Laplacian-level quantum hydrodynamic theory for plasmonics

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An accurate description of the optical response of subwavelength metallic particles and nanogap structures is a key problem of plasmonics. Quantum hydrodynamic theory (QHT) has emerged as a powerful method to calculate the optical response of metallic nanoparticles since it takes into account nonlocality and spill-out effects. Nevertheless, the absorption spectra of metallic particles from QHT is affected, at energies higher than the main plasmon peak, by several additional peaks, which are instead largely damped in reference time-dependent density-functional theory calculations. Moreover, we show here that these peaks have a strong dependence on the simulation domain-size so that the numerical convergence of QHT calculations is problematic. In this article, we introduce a QHT method accounting for kinetic energy contributions depending on the Laplacian of the electronic density, thus beyond the gradient-only dependence of conventional QHT. In this way, only the main plasmon peak is obtained, with a numerically stable absorption spectrum and more accurate intensities of the plasmon peak. Thus, the Laplacian-level QHT represents a novel, efficient and accurate platform to study plasmonic systems.

I. INTRODUCTION

Metal nanoparticles (NPs) play a crucial role in the enhancement of the optical field due to plasmonic effects [1], which make them an ideal platform for nonlinear optics [2, 3], hot-electron enhancement for photovoltaics [4, 5], surface-enhanced Raman scattering [6], and imaging [7]. When it comes to nanoscale, nonlocal and quantum effects play a crucial role in light-matter interaction [8]. Among theoretical approaches [9–17], time-dependent density-functional theory (TD-DFT) [18, 19] stands out, since it allows to accurately resolve the optical response of plasmonic structures at nanoscale, including both quantum and atomistic effects [11, 16, 20–24]. However, TD-DFT is computationally expensive, since all occupied orbitals need to be evaluated.

Another approach would be to treat the electron system semi-classically: a fluid, characterized by the macroscopic local quantities such as the electron density \( n(\mathbf{r},t) \) and the electron velocity field \( \mathbf{v}(\mathbf{r},t) \) [25–28] but at the same time considering quantum effects through energy functionals of the electron density fluctuations. This approach is known as hydrodynamic theory (HT). The HT is part of a larger class of methods based on the orbital-free (OF) [29–31] description of quantum electronic systems dating back to the works of Thomas [32] and Fermi [33]. Although the interest in OF-DFT methods has gradually decreased in favor of Kohn-Sham (KS) orbital-based methods, the last decades have witnessed a reinvigorated interest due to the ideal scaling of computational resources with respect to the size of the electronic system offered by the OF-DFT approach [34]. Most of the research efforts in this field, however, have been devoted to static properties [35–38] and, more recently, also to response properties with the time-dependent OF-DFT [39–42]. In both cases, the central quantity that controls the accuracy of these methods is the noninteracting kinetic energy (KE) functional.

The most simple KE functional is the Thomas-Fermi (TF) functional, which accounts for the Pauli exclusion principle for a homogeneous system of noninteracting electrons [29] and it yields the electron quantum pressure \( p(\mathbf{r},t) \propto n(\mathbf{r},t)^{5/3} \) [43] that accounts for the nonlocal electron response. It has been demonstrated that TF-HT is able to provide surprisingly accurate predictions that match well experiments with noble metal NPs, such as Au [44] and Ag [45], both qualitatively and quantitatively. Nevertheless, for alkali metals or aluminum, the TF-HT predicts a blueshift of the localized surface plasmon resonance with respect to the classical Mie resonance [46], in contradiction with the redshift from the experiments [47] and TD-DFT calculations [48]. The origin of this difference lies in neglecting the spill-out of the plasmon-induced charges at the NP surface [46]. In fact, the TF-HT approach employs (with some recent exception [49]) a spatially uniform electronic density inside the NP and zero outside (i.e., hard-wall boundary) [15].

To properly address spill-out effects, the spatial dependence of electron density as well as a correction to the KE functional, in order to describe the density variation effects, must be introduced. The simplest functional that depends on the gradient of the density is the von Weizsäcker (vW) functional [29, 50]. The TF-HT with a fraction \( \lambda, \) with \( 0 < \lambda \leq 1 \) of the vW correction (i.e., the TF\textit{vW} KE functional) is usually referred to in the literature as the QHT since the vW functional does not have a classical counterpart. The QHT has been largely used in plasma physics [51–56], and more recently, for plasmonic response properties of metal NPs of different

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geometries [57–63], as well as for surfaces [64–66] and strongly coupled plasmonic structures [62, 67, 68]. It has been shown that the QHT can predict plasmon resonance, spill-out, and retardation effects in noble and simple metal NPs, matching very well with TD-DFT calculations [59, 62]. There are also other works on the development of the QHT that consider the viscous contribution of electron fluid [67, 69] and formulation of HT for nonlinear phenomena [70–72].

However, it is important to highlight that the QHT results depend on the approximation made for the KE functional (e.g., $\lambda$ parameter) as well as on the electronic density, which is an input quantity. The input electronic density can be obtained from a preceding OF-DFT calculation using the same KE functional used for the response, i.e., the self-consistent QHT approach [58]. Other approaches can use the exact KS density [59] or, more efficiently, from a model density [57, 59].

Although QHT can describe different quantum effects relevant in plasmonics, the QHT is not unaffected by drawbacks:

i) Various QHT works [58–61, 66], show the presence of additional resonances above the main plasmon peak and below the plasma frequency ($\omega_p$): these resonances originate from the spatial variation of the electronic density as first pointed out by Bennet [73]. Using the hard-wall boundary, no Bennet states are present for NPs in QHT [74–76] nor in TF-HT [76–79]: in these approaches, several peaks (volume plasmons) occur due to nonlocality, but only at frequencies larger than $\omega_p$. Such Bennet states are thus peculiar to hydrodynamic models with nonuniform density. Instead, in TD-DFT calculations of large jellium spheres, only a shoulder above the main plasmon peak (around 4 eV) is present [16] and it has been attributed to the interaction between single-particle transitions and surface modes [80–83]. To better illustrate this point (often overlooked in the literature), we report in Fig. 1 (a) a direct comparison of the absorption spectra of a Na jellium nanosphere between reference TD-DFT and QHT theory. TD-DFT can be considered as a reference for QHT because the latter can be directly derived from TD-DFT equations (and for the two-electron case the methods coincide) [56, 67, 84]. Although the energy position of the main peak, the localized surface plasmon (LSP), is very well reproduced, additional peaks are not present in the reference TD-DFT spectrum. Results in Fig. 1 (a) represent the current state-of-the-art of QHT calculations: clearly, the presence of the other peaks strongly limit the QHT accuracy and applicability.

ii) For energies above a critical frequency $\omega_c$ [59, 65], the induced density (i.e., the first-order change of the electronic density due to the excitation) have both an oscillating and exponentially decaying behavior, as shown in Fig. 1 (b), which is problematic to treat numerically. We will show in this paper, that all the energy position of all the peaks above the critical frequency strongly changes with the computational domain size so that a numerically converging QHT spectrum is challenging to obtain.

iii) The TF$\lambda$W functional is known to be quite a rough approximation to the exact KE, and different limitations of this functional have been shown in different contexts, e.g., lack of dynamical corrections [40, 55, 65, 85] and incorrect response for homogeneous electron gas [30, 86, 87]. Thus, the great accuracy of QHT calculations with the TF$\lambda$W functional obtained in some cases should be related to some error cancellation and, therefore, cannot have general validity.

In order to overcome these limitations, in this article, we complement the QHT approach with the recently developed Laplacian-level KE functionals [87], that performed well for semiconductors and metals in the framework of OF-DFT. In particular, the Pauli-Gaussian second-order and Laplacian (PGSL) functional has an improved Lindhard response [87], which is a fundamen-
tal property for the description of metallic systems.

We derive the Laplacian-level QHT linear-response equations in the frequency-domain: this is a completely novel implementation for the QHT, so far only limited to the TFvW KE functionals. Note that Laplacian-level KE functionals are much simpler than fully non-local functional based on the Lindhard response in the reciprocal space [30, 85, 86] and can be easily applied to finite systems [87]. We demonstrate that in the QHT-PGSL approach, only the main plasmon peak appears in the absorption spectrum, which is stable to the changes of computational domain size. In fact, in QHT-PGSL, the induced density decays in the same way for all frequencies, and no critical frequencies exist anymore. Moreover, as we will show later, in QHT-PGSL, the intensity of the main plasmon peak is more accurate than the conventional QHT approach.

The article is organized as follows: in Section II we introduce the equations governing the Laplacian-level QHT theory, which contains also the conventional QHT approach as a special case; in Section III we discuss theoretically the properties of the induced density in the tail region in spherical systems, showing that the QHT-PGSL has an unexpected and completely different behavior with respect to the conventional QHT; in Section IV, we provide numerical details of our implementation which can efficiently describe systems with spherical and cylindrical symmetry; in Section V, we compare in detail the absorption spectra of Na jellium nanospheres from TD-DFT, QHT and QHT-PGSL, showing their different dependence on the computational domain size as well as their oscillator strength; in Section VI, we describe the numerical results of the induced density decay for Na jellium nanospheres which confirms the theoretical prediction of Section III; in Section VII, we study the energy and oscillator strength as a function of particle size; in Section VIII, we present results for spherical dimers. Finally, conclusion and future perspectives are drawn in Section IX.

II. PAULI-GAUSSIAN AND LAPLACIAN-LEVEL FUNCTIONALS IN QUANTUM HYDRODYNAMICS

The linearized QHT response [28, 88] is governed by the following equations [58, 59] for the electric field $\mathbf{E}$ and polarization vector $\mathbf{P}$:

$$\nabla \times \nabla \times \mathbf{E} - \frac{\omega^2}{c^2} \mathbf{E} = \omega^2 \mu_0 \mathbf{P},$$

(1a)

$$\frac{\varepsilon_0}{m_e} \nabla \left( \frac{\delta G[n]}{\delta n} \right)_1 + (\omega^2 + i\gamma \omega) \mathbf{P} = -\varepsilon_0 \omega_0^2 \mathbf{E},$$

(1b)

where $c$ is the speed of light, $\varepsilon_0$ and $\mu_0$ are the vacuum permittivity and permeability, $m_e$ and $e$ are the electron mass and charge (in absolute value), $\gamma$ is the phenomenological damping rate and $\omega_0 (\mathbf{r}) = \sqrt{\varepsilon \varepsilon_0 n_0 (\mathbf{r}) / (m_e \varepsilon_0)}$ is the plasma frequency with $n_0 (\mathbf{r})$ being the ground-state (equilibrium) electron density. $\left( \frac{\delta G[n]}{\delta n} \right)_1$ is the first-order term for the potential associated to the energy functional $G[n]$ given by:

$$G[n] = T_s [n] + E_{\text{XC}}^{\text{LDA}} [n],$$

(2)

where $E_{\text{XC}}^{\text{LDA}} [n]$ is the exchange-correlation (XC) energy functional in local density approximation (LDA), while $T_s$ is the noninteracting KE functional.

In general, the exact energy functional can be written as:

$$T_s[n] = T_s^{\text{TF}} [n] + T_s^{\text{vW}} [n] + C_s [n] + C_d [n, \omega],$$

(3)

where $C_s$ and $C_d$ represent static and dynamic corrections, respectively. Although some schemes have been proposed [40, 67, 85], the first-principle derivation of dynamic corrections presents fundamental challenges, especially for finite-size systems. In this article, we consider only static corrections, in particular at the Laplacian-level, where the KE has the form:

$$T_s [n] = \int \tau (n, u, q) d^3 r,$$

(4)

where $w = \nabla n \cdot \nabla n$ and $q = \nabla^2 n$. The function $\tau (n, u, q)$ is approximated as the sum of vW [50], Pauli-Gaussian (PG$\alpha$) and Laplacian (L$\beta$) terms [87]:

$$\tau (n, u, q) = \tau^{\text{vW}} (n, u) + \tau^{\text{PG}} (n, u) + \tau^{\text{L}} (n, q),$$

(5)

where:

$$\tau^{\text{vW}} (n, u) = A n^{-1} u, \quad \tau^{\text{PG}} (n, u) = B n^{5/3} c^{\alpha} n^{-8/3} u, \quad \tau^{\text{L}} (n, q) = D \beta n^{-5/3} q^2,$$

(6a)-(6c)

with the coefficients being $A = E_h a_0^3 / 8$, $B = 3 (3\pi^2)^{2/3} E_h a_0^2 / 10$, $C = - (3\pi^2)^{-2/3} / 4$ and $D = 3 (3\pi^2)^{-2/3} E_h a_0^2 / 160$. $E_h = h^2 / m_e a_0^2$ is the Hartree energy and $a_0$ is the Bohr radius. It is useful to identify the following cases:

- $\alpha = 0$, $\beta = 0$. Eqs. (2) - (6) reduce to the models employed in previous works [59, 62, 65], i.e., $G[n]$ is approximated as the sum of TF, vW and XC functionals. In line with the literature, we will indicate this case as QHT. Note that here we use the full vW term, i.e., $\lambda = 1$. Other implementations in literature use $\lambda = 1/9$, but as shown in Ref. 59 $\lambda = 1$ is required to better reproduce TD-DFT results.

