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Fast computations of the dielectric response of systems with spherical or axial symmetry

Y. Pavlyukh[*] and J. Berakdar
Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Str. 4, 06120 Halle, Germany

K. Köksal
Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Str. 4, 06120 Halle, Germany and Physics Department, Bitlis Eren University, 13000 Bitlis, Turkey

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When the size of a system does not permit a quantum-mechanical treatment it is still possible to obtain an accurate description of the collective electronic excitations by using a semiclassical approximation for the density-density response function. The dielectric function in this approach is a nonlocal quantity dependent on the electron density as a single parameter. The optical response is described by the Fredholm integral equation as demonstrated by Mukhopadhyay and Lundqvist [Nuovo Cimento B **27**, 1 (1975)]. The optical response has to be evaluated numerically, except for few models amenable to analytic solutions (typically with the density abruptly varying at the interface). We demonstrate that for the systems with a spherical or an axial symmetry this equation can be reduced to the Volterra integral equation, which furthermore can be solved as a system of differential equations. This observation leads to an efficient numerical scheme that scales as $\mathcal{O}(N)$, where N is the number of mesh points for the density. This is to be contrasted with $\mathcal{O}(N^3)$ scaling in commonly used brute-force implementations.

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I. INTRODUCTION

The dielectric response of electronic matter[1] is a key quantity for a wide range of phenomena including the energy ω and momentum $\mathbf{k}$ exchange with a traversing particle and the refraction and absorption of light. The recent reviews on the interaction of nanoparticles with light[2] or electrons[3] provide an overview on the topics including the relevance for the nanotechnology and plasmonics. In the linear response regime, the key quantity in the treatment of the dielectric response, regardless of the type of excitations, is the density-density response $\chi(\mathbf{r},\mathbf{r}';\omega)$ function. When the exciting light wave-length exceeds well the nanoparticle size the dipole approximation is justified and only the dipole term ($\ell = 1$) in a spherical harmonics expansion of $\chi(\mathbf{r},\mathbf{r}';\omega)$ is required. This is not so for excitations using the scanning tunneling microscopy and the electron energy loss spectroscopy that may involve a full range of angular momenta ℓ.

Quantum theory accounts inherently for the nonlocality of the dielectric function that can in principle be calculated fully *ab initio*. However, due to enormous computational cost, a fully atomistic approach is feasible only for small molecular systems. As a first approximation to treat nanoparticles one may assume a delocalized electron with boundary conditions compatible with the system symmetry (*jellium model*). In fact, this assumption is reasonable even for molecular structures, as we have shown recently[4,5] for fullerenes. The usefulness of the jellium model was demonstrated by the pioneering works of Ekardt on sodium clusters[6,7] or of Puska and Nieminen on C_{60}.[8] Relatively simple electronic structure (absence of the localized d-electrons) substantiates the approach. Another important prerequisite is a trick suggested by Zangwill and Soven[9] to avoid summation over the infinite number of unoccupied states for the calculation of the noninteracting density-density response function $\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega)$. Over the years several authors perfected the method (now the treatment of systems containing millions of electrons is possible[10]), and applied it to a range of geometries: starting from the simple spherical symmetry (spherical clusters, nanoshells) to systems without any symmetry[11] and used theories from the random phase approximations (RPA) to time-dependent density functional theory (TDDFT).

Our paper deals with a situation where a system has dimensions prohibitively large for atomistic approach, but still is treatable on the quantum level within the jellium model. For frequencies of external fields ω exceeding the single-particle gap E_g ($\omega \gg E_g$) the semiclassical approximation becomes well justified and allows one to write the frequency-dependent nonlocal dielectric function solely in terms of the electron density.[12] This in turn allows one to formulate an integral equation for the optical response as was demonstrated for a number of relevant geometries by Mukhopadhyay and Lundqvist.[13] In comparison with RPA or TDDFT this semiclassical approximation (SCA) is substantially simpler as it is free from summations over the electronic states. Recent comparison of the two approaches reveals a remarkable agreement between them.[10] This is mostly expressed in the energy positions of collective resonances. Quantum effects such as discreteness of the electronic structure are manifested as small deviations at the resonances' wings. In the case of abruptly varying density (expressible as a combination of the step functions) the SCA integral equation can be reduced to an algebraic one. Analytical solutions in this case are in agreement with the classical Mie theory using the Drude dielectric function.

In view of its simplicity and accuracy SCA is potentially a practical tool for nanoplasmonics. However, its use was hindered by the difficulties of solving the integral equation and was considered to be a *formidable task*.[14] In fact, conventional methods require discretization of the integral equation and solution of the resulting system of linear equations. The method unfavorably scales as $\mathcal{O}(N^3)$ with the number of mesh points and is, thus, not practical for large systems, where one necessarily uses very fine meshes to describe nonsmooth electron densities at the interfaces. In the present work we go one step further toward an analytic solution of the problem for systems with symmetries. We show that the SCA integral equation can be reduced to a system of two coupled differential equations. Although in general their solution cannot be obtained analytically it still presents a huge computation saving as the problem can be solved with $\mathcal{O}(N)$ complexity.

The work is organized as follows. In Sec. II we give very general derivation of the SCA integral equation without imposing any restriction on the locality of light-matter interaction. Equations are written in the form to demonstrate parallels between the spherical and axial symmetry. In Sec. III we discuss methods of solutions. To illustrate our approach we compute the optical response of the Na_{2869}^{-} cluster in Sec. IV. The discussion in this section is also concerned with another important aspect of the problem: the validity of the jellium model as such. It is not uncommon that the jellium model is used to (i) discuss noble metal systems where d-electrons cannot be considered as delocalized and (ii) discuss quantum effects such as spill out of the electron density which cannot be accessed without the knowledge of the true ionic potential. Thus this section is devoted to the verification of these issues.

