the absorption is manifestly quantum and is determined by the two-level physics.
A. Continuous spectrum

For a continuous spectrum, the transition probability per unit time from the state $|i\rangle$ to the states $|f\rangle$ in the interval of energies $d\varepsilon_f$ is given by ($\hbar = 1$)

$$dw_{if} = 2\pi |F_{if}|^2 \delta (\varepsilon_f - \varepsilon_i - \omega) \nu (\varepsilon_f) d\varepsilon_f$$

(14)

where $\nu$ is the level density and $\nu (\varepsilon_f) d\varepsilon_f$ is the number of final states in the energy interval $d\varepsilon_f$. The matrix element $F_{if}$ corresponds to the periodic perturbation of frequency $\omega$.

$$\hat{V} = \hat{F} e^{-i\omega t} + \hat{F}^* e^{i\omega t}$$

(15)

In the present case, $F = \overline{p} \cdot E_0$, where $\overline{p}$ is the dipole moment of a single particle. Using eq. (14) the absorption is found as,

$$Q_{cont} = 2\pi \int \int |F_{if}|^2 (\varepsilon_f - \varepsilon_i) \delta (\varepsilon_f - \varepsilon_i - \omega) \nu (\varepsilon_i) \nu (\varepsilon_f) [n (\varepsilon_i) - n (\varepsilon_f)] d\varepsilon_i d\varepsilon_f$$

(16)

where $\nu (\varepsilon_i) d\varepsilon_i$ is the number of initial states in the interval $d\varepsilon_i$ and $n$ is the Gibbs thermal occupancy of the state.

For electrons in the Fermi sea, the integration reduces to the one over the single-electron states $|i\rangle$ and $|f\rangle$ with the matrix element being that of a single-electron dipole moment $e\hat{R}$. Since each particle has a different impurity configuration, we average over the disorder (denoted by the angular brackets) to find the following expression for the mean value of absorption:

$$\langle Q_{cont} \rangle = \frac{2\pi}{3} \omega^2 \nu^2 E_0^2 \int \int |\hat{R}_{if}|^2 (\varepsilon_f - \varepsilon_i) \delta (\varepsilon_f - \varepsilon_i - \omega) \nu (\varepsilon_i) \nu (\varepsilon_f) [f (\varepsilon_i) - f (\varepsilon_f)] d\varepsilon_i d\varepsilon_f$$

(17)

where $f (\varepsilon)$ is the Fermi thermal occupancy factor. Integration in eq. (17) is performed by changing the integration variables to $y = \varepsilon_f + \varepsilon_i$ and $x = \varepsilon_f - \varepsilon_i$ yielding

$$\langle Q_{cont} \rangle = \frac{2\pi}{3} \omega^2 \nu^2 E_0^2 |\hat{R}_{if}|^2 \frac{\nu (0) \nu (\omega)}{\nu^2}$$

(18)

where the mean position of the Fermi level is chosen to be at zero.

Notice that, in the usual manner [3, 4], we decoupled the matrix element from the level-density correlation function. Moreover, the former is evaluated in the semi-classical approximation, which is justified for the large quantum numbers corresponding to the Fermi level [3, 4]. Finally, $\hat{R}$ must include the effect of screening of the external field $E_0$ [4].

$$\hat{R} = \frac{1}{2} f (r) \hat{r}$$

(19)

A more rigorous quantum-mechanical response-function formulation in Ref. [10] confirms the validity of this procedure.

From the semi-classical expression [3, 4]

$$|\hat{R}_{if}|^2 = \frac{1}{\pi \nu} \int \int (\hat{R} \cdot \hat{R}') d(r, r'; 0) dr' dr$$

(20)

and eqs. (6) and (18), it follows that

$$\langle Q_{cont} \rangle = Q_{RD} \frac{\nu (0) \nu (\omega)}{\nu^2}$$

(22)

showing that, aside from the quantum correction in the correlation function $\nu^{-2} \langle v (0) v (\omega) \rangle$, the result obtained in this approximation coincides with $Q_{RD}$. This is in agreement with Ref. [3].

The expression for $\langle v (0) v (\omega) \rangle$ for any value of level broadening $\gamma$ was derived in Ref. [11]. For $\gamma \gg \Delta$, it is given by a perturbation theory expression [12]

$$\frac{\langle v (0) v (\omega) \rangle}{\nu^2} = 1 + \frac{1}{\eta \pi^2} \text{Re} \frac{\Delta^2}{(-\omega + \gamma)^2}$$

(23)
where \( \eta = 1, 2, 4 \) for Gaussian orthogonal (GOE), unitary (GUE) and symplectic (GSE) ensembles, respectively. When \( \gamma \lesssim \Delta \), the second term in the parentheses acquires an ensemble-specific oscillatory behavior \[13\]. However, for \( \omega \gg \Delta \) it is still small in the order \( \Delta^2 / \omega^2 \) which supports the validity of the present approximation, even though the spectrum becomes discrete in this limit.