- $\alpha \neq 0$, $\beta = 0$. It corresponds to the case where the QHT is improved with the addition of the PG$\alpha$ functional. We will refer to this case as QHT-PG$\alpha$. 

\( \alpha \neq 0, \beta \neq 0 \). This is the more complex case in which the Laplacian-level correction \( L_\beta \) is included in the energy functional. This case will be referred to as QHT-PGoL_\beta.

In order to calculate the potential, we take the functional derivative of \( T_s[n] \) [89] and obtain:

\[
\frac{\delta T_s}{\delta n} = \tau_n + w_{\tau n q} - 2 w_{\tau n w} + \tau_{n q} - 2 q \tau_w + 2 \tau_{n q} \nabla n \cdot \nabla q - 2 \tau_{w w} \nabla n \cdot \nabla w + \tau_{q q} \nabla^2 q, \tag{7}
\]

where the subscripts \( i = n, q \) denote the corresponding partial derivatives. The detailed derivation of Eq. (7) is given in Sec. I of supplementary materials (SM) [90]. The first-order term of the potential, \( \left( \frac{\delta T_s}{\delta n} \right)_1 \), is obtained using a perturbation approach where the perturbed density is taken as \( n = n_0 + n_1 \), with \( n_1 = \frac{1}{\varepsilon_0} \nabla \cdot P \) being the electron density perturbation. After some tedious algebra and neglecting higher-order terms, we obtain the following expression for the linear potential (we refer to SM Sec. I and II for the full derivation [90]):

\[
\left( \frac{\delta T_s}{\delta n} \right)_1 = \left( \frac{\delta T_{TFvW}}{\delta n} \right)_1 + \left( \frac{\delta T_{PGs}}{\delta n} \right)_1 + \left( \frac{\delta T_{L_\beta}}{\delta n} \right)_1, \tag{8}
\]

where:

\[
\left( \frac{\delta T_{TFvW}}{\delta n} \right)_1 = \tau_{n n} n_1 - 2 \tau_{n w} (|n_0|) \nabla n_0 \nabla n_1 - 2 \tau_{n w} (|n_0|) \nabla n_0 \nabla n_1 - 2 \tau_{w w} \nabla^2 n_1, \tag{9a}
\]

\[
\left( \frac{\delta T_{PGs}}{\delta n} \right)_1 = -2 \tau_{n w} (|n_0|) \nabla n_0 \nabla n_1 \nabla^2 n_0 + \nabla (|n_0|^2) \cdot \nabla n_1 + 2 \nabla n_0 \nabla (|n_0|^2) \tag{9b}
\]

\[
\left( \frac{\delta T_{L_\beta}}{\delta n} \right)_1 = \tau_{n q} (|n_0|^2) n_1 + \tau_{q q} (|n_0|^2) n_1 + 2 \tau_{n q} (|n_0|^2) n_1 + 2 \tau_{n q} (|n_0|^2) n_1 \tag{9c}
\]

where the superscript (0) indicates that the function is evaluated at \( n = n_0 \). First-order term \( \left( \frac{\delta E_{XC}[n]}{\delta n} \right)_1 \) for XC potential is obtained via Perdew-Zunger LDA parametrization [91] and full expression of it can be found in Ref. 59. Note that if \( \alpha = \beta = 0 \), only the first term in Eq. (8) survives; \( \left( \frac{\delta T_{TFvW}}{\delta n} \right)_1 \) then corresponds to the TFvW (with \( \lambda = 1 \)) functional used in previous works [58, 59, 65]. Clearly, \( \left( \frac{\delta T_{PGs}}{\delta n} \right)_1 \) and \( \left( \frac{\delta T_{L_\beta}}{\delta n} \right)_1 \) are the contribution associated with the PG and L corrections respectively.

The parameters \( \alpha \) and \( \beta \) can be determined in a nonempirical way by imposing exact asymptotic solutions. In particular, we set \( \alpha = 40/27 \) in order to satisfy second-order gradient expansion [87, 92] and use PGS for PG(40/27). Moreover, we follow the results of Ref. 87 and fix \( \beta = 0.25 \) such that the overall correction functional PGSL0.25 accurately reproduces the linear response function of a noninteracting homogeneous electron gas at both small and large wavevectors [87]. For brevity, we will use the acronym PGS for PGSL0.25.

**III. ASYMPTOTIC ANALYSIS**

We take the divergence of Eq. (1b), and we use the quasistatic approximation (so that \( \varepsilon_0 \nabla \cdot E = \nabla \cdot P = e n_1 \)), obtaining:

\[
\nabla \cdot \frac{e n_0}{m_e} \nabla \left( \frac{\delta G}{\delta n} \right)_1 = -\omega^2 e n_1 - \frac{e^2}{\varepsilon_0} \left( \frac{e}{\varepsilon_0} n_0 n_1 + \nabla n_0 \cdot E \right). \tag{10}
\]
To obtain the asymptotic form of Eq. (10) we assume that [59]:

\[ n_0(r) \rightarrow A_0 \exp(-\kappa r), \quad (11) \]

\[ n_1(r) \rightarrow B_0 \exp(-\nu \kappa r), \quad (12) \]

where \( \kappa > 0 \) is the decay constant of the ground-state density, and \( \nu \kappa \) is the decay constant of the (dipole excited) induced density.

The right-end side (RHS) of Eq. (10) is asymptotically vanishing and it decays as

\[ -\omega^2 e n_1 + \frac{3 e^2 \kappa d_1}{4 \pi \epsilon_0 m_e} \frac{n_0 \cos(\theta)}{r^3}, \quad (13) \]

where \( d_1 \) is the dipole moment of \( n_1 \) (see Ref. 59). For the left-end side (LHS) of Eq. (10) we obtain (after some algebra, see SM, Sec. III [90]):

\[ \nabla n_0 \nabla \left( \frac{\delta T_{\text{XC}}^{\text{DA}}}{\delta n} \right) \rightarrow \left( -\frac{\nu^4}{4} + \frac{\nu^2}{2} - \frac{\nu^2}{4} \right) \kappa^4 n_1 \]

\[ \nabla n_0 \nabla \left( \frac{\delta T_{\text{PG}}^s}{\delta n} \right) \rightarrow \beta \frac{\sqrt{3}}{\pi^{4/3}} \left( \frac{243\nu^6 - 1377\nu^5 + 2025\nu^4 + 765\nu^3 - 3885\nu^2 + 2865\nu - 650}{19440} \right) \frac{n_1}{n_0^{2/3}} \quad (15) \]

while the terms with \( E_{\text{XC}}^{\text{DA}} \) and \( T_s^{\text{PG}} \) decay exponentially faster than \( n_1 \). We underline that Eqs. (14) and (15) represent only the leading terms in the asymptotic region.

The case with \( \beta = 0 \) has been described in Ref. [59]: when \( \hbar \omega \) is higher than a critical excitation energy

\[ \hbar \omega_c = h \frac{\kappa^2}{8} \sqrt{\frac{E_{\text{h}} \alpha_0^2}{m_e}} \quad (16) \]

the asymptotic decay is complex-valued and oscillating. Otherwise, the asymptotic decay is exponential, and \( \nu \) depends on \( \omega \).

When \( \beta > 0 \), we found, interestingly, that the \( L/\beta \) term gives an exponentially increasing contribution, due to the division by \( n_0^{2/3} \), which dominates over the term in Eq. (14) as well as the term at the RHS. Thus, the asymptotic solution does not depend on \( \omega \), as in the conventional QHT approach with the TFvW functional, but it is related to the solution of the sixth-degree polynomial in \( \nu \) in Eq. (15), which are:

\[ -1.320, +0.543, +2/3, 1.123, +5/3, +2.987. \quad (17) \]

Only for those values of \( \nu \), the LHS term vanishes asymptotically, as it does the RHS. Some of these solutions are not possible or unstable, i.e., those with \( \nu \geq 2/3 \), as the term \( n_1/n_0^{2/3} \) will not decay asymptotically. The other three values of \( \nu \) give the right asymptotic solution, but a high order analytical analysis or a full numerical solution is required to select the actual value of \( \nu \). Interestingly, all these solutions have \( \nu > 1 \), which is another difference with respect to the QHT approach with the TFvW functional [59], where \( \nu < 1 \).

IV. NUMERICAL IMPLEMENTATION

The system of Eqs. (1) with Eq. (2) and expressions (9) is solved for a plane wave excitation using a commercial implementation of the finite-element method (FEM) [93].

![Figure 2. KS n_0^{KS} and model n_0^{Mod} ground-state densities for a Na jellium sphere with N_e = 1074 electrons. The inset shows the variation of densities in the logarithmic scale. Values are normalized to the bulk density n_b = (4/3\pi r_b^3)^{-1}.](image)

In order to easily compute absorption spectra for spheres and sphere dimers, we have implemented our equations using the **2.5D technique**, which significantly reduces the computational time for axisymmetric structures [59, 94, 95]. A detailed explanation of the FEM implementation can be found in the Appendix B. A completely independent implementation has also been carried out using a finite-difference method for spherical systems in the quasi-static approximation [96]: the results obtained with the two methods are numerically the same. In order to solve the system of Eqs. (1) an ex-
expression for ground-state density function \( n_0(r) \) is required. Throughout the article we consider the following two ground-state density functions: i) the exact KS density \( n_{0,KS}(r) \) calculated using a DFT in-house code \([59]\), and ii) a model density defined as \([57, 59]\):

\[
n_{0,\text{Mod}}(r) = \frac{1}{1 + \exp(\kappa_{\text{Mod}}(r - R))},
\]

normalized with a condition \( \int n_{0,\text{Mod}}^2 dV = N_e \), where \( N_e \) is the number of electrons. For \( \kappa_{\text{Mod}} \) value is fixed fitted with asymptotic decay of the KS electronic density decay \([59]\). Fig. 2 shows \( n_{0,KS}^2 \) and \( n_{0,\text{Mod}}^2 \) densities for a Na (Wigner-Seitz radius \( r_s = 4 \) a.u.) jellium nanosphere with \( N_e = 1074 \) electrons (nanosphere radius \( R = 2.167 \) nm). Note that \( n_{0,\text{Mod}}^2 \) does not display Friedel oscillations inside the nanosphere volume (surface marked with vertical line), which are instead present in \( n_{0,KS}^2 \). The inset shows that the asymptotic decay is the same for both cases.

V. ABSORPTION SPECTRA

In Fig. 3 we report the comparison of the normalized absorption cross-section for a Na jellium nanosphere with \( N_e = 1074 \) electrons as obtained using QHT, QHT-PGS, QHT-PGSL as well as the TD-DFT approaches (see Appendix A for definitions and details).

![Figure 3](image)

Figure 3. Normalized absorption cross-section \( \sigma/\sigma_0 \) (see the Appendix for definitions) for a Na jellium sphere with \( N_e = 1074 \) electrons as obtained from TD-DFT, QHT, QHT-PGS and QHT-PGSL using KS and model ground-state densities.

Fig. 3 shows that the energy of the localized surface plasmon (LSP) resonance (first main peak) for QHT and QHT-PGS are in good agreement (within 10 meV) with TD-DFT (\( \approx 3.22 \) eV), which is broader due to quantum-size effects, while KS/QHT-PGSL and Mod/QHT-PGSL give the LSP peaks at \( \approx 3.374 \) eV and \( \approx 3.313 \) eV, respectively, which are blue-shifted with respect to TD-DFT results (for further analysis of the position of LSP peak, see Sec. VII). As discussed in the Introduction, QHT gives accurate energy of the LSP and predicts additional peaks at higher energies, which are not present in the TD-DFT. Almost the same situation is obtained from QHT-PGS, meaning that even the more general gradient approximation in Eq. (6b) does not solve the problem of additional peaks. On the other hand, the QHT-PGSL absorption spectrum is quite different. The main difference between QHT and QHT-PGSL is not the energy shift of the LSP, but the absence of additional resonances in the latter.

Although the QHT predicts very well the LSP resonance when compared to more sophisticated TD-DFT approaches, the presence of additional peaks is a major shortcoming. These peaks have, in fact, energy higher than \( \hbar \omega_c \approx 3.55 \) eV (see Ref. \([59]\)) and thus can hardly be treated in an efficient numerical scheme.

![Figure 4](image)

Figure 4. The effect of computational domain size (L) on the normalized absorption spectra as obtained from KS/QHT (a) and Mod/QHT (b) for a Na jellium nanosphere with \( N_e = 1074 \) electrons.