We use atomic units, i.e.,$\hbar = e = m_e = 4\pi\varepsilon_0 = 1$ throughout. The Appendixes contain mathematical details that make the exposition in Secs. II and III self-contained.

II. DIELECTRIC RESPONSE

The key quantity for our discussion is the *dielectric function*. In the random phase approximation (RPA) it is given by [cf. Eq. (5.19) of Ref. 15]

$$\varepsilon(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int v(\mathbf{r}-\mathbf{r}_1)\chi^{(0)}(\mathbf{r}_1,\mathbf{r}';\omega)d\mathbf{r}_1, \tag{1}$$

where $v(\mathbf{r}-\mathbf{r}_1)$ is the Coulomb potential and $\delta(\mathbf{r}-\mathbf{r}') \equiv \delta(x-x')\delta(y-y')\delta(z-z')$.

The summation over the spin indices yields a prefactor 2 in front of the *noninteracting density-density response* function [known as Lindhard function for the homogeneous electron gas in three dimensions (3D)]:

$$\begin{aligned}\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega) = 2\sum_{i,j}\frac{f_i - f_j}{\omega + E_i - E_j + i\eta}\\ \times \psi_i(\mathbf{r})\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')\psi_i^*(\mathbf{r}'),\end{aligned} \tag{2}$$

where f is the Fermi function and i, j refer to collections of quantum numbers that uniquely characterize electronic states of the system. The infinitesimally small positive number η shifts the poles from the real axis and ensures, thus, the causality of the response function. In what follows we will assume it can be incorporated in the ω variable. Likewise, in the random phase approximation the *density-density response* function can be obtained as

$$\begin{aligned}\chi(\mathbf{r},\mathbf{r}';\omega) = \chi^{(0)}(\mathbf{r},\mathbf{r}';\omega) + \int d\mathbf{r}_1\int d\mathbf{r}_2\, \chi(\mathbf{r},\mathbf{r}_1;\omega)\\ \times v(\mathbf{r}_1-\mathbf{r}_2)\chi^{(0)}(\mathbf{r}_2,\mathbf{r}';\omega)\end{aligned} \tag{3}$$

or

$$\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega) = \int d\mathbf{r}_1\, \chi(\mathbf{r},\mathbf{r}_1;\omega)\varepsilon(\mathbf{r}_1,\mathbf{r}';\omega). \tag{4}$$

For time-reversal invariant systems the density-density response functions are symmetric $\chi(\mathbf{r},\mathbf{r}';\omega) = \chi(\mathbf{r}',\mathbf{r};\omega)$ and $\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega) = \chi^{(0)}(\mathbf{r}',\mathbf{r};\omega)$ (cf. Sec. 3.2.4 of Ref. 15).

When for the light-matter interaction the multipole expansion is adopted the *ℓ-pole frequency-dependent polarizability* is defined as

$$\alpha_{\ell m}(\omega) = -\int d\mathbf{r}\int d\mathbf{r}'\, Q^*_{\ell m}(\mathbf{r})\chi(\mathbf{r},\mathbf{r}';\omega)Q_{\ell m}(\mathbf{r}'),$$

where the *multipole electric moments* of the electromagnetic field are defined as (Sec. 46 of Ref. 16)

$$Q_{\ell m}(\mathbf{r}) = \sqrt{\frac{4\pi}{2\ell+1}}\, r^\ell Y_{\ell m}\left(\frac{\mathbf{r}}{r}\right).$$

The density-density response function $\chi(\mathbf{r},\mathbf{r}';\omega)$ is a complex two-particle quantity. If one is only interested in the optical response it is advantageous to work with a simpler function,

$$\delta n_{\ell m}(\mathbf{r}';\omega) = -\int d\mathbf{r}\, Q^*_{\ell m}(\mathbf{r})\chi(\mathbf{r},\mathbf{r}';\omega),$$

having a meaning of the *induced density* (position-dependent). Because this is a function of only one spatial variable the equations simplify considerably. They can be obtained by integrating Eq. (4) over $\mathbf{r}$. Symmetry considerations can lead to further simplifications: it is often possible to reduce the integration over the intermediate coordinate $\mathbf{r}_1$ to a one-dimensional integral. This is detailed in the Appendixes for spherical and cylindrical symmetries.

Let us now introduce our basic approximation. SCA implies a high frequency condition $|E_i - E_j| \ll \omega$. This allows us to approximate the denominator in Eq. (2) as

$$\frac{f_i - f_j}{\omega + E_i - E_j} \approx \frac{f_i - f_j}{\omega}\left(1 - \frac{E_i - E_j}{\omega}\right). \tag{5}$$

By following Ref. 12 we obtain the expression for the nonlocal dielectric function

$$\begin{aligned}\varepsilon(\mathbf{r},\mathbf{r}';\omega) = \left[1 - \frac{4\pi}{\omega^2}n(\mathbf{r})\right]\delta(\mathbf{r}-\mathbf{r}')\\ + \frac{1}{\omega^2}\nabla_{\mathbf{r}'}v(\mathbf{r}-\mathbf{r}')\cdot\nabla n(\mathbf{r}').\end{aligned} \tag{6}$$

A simple algebraic property of the matrix inverse and Eq. (4) may lead to the impression that the dielectric function should in general be symmetric. The explicit form (6) seems to contradict this statement, however. In fact, such a peculiar property of the dielectric function was also observed for other geometries. The contradiction can be resolved by observing that, on very general ground, $\chi(\mathbf{r},\mathbf{r}';\omega)$ is not an invertible matrix (as discussed in, e.g., the optimized effective potential method[17] where this is one of the major problems). For singular matrices the inverse can still be defined, however not unambiguously. Thus we arrive at Eq. (6) by making a reasonable physical approximation; however, we do not impose additional constraints (such as in the Moore-Penrose theory of pseudoinverse matrices) to make $\varepsilon(\mathbf{r},\mathbf{r}';\omega)$ symmetric.