Notice that one of the conditions specified earlier, \( \omega \ll D/a^2 \), has been used for the diffusive evaluation of the dipole matrix element and also in the use of the "zero-mode" approximation for the correlation function \[22\] where the kinetic terms \( \sim D/a^2 \) are omitted relative to \( \omega \). The other condition, \( \gamma < \omega \), is needed to justify the Fermi golden rule approximation for the evaluation of the absorption in eqs. (16) and (17). Namely, the assumption of a sharp peak in the transition probability at \( \epsilon_f - \epsilon_i = \omega \) would not be meaningful otherwise. Notice that, more rigorously, the \( \delta \)-function should have been replaced by \( \gamma / \pi (\gamma^2 + (\epsilon_f - \epsilon_i - \omega)^2) \). However, this would not effect the parametric dependence of the quantum correction.

### B. Discrete spectrum

By definition, the level density assumes averaging over many levels. When \( \gamma, \omega \lesssim \Delta \), on the other hand, the energy spectrum must be treated as discrete and the transitions leading to absorption occur predominantly to the nearest level \[14\]. This is in complete analogy with the thermodynamical quantities which are evaluated using a few-level approximation \[14\]. Therefore, one needs to use another descriptor of level statistics, namely the probability distribution function.

For GOE, for instance, this implies \( Q \sim \omega^3 \).

#### 1. \( T \gg \Delta \)

In this case,

\[
\langle Q_{\text{disc}}^{(1)} \rangle = \frac{2\pi}{3} e^2 E_0^2 \left| \mathbf{R}_{ij} \right|^2 \Delta \sum_i \int x \delta(x - \omega) P(x) \left[ f(\epsilon_i) - f(\epsilon_i + x) \right] dx
\]

where summation is over all nearest-level pairs within \( \sim T \) of the Fermi level. Replacing it by integration, \( \sum_i \to \int \right\) dv, denoting \( x = (\epsilon_f - \epsilon_i) \) and performing integration on \( y = \epsilon_f + \epsilon_i \) first, we obtain

\[
\langle Q_{\text{disc}}^{(1)} \rangle = \frac{2\pi}{3} e^2 v^2 E_0^2 \left| \mathbf{R}_{ij} \right|^2 \Delta \int \int x \delta(x - \omega) P(x) \left[ f(\epsilon_i) - f(\epsilon_f) \right] dx \epsilon_i dx
\]

\[
= \frac{2\pi}{3} e^2 v^2 E_0^2 \left| \mathbf{R}_{ij} \right|^2 \Delta \int x^2 \delta(x - \omega) P(x) dx = Q_{\text{RD}} \Delta P(\omega)
\]

For GOE, for instance, this implies \( \langle Q_{\text{disc}}^{(1)} \rangle \sim \omega^3 \).

#### 2. \( T < \Delta \)

In this case, the only transitions of significance are those from the (occupied) Fermi level to the next (unoccupied) level. The implication of the latter is two-fold. First, there is no summation over the initial states \[3\], \( \sum_i \). Second, the thermal factors are those of the two-level system,

\[
f(0) = \frac{1}{1 + e^{-\frac{\omega}{T}}} , \ f(x) = \frac{e^{-\frac{x}{T}}}{1 + e^{-\frac{x}{T}}}
\]

\[\text{Notice that if one formally extends the expression for the level-density correlation function to } \omega < \Delta, \text{ the following relationship exists } \[3\] \text{ between the former and the probability density } P: \lim_{\epsilon_f - \epsilon_i \to 0} \left( \left( \epsilon_i, \epsilon_f \right) \right) \left( \epsilon_i - \epsilon_f \right) = \lim_{\epsilon_f - \epsilon_i \to 0} \left( P(\epsilon_f - \epsilon_i) \Delta \right)\]
Consequently, we find the following expression for the absorption

\[
\langle Q^{(2)}_{\text{disc}} \rangle = \frac{2\pi}{3} v E_0^2 |\hat{R}_{ij}|^2 \int x \delta (x - \omega) P(x) [f(0) - f(x)] dx
\]

(28)

\[
= Q_{RD} v^{-1} \Delta \omega P(\omega) \tanh \left( \frac{\omega}{2T} \right)
\]

(29)

\[
= Q_{RD} \Delta \omega P(\omega), \quad \omega < T
\]

(30)

\[
\simeq Q_{RD} \Delta \omega P(\omega), \quad T < \omega
\]

For the orthogonal ensemble, the second of eq. (30) implies that

\[
\langle Q^{(2)}_{\text{disc}} \rangle = \frac{\pi^2}{12} Q_{\text{class}}
\]

(31)

The temperature dependence of the quantum absorption given by eqs. (28) and (30) has been described in Ref. [5].

IV. CONCLUSIONS

We have argued that the quantum effects on electric-dipole absorption are significant only when \( \omega < \Delta \). The main assumption of this derivation is that the matrix element of the dipole moment can be evaluated classically, in accordance with eq. (21), where the Thomas-Fermi screening is taken into account as well. The quantum effects are manifested through the use of the probability distribution function for the energy spacing to the next-nearest level and the use of thermal occupation factors of the two-level systems.

As was pointed out in I, since there is no screening for the magnetic-dipole absorption, in classical electrodynamics the latter becomes dominant for very small particle sizes. It is, therefore, important, to investigate the quantum effects on the magnetic-dipole absorption. This will be done in a future publication.

V. ACKNOWLEDGMENTS

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