In fact, this is shown in Fig. 4, where QHT normalized absorption cross-section \( \sigma/\sigma_0 \) for the same jellium nanosphere are calculated for increasing size of the simulation domain. These calculations have been done with a novel finite-difference code for spherical systems \([96]\), which reproduces exactly the FEM results reported in this work but is more accurate in the asymptotic region. Results were obtained with KS (upper panel) and model (lower panel) ground-state densities. Clearly, as the domain size increases, more and more modes appear (and with reduced intensities) in the spectrum without any limit. Thus the absorption spectrum is very sensitive to the domain-size. We note that no previous report in literature has considered the numerical convergence of Bennet states in QHT calculations. With an infinite computational domain size, there should be an infinite number of states with infinitely small peak intensity, i.e., no peaks can be distinguished anymore, and only an unstructured shoulder could be present.
This is indeed shown in Fig. 5 where we report the QHT and TD-DFT results for two different computational domain size. We have used a larger broadening for QHT (namely \( \gamma = 0.2 \text{ eV} \)) so that it will give the same intensity at the LSP peak as TD-DFT. While the TD-DFT results are converged with standard domain size, convergence seems to appear for QHT only with a domain size of 200 a.u., where no more Bennet peaks can be distinguished and only a shoulder is present. However, this shoulder which starts at \( h\omega_c \) is significantly higher (about a factor of 2.5) than the TD-DFT one, which starts later, at about 3.7 eV. Clearly a domain size of 200 a.u. to obtain a converged absorption spectrum is not reasonable for any applications in plasmonics, and it has been obtained only with a specialized code for reference calculations [96].

In Fig. 5, we also report the QHT/PGSL* results, where the * indicates that the spectra have been redshifted by 0.15 eV in order to have the same LSP energy position of QHT; the broadening is \( \gamma = 0.24 \text{ eV} \) so that also the peak intensity is the same. The plot shows that the QHT-PSGL* does not change at all with the computational domain size, and overall it is much closer to TD-DFT than QHT.

A more quantitative comparison of methods can be done by considering the integrated absorption cross-section:

\[
I(\omega) = \int_0^\omega \sigma(\omega')d\omega',
\]

which will converge to \((\pi e^2)/(2\epsilon_0 m_e c)N_e\) for \( \omega \to \infty \), where \( N_e \) is the number of electrons [81, 97, 98].

The integrated absorption is plotted in Fig. 6, and it shows that \( I(\omega) \) for QHT and QHT-PSGL* converge to the same value for high energies. However, while the integrated absorption curve for TD-DFT and QHT-PSGL* are very close to each other, the growth in QHT is much slower, meaning that the oscillator strength (i.e., the energy-integrated intensity) in QHT is split in several Bennet modes, whereas the single peak in QHT-PSGL* contains it all. In fact, the integrated absorption for QHT at \( \omega = \omega_c \) is about 15% smaller than QHT-PSGL* and TD-DFT.

In Sec. VII, a more detailed analysis of oscillator strength and absorption cross-section for different number of electrons is presented. Here, we remark that these features are not limited to spherical NPs, but could happen in other geometries or materials: in fact, for \( \omega_c \) the identical expression was obtained for a jellium sphere [59] and slab [65]. Thus, in general, one could have for LSP \( \omega_{sp} \simeq \omega_c \) or even \( \omega_{sp} > \omega_c \). In such cases, the QHT will not accurately predict the LSP energy.

VI. INDUCED CHARGE DENSITY

As discussed in the Sec. III, the decay of conventional QHT induced densities is frequency-dependent, and solutions are pure exponentially decaying at the metal surface only if the incident plane wave energy is lower than \( h\omega_c \), whereas using the PGSL functional a fixed exponential decay should be obtained.

This can be verified numerically by plotting the computed induced charge density \( n_1 \) (associated with the absorption). In Fig. 7 we plot \( |n_1| \) (in the logarithmic scale) as obtained from the KS/QHT and KS/QHT-PSGL for a Na jellium nanoparticle with \( N_e = 1074 \). To have clear comparison of decay rates, the curves for \( |n_1| \) are shifted to have the maximum at \( z = R \) and normalized to \( |n_1(R)| \), while \( n_0 \) density is only normalized to \( n_0(R) \).

For the KS/QHT induced density the decay slope shows a clear dependence on the incident energy \( h\omega \), becoming oscillatory for \( h\omega > h\omega_c = 3.55 \text{ eV} \) (such
Figure 7. Modulus of induced charged density at different energies for a Na jellium sphere with \( N_e = 1074 \) electrons as calculated from KS/QHT (a), KS/QHT-PGSL (b) and TD-DFT (c). The blue curves correspond to the densities associated to the LSP excitation energy. The critical frequency is \( \hbar \omega_c = 3.55 \) eV, see Ref. [59].

KS/QHT induced densities are not converged with respect to the computational domain size, as discussed in Sec. V).

On the other hand, the KS/QHT-PGSL calculations yield the same slope for all excitation energies, as analytically demonstrated in Sec. III. A numerical fit of the decay gives a value of \( \nu \) close to +1.12, i.e., the slowest from asymptotically decaying solutions (with \( \nu > 2/3 \)) (17).

It is important to note that the TD-DFT calculations (Fig. 7 (c)) give qualitatively similar results as the QHT-PGSL. In fact, for TD-DFT we get the same decay slope for the induced density (at least for \( \hbar \omega < \hbar \omega_p \)). However, as discussed in Sec. III in QHT-PGSL we have \( \nu > 1 \) while \( \nu < 1 \) in the conventional QHT, meaning that spill-out effects are somehow smaller in QHT-PGSL. Nonetheless, we need to point out that this feature is peculiar to PGSL, which is one of the few Laplacian-level KE functionals, and PGSL has not been developed for QHT calculations. Thus, other Laplacian-level KE functional can be developed with better features.

Another important aspect is the numerical stability of the QHT-PGSL approach: not only the absorption spectra does not depend on the domain-size, but the fact that the decay constant is fixed and independent from the frequency allows to use mixed boundary condition for an exponential decay (i.e., \( \hat{r} \cdot \nabla n_1 + \nu \kappa n_1 = 0 \)), allowing to have converged results even with a very small domain-size.

The impact of the Laplacian-level corrections studied in this article is not limited to the density tail decay but can be easily appreciated in the linear scale as well. In Fig. 8, we report the imaginary part of the induced charge density \( n_1 \), Figs. 8 (a) - (d), and norm of the total (incident + scattered) field for the KS ground-state density (for the model density see Fig. S1 of the SM [90]). The cross-section plane for the map plots in Figs. 8 (b) - (g) is perpendicular to the incident plane wave propagation. We clearly observe that the spill-out is less pronounced for QHT-PGSL, as the imaginary part of \( n_1 \) is more squeezed into the nanosphere volume. Consequently, for QHT-PGSL the peak value of \( \text{Im}(n_1) \) and field enhancement are the biggest. This behavior is directly related to the blue shift of LSP resonance obtained using QHT-PGSL with respect to QHT and QHT-PGS shown in Fig. 3.

VII. ELECTRON NUMBER VARIATION EFFECTS

An important aspect in nanoplasmonic systems is the LSP resonance dependence on the NP size [47, 48, 99]. As already mentioned in the introduction, LSP for Na jellium nanosphere must undergo red shift with respect to Mie theory results. In Fig. 9 (a) (horizontal axis is in the logarithmic scale), we show the LSP resonance energy of various Na jellium nanospheres with the number of electrons \( N_e \) varying from 254 to 6174 \((R = r_s N_e^{1/3})\) as computed from TD-DFT, Mod/QHT, Mod/QHT-PGS and Mod/QHT-PGSL. We see that for all approaches, LSP energy is lower than Mie theory value \( \hbar \omega_{\text{Mie}} = 3.4 \) eV (shown as a horizontal line). The mean average error with respect reference TD-DFT are of 8, 12, 85 meV, for Mod/QHT, Mod/Pgs, and Mod/Pgsl, respectively. Thus, the accuracy of Mod/QHT is extremely high, which is somehow surprising, considering the shortcomings of the TFvW functional. The PGS functional, which
has some better properties than the TFvW functional [87], yield similar but somehow smaller accuracy. Finally, PGSL overestimates the LSP peak, but an overestimation of 85 meV is quite small, considering that that choice of the exchange-correlation functional can shift the results even more [100–103].

To describe the accuracy of a given theoretical method for the calculation of the absorption spectra, not only the energy of the LSP peak have to be considered, but also the oscillator strength, $f_{osc}$, associated to it. The oscillator-strength is readily available in an eigenvalue formulation of QHT [57, 104]. Our QHT implementation is frequency-dependent, and, therefore, the oscillator strength is not directly computed, but it can be extracted from the absorption spectra using the fitting procedure described in Sec. IV of the SM [90]. The oscillator strength of the LSP peak can also be extracted from the TD-DFT spectra, if the onset of the plasmon shoulder is considered (Sec. IV of the SM [90]). Previous attempts to compute the $f_{osc}$ of the LSP peak are based on the sum-rule approaches [83].

In Fig. 9 (b), we report $f_{osc}$ of the LSP peak, as obtained from TD-DFT, Mod/QHT, Mod/QHT-PGS, and Mod/QHT-PGSL. Fig. 9 (b) shows that for all methods LSP converges to the Mie results for large $N_e$. However, $f_{osc}$ for Mod/QHT and Mod/QHT-PGS is largely underestimated, as the main-plasmon peak is subdivided in different peaks, as previously discussed. On the other hand, the main-peak of Mod/QHT-PGSL contains almost all the oscillator strength. The mean absolute relative error for these systems are 6.7%, 6.4%, and 2.9% for Mod/QHT, Mod/PDS, and Mod/PGS. Thus PGSL overestimates the energies with respect to QHT but gives a better description of the oscillator strength.

Results using the KS-density (not reported) are similar, but in this case the KS/QHT-PGSL overestimates the TD-DFT even more, as also shown in Fig. 3. This can be traced back to the higher oscillating behavior of
the KS density inside the NP, as shown in Fig. 1. Such quantum oscillations induce higher values of the Laplacian and thus higher contributions to the energy. On the other hand, with the model density, both the gradient and the Laplacian are very small inside the NP. An ‘exact’ KE functional should be able to describe both situations, but this is not the case of the PGSL functional, which has not been optimized for jellium nanosphere nor for the QHT approach.

In any case, for applications involving large systems, only the model density can be used since the calculation of \( n_{KS} \) via KS-DFT or OF-DFT would require additional computational effort.

VIII. APPLICATION TO SPHERICAL DIMER

Our FEM implementation allows to calculate absorption spectra for axisymmetric structures. An important example of such a system is a nanosphere dimer. The NP dimer has been widely studied in literature since it supports gap plasmons that can squeeze light down to sub-nanometer volumes, making it an ideal system for exploring quantum and nonlocal phenomena [21, 67, 105–107]. Here we consider a dimer of Na jellium spheres with 1074 electrons each. In Fig. 10 (a) we present the comparison of the absorption cross-section as calculated from the Mod/QHT, Mod/QHT-PGS and Mod/QHT-PGSL (the cross-section is normalized to the \( 2\sigma_0 = \pi R^2 \) with \( R \) being the radius of a single sphere). The plane wave that excites the structure is polarized along the \( z \)-axis, and the input ground-state density is a sum of model densities (18) of two spheres. As we can see, the Mod/QHT and Mod/QHT-PGS give oscillations in the spectrum, which are absent in Mod/QHT-PGSL approach. Our convergence analysis showed that these oscillations, as in the case of the sphere (see Fig. 3), persist with the change of the computational domain. These oscillations should not be confused with the small undulation next to the main plasmon peak that is more clearly visible in \( \text{gap} = 1 \text{ nm} \) case (Fig. 10 (a)). This undulation comes from the charge-transfer plasmon and gets higher for smaller sizes of the gap [21]. For all considered cases of gap size, Mod/QHT-PGSL gives blueshifted plasmon resonance energy with respect to other methods. The respective values of the plasmon resonance are shown in the map plots of the total field enhancement in Fig. 10. There we also see that the field gets more enhanced for Mod/QHT-PGSL as for other approaches. Clearly, as Table I shows, more field is concentrated in the gap for Mod/QHT-PGSL. In turn, this means that more energy is moved to the main plasmon peak, hence, it is blue shifted for Mod/QHT-PGSL with respect to Mod/QHT and Mod/QHT-PGS as shown in absorption curves.

IX. CONCLUSIONS AND FUTURE PERSPECTIVES

We have extended the quantum hydrodynamic theory to Laplacian-level kinetic energy functionals. In particular, we studied the PGSL functional, which is accurate for OF-DFT calculations and well reproduced the linear response of the homogeneous electron gas [87]. We investigated in detail Na jellium nanospheres and results are compared to reference TD-DFT calculations. The obtained results are focused around two main findings:

1. QHT and QHT-PGS that are gradient-level functionals of electron density, together with an LSP resonance give additional resonances in the absorption spectrum of Na jellium nanospheres. Well defined additional resonances are not present in TD-DFT nor in QHT with an infinite computational domain-size. In both cases, only a shoulder is present at the high energy side to the plasmon peak, with the TD-DFT result being much smaller and at higher energy than in QHT. On the other hand, complementing QHT with a Laplacian-level functional (QHT-PGSL) of electron density yields only the LSP peak in the absorption spectrum, yielding an overall spectrum and oscillator strength closer to TD-DFT.