III. SOLUTION OF GENERIC INTEGRAL EQUATION

The examples discussed in Appendix A demonstrate that finding the optical response for the relevant geometries within SCA can be reduced to the solution of the following integral equation:

$$\alpha(r;\omega) = \alpha^{(0)}(r;\omega)\left[1 - \int_0^\infty dr' G(r,r')\alpha(r';\omega)\right], \quad (7)$$

where $\alpha^{(0)}(r;\omega)$ is a known function of the density. The reduction to this form might require an appropriate scaling of the unknown function $\alpha(r;\omega)$ [cf. Eqs. (B6) and (B11)]. The ω parameter is in general a complex number as it includes also the small broadening $i\eta$. Therefore, the response functions are also complex. Furthermore, it is important to notice the structure of the Green's function

$$G(r,r') = f(r)g(r')\theta(r - r') - h\theta(r' - r), \quad (8)$$

where $f(r)$ and $g(r')$ are typically given by the power functions. Equation (7) belongs to the class of the *Fredhoml integral equations of the second kind*.[18] The analytical solution of our particular form is not known and one has to resort to numerical methods. A standard approach, also broadly used for the computations of the polarizabilities,[10,14] is *the quadrature method*. Here one proceeds by using some quadrature rules for the integral, discretizing the kernel, and by posing the problem as a system of linear algebraic equations. The advantage of this approach is its universality, however, it is obliterated by the high computational cost. A mesh containing N points leads to a system of N linear equations which can only be solved at $\mathcal{O}(N^3)$ cost. A further disadvantage of the method is in the difficulty to apply an iterative refinement procedure: it is often necessary to obtain the solutions for a large number of ω values. For finite η the response functions are continuous functions of the frequencies. Thus, one may want to use a known solution at $\omega = \omega_i$ to find a solution for a neighboring point $\omega = \omega_{i+1}$. The implementation of this approach within the quadrature approach requires the use of sophisticated methods, and also may suffer from instabilities and cannot be implemented within standard numerical libraries. Therefore, we propose a method that is free from these deficiencies: (i) it scales linearly with the number of mesh points, (ii) the iterative refinement can be implemented straightforwardly, and (iii) the method is numerically stable.

Let us write Eq. (7) in the form

$$\alpha(r;\omega) = \alpha^{(0)}(r;\omega)[1 + ha(\omega)] - \alpha^{(0)}(r;\omega)\int_0^r dr'[f(r)g(r') + h]\alpha(r';\omega). \quad (9)$$

If $a(\omega) = \int_0^\infty \alpha(r;\omega)dr$ were a known function Eq. (9) would belong to the type of the *Volterra integral equations of the second kind* with a degenerate kernel[18] which admits an analytic solution. Let us assume that on the nth iteration step an approximate value $a^{(n)}$ has already been known. We solve the integral equation (9) in a standard way by introducing the two auxiliary functions:

$$w_1(r,\omega) = \int_0^r dr' g(r')\alpha(r';\omega), \quad (10a)$$

$$w_2(r,\omega) = \int_0^r dr' \alpha(r';\omega). \quad (10b)$$

Then the unknown function is given by

$$\alpha(r;\omega) = \alpha^{(0)}(r;\omega)[1 + ha^{(n)}(\omega) - f(r)w_1(r,\omega) - hw_2(r,\omega)] \quad (11)$$

and the improved approximation to $a(\omega)$ by

$$a^{(n+1)}(\omega) = \lim_{r\to\infty} w_2(r,\omega). \quad (12)$$

Two auxiliary functions can be found as solutions to the system of the ordinary differential equations:

$$w_1'(r,\omega) = \alpha^{(0)}(r;\omega)g(r) \times [1 + ha^{(n)}(\omega) - f(r)w_1(r,\omega) - hw_2(r,\omega)], \quad (13a)$$

$$w_2'(r,\omega) = \alpha^{(0)}(r;\omega) \times [1 + ha^{(n)}(\omega) - f(r)w_1(r,\omega) - hw_2(r,\omega)]. \quad (13b)$$

These relations are derived by differentiating Eq. (10) and using Eq. (11). To solve Eq. (13) with the initial conditions $w_i(r,\omega) = 0$ the standard *fourth-order Runge-Kutta* method can be used. This turned out to be a good compromise between the speed and the accuracy. Let us focus now on the second component of our approach: the iterative update of $a(\omega)$. To explicitly show the functional dependence of $w_2(r,\omega)$ on $a(\omega)$ it can be written as

$$a = \lim_{r\to\infty} w_2[a](r,\omega). \quad (14)$$

This relation can be viewed as a nonlinear algebraic equation for the complex $a(\omega)$. In general, the brute-force update (12) does not achieve convergence; with only one starting point it is successful under special conditions only. Therefore, we use here a simple and an efficient method for finding the complex roots based on a quadratic interpolation with three distinct points needed to start the iteration. This approach is known as the *Müller's method*. The convergence can be greatly accelerated if already known $a(\omega_i)$ is used to initialize the computation of $a(\omega_{i+1})$:

$$a^{(1)}(\omega_{i+1}) = a(\omega_i), \quad a^{(2,3)}(\omega_{i+1}) = (1 \pm \lambda)a(\omega_i),$$

where λ is a small parameter (typically $\lambda = 0.1$). Our numerical tests indicate an excellent stability of the method. Typically one ω point is converged with an accuracy of 10^{-12} within 10 iterations and the whole calculation linearly scales with the number of mesh points. This makes it a perfect candidate for the investigation of the optical properties of complex 3D objects not necessarily possessing a high symmetry. To the best of our knowledge, a classical electrodynamics finite element method had no alternatives in this case. A complete numerical solution of the 2D problem with an axial symmetry will be presented elsewhere. Here, we demonstrate the usability of our approach by applying it to a spherically symmetric metal cluster.