2. The theoretical and numerical asymptotic analysis of the induced charge density as obtained from QHT, shows that the decay slope is changing at different energies of incident radiation. Contrarily, QHT-PGSL shows the same decay slope for all energies. Despite the spill-out effects are somehow underestimated in QHT-PGSL, this strongly simplifies the boundary condition, so that converged calculation can be obtained with a very small domain-size.

Our results thus demonstrate that the convergence of the QHT absorption spectra is problematic, and most of the QHT results reported so far are thus not accurate enough for energies above LSP resonance. The Laplacian-level QHT, on the other hand, does not suffer from these problems and can be successfully applied to investigate quantum and spill-out effects in different sys-

| Method        | gap | \(|E|/E_0| \n|----------------|-----|----------------|
|----------------|-----|----------------|
| Mod/QHT        | 1.0 nm | 33.9 |
| Mod/QHT       | 1.5 nm | 22.5 |
| Mod/QHT-PGS   | 2.0 nm | 16.5 |
| Mod/QHT-PGS   | 1.0 nm | 35.4 |
| Mod/QHT-PGS   | 1.5 nm | 23.2 |
| Mod/QHT-PGS   | 2.0 nm | 16.9 |
| Mod/QHT-PGSL  | 1.0 nm | 38.8 |
| Mod/QHT-PGSL  | 1.5 nm | 25.5 |
| Mod/QHT-PGSL  | 2.0 nm | 18.7 |

Table I. The average value of \(|E|/E_0| in the dimer gap as calculated from Mod/QHT, Mod/QHT-PGS and Mod/QHT-PGSL.
Figure 10. Normalized absorption cross-section $\sigma/\sigma_0$ (in the logarithmic scale) and norm of the total field $|E|/E_0$ for dimers of Na jellium spheres with $N_e = 1074$ electrons as obtained from the Mod/QHT, Mod/QHT-PGS and Mod/QHT-PGSL. From top to bottom: panel (a) refers to gap = 1 nm, (b) to gap = 1.5 nm and (c) refers to gap = 2 nm.

tems, as shown in Sec. IX, where we report the results for NP dimers.

From a computational point-of-view, QHT-PSGL is close to the widely used TF-HT with hard-wall: in fact, the size of the computational domain can be set very close to the size of the nanoparticles, as discussed in Sec. VI. However, QHT-PGSL solves the two main drawbacks of the TF-HF approach: the neglect of spill-out effects and the blueshift of LSP energies.

QHT-PGSL thus allows an efficient and numerically converged computation of collective excitations in quantum systems: the main drawbacks of QHT-PGSL are related to the too fast decay of the induced density, which then causes reduced spill-out effects and increased plasmon energy. However, we point out that the QHT-PGSL functional, used in this work, has not been developed for QHT, but for bulk properties of bulk metal and semiconductors. We believe the Laplacian-level QHT results can be improved considering more sophisticated functional that could depend, for example, on a different function of $q$ and/or on a product of $w$ and $q$.

The Laplacian-level QHT is thus a new platform, very promising for the future, as the Laplacian ingredient includes much more degree of freedom in developing accurate KE functionals, than more conventional functionals-based on density-gradient. So far, however, the development of semilocal KE functional focused only on ground-state properties, considering only the total KE energy and the KE potential (i.e., the first functional derivatives). Instead, for the QHT response properties, the KE kernel (i.e., the second functional derivative) is required, but, so far, it has not been considered at all in the semilocal KE functional development [87, 108–113]. In addition, it is crucial to understand the role of static and dynamic corrections to the energy functional. Although, here, we have considered only static corrections at the second-order gradient and Laplacian-level, the analysis of dynamic correction represents another important route to explore. Overall, we believe that our current results will help to better understand the role of functional dependence on electron density in plasmonic systems.

**Appendix A: Absorption spectrum**

In QHT, the absorption cross-section is calculated as

$$\sigma(\omega) = \frac{\omega}{2I_0} \int \text{Im} \{ \mathbf{E} \cdot \mathbf{P}^* \} \, dV,$$

with $I_0$ being the intensity for the incident plane wave with frequency $\omega$. The electric field $\mathbf{E}$ and the polarization vector $\mathbf{P}$ are obtained solving Eqs. (1a, 1b). Considering the very small size of the of the investigated nanoparticles, only dipole modes are excited. An important parameter for the shape of the absorption spectra...
is the damping parameter ($\gamma$), see Eq. 1b. If not stated differently, in all QHT calculations, we use $\gamma = 66$ meV.

The normalized absorption cross-section (absorption efficiency) is then obtained by normalizing $\sigma$ to the geometric cross-section of a nanosphere $\sigma_0 = \pi R^2$ with $R$ being the radius of the nanosphere.

The TD-DFT absorption spectra have been computed with a finite-difference in-house code (with spherical symmetry) introduced in Ref. 59; a radial uniform grid is used to represent KS orbitals and densities. In TD-DFT, no retardation effects are included, and only longitudinal electric field are considered [19]. The absorption cross-section [114–117], is calculated as

$$
\sigma(\omega) = \frac{\omega}{\epsilon_0} \text{Im} \{\alpha_{zz}(\omega)\},
$$

where the polarizability is given by

$$
\alpha_{zz}(\omega) = -e^2 \int drdr'z \chi(r, r', \omega) z',
$$

with $\chi(r, r', \omega) = \delta n(r)/\delta (eV_{\text{ext}}(r'))$ being the interac-
ting density response function [19], which is obtained solving the Dyson equation

$$
\chi = \chi_0 + \chi_0 (v_{\text{coul}} + f^{\text{LDA}}_{\text{XC}}) \chi.
$$

In Eq. (A4) $v_{\text{coul}}$ is the Coulomb interaction, $f^{\text{LDA}}_{\text{XC}}$ is the adiabatic LDA XC kernel, and $\chi_0$ is the non-interacting density response function, which is computed using Green’s function [115] using occupied KS orbitals from the ground-state calculation (again using LDA). The broadening parameter for the Green’s function calculations is, if not stated differently, $\Gamma_0 = 33$ meV.

**Appendix B: FEM implementation**

In order to lower the order of derivatives we multiply Eq. (1b) by test function $\tilde{\mathbf{P}}$ and integrate by parts, which gives us:

$$
\int \left\{ -\frac{e}{m_e} \left( \frac{\delta G[n]}{\delta n} \right)_l \left( \nabla \cdot \tilde{\mathbf{P}} \right) + \frac{1}{n_0} \left[ (\omega^2 + i\gamma \omega) \mathbf{P} + \epsilon_0 \omega_p^2 \mathbf{E} \right] \cdot \tilde{\mathbf{P}} \right\} dV = 0,
$$

where we assumed that the integral on the boundary goes to zero. Even after integration by parts ($\left( \frac{\delta G[n]}{\delta n} \right)_l$) potential contains derivatives up to the fourth-order of $n_1$ (see the Exps. (9)), so auxiliary variables should be added to lower the order of differentiation. By introducing two variables $\mathbf{F} = \nabla n_1$ and $\mathbf{O} = \nabla (\nabla^2 n_1) = \nabla \cdot \mathbf{F}$ we have only first-order derivatives. Considering axisymmetric of considered structures, we adopt 2D 5 technique [59, 94, 95], and the dependence of $\mathbf{E}, \mathbf{P}, \mathbf{F},$ and $\mathbf{O}$ on azimuthal coordinate is taken in $e^{-im\phi}$ form with $m \in \mathbb{Z}$. The dependence on $m$ for test functions $\tilde{\mathbf{E}}, \tilde{\mathbf{P}}, \tilde{\mathbf{F}},$ and $\tilde{\mathbf{O}}$ is of $e^{im\phi}$ form. Thus, instead of a three-dimensional problem, we can have $2m_{\text{max}} + 1$ problems (with $m_{\text{max}}$ being the maximum value for $m$). Moreover, for the dimensions considered in the current work $m_{\text{max}} = 0$ is enough for the convergence of results. Finally, only one two-dimensional problem needs to be solved. Hence, we come to the following system of equations:

$$
2\pi \int \left\{ \left( \nabla \times \mathbf{E}^{(0)} \right) \cdot \left( \nabla \times \tilde{\mathbf{E}}^{(0)} \right) - \left( k_0^2 \mathbf{E}^{(0)} + \mu_0 \omega^2 \mathbf{P}^{(0)} \right) \cdot \tilde{\mathbf{E}}^{(0)} \right\} \rho dp dz = 0,
$$

$$
2\pi \int \left\{ -\frac{e}{m_e} \left( \frac{\delta G[n]}{\delta n} \right)_l^{(0)} \left( \nabla \cdot \tilde{\mathbf{P}}^{(0)} \right) + \frac{1}{n_0} \left[ (\omega^2 + i\gamma \omega) \mathbf{P}^{(0)} + \epsilon_0 \omega_p^2 \left( \mathbf{E}^{(0)} + \mathbf{E}_{\text{inc}}^{(0)} \right) \right] \cdot \tilde{\mathbf{P}}^{(0)} \right\} \rho dp dz = 0,
$$

$$
2\pi \int \left\{ \left( \nabla \cdot \mathbf{P}^{(0)} \right) \left( \nabla \cdot \tilde{\mathbf{F}}^{(0)} \right) + \epsilon \mathbf{F}^{(0)} \cdot \tilde{\mathbf{F}}^{(0)} \right\} \rho dp dz = 0,
$$

$$
2\pi \int \left\{ \left( \nabla \cdot \mathbf{F}^{(0)} \right) \left( \nabla \cdot \tilde{\mathbf{O}}^{(0)} \right) + \mathbf{O}^{(0)} \cdot \tilde{\mathbf{O}}^{(0)} \right\} \rho dp dz = 0,
$$

where (0) superscript denotes the zero-order coefficients of the $\mathbf{v}(\rho, \phi, z) = \sum_{m \in \mathbb{Z}} V^{(m)}(\rho, z) e^{-im\phi}$ vector field expansion of cylindrical harmonics. We found that curl elements for Eq. (B2a) and divergence elements [93] for other equations of the system (B2) are the best choice for stable solutions.
For the wave equation Eq. (B2a), simulation domain radius \( R_{\text{dom}} \) is defined via \( R_{\text{dom}} = R + 500a_0 \) condition. \( R = r_s N_1^{1/3} \) is the radius of the nanosphere, and, for dimers, it is the radius of one of the spheres. Perfectly matched layers (PML) are used in order to emulate an infinite domain and avoid unwanted reflections. PML thickness is set to \( t_{\text{PML}} = 200a_0 \) for all the considered systems. Also, zero flux boundary condition is imposed on the electric field at the outer boundary of the PML. For Eqs. (B2b) - (B2d), simulations are done in a smaller domain, considering faster decay of variables \( P, F, \) and \( O \) compared to the electric field. The domain, as depicted in Fig. S2 (a) of SM [90], is a semicircle (consider the axial symmetry), for the nanospheres and, for the dimers, is the union of 2 circles centered at the centers of nanospheres. Moreover, to facilitate the calculations, only the "quarter" of the dimer is simulated with a corresponding perfect electric conductor condition at the intersection segment of 2 circles, as shown in Fig. S2 (b) of SM [90]. The radii for the circles is \( r_{\text{dom}} = r + 25a_0 \) for QHT and QHT-PGS, but for QHT-PGSL, it is in the range \( r_{\text{dom}} \approx r + 12a_0 \). The simulation domain is smaller for QHT-PGSL, because \( \nu \approx 1.12 \) decay slope is bigger in this case (see Sec. VI). Dirichlet boundary conditions \( P = 0, F = 0 \) and \( O = 0 \) are set on the simulation domain boundary. As stated in Section VI, mixed boundary condition with a fixed exponential decay can be used for QHT-PGSL, so that a very small simulation domain is enough for converged calculations.

[1] Alexei A. Maradudin, J. Roy Sambles, and William L. Barnes, eds., *Modern Plasmonics*, Handbook of Surface Science No. ser. ed.: Maradudin, Alexei A.; Vol. 4 (Elsevier, Amsterdam, 2014).

[2] Martti Kauranen and Anatoly V. Zayats, “Nonlinear plasmonics,” *Nature Photon.* 6, 737–748 (2012).

[3] Mengxin Ren, Eric Plum, Jingjin Xu, and Nikolay I. Zheludev, “Giant nonlinear optical activity in a plasmonic metamaterial,” *Nat. Commun.* 3, 833 (2012).