IV. OPTICAL ABSORPTION OF A SODIUM CLUSTER

We apply our method to the Na_{2869}^{-} cluster: a system which simultaneously possesses a magic structural number of the atoms and completely filled electronic shells. As discussed by Martin (Ref. 19) for a small number of atoms the stability of the sodium cluster is determined by the completion of its electronic shells. The simplest way to classify the electronic states is to name them according to the states of the spherical potential well,[20] i.e., by pairs of a principal and an angular momentum quantum number (n,ℓ). For a larger number of atoms the geometric effects dominate. The system's stability is determined by the completion of the concentric atomic shells. Several structural orderings are possible and it is experimentally known that the sodium clusters are organized according to an icosahedral symmetry: a central atom is surrounded by 12 neighboring atoms at the corners of the icosahedron, this 13-atom core is covered by a second layer of 42 atoms, forming again a perfect icosahedron, and so on. In general, for an icosahedron composed of K shells the total number of atoms is given by

$$n_K = \frac{K(10K^2+11)}{3} - 5K^2 - 1.$$

In addition to these nice properties our 10-shell system [Fig. 1(a), $n_{10} = 2869$] possesses complete electronic shells in the configuration [Fig. 1(c)] where the angular momentum states up to $\ell = 19$ are filled accommodating, thus, 2870 electrons. Let us compare (a) the geometric, (b) the ground state electronic, and (c) the excited states optical properties for various scenarios.

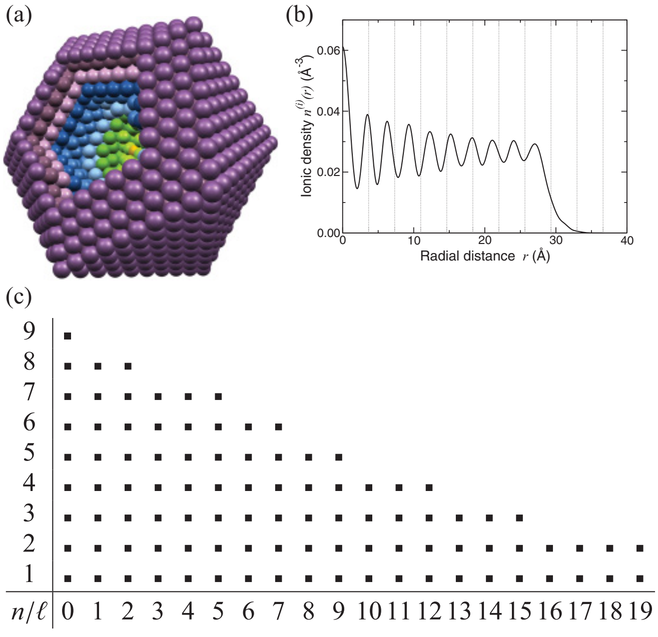

FIG. 1. (Color online) (a) Geometrical structure of 10-shell icosahedral Na_{2869}^{-} cluster. Positions of atoms were generated by a cluster coordinate generator.[21] (b) Radial distribution function of the ionic density computed with intershell spacing fixed at the nearest neighbor distance (interval between thin vertical lines) of the bulk lattice ($a_s = a_{nn} = \sqrt{3}/2a_b$). (c) Electronic configuration of the system. Each square denotes an occupied (n,ℓ) state.

(a) Geometric properties. The standard jellium model assumes that the ionic density is homogeneously distributed within the volume of a sphere and abruptly drops to zero at its boundaries.[20] The electronic properties are then determined by a single parameter: the ionic density which is selected to match the bulk value (for Na $r_s = 3.96$) and, hence, is related to the bulk lattice constant (for Na $a_b = 4.230$ Å) and to the number of valence electrons per unit cell. For our comparative study we fix the averaged ionic density and adjust all the other parameters.

The icosahedral packing observed in clusters is more dense than in the regular bulk lattices (bcc for Na). To match the bulk value of the density the intershell distance (a_s) has to be expanded by 4.7% as compared to the bulk nearest neighbor distance (a_{nn}). This value we obtain by computing the averaged ionic density based on the radial distribution function, where we set the edge of the density cloud at the last inflection point of the function. The radial distribution $n^{(i)}(r)$ was computed applying the Gaussian broadening with the width $\sigma \sim 1$ Å to the idealized atomic positions $\mathbf{r}_a$,

$$n^{(i)}(r) = \int d\Omega \sum_{a=1}^{N_a} \left(\frac{1}{\sqrt{2\pi}\sigma}\right)^3 \exp\left(-\frac{|\mathbf{r}-\mathbf{r}_a|^2}{2\sigma^2}\right).$$

For the angular integration we use the Fibonacci grids introduced by Hannay and Nye[22] (see also Ref. 5). As anticipated, the ionic density exhibits an oscillatory behavior [Fig. 1(b)]. There is a small variation in the period of oscillation around the average value of $0.75a_b$.

(b) Ground state electronic properties. Let us assess the influence of the ionic density oscillations on the electronic properties. We compare here the electronic distribution (Fig. 2) resulting from the self-consistent local density approximation (LDA) calculations based on the jellium model for the ionic density and on the realistic ionic density derived by smearing out the positive charges at idealized icosahedral positions. Our LDA calculations use the same exchange-correlation potential and the methodology as in Ref. 20. The radial Kohn-Sham (or Schrödinger) equations are solved by the renormalized *Numerov method*.[23] At the later stages of the self-consistent calculations we used a modification of the *Pulay method*[24] to accelerate the convergence.

Our calculations reveal interesting features of the jellium model approach. We find that the electronic density reproduces closely the oscillations of the positive background. The oscillations are in-phase, their magnitude is damped compared to the ionic distribution, and they are also reflected in the Kohn-Sham potential. In the next paragraph we will argue that they are also manifested in the optical response. In the asymptotic region the electron and the ionic densities are almost indistinguishable. We also notice that the spill-off region is significantly extended compared to the standard jellium model. This is in the first place a geometric not an electronic effect which originates from the deviation of the cluster's shape from the spherical or, in other words, from the reduced coordination number of the surface atoms. The Kohn-Sham potential for the system with a realistic ionic density is shallower compared to the standard jellium model. Consequently, the work function in the latter case is increased by roughly 1 eV.

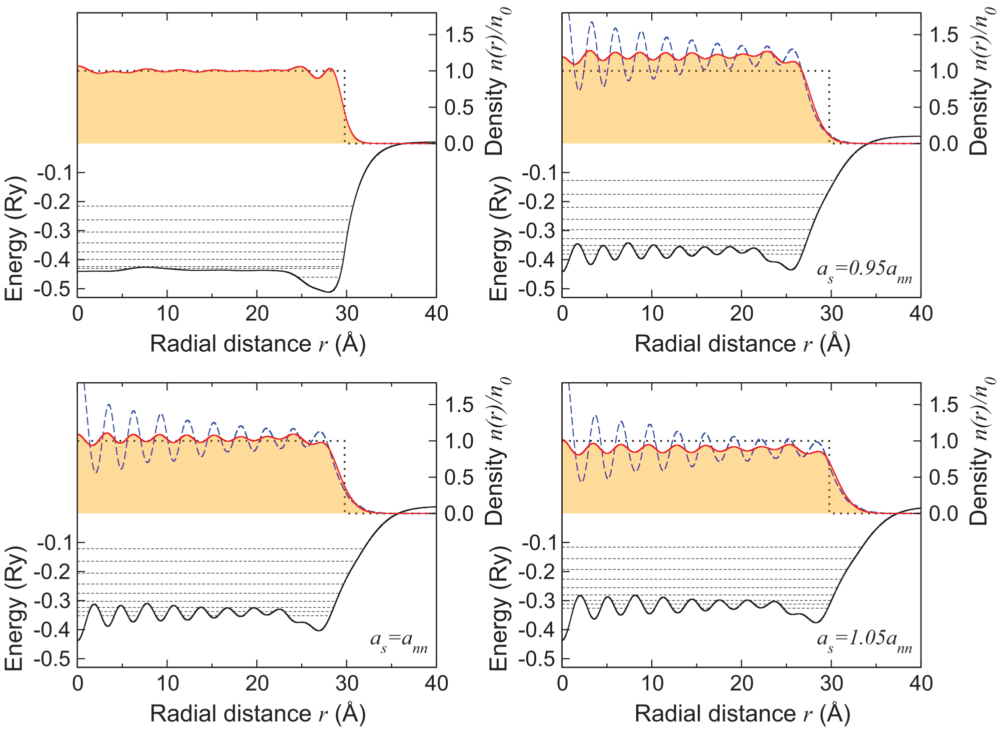

FIG. 2. (Color online) Electronic structure of the Na_{2869}^{-} cluster: solid line denotes the self-consistent Kohn-Sham potential, the electronic states for $\ell = 0$ shown as thin dashed lines; the filled area denotes the converged electronic density; the long-dashed line shows the ionic density; the dotted line marks the ideal jellium background. The four panels correspond to different approximations to the ionic density.

(c) Optical properties. Variation of the electronic density has a profound impact on the optical response (Fig. 3). The optical spectrum in all four scenarios is characterized by a major surface plasmon resonance at around the classical value $\omega_s = \omega_p/\sqrt{3}$ and some features at the bulk plasmon frequency ω_p. Such "artificial features" were also observed in metallic shell systems. For our system they are only visible when plotted on the log scale. We performed a sequence of calculations by varying the broadening parameter and found only a tiny influence of the spectrum. This signifies the intrinsic broadening of the optical absorption peaks in SCA. Contrary to a fully quantum approach where finite systems necessarily possess electronic excitations of the discrete spectrum (albeit very densely spaced) the response function in SCA has branch cuts rather than poles. This can be traced back to a specific form of the free term $\alpha^{(0)}(r;\omega)$ in the SCA integral equation having a branch cut in the complex ω plane. Its range is determined by the availability and the continuity of the electron density $\omega_p^2(r) = 4\pi n(r)$. It is then obvious that the realistic ionic density leads to a variation of the electron density in a wider range and as a consequence to broader plasmonic resonances.