[4] Mark L. Brongersma, Naomi J. Halas, and Peter Nordlander, “Plasmon-induced hot carrier science and technology,” *Nature Nanotech.* 10, 25–34 (2015).

[5] Ilya Goykhman, Boris Desiatov, Jacob Khurgin, Joseph Shappir, and Uriel Levy, “Locally Oxidized Silicon Surface-Plasmon Schottky Detector for Telecom Regime,” *Nano Lett.* 11, 2219–2224 (2011).

[6] Hongxing Xu, Erik J. Bjerneld, Mikael Käll, and Lars Börjesson, “Spectroscopy of Single Hemoglobin Molecules by Surface Enhanced Raman Scattering,” *Phys. Rev. Lett.* 83, 4357–4360 (1999).

[7] Satoshi Kawata, Yasushi Inouye, and Prabhat Verma, “Size-Dependent Optical Properties of Aluminum Nanoparticles: From Classical to Quantum Description,” *ACS Photonics* 4, 1484–1493 (2017).

[8] Rajarshi Sinha-Roy, Pablo García-González, Hans-Christian Weisssker, Frank Rabilloud, and Antonio I. Fernández-Domínguez, “Classical and ab Initio Plasmonics Meet at Sub-nanometric Noble Metal Rods,” *ACS Photonics* 4, 1484–1493 (2017).

[9] Mengxin Ren, Eric Plum, Jingjin Xu, and Nikolay I. Zheludev, “Giant nonlinear optical activity in a plasmonic metamaterial,” *Nat. Commun.* 3, 833 (2012).
nally Doped Silicon Nanocrystals," ACS Photonics 6, 1474–1484 (2019).
[25] E. Madelung, “Quantentheorie in hydrodynamischer Form,” Z. Phys. 40, 322–326 (1927).
[26] F. Bloch, “Bremsvermögen von Atomen mit mehreren Elektronen,” Z. Phys. 81, 363–376 (1933).
[27] H. Jensen, “Eigenschwingungen eines Fermi-Gases und Anwendung auf die Blochsche Bremsformel für schnelle Teilchen,” Z. Phys. 106, 620–632 (1937).
[28] S. C. Ying, “Hydrodynamic response of inhomogeneous metallic systems,” Nuov. Cim. B 23, 270–281 (1974).
[29] Robert G. Parr and Weitao Yang, Introduction to Quantum Theory: A Route to Multi-Million Atom Non-Periodic Density Functional Calculations (Springer, 2014).
[30] Yan Alexander Wang, Niranjan Govind, and Emily A. Carter, “Orbital-free kinetic-energy functionals for the nearly free electron gas,” Phys. Rev. B 58, 13465 (1998).
[31] Tomasz A. Wesolowski and Yan Alexander Wang, eds., Recent Progress in Orbital-free Density Functional Theory (World Scientific, Singapore, 2013).
[32] L. H. Thomas, “The calculation of atomic fields,” Math. Proc. Camb. Phil. Soc. 23, 542–548 (1927).
[33] E. Fermi, “Un Metodo Statistico per la Determinazione di alcune Proprietà dell’Atomo,” Rend. Accad. Naz. Lincei 6, 602–607 (1927).
[34] Vikram Gavini, Kaushik Bhattacharya, and Michael Ortiz, “Quasi-continuum orbital-free density-functional theory: A route to multi-million atom non-periodic DFT calculation,” J. Mech. Phys. Solids 55, 697–718 (2007).
[35] Junchao Xia and Emily A. Carter, “Density-decomposed orbital-free density functional theory for covalently bonded molecules and materials,” Phys. Rev. B 86, 235109 (2012).
[36] Ilgyou Shin and Emily A. Carter, “Enhanced von Weizsäcker-Wang-Govind-Carter kinetic energy density functional for semiconductors,” J. Chem. Phys. 140, 18A531 (2014).
[37] Lucian A. Constantin, Eduardo Fabiano, and Fabio Di Bella, “Nonlocal kinetic energy functional from the jellium-with-gap model: Applications to orbital-free density functional theory,” Phys. Rev. B 97, 205137 (2018).
[38] William C. Witt, Beatriz G. del Rio, Johannes M. Dieterich, and Emily A. Carter, “Orbital-free density functional theory for materials research,” J. Mater. Res. 33, 777–795 (2018).
[39] A. Domps, P.-G. Reinhard, and E. Suraud, “Time-Dependent Thomas-Fermi Approach for Electron Dynamics in Metal Clusters,” Phys. Rev. Lett. 80, 5520–5523 (1998).
[40] Daniel Neuhauser, Shlomo Pistiner, Arunima Coomar, Xu Zhang, and Gang Lu, “Dynamic kinetic energy potential for orbital-free density functional theory,” J. Chem. Phys. 134, 144101 (2011).
[41] Hongping Xiang, Mingliang Zhang, Xu Zhang, and Gang Lu, “Understanding Quantum Plasmonics from Time-Dependent Orbital-Free Density Functional Theory,” J. Phys. Chem. C 120, 14330–14336 (2016).
[42] Xu Zhang, Hongping Xiang, Mingliang Zhang, and Gang Lu, “Plasmonic resonances of nanoparticles from large-scale quantum mechanical simulations,” Int. J. Mod. Phys. B 31, 1740003 (2017).
[43] Neil W. Ashcroft and N. David Mermin, Solid State Physics (Holt, Rinehart and Winston, New York, 1976).
[44] C. Ciraci, R. T. Hill, J. J. Mock, Y. Urzhumov, A. I. Fernandez-Domínguez, S. A. Maier, J. B. Pendry, A. Chilkoti, and D. R. Smith, “Probing the Ultimate Limits of Plasmonic Enhancement,” Science 337, 1072–1074 (2012).
[45] Soren Raza, Nicolas Stenger, Shima Kadkhodazadeh, Saren V. Fischer, Natalie Kostesha, Anti-Pekka Jauho, Andrew Burrows, Martijn Wubs, and N. Asger Mortensen, “Blueshift of the surface plasmon resonance in silver nanoparticles studied with EELS,” Nanophotonics 2, 131–138 (2013).
[46] T. V. Teperik, P. Nordlander, J. Aizpurua, and A. G. Borisov, “Robust Subnanometric Plasmon Ruler by Rescaling of the Nonlocal Optical Response,” Phys. Rev. Lett. 110, 263901 (2013).
[47] Thomas Reiners, Christoph Ellert, Martin Schmidt, and Hellmut Haberland, “Size Dependence of the Optical Response of Spherical Sodium Clusters,” Phys. Rev. Lett. 74, 1556–1561 (1995).
[48] Jian-Hao Li, Michitoshi Hayashi, and Guang-Yu Guo, “Plasmonic excitations in quantum-sized sodium nanoparticles studied by time-dependent density functional calculations,” Phys. Rev. B 88, 155437 (2013).
[49] Christin David and F. Javier García de Abajo, “Surface Plasmon Dependence on the Electron Density Profile at Metal Surfaces,” ACS Nano 8, 9558–9566 (2014).
[50] C. F. von Weizsäcker, “Zur Theorie der Kernmassen,” Z. Phys. 96, 431–438 (1935).
[51] G. Manfredi, “How to model quantum plasma,” Fields Inst. Comm. 46, 263 (2005).
[52] Michael Bonitz, Jose Lopez, Kurt Becker, and Hauke Thomasen, eds., Complex Plasmas: Scientific Challenges and Technological Opportunities, Springer Series on Atomic, Optical, and Plasma Physics, Vol. 82 (Springer International Publishing, Cham, 2014).
[53] P. K. Shukla and B. Eliasson, “Novel attractive force between ions in quantum plasmas,” Phys. Rev. Lett. 108, 165007 (2012).
[54] D. Michta, F. Graziani, and M. Bonitz, “Quantum Hydrodynamics for Plasmas - a Thomas-Fermi Theory Perspective: Quantum Hydrodynamics for Plasmas - a Thomas-Fermi Theory Perspective,” Contrib. Plasma Phys. 55, 437–443 (2015).
[55] Zh. A. Moldabekov, M. Bonitz, and T. S. Ramazanov, “Theoretical foundations of quantum hydrodynamics for plasmas,” Phys. Plasmas 25, 031903 (2018).
[56] M. Bonitz, Zh. A. Moldabekov, and T. S. Ramazanov, “Quantum hydrodynamics for plasmas— Quo vadis ?” Phys. Plasmas 26, 090601 (2019).
[57] Arup Banerjee and Manoj K. Harbola, “Hydrodynamical approach to collective oscillations in metal clusters,” Phys. Lett. A 372, 2881–2886 (2008).
[58] Giuseppe Toscano, Jakob Straubel, Alexander Kwiatkowski, Carsten Rockstuhl, Ferdinand Evers, Hongxing Xu, N. Asger Mortensen, and Martijn Wubs, “Resonance shifts and spill-out effects in self-consistent hydrodynamic nanoplasmics,” Nat. Commun. 6, 7132 (2015).
[59] Cristian Ciraci and Fabio Di Bella, “Quantum hydrodynamic theory for plasmonics: Impact of the electron density tail,” Phys. Rev. B 93, 205405 (2016).
[60] Kun Ding and C. T. Chan, “Plasmonic modes of polyg-
onal rods calculated using a quantum hydrodynamics method," Phys. Rev. B 96, 125134 (2017).

[61] Kun Ding and C. T. Chan, “Optical forces, torques, and force densities calculated at a microscopic level using a self-consistent hydrodynamics method,” Phys. Rev. B 97, 155118 (2018).

[62] Muhammad Khalid, Fabio Della Sala, and Cristian Ciraci, “Optical properties of plasmonic core-shell nanomatrixyoshkas: A quantum hydrodynamic analysis,” Opt. Express 26, 17322 (2018).

[63] Muhammad Khalid and Cristian Ciraci, “Numerical Analysis of Nonlocal Optical Response of Metallic Nanoshells,” Photonics 6, 39 (2019).

[64] Ying-Ying Zhang, Sheng-Bai An, Yuan-Hong Song, Nai-jing Kang, Z. L. Mikovi, and You-Nian Wang, “Plasmon excitation in metal slab by fast point charge: The role of additional boundary conditions in quantum hydrodynamic model,” Phys. Plasmas 21, 102114 (2014).

[65] Wei Yan, “Hydrodynamic theory for quantum plasmonics: Linear-response dynamics of the inhomogeneous electron gas,” Phys. Rev. B 91, 115416 (2015).

[66] D. I. Palade, “Multiple surface plasmons in an unbounded quantum plasma half-space,” Phys. Plasmas 23, 074504 (2016).

[67] Cristian Ciraci, “Current-dependent potential for nonlocal absorption in quantum hydrodynamic theory,” Phys. Rev. B 95, 245404 (2017).

[68] Cristian Ciraci, Radoslaw Jurga, Muhammad Khalid, and Fabio Della Sala, “Plasmonic quantum effects on single-emitter strong coupling,” Nanophotonics 8, 1821–1833 (2019).

[69] Domenico de Ceglia, Michael Scalaora, Maria A. Vincenti, Salvatore Campione, Kyle Kelley, Evan L. Runnerstrom, Jon-Paul Maria, Gordon A. Keeler, and Ting S. Luk, “Viscoelastic optical nonlocality of low-loss epsilon-near-zero nanofilms,” Sci. Rep. 8, 9335 (2018).

[70] A. Bergara, J.M. Pitarke, and R.H. Ritchie, “Nonlinear quantum hydrodynamical model of the electron gas,” Nucl. Instrum. Methods Phys. Res. 115, 70–74 (1996).

[71] N. Crouseilles, P.-A. Hervieux, and G. Manfredi, “Quantum hydrodynamic model for the nonlinear electron dynamics in thin metal films,” Phys. Rev. B 78, 155412 (2008).

[72] Muhammad Khalid and Cristian Ciraci, “Second-harmonic generation enhancement driven by quantum electron spill-out at metal surfaces,” (2020), arXiv:2004.07012 [physics.optics].

[73] Alan J. Bennett, “Influence of the Electron Charge Distribution on Surface-Plasmon Dispersion,” Phys. Rev. B 1, 203–207 (1970).

[74] Afshin Moradi, “Quantum nonlocal effects on optical properties of spherical nanoparticles,” Phys. Plasmas 22, 022119 (2015).

[75] Mario Kupresak, Xuezhi Zheng, Guy A. E. Vandenbosch, and Victor V. Moshchalkov, “Appropriate Nonlocal Hydrodynamic Models for the Characterization of Deep-Nanometer Scale Plasmonic Scatterers,” Adv. Theory Simul. 3, 1900172 (2020).

[76] Afshin Moradi, Canonical Problems in the Theory of Plasmonics, Springer Series in Optical Sciences, Vol. 230 (Springer International Publishing, Cham, 2020).

[77] R. Ruppin, “Optical Properties of a Plasma Sphere,” Phys. Rev. Lett. 31, 1434–1437 (1973).

[78] Basab B. Dasgupta and Ronald Fuchs, “Polarizability of a small sphere including nonlocal effects,” Phys. Rev. B 24, 554–561 (1981).