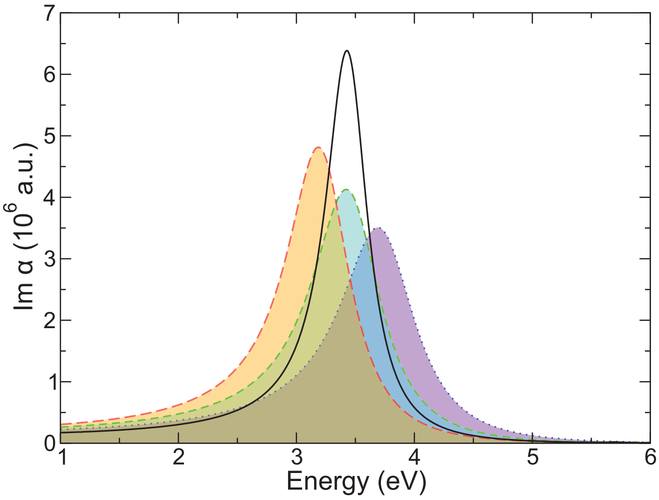

FIG. 3. (Color online) Optical response of the Na_{2869}^{-} cluster obtained by solving Eq. (7) with the Green's function (B5). The polarizability is only weakly dependent on the broadening parameter η (set to 0.001 a.u. here). We do not present here the spectra in the small energy range as SCA loses its validity there [cf. Eq. (5)]. The solid line: the standard jellium model; the dotted line: $a_s = 0.95a_{nn}$; the short dashed line: $a_s = a_{nn}$; the long dashed line: $a_s = 1.05a_{nn}$.

The broadening of the excited states in the optical experiments is associated with different factors: the temperature, disorder, the electronic correlations. However, to the best of our knowledge, this phenomenon was never put in such a tight relation with the geometric ordering.

V. CONCLUSIONS

We proposed an approach for the calculation of the multipole optical response in the semiclassical approximation. The method linearly scales with the system size and can be extended to systems with lower symmetries. As an illustration we applied our approach to study the collective electronic excitations in the icosahedrally ordered Na_{2869}^{-} cluster. We investigated the influence of the ionic structure on the ground state electronic properties and on the properties of excited states. We found a significant broadening of the plasmon resonances and demonstrated that it is enhanced when the positive background is treated more realistically.

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APPENDIX A: INTEGRATION OF $\chi^{(0)}$

The term proportional to $1/\omega$ in the expansion of $\chi^{(0)}$ vanishes in view of the completeness of the electron wave functions:

$$\sum_i \psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2) = \delta(\mathbf{r}_1-\mathbf{r}_2). \tag{A1}$$

Therefore, we consider the remaining part that is proportional to $1/\omega^2$:

$$\begin{aligned}\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega) \approx -\frac{2}{\omega^2}\sum_{i,j}(E_i-E_j)(f_i-f_j)\\ \times\psi_i(\mathbf{r})\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')\psi_i^*(\mathbf{r}').\end{aligned} \tag{A2}$$

Let us evaluate the integral of the generic type,

$$\Phi(\mathbf{r}') = \int d\mathbf{r}\,\phi(\mathbf{r})\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega). \tag{A3}$$

In view of the Schrödinger equation we have

$$\int d\mathbf{r}\,\phi(\mathbf{r})(E_i-E_j)\psi_i(\mathbf{r})\psi_j^*(\mathbf{r}) = -\frac{1}{2}\int d\mathbf{r}\,\phi(\mathbf{r})\nabla\cdot\boldsymbol{\xi}_{ij}(\mathbf{r}),$$

where

$$\boldsymbol{\xi}_{ij}(\mathbf{r}) = \psi_i(\mathbf{r})\nabla\psi_j^*(\mathbf{r}) - \psi_j^*(\mathbf{r})\nabla\psi_i(\mathbf{r}).$$

Utilizing the Gauss theorem and the antisymmetry of $\boldsymbol{\xi}_{ij}(\mathbf{r})$ with respect to an exchange of the indices in the case of real functions, we obtain

$$\Phi(\mathbf{r}') = -\frac{2}{\omega^2}\sum_i f_i \sum_j \psi_j(\mathbf{r}')\psi_i^*(\mathbf{r}')\int d\mathbf{r}\,\boldsymbol{\xi}_{ij}(\mathbf{r})\cdot\nabla\phi(\mathbf{r}).$$

Summation over j is performed using the completeness relation (A1), while the summation over i yields the electron density:

$$2\sum_i f_i\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) = n(\mathbf{r}). \tag{A4}$$

It is useful to rewrite $\boldsymbol{\xi}_{ij}(\mathbf{r})$ in the form

$$\boldsymbol{\xi}_{ij}(\mathbf{r}) = \nabla(\psi_i\psi_j)(\mathbf{r}) - 2\psi_j(\mathbf{r})\nabla\psi_i(\mathbf{r})$$

and to use the Green's theorem to integrate the first term:

$$\begin{aligned}&\sum_i f_i \sum_j \psi_i(\mathbf{r}')\psi_j(\mathbf{r}')\int d\mathbf{r}\,\nabla(\psi_i\psi_j)(\mathbf{r})\cdot\nabla\phi(\mathbf{r})\\ &\quad= \sum_i f_i\,\psi_i(\mathbf{r}')\int d\mathbf{r}\,\psi_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\nabla^2\phi(\mathbf{r})\\ &\quad= \frac{1}{2}n(\mathbf{r}')\nabla^2\phi(\mathbf{r}').\end{aligned} \tag{A5}$$

The second term integrates as follows:

$$\begin{aligned}&2\sum_i f_i \sum_j \psi_i(\mathbf{r}')\psi_j(\mathbf{r}')\int d\mathbf{r}\,\psi_j(\mathbf{r})\nabla\psi_i(\mathbf{r})\cdot\nabla\phi(\mathbf{r})\\ &\quad= 2\sum_i f_i\psi_i(\mathbf{r}')\int d\mathbf{r}\,\delta(\mathbf{r}-\mathbf{r}')\nabla\psi_i(\mathbf{r})\cdot\nabla\phi(\mathbf{r})\\ &\quad= \frac{1}{2}\nabla n(\mathbf{r}')\cdot\nabla\phi(\mathbf{r}').\end{aligned} \tag{A6}$$