[79] Soren Raza, Giuseppe Toscano, Antti-Pekka Jaaho, Martijn Wubs, and N. Asger Mortensen, “Unusual resonances in nanoplasmonic structures due to nonlocal response,” Phys. Rev. B 84, 121412 (2011).

[80] D. E. Beck, “Self-consistent calculation of the eigenfrequencies for the electronic excitations in small jellium spheres,” Phys. Rev. B 35, 7325–7333 (1987).

[81] Matthias Brack, “The physics of simple metal clusters: Self-consistent jellium model and semiclassical approaches,” Rev. Mod. Phys. 65, 677–732 (1993).

[82] C. Yannouleas, E. Vigezzi, and R. A. Broglia, “Evolution of the optical properties of alkali-metal microclusters towards the bulk: The matrix random-phase-approximation description,” Phys. Rev. B 47, 9849–9861 (1993).

[83] P.-G. Reinhard, O. Genzken, and M. Brack, “From sum rules to rpa: 3. optical dipole response in metal clusters,” Ann. Phys. 508, 576607 (1996).

[84] Manoj K. Harbola, “Differential virial theorem and quantum fluid dynamics,” Phys. Rev. A 58, 1779–1798 (1998).

[85] D. I. Palade, “Nonlocal orbital-free kinetic pressure tensors for the Fermi gas,” Phys. Rev. B 98, 245101 (2018).

[86] Yan Alexander Wang and Emily A. Carter, “Orbital-Free Kinetic-Energy Density Functional Theory,” in Theoretical Methods in Condensed Phase Chemistry, Vol. 5, edited by Steven D. Schwartz (Kluwer Academic Publishers, Dordrecht, 2002) pp. 117–184.

[87] Lucian A. Constantin, Eduardo Fabiano, and Fabio Della Sala, “Semilocal Pauli-Gaussian Kinetic Functionals for Orbital-Free Density Functional Theory Calculations of Solids,” J. Phys. Chem. Lett. 9, 4385–4390 (2018).

[88] M. J. Stott and E. Zaremba, “Linear-response theory within the density-functional formalism: Application to atomic polarizabilities,” Phys. Rev. A 21, 12–23 (1980).

[89] Fabio Della Sala, Eduardo Fabiano, and Lucian A. Constantin, “Kinetic-energy density dependent semi-local exchange-correlation functionals,” Int. J. Quantum Chem. 116, 1641–1694 (2016).

[90] “See Supplementary Material at [URL will be inserted by publisher] for a Na jellium nanosphere, imaginary part of induced charge density n1 and norm of the total field as calculated from Mod/QHT, Mod/QHT-PGS and Mod/QHT-PGSL; a schematic image of simulation domain for a nanosphere and nanosphere dimer; derivation of the Exp. (7) for the functional derivative \( \frac{\delta T}{\delta n} \) of noninteracting KE functional \( T \); derivation of the Exp. (15) for the asymptotic form of the laplacian term for spherical system; fitting procedure to extracted the oscillator strength from the absorption spectra of Na jellium nanosphere.”

[91] J. P. Perdew and Alex Zunger, “Self-interaction correction to density-functional approximations for many-electron systems,” Phys. Rev. B 23, 5048–5079 (1981).

[92] D. A. Kirzhnits, “Quantum corrections to the thomas-fermi equation,” Sov. Phys. JETP 5, 64 (1957).

[93] COMSOL Multiphysics, https://www.comsol.com.

[94] Cristian Ciraci, Yaroslav A Urzhumov, and David R Smith, “Effects of classical nonlocality on the optical response of three-dimensional plasmonic nanodimers,”
Cristian Circi, Yaroslav Urzhumov, and David R. Smith, “Far-field analysis of axially symmetric three-dimensional directional cloaks,” Opt. Express 21, 9397 (2013).

Fabio Della Sala, “Finite difference quantum hydrodynamics for spherical systems,” in preparation (2020).

O. Bohigas, A.M. Lane, and J. Martorell, “Sum rules for nuclear collective excitations,” Physics Reports 51, 267–316 (1979).

Zhong-Jian Yang, Tomasz J. Antosiewicz, Ruggero Verre, F. Javier García de Abajo, S. Peter Apell, and Mikael Käll, “Ultimate Limit of Light Extinction by Nanophotonic Structures,” Nano Lett. 15, 7633–7638 (2015).

Jonathan A. Scholl, Ai Leen Koh, and Jennifer A. Dionne, “Quantum plasmon resonances of individual metallic nanoparticles,” Nature 483, 421–427 (2012).

S. J. A. van Gisbergen, J. M. Pacheco, and E. J. Adèle D. Laurent and Denis Jacquemin, “TD-DFT benchmarks: A review,” Int. J. Quantum Chem. 113, 2019–2039 (2013).

Oscar Baseggio, Martina De Vetta, Giovanna Fronzoni, Mauro Stener, Luca Sementa, Alessandro Fortunelli, and Arrigo Calzolari, “Photoabsorption of Icosahedral Noble Metal Clusters: An Efficient TDDFT Approach to Large-Scale Systems,” J. Phys. Chem. C 120, 12773–12782 (2016).

Kun Ding and C T Chan, “An eigenvalue approach to quantum plasmonics based on a self-consistent hydrodynamics method,” J. Phys. Condens. Matter 30, 084007 (2018).

O. Pérez-González, N. Zabala, A. G. Borisov, N. J. Halas, P. Nordlander, and J. Aizpurua, “Optical Spectroscopy of Conductive Junctions in Plasmonic Cavities,” Nano Lett. 10, 3090–3095 (2010).

Hyeon-Ho Jeong, Melanie C. Adams, Jan-Philipp Günther, Mariana Alarcón-Correa, Insook Kim, Eunjin Choi, Cornelia Miksch, Alison F. Mark, Andrew G. Mark, and Peer Fischer, “Arrays of Plasmonic Nanoparticle Dimers with Defined Nanogap Spacers,” ACS Nano 13, 11453–11459 (2019).

L. Schumacher, J. Jose, D. Janoschka, P. Dreher, T. J. Davis, M. Ligges, R. Li, M. Mo, S. Park, X. Shen, S. Weathersby, J. Yang, X. Wang, F. Meyer zu Heringdorf, K. Sokolowski-Tinten, and S. Schlücker, “Precision Plasmonics with Monomers and Dimers of Spherical Gold Nanoparticles: Nonequilibrium Dynamics at the Time and Space Limits,” J. Phys. Chem. C 123, 13181–13191 (2019).

John P. Perdew and Lucian A. Constantin, “Laplacian-level density functionals for the kinetic energy density and exchange-correlation energy,” Phys. Rev. B 75, 155109 (2007).

V. V. Karasiev, R. S. Jones, S. B. Trickey, and Frank E. Harris, “Properties of constraint-based single-point approximate kinetic energy functionals,” Phys. Rev. B 80, 245120 (2009).

Antonio C. Cancio, Dane Stewart, and Aeryk Kuna, “Visualization and analysis of the kohn-sham kinetic energy density and its orbital-free description in molecules,” J. Chem. Phys. 144, 084107 (2016).

Junji Seino, Ryo Kageyama, Mikito Fujinami, Yasuhiro Ikabata, and Hiromi Nakai, “Semi-local machine-learned kinetic energy density functional with third-order gradients of electron density,” J. Chem. Phys. 148, 241705 (2018).

Pavlo Golub and Sergei Manzhos, “Kinetic energy densities based on the fourth order gradient expansion: performance in different classes of materials and improvement via machine learning,” Phys. Chem. Chem. Phys. 21, 378 (2018).

Lucian A. Constantin, Eduardo Fabiano, and Fabio Della Sala, “Performance of semilocal kinetic energy functionals for orbital-free density functional theory,” J. Chem. Theory Comput. 15, 30443055 (2019).

A. Zangwill and Paul Soven, “Density-functional approach to local-field effects in finite systems: Photoabsorption in the rare gases,” Phys. Rev. A 21, 1561–1572 (1980).

W. Ekardt, “Size-dependent photoabsorption and photoemission of small metal particles,” Phys. Rev. B 31, 6360–6370 (1985).

G. Bertsch, “An RPA program for jellium spheres,” Comput. Phys. Commun. 60, 247–255 (1990).

E. Prodan and P. Nordlander, “Electronic structure and polarizability of metallic nanoshells,” Chem. Phys. Lett. 352, 140–146 (2002).
FIG. S1: Na jellium sphere with \( N_e = 1074 \) electrons. Imaginary part of induced charge density \( n_1 \) and norm of the total field \( E \) normalized to incident field amplitude \( E_0 \) at LSP resonance as calculated from Mod/QHT, Mod/QHT-PGS, and Mod/QHT-PGSL.

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FIG. S2: Schematic image of the simulation domain for a spherical nanoparticle (NP) - (a) and NP dimer - (b). R denotes the radius of the NP, \( r_{\text{dom}} \) - the radius of the simulation domain for \( \textbf{P}, \textbf{F}, \) and \( \textbf{O} \) variables, \( R_{\text{dom}} \) - the simulation domain for \( \textbf{E} \), and \( t_{\text{PML}} \) is the thickness of the perfectly matched layer (PML).

S1. FUNCTIONAL DERIVATIVE

Here we derive the functional derivative of \( T_s [n] \) (Exp. (7) of the main manuscript). Following Ref. 1 we have

\[
\frac{\delta T_s}{\delta n} = \frac{\partial \tau}{\partial n} - \nabla \cdot \frac{\partial \tau}{\partial (\nabla n)} + \nabla^2 \frac{\partial \tau}{\partial (\nabla^2 n)},
\]

(S1)

where \( \frac{\partial \tau}{\partial n} = \tau_i (i = n, w, q) \). In Exp. (S1)

\[
\nabla \cdot \frac{\partial \tau}{\partial (\nabla n)} = \nabla \cdot \left( \tau_w \frac{\partial w}{\partial (\nabla n)} \right) = 2 \nabla \cdot (\tau_w \nabla n) = 2 (\tau_w \nabla^2 n + \nabla \tau_w \cdot \nabla n)
\]

(S2)

\[
\nabla^2 \frac{\partial \tau}{\partial (\nabla^2 n)} = \nabla \cdot \left( \nabla \frac{\partial \tau}{\partial (\nabla^2 n)} \right) = \nabla \cdot (\nabla \tau_q) = \nabla \cdot (\tau_{qn} \nabla n + \tau_{qw} \nabla n + \tau_{qq} \nabla q)
\]

(S3)

Thus, Exp. (S1) simplifies to

\[
\frac{\delta T_s}{\delta n} = \tau_n - 2 (\tau_{wn} \nabla^2 n + \tau_{wn} \text{w} + \tau_{ww} (\nabla n \cdot \nabla w) + \tau_{ww} (\nabla n \cdot \nabla q))
\]

(S4)

Considering that our choice for \( \tau (n, w, q) \) (Exps. (5) and (6) of the main manuscript),
\[ \tau(n, w, q) = An^{-1}w + Bn^{5/3}e^{\alpha Cn^{-8/3}w} + Dn^{-5/3}q^2 \]

(S5)
is quadratic with respect to \( q \), and mixed derivatives of it that involve both \( q \) and \( w \) are zero, the final expression of \( \frac{\delta T_s}{\delta n} \) is (as Exp. (7) of the main manuscript):

\[ \frac{\delta T_s}{\delta n} = \tau_n + w\tau_{nnq} - 2w\tau_{nw} + \tau_{nwq} - 2q\tau_w + 2\tau_{nqq} (\nabla n \cdot \nabla q) - 2\tau_{ww} (\nabla n \cdot \nabla w) + \tau_{qq} \nabla^2 q. \]

(S6)

**S2. LINEARIZATION**

Here we derive the Exps. (9a) - (9c) of the main manuscript. For the linearization, \( \frac{\delta T_s}{\delta n} \) is expressed in Taylor series around \( n_0 \) ground state density (unperturbed), such that \( n = n_0 + n_1 \):

\[
\left( \frac{\delta T_s}{\delta n} \right)_1 = (\tau_n)_1 + (w\tau_{nnq})_1 - 2(w\tau_{nw})_1 + (q\tau_{nw})_1 - (q\tau_{w})_1 + 2(\tau_{nqq} \nabla n \cdot \nabla q)_1 - 2(\tau_{ww} \nabla n \cdot \nabla w)_1 + (\tau_{qq} \nabla^2 q)_1.
\]

(S7)

Keeping only terms linear with respect to \( n_1 \), we have for \( (\tau_n)_1 \):

\[
(\tau_n)_1 = \tau_{nn}^{(0)} (n - n_0) + \tau_{nw}^{(0)} (w - w_0) + \tau_{nq}^{(0)} (q - q_0) = \\
\tau_{nn}^{(0)} n_1 + \tau_{nw}^{(0)} \nabla (n_0 + n_1) \cdot \nabla (n_0 + n_1) - |\nabla n_0|^2 + \tau_{nq}^{(0)} \left[ \nabla^2 (n_0 + n_1) - \nabla^2 n_0 \right] + \tau_{nq}^{(0)} \nabla n_0 \nabla n_1.
\]