The following simple expression is then obtained:

$$\Phi(\mathbf{r}') = \frac{1}{\omega^2}[\nabla n(\mathbf{r}')\cdot\nabla\phi(\mathbf{r}') - n(\mathbf{r}')\nabla^2\phi(\mathbf{r}')]. \tag{A7}$$

By using $\phi(\mathbf{r}_1) = v(\mathbf{r}-\mathbf{r}_1)$, $\nabla_1\phi(\mathbf{r}_1) = -\nabla_1 v(\mathbf{r}-\mathbf{r}_1)$, and $\nabla_1^2\phi(\mathbf{r}_1) = \nabla_1^2 v(\mathbf{r}-\mathbf{r}_1) = -4\pi\delta(\mathbf{r}-\mathbf{r}_1)$ in Eq. (A7) we prove the semiclassical expression for the dielectric function (6). In the following section we apply Eq. (A7) to derive the equations for the multipole polarizabilities.

APPENDIX B: INTEGRAL EQUATIONS FOR THE MULTIPOLE POLARIZABILITIES

In the main text we demonstrated how the ℓ-pole polarizability can be obtained from the integral equation for the induced density. Here, we explicitly derive these equations for the spherical and the axial symmetry.

(d) Spherical symmetry $[n(\mathbf{r}) = n(r)]$. The response functions are invariant under the rotations of the system as a whole. Thus they can be expanded as

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \sum_{l,\mu}\chi_{l\mu}(r,r';\omega)Y_{l\mu}^*(\Omega)Y_{l\mu}(\Omega').$$

Hence the induced density can be written in a simpler form:

$$\delta n_{\ell m}(\mathbf{r}';\omega) = \sqrt{\frac{4\pi}{2\ell+1}}\delta n_{\ell m}(r';\omega)Y_{\ell m}(\Omega').$$

The integral equation for $\delta n_{\ell m}(r';\omega)$ follows from Eq. (4). The left-hand side (LHS) requires the evaluation of

$$\begin{aligned}\delta n_{\ell m}^{(0)}(r';\omega) = -\frac{4\pi}{2\ell+1}\int d\Omega' Y_{\ell m}^*(\Omega')\\ \times\int d\mathbf{r}\,r^\ell Y_{\ell m}(\Omega)\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega).\end{aligned} \tag{B1}$$

Thus the final result (A7) of the previous section can be used for the integration over $\mathbf{r}$. Because of the symmetry of the density it is sufficient to take only the radial component of the gradient

$$\nabla = \mathbf{e}_r\frac{\partial}{\partial r} + \frac{1}{r}\nabla_{\boldsymbol{\Omega}}$$

in the first term of Eq. (A7). Here $\mathbf{e}_r \equiv \mathbf{r}/r$ and $\nabla_{\boldsymbol{\Omega}}$ acts only on the angular variables. The second term of Eq. (A7) vanishes because of the form of the Laplacian in spherical coordinates:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\mathbf{L}^2,$$

where $\mathbf{L}$ is the operator of the angular momentum. After the angular integration we obtain

$$\delta n_{\ell m}^{(0)}(\mathbf{r};\omega) = -\frac{4\pi}{2\ell+1}\frac{\ell}{\omega^2}r^{\ell-1}\frac{dn}{dr}. \tag{B2}$$

The integral kernel from the right-hand side (RHS) of Eq. (4) requires the evaluation of

$$K_\ell(r_1,r') = \int d\Omega_1 Y_{\ell m}(\Omega_1) \times \int d\Omega' \nabla_{\mathbf{r}'} v(\mathbf{r}_1 - \mathbf{r}')\cdot \nabla n(\mathbf{r}') Y^*_{\ell m}(\Omega'). \tag{B3}$$

It can be integrated using the spherical harmonics expansion of the Coulomb potential [see Sec. 3.6 of Jackson (Ref. 25)],

$$v(\mathbf{r}-\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_l \sum_{\mu=-l}^{l} \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}} Y^*_{l\mu}(\Omega) Y_{l\mu}(\Omega'),$$

where $r_<$ ($r_>$) is smaller (larger) of r and r'. The gradient of spherical harmonics need not to be considered in view of the symmetry of the density; the angular integration can be done beforehand and we obtain for Eq. (B3)

$$\begin{aligned} K_\ell(r_1,r') &= \frac{4\pi}{2\ell+1}\frac{dn}{dr'}\frac{\partial}{\partial r'}\left(\frac{r_<^l}{r_>^{l+1}}\right) \\ &= -\frac{4\pi}{2\ell+1}\frac{dn}{dr'}\frac{r'^{\ell-1}}{r_1^{\ell+1}} G_\ell^{\mathrm{sph}}(r',r_1), \end{aligned} \tag{B4}$$

with the spherical ℓ-pole Green's function defined as

$$G_\ell^{\mathrm{sph}}(r,r') = (\ell+1)\theta(r-r')\left(\frac{r'}{r}\right)^{2\ell+1} - \ell\theta(r'-r). \tag{B5}$$

Using Eqs. (B2) and (B4) we obtain

$$\alpha_\ell^{\mathrm{sph}}(r;\omega) = \alpha_\ell^{(0,\mathrm{sph})}(r;\omega) \times \left[\ell - \int_0^\infty dr' \left(\frac{1}{r'}\right)^{\ell-1} G_\ell^{\mathrm{sph}}(r,r')\alpha_\ell^{\mathrm{sph}}(r';\omega)\right], \tag{B6}$$

with $\alpha_\ell^{\mathrm{sph}}(r;\omega) = \delta n_{\ell 0}(r;\omega)$ and

$$\alpha_\ell^{(0,\mathrm{sph})}(r;\omega) = -\frac{4\pi}{2\ell+1}\frac{r^{\ell-1}dn(r)/dr}{\omega^2-\omega_p^2(r)},$$

where we introduced the *local plasmon frequency* in analogy to the expression for homogenous systems $\omega_p^2(r) = 4\pi n(r)$. In the case of the dipolar response our result (B6) coincides with Eq. (5) of Prodan and Nordlander (Ref. 10).