(S8)

where the superscript \((0)\) denotes that the function is evaluated at \( n = n_0 \). Similarly, for other terms in Exp. (S7) (and cancelling out partial derivatives that are zero) we get:

\[
(w\tau_{nnq})_1 = (w\tau_{nnq})^{(0)} n_1 + 2(\nabla n_0 \cdot \nabla n_1) (\tau_{nnq} + w\tau_{nnqw})^{(0)} + (w\tau_{nnqw})^{(0)} \nabla^2 n_1 = \\
\left[ \nabla n_0 \tau_{nnq}^{(0)} n_1 + 2(\nabla n_0 \cdot \nabla n_1) \tau_{nnq}^{(0)} + \nabla n_0 \nabla n_1 \tau_{nnq}^{(0)} \nabla^2 n_1, \right.
\]

(S9)

\[
-2(w\tau_{nw})_1 = -2 \left[ w\tau_{nw}^{(0)} n_1 + 2(\nabla n_0 \cdot \nabla n_1) (\tau_{nw} + w\tau_{nww})^{(0)} + (w\tau_{nwq})^{(0)} \nabla^2 n_1 \right] = \\
-2 \nabla n_0 \left[ 2 \tau_{nw}^{(0)} n_1 + 2(\nabla n_0 \cdot \nabla n_1) \tau_{nw}^{(0)} - 4(\nabla n_0 \cdot \nabla n_1) \tau_{nw}^{(0)} \nabla^2 n_1 \right]
\]

(S10)

\[
(q\tau_{nw})_1 = \nabla^2 n_0 \tau_{nqw}^{(0)} n_1 + 2(\nabla n_0 \cdot \nabla n_1) \nabla^2 n_0 \tau_{nqw}^{(0)} + \tau_{nq}^{(0)} \nabla^2 n_1 + \nabla^2 n_0 \tau_{nqw}^{(0)} \nabla^2 n_1 = \\
\nabla^2 n_0 \tau_{nqw}^{(0)} n_1 + \tau_{nq}^{(0)} \nabla^2 n_1 + \nabla^2 n_0 \tau_{nqw}^{(0)} \nabla^2 n_1,
\]

(S11)

\[
-2(q\tau_{w})_1 = -2 \nabla^2 n_0 \tau_{qw}^{(0)} n_1 - 4(\nabla n_0 \cdot \nabla n_1) \nabla^2 n_0 \tau_{qw}^{(0)} \nabla^2 n_1 - 2 \nabla n_0 \tau_{qw}^{(0)} \nabla^2 n_1 = \\
-2 \nabla^2 n_0 \tau_{qw}^{(0)} n_1 - 4(\nabla n_0 \cdot \nabla n_1) \nabla^2 n_0 \tau_{qw}^{(0)} - 2 \tau_{qw}^{(0)} \nabla^2 n_1,
\]

(S12)

\[
2(\tau_{nqq} (\nabla n \cdot \nabla q))_1 = 2 \left[ \tau_{nqq}^{(0)} (\nabla n_0 \cdot \nabla (\nabla^2 n_0)) n_1 + \tau_{nqq}^{(0)} \left[ (\nabla n \cdot \nabla q) \nabla n_0 \right] \cdot n_1 \right] + \tau_{nqq}^{(0)} (\nabla n_0 \cdot \nabla (\nabla^2 n_0)) \nabla^2 n_1 + \tau_{nqq}^{(0)} \left[ (\nabla n \cdot \nabla q) \nabla n_0 \cdot \nabla (\nabla^2 n_1) \right]
\]

(S13)
\[ -2 (\tau_{ww} (\nabla n \cdot \nabla w))_1 = -2 \left[ \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (|\nabla n_0|^2)) n_1 + \left( (\tau_{ww}(\nabla n \cdot \nabla w))_{\nabla n}^{0} \right) \cdot \nabla n_1 \right. \\
\left. + \left( (\tau_{ww}(\nabla n \cdot \nabla w))_{\nabla w}^{0} \right) \cdot \nabla^2 n_1 + \left( (\tau_{ww}(\nabla n \cdot \nabla w))_{\nabla w}^{0} \right) \cdot (\nabla w - \nabla w_0) \right] \\
= -2 \left[ \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (|\nabla n_0|^2)) n_1 + 2 \tau_{ww}^{0} (\nabla n_0 \cdot \nabla n_1) \left( \nabla n_0 \cdot \nabla (|\nabla n_0|^2) \right) \right. \\
\left. + \tau_{ww}^{0} (\nabla (|\nabla n_0|^2) \cdot \nabla n_1) + \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (\nabla n_0 + n_1) \cdot \nabla (n_0 + n_1) - |\nabla n_0|^2)) \right] \right] \\
(S14) \\
= -2 \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (|\nabla n_0|^2)) n_1 - 4 \tau_{ww}^{0} (\nabla n_0 \cdot \nabla n_1) \left( \nabla n_0 \cdot \nabla \left( |\nabla n_0|^2 \right) \right) \\
- 2 \tau_{ww}^{0} (\nabla \left( |\nabla n_0|^2 \right) \cdot \nabla n_1) - 2 \tau_{ww}^{0} \left( \nabla n_0 \cdot \nabla (2 (\nabla n_0 \cdot \nabla n_1)) \right) \\
- 2 \tau_{ww}^{0} \left( \nabla \left( |\nabla n_0|^2 \right) \cdot \nabla n_1 \right) - 4 \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (\nabla n_0 \cdot \nabla n_1)) \\
- \tau_{qq}^{0} \nabla^2 (\nabla^2 n_0) n_1 + \tau_{qq}^{0} \nabla^2 (\nabla^2 n_1) \\
(S15) \\
\] 

Substituting Exp. (S8) - (S15) into Exp. (S7) we get:

\[ \left( \frac{\delta T}{\delta n} \right)_1 = n_1 \tau_{nn}^{0} + 2 \tau_{nw}^{0} (\nabla n_0 \cdot \nabla n_1) + \tau_{nq}^{0} \nabla^2 n_1 \\
+ |\nabla n_0|^2 \tau_{nnq}^{0} n_1 + 2 (\nabla n_0 \cdot \nabla n_1) \tau_{nnq}^{0} + |\nabla n_0|^2 \tau_{nqq}^{0} \nabla^2 n_1 \\
- 2 |\nabla n_0|^2 \tau_{nnw}^{0} n_1 - 4 (\nabla n_0 \cdot \nabla n_1) \tau_{nnw}^{0} - 4 (\nabla n_0 \cdot \nabla n_1) |\nabla n_0|^2 \tau_{nnw}^{0} \\
+ \nabla^2 n_0 \tau_{nnq}^{0} n_1 + \tau_{nq}^{0} \nabla^2 n_1 + \nabla^2 n_0 \tau_{nqq}^{0} \nabla^2 n_1 \\
- 2 \nabla^2 n_0 \tau_{nnw}^{0} n_1 - 4 (\nabla n_0 \cdot \nabla n_1) \nabla^2 \tau_{nnw}^{0} - 2 \tau_{ww}^{0} \nabla^2 n_1 \\
+ 2 \tau_{nnq}^{0} \left( \nabla n_0 \cdot \nabla \left( \nabla^2 n_0 \right) \right) n_1 + 2 \tau_{nqq}^{0} \left( \nabla n_1 \cdot \nabla \left( \nabla^2 n_0 \right) \right) n_1 + 2 \tau_{nqq}^{0} \left( \nabla n_0 \cdot \nabla \left( \nabla^2 n_1 \right) \right) \\
- 2 \tau_{ww}^{0} \left( \nabla \left( |\nabla n_0|^2 \right) \cdot \nabla n_1 \right) - 4 \tau_{ww}^{0} (\nabla n_0 \cdot \nabla (\nabla n_0 \cdot \nabla n_1)) \\
+ \tau_{nqq}^{0} \nabla^2 (\nabla^2 n_0) n_1 + \tau_{nqq}^{0} \nabla^2 (\nabla^2 n_1) . \\
(S16) \\
\] 

Terms with partial derivative factors \( \tau_{nn}^{0} \), \( \tau_{nw}^{0} \), and \( \tau_{ww}^{0} \) determine potential \( \frac{\delta T_{\text{PFC}}}{\delta n} \), and \( \tau_{nq}^{0} \), \( \tau_{qq}^{0} \), \( \tau_{nnq}^{0} \), \( \tau_{nqq}^{0} \), and \( \tau_{nqq}^{0} \) - potential \( \frac{\delta T_{\text{PF}}}{\delta n} \).
S3. ASYMPTOTIC FORM OF THE LAPLACIAN TERM FOR SPHERICAL SYSTEM

For spherical systems we have that

\[ \nabla n_0(r) \nabla \left( \frac{\delta T_{L3}^{k0}}{\delta n} \right)_1 = \sum_{n=0}^{6} F_k[r, n_0(r)] \frac{d^k n_1(r)}{dr^k}, \]  

(S17)

where \( n_1(r) = n_1(r) \cos(\theta) \) and

\[ F_0 = \frac{1}{80} \frac{\sqrt{3} \beta}{\pi^{4/3} (n_0(r))^{2/3}}, \]  

(S18)

\[ F_5 = \frac{1}{240} \frac{\sqrt{3} \beta}{r \pi^{4/3} (n_0(r))^{5/3}}, \]  

(S19)

\[ F_4 = -\frac{1}{240} \frac{\sqrt{3} \beta}{r^2 \pi^{4/3} (n_0(r))^{8/3}} \left( 18 (n_0(r))^2 - 65 \left( \frac{d}{dr} n_0(r) \right)^2 r^2 + 40 \left( \frac{d^2}{dr^2} n_0(r) \right) r^2 n_0(r) + 108 \left( \frac{d}{dr} n_0(r) \right) r n_0(r) \right), \]  

(S20)

\[ F_3 = \frac{1}{2160} \frac{\sqrt{3} \beta}{r^{-2} \pi^{4/3} (n_0(r))^{-11/3}} \left( -1400 \left( \frac{d}{dr} n_0(r) \right)^3 r^2 - 450 \left( \frac{d^3}{dr^3} n_0(r) \right) r^2 (n_0(r))^2 \right. \]  

+ \[ 1935 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^2}{dr^2} n_0(r) \right) r^2 n_0(r) + 324 \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^2 \]  

- \[ 1980 \left( \frac{d^2}{dr^2} n_0(r) \right) r (n_0(r))^2 + 3690 \left( \frac{d}{dr} n_0(r) \right)^2 r n_0(r) \right), \]  

(S21)

\[ F_2 = \frac{1}{6480} \frac{\sqrt{3} \beta}{\pi^{-4/3} (n_0(r))^{-14/3} r^{-3}} \left( 4840 \left( \frac{d}{dr} n_0(r) \right)^4 r^3 - 1080 \left( \frac{d^4}{dr^4} n_0(r) \right) (n_0(r))^3 r^3 \right. \]  

+ \[ 3780 \left( \frac{d^2}{dr^2} n_0(r) \right)^2 (n_0(r))^2 r^3 - 28560 \left( \frac{d}{dr} n_0(r) \right)^3 n_0(r) r^2 + 2808 \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^3 \]  

+ \[ 2160 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^3 r - 14640 \left( \frac{d}{dr} n_0(r) \right)^2 \left( \frac{d^2}{dr^2} n_0(r) \right) n_0(r) r^3 \]  

+ \[ 5805 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^2 r^3 - 5940 \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^3 r^2 \]  

\[ - 270 \left( \frac{d}{dr} n_0(r) \right)^2 (n_0(r))^2 r + 32580 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^2 r^2 \right), \]  