(e) Axial symmetry [$n(\mathbf{r}) = n(\rho)$]. Unlike in the spherical case the orientation of the coordinate system is important. We consider an electromagnetic wave with a normal incidence on the cylinder's surface. It is possible to obtain the equations for the general ℓ-pole response. However, only in the dipolar $(\ell,m) = (1,0)$ case (to be considered here) can they be written in a simple form. This can be traced back to the fact that only for $\ell = 1$ the multipole electric moments are the invariant under the system's symmetry.

We proceed by expanding the response functions as

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \sum_m \chi_m(\rho,\rho';\omega)e^{im(\varphi'-\varphi)}.$$

This reflects the axial symmetry of the system which allows us to represent the induced density as

$$\delta n_{10}(\mathbf{r}';\omega) = \delta n_{10}(\rho';\omega)\cos(\varphi').$$

The integral equation for $\delta n_{10}(\rho';\omega)$ follows from Eq. (4). The LHS requires the evaluation of

$$\delta n_{10}^{(0)}(\rho';\omega) = -\int_0^{2\pi}\frac{d\varphi'}{\pi}\int d\mathbf{r}\, r\, \cos(\varphi) \times \chi^{(0)}(\mathbf{r},\mathbf{r}';\omega)\cos(\varphi'), \tag{B7}$$

where we expressed the spherical harmonics in terms of the Legendre polynomials:

$$Y_{10}(\Omega) = \sqrt{\frac{3}{4\pi}}P_1(\cos\varphi) = \sqrt{\frac{3}{4\pi}}\cos\varphi.$$

Only the radial components of the gradient contribute. After the integration we obtain

$$\delta n_{10}^{(0)}(\rho';\omega) = -\frac{1}{\omega^2}\frac{dn(\rho)}{d\rho}. \tag{B8}$$

The integral kernel from the RHS of Eq. (4) requires the evaluation of

$$K_1(\rho_1,\rho') = \int_{-\infty}^{\infty} dz_1 \int_0^{2\pi} d\varphi_1 \cos(\varphi_1) \times \int_0^{2\pi}\frac{d\varphi'}{\pi}\nabla_{\mathbf{r}'} v(\mathbf{r}_1-\mathbf{r}')\cdot\nabla n(\mathbf{r}')\cos(\varphi'). \tag{B9}$$

We use here the double summation expansion of the Coulomb potential in the cylindrical coordinates (Ref. 26 and problem 3.16 in Ref. 25):

$$v(\mathbf{r}-\mathbf{r}') = \sum_{m=-\infty}^{\infty} e^{im(\varphi-\varphi')}\int_0^\infty dk\, J_m(k\rho)J_m(k\rho')e^{-k(z_>-z_<)},$$

where J_m is the order m Bessel function of the first kind and $z_<$ ($z_>$) is smaller (larger) of z and z'. The integration over the angles can be done beforehand and by using $J_{-m}(x) = J_m(x)$ which leads to

$$K_1(\rho_1,\rho') = 2\pi\int dz_1 e^{-k(z_>-z_<)} \times \int_0^\infty dk \frac{d}{d\rho'}[J_1(k\rho_1)J_1(k\rho')]\frac{dn}{d\rho'}.$$

The integration over z_1 is a trivial matter and by using a differentiation formula for the Bessel functions $J_m'(x) = J_{m-1}(x) - J_{m+1}(x)$ we obtain

$$K_1(\rho_1,\rho') = 2\pi\frac{dn}{d\rho'}\int_0^\infty dk\, J_1(k\rho_1)[J_0(k\rho') - J_2(k\rho')].$$

The integration using Eq. 6.512(3) of Gradsteyn and Ryzhik[27] leads to

$$\begin{aligned} K_1(\rho_1,\rho') &= -\frac{2\pi}{\rho_1}\frac{dn}{d\rho'}\left[\left(\frac{\rho_1}{\rho'}\right)^2\theta(\rho'-\rho_1) - \theta(\rho_1-\rho')\right] \\ &= -\frac{2\pi}{\rho_1}\frac{dn}{d\rho'}G_1^{\mathrm{cyl}}(\rho',\rho_1). \end{aligned} \tag{B10}$$

Using Eqs. (B8) and (B10) we obtain

$$\alpha_1^{\mathrm{cyl}}(\rho;\omega) = \alpha_1^{(0,\mathrm{cyl})}(\rho;\omega) \times \left[1 - 2\int_0^\infty d\rho' G_1^{\mathrm{cyl}}(\rho,\rho')\alpha_1^{\mathrm{cyl}}(\rho';\omega)\right], \tag{B11}$$

where $\alpha_1^{\mathrm{cyl}}(\rho;\omega) = \pi\delta n_{10}(\rho;\omega)$ and

$$\alpha_1^{(0,\mathrm{cyl})}(\rho;\omega) = -\frac{\pi}{\omega^2 - \omega_p^2(\rho)}\frac{dn}{d\rho},$$

in an agreement with the expression given by Vasvári.[14]

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[*] yaroslav.pavlyukh@physik.uni-halle.de

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