(S22)
\[ F_1 = -\frac{1}{1296} \sqrt{\beta} \pi^{-4/3} (n_0(r))^{-14/3} r^{-4} \left( 108 \left( \frac{d^5}{dr^5} n_0(r) \right) (n_0(r))^3 r^4 + 3180 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^2 r^4 + 783 \left( \frac{d^4}{dr^4} n_0(r) \right) (n_0(r))^2 r^4 - 432 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^3 r^4 \right) \]

\[ + \frac{3528}{r^3} (n_0(r))^2 - 1296 \left( \frac{d^2}{dr^2} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^2 r^4 + 648 \left( \frac{d^4}{dr^4} n_0(r) \right) (n_0(r))^3 r^3 - 4136 \left( \frac{d}{dr} n_0(r) \right)^3 \left( \frac{d^2}{dr^2} n_0(r) \right) r^4 - 10208 \left( \frac{d}{dr} n_0(r) \right)^4 \]

\[ + \frac{1332}{r} \left( \frac{d}{dr} n_0(r) \right)^2 r + 2736 \left( \frac{d^3}{dr^3} n_0(r) \right) n_0(r) r^4 - 432 \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^3 r^2 + 432 \left( \frac{d}{dr} n_0(r) \right)^3 n_0(r) r^2 + 720 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^2 r^2 \]

\[ + 18288 \left( \frac{d}{dr} n_0(r) \right)^2 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^3 r^3 - 4806 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^2 r^3 \right), \] (S23)

\[ F_0 = -\frac{1}{3888} \sqrt{\beta} \pi^{-4/3} (n_0(r))^{-12/5} r^{-5} \left( 13176 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^2}{dr^2} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^2 r^5 + 2646 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^3 r^3 - 83424 \left( \frac{d}{dr} n_0(r) \right)^3 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^4 r^4 \right) \]

\[ - 4860 \left( \frac{d^4}{dr^4} n_0(r) \right) \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^3 r^4 + 4968 \left( \frac{d}{dr} n_0(r) \right) \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^3 r^2 \]

\[ - 2880 \left( \frac{d}{dr} n_0(r) \right)^2 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^2 r^3 + 25488 \left( \frac{d}{dr} n_0(r) \right)^2 \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^2 r^4 \]

\[ + 36648 \left( \frac{d^2}{dr^2} n_0(r) \right)^2 \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^2 r^4 - 783 \left( \frac{d^5}{dr^5} n_0(r) \right) \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^3 r^5 \]

\[ - 12408 \left( \frac{d}{dr} n_0(r) \right)^3 \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^3 r^5 - 21252 \left( \frac{d^2}{dr^2} n_0(r) \right)^2 \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^2 r^5 \]

\[ - 1728 \left( \frac{d^2}{dr^2} n_0(r) \right) \left( \frac{d^4}{dr^4} n_0(r) \right) (n_0(r))^3 r^5 + 4104 \left( \frac{d^4}{dr^4} n_0(r) \right) \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^2 r^5 \]

\[ - 9504 \left( \frac{d^2}{dr^2} n_0(r) \right) \left( \frac{d^3}{dr^3} n_0(r) \right) (n_0(r))^3 r^5 - 1080 \left( \frac{d^3}{dr^3} n_0(r) \right)^2 (n_0(r))^2 r^5 \]

\[ + 2772 \left( \frac{d^2}{dr^2} n_0(r) \right)^3 (n_0(r))^2 r^5 + 81 \left( \frac{d^6}{dr^6} n_0(r) \right) (n_0(r))^4 r^5 \]

\[ - 2484 \left( \frac{d}{dr} n_0(r) \right)^3 (n_0(r))^3 r + 1944 \left( \frac{d^2}{dr^2} n_0(r) \right)^2 (n_0(r))^3 r^3 + 1296 \left( \frac{d^2}{dr^2} n_0(r) \right) (n_0(r))^4 r^4 \]

\[ - 648 \left( \frac{d^4}{dr^4} n_0(r) \right) (n_0(r))^4 r^4 + 48 \left( \frac{d^5}{dr^5} n_0(r) \right) (n_0(r))^4 r^4 \]

\[ + 17248 \left( \frac{d}{dr} n_0(r) \right)^4 \left( \frac{d^2}{dr^2} n_0(r) \right) r^5 - 5472 \left( \frac{d}{dr} n_0(r) \right)^3 (n_0(r))^2 r^2 \]

\[ - 1584 \left( \frac{d}{dr} n_0(r) \right)^4 (n_0(r))^3 r^3 + 34496 \left( \frac{d}{dr} n_0(r) \right)^5 r^4 - 1296 \left( \frac{d}{dr} n_0(r) \right) (n_0(r))^4 \right), \] (S24)
The above expressions are valid everywhere (for spherical systems). In the asymptotic region, we can use $n_0(r) = A_0 \exp(-\kappa r)$, obtaining:

$$F_6 = \frac{1}{80 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3}$$

$$F_5 = \frac{1}{240 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^2$$

$$F_4 = \frac{1}{240 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^2$$

$$F_3 = \frac{1}{2160 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^2$$

$$F_2 = \frac{1}{240 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^2$$

$$F_1 = -\frac{1}{1296 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^4$$

$$F_0 = -\frac{1}{1944 \pi^{4/3}} (A_0 e^{-\kappa r})^{2/3} r^5$$

(S25) (S26) (S27) (S28) (S29) (S30) (S31)

In the asymptotic region, we have also to consider only the lowest $1/r$ power, thus obtaining the Exp. (15) in the main manuscript.

S4. FITTING PROCEDURE TO EXTRACT THE OSCILLATOR STRENGTH

We fit the photoabsorption cross-section (of all QHT approaches and reference TD-DFT) with the function

$$f(\omega) = \frac{2}{\pi} \frac{\omega^2 \gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2},$$

where $\gamma$ is the broadening parameter and $\omega_0$ the peak position. Note that $f(\omega)$ has a maximum at $\omega = \omega_0$ and $f(\omega_0) = 2/(\pi \gamma)$. This function integrates to 1 in the range $0 < \omega < +\infty$ and originates from the Drude classical solution of a nanosphere, whose photoabsorption cross-section in CGS units is [2]:

$$\sigma(\omega) = \frac{4\pi}{c} \text{Im} \left[ R^3 \epsilon(\omega) - 1 \right] \frac{\epsilon(\omega) + 2}{\epsilon(\omega) + 2} f(\omega) = \frac{2\pi^2 \omega_p^2}{3c} f(\omega) = \frac{2\pi^2}{c} \frac{e^2}{m_e} N \sigma_m \sigma f(\omega),$$

(S32) (S33)

where we used that $\omega_0 = w_p/\sqrt{3}$, $\omega_p = \sqrt{4\pi e^2/m_e (N/V)}$ and $V = (4\pi/3)R^3$. For a jellium nanosphere of very large $R$, QHT and TD-DFT will reach the classical limit [3], thus the function $f(\omega)$ is the right function to be used in the fitting procedure, where we minimize:

$$E = \frac{\int_{\omega_0}^{\omega_b} [f_{\text{osc}}(\omega) - \sigma_m(\omega)] d\omega}{\int_{\omega_0}^{\omega_b} \sigma_m(\omega) d\omega},$$

(S34)

where $\sigma_m(\omega)$ is the input absorption spectra (QHT or TD-DFT). The error depends on three parameters $f_{\text{osc}}, \omega_0$, and $\gamma$. For the range, we consider $\omega_a = 1$ eV whereas $\omega_b$ is the energy position where other peaks/shoulders starts after the LSP resonance. In this way, only the LSP peak is included in the fit, whereas other high-energy peaks or shoulders are not considered. As an example, we show in Fig. S3 the QHT spectra for $N_e = 1074$. The resulting fit is very accurate for all energies less than $\omega_b$. Other peaks above $\omega_b$ are not included in the peaks, so that the oscillator strength of the first main peak can be obtained. For QHT, one can also do a fit with several $f(\omega)$, one for each peak, obtaining the same results.

The situation complicates for the TD-DFT spectrum. In Fig. S4 a), we report the TD-DFT spectrum for $N_e = 6174$ (i.e., the largest system considered) and the corresponding fit (green dashed-line) with Eq. (S32). The error in the fit is 2.1% in the fitting range and fitted $f_{\text{osc}}$ is 890. The fitting curve is not very accurate as the TD-DFT values (for low and high energies) are not well reproduced.
In order to improve the fit, we considered an energy-dependent broadening [4], i.e., $\gamma = g(\omega)$ and to model the function $g(\omega)$, we inverted Eq. (S32) as a function on $\omega$. For an arbitrary spectrum $\sigma(\omega)$ with $f_{osc} = \int_{0}^{\infty} \sigma(\omega)d\omega$ we define the function:

$$\Gamma(\omega) = \frac{\pi(\omega_0^4 - \omega^4)}{\omega^3} \frac{\sigma(\omega)^2}{f_{osc}\frac{d\sigma(\omega)}{d\omega}}.$$  \hfill (S35)

It can be easily verified that if $\sigma(\omega) = f_{osc}f(\omega)$, then we obtain a constant function $\Gamma(\omega) = \gamma$. In Fig. S4 b), we report the function $\Gamma(\omega)$ for the TD-DFT absorption spectra using Eq. (S35). There are some spikes at $\omega = \omega_0$ due to the presence vanishing first derivative at the main plasmon peak. For high- and low-energy, we see that $\Gamma(\omega)$ approaches exactly $2\Gamma_0$, where $\Gamma_0$ is the broadening used in TD-DFT calculation. Thus, we define a model $g(\omega)$ with the following limits $g(\omega \leq \omega_{low}) = 2\Gamma_0$, where $\omega_{low}$ is close to $\omega_a$ and $g(\omega > \omega_p) = 2\Gamma_0$, where $\omega_p$ is the plasma frequency. In between these limits, the function $g(\omega)$ grows up to the maximum values of $g(\omega_1) = \gamma$, where $\omega_1$ is fixed to be $\omega_b$ i.e. the energy where the shoulder in the spectrum starts. If the TD-DFT absorption spectrum is fitted with such function, we obtain the red-curve in Fig. S4a) with an error reduced by a factor of 4 (0.6%) and also a reduced oscillator strength ( $f_{osc} = 872$). The non-linear fit is done using four parameters: $f_{osc}, \omega_0, \gamma$, and $\omega_{low}$. Note also that the function $f(\omega)$ has to be renormalized to integrate to 1 when a frequency dependent broadening is used. In Fig. S4 b) we report the function $\Gamma(\omega)$ obtained from the fitted curve. The agreement with the TD-DFT results is very good, for all energies before and after the plasmon shoulder.

In Table S1, we report all the parameters for the fits of the TD-DFT spectra. Note that for the fits, we compute the TD-DFT with a broadening of $\Gamma_0 = 0.1$ eV, to have a smooth curve, which is required especially for small spheres. The $f_{osc}$ of the LSP peak is thus very accurate (about 1%) for systems where the plasmon shoulder is clearly observed (i.e., for $N_e > 1000$).

[1] Fabio Della Sala, Eduardo Fabiano, and Lucian A. Constantin, “Kinetic-energy-density dependent semi-local exchange-correlation functionals,” Int. J. Quantum Chem. 116, 1641–1694 (2016).
[2] Uwe Kreibig and Michael Vollmer, Optical Properties of Metal Clusters, edited by J. Peter Toennies, U. Gonser, R. M. Osgood, M. B. Panish, H. Sakaki, and Helmut K. V. Lotsch, Springer Series in Materials Science, Vol. 25 (Springer Berlin Heidelberg, Berlin, Heidelberg, 1995).
[3] Matthias Brack, “The physics of simple metal clusters: self-consistent jellium model and semiclassical approaches,” Rev. Mod. Phys. 65, 677–732 (1993).
[4] E. Zaremba and B. N. J. Persson, “Dynamic polarizability of small metal particles,” Phys. Rev. B 35, 596–606 (1987).
FIG. S4: a) TD-DFT photoabsorption cross section (black line) for $N_e=6174$ and using $\Gamma_0=0.1\text{eV}$ and its fits using a constant broadening (dashed-green line) and an energy-dependent broadening (red line). The fits consider only the region from 1 eV up to $\omega_b=4.1\text{eV}$, which represent the onset of the plasmon shoulder. b) Function $\Gamma(\omega)$ obtained from the three curve in panel a).

| $N_e$ | $\omega_0$ | $\gamma$ | $f_{osc}$ | $\omega_1$ | $\omega_b$ |
|-------|-----------|--------|--------|--------|--------|
| 254   | 3.08797   | 0.88216| 35.94383| 2.59131| 3.83797|
| 338   | 3.13421   | 0.52539| 47.51501| 1.83333| 3.60421|
| 556   | 3.18204   | 0.44196| 76.59263| 1.00001| 3.95204|
| 832   | 3.20140   | 0.44291| 117.08588| 1.33059| 3.97140|
| 1074  | 3.21699   | 0.37609| 149.89713| 1.56759| 3.72699|
| 1284  | 3.23376   | 0.36143| 177.38700| 1.44677| 3.72376|
| 1516  | 3.24390   | 0.36138| 210.54419| 1.00000| 4.04390|
| 1760  | 3.24730   | 0.36607| 244.62864| 1.40239| 4.04730|
| 2048  | 3.25425   | 0.36936| 286.90874| 1.25072| 4.05425|
| 2654  | 3.26583   | 0.35402| 371.71087| 1.22778| 3.89583|
| 3404  | 3.27786   | 0.35134| 480.75394| 1.07239| 4.07786|
| 4570  | 3.28959   | 0.33304| 643.47974| 1.35421| 4.08959|
| 5470  | 3.29687   | 0.32296| 771.47150| 0.99999| 4.09687|
| 6174  | 3.30032   | 0.31742| 871.93036| 1.06694| 4.10032|

TABLE S1: Parameters from the fits of the TD-DFT photo-absorption cross section. All values but $f_{osc}$ in eV.