Dielectric function of spherical dome shells with quantum size effects

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Abstract: Metallic spherical dome shells have received much attention in recent years because they have proven to possess highly impressive optical properties. The expected distinctive changes occurring owing to quantum confinement of conduction electrons in these nanoparticles as their thickness is reduced, have not been properly investigated. Here we carry out a detailed analytical derivation of the quantum contributions by introducing linearly shifted Associated Legendre Polynomials, which form an approximate orthonormal eigenbasis for the single-electron Hamiltonian of a spherical dome shell. Our analytical results clearly show the contribution of different elements of a spherical dome shell to the effective dielectric function. More specifically, our results provide an accurate, quantitative correction for the dielectric function of metallic spherical dome shells with thickness below 10 nm.

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1. Introduction

Metallic spherical dome shells of nanometer sizes have received considerable attention because of their anisotropic, highly tunable, and distinctive optical properties such as unique light-focusing ability, highly enhanced localized electric field near the rims, and increased absorption at longer wavelengths compared with their shell or sphere counterparts [1–7]. Such properties are expected to have potential applications in the diverse fields of solar energy harvesting [8–10], solar glazing [11], spacer design [12, 13], surface-enhanced Raman scattering spectroscopy (SERS) [8, 14], optical communications [15], three-dimensional nano-antennas [16] etc. The spherical metallic dome shell, also known as a nano-cup or a semi-shell, is a thin spherical metallic shell that surrounds a dielectric sphere only partly (see Fig.1). Optical properties of such metallic dome shells depend on both its geometric dimensions and intrinsic material properties. As a result, they can be easily tuned by varying geometrical parameters (such as the inner or outer radius, cut-off angle, and orientation with respect to light), in addition to the materials used for the core and the surrounding medium [2].

When dimensions of nanoparticles are large, the geometrical and material properties are independent of each other. But when these dimensions are comparable to electron's mean free path, intrinsic material properties such as the dielectric function become dependent on the geometric properties due to the electron confinement effects. Further reduction of the dimensions until they become comparable to the wavelength of the electron wave function, leads to quantum confinement effects. For example, Ref. [17] provides electron energy loss spectroscopy (EELS) experiment based evidence for surface plasmon peak shifts of Ag nanospheres due to quantum confinement effects. Further evidence of such coupling has been experimentally observed in shapes such as nanoshells [18, 19], nanowires [20], [21] that have close geometric resemblance to dome shells. Particularly, in Ref. [19], it was experimentally observed that thickness reductions in nanoshells caused broadening of absorbance peaks. Also in Refs. [21] and [20] oscillatory behavior owing to quantum effects in conductance was experimentally observed. Although no experimental data is available for spherical dome shells, such effects are expected to occur with them as well.

Electron confinement results in increased scattering of electrons at the external boundaries of the particle (so-called surface scattering) compared to the bulk metal. Quantum confinement leads to discretization of the conduction band of metals, which also affects the motion of electrons in addition to increased surface scattering [22], both of which also depend on the particle shape [23,24].

When the electron confinement effects are not dominant, one can safely use bulk material properties and predict the optical response of nanoparticles by solving the Maxwell equations. Existing analytical methods for solving Maxwell equations (such as Mie theory) can give exact solutions only for a few highly symmetric structures such as spheres or shells. The analytical tractability of Maxwell's equations is non-existent for reduced symmetry systems such as spherical dome shells. As a result, numerical methods such as discrete-dipole approximation, T-matrix method, or a finite-element method have to be used.

Also, models such as plasmon hybridization can be conceptually used to understand the optical behavior of certain composite nanostructures. The dome shell consist of two surfaces (inside and out), very much similar to fully spherical nano-shells considered by Prodan *et al.* in Ref. [25]. In the case of a hollow dome-shell, we can explain the appearance of plasmonic modes by considering the interaction of solid shell with a vacuum void cavity, as discussed in Ref. [26]. Interaction of dipolar plasmon mode of the nanohole with the dipolar and quadrupolar plasmon modes of the nanoshell leads to four plasmon modes with different energy levels.

All these methods require a critical material property as input, namely the dielectric function of the particle. The objective of this paper is to obtain a realistic dielectric function for thin

spherical dome shells with a small cut-off angle, considering all of the shape and size effects.

Experimentally measured dielectric values are available for bulk materials in the literature [27]. Approximate theoretical estimates have also been developed for metals based on the classical free-electron Drude model [28]. However, these estimates require size and shapedependent adjustments to account for the electron confinement effects before they can be used to obtain the optical properties of nanoparticles with reduced dimensions (below 50 nm for gold [29] and silver [17]). Even with such corrections, they fail to accurately predict the properties of nanoparticles when the size is reduced to below 10 nm [17] and quantum confinements effects appear.

An alternative is to use an *ab initio* approach based on density functional theory [30]. Such a theory will use detailed potential information inside the nanoparticle and consider the whole system as a quantum-mechanical many-body problem to calculate various quantities of interest. However, a many-body approach is likely to be limited to nanoparticle sizes of less than 2 nm due to its excessively high computational costs. Most importantly, such a full-blown numerical analysis will lead to loss of physical insight that is very valuable to engineer these systems. Therefore, we have adopted in this work, a much simpler single-electron model, which assumes a non-interacting electron gas confined under a uniform background potential. We use this model to obtain numerically the size and shape dependent dielectric values for thin metallic spherical dome shells with thickness in the range of 2–10 nm and a small cut-off angle. This model has been successfully adopted for other geometries such as nanospheres [17] and nanorods as well [31].

2. Classical model for dielectric function

In general, the dielectric function of a metal has contributions from both the interband(inter) and intraband(intra) electron transitions and can be written as,

$$\varepsilon(\omega) = \varepsilon_{\text{inter}}(\omega) + \varepsilon_{\text{intra}}(\omega), \tag{1}$$

where ω is the angular frequency of incident electric field. The interband component dominates for semiconductors but is often ignored for metals. It cannot be neglected for noble metals (such as Ag, Au and Cu) because they exhibit more complex electronic features than other metals owing to completely occupied d-orbital electrons [32]. The interband effects on the permittivity coincide with the bulk values when particle dimensions are above a few nanometers [30]. Therefore, we assume that the interband component is size independent in the 2–10 nm range for the metals under consideration.

The intraband component in Eq. (1) corresponds to electron transitions in incompletely filled bands, or to those in filled bands that overlap partially with an empty band. These transitions can be triggered by photons of very small energies because the energy difference between the initial and final electronic states is small compared to interband transitions. The intraband contribution is well described by the Drude model and has the form [33],

$$\varepsilon_{\text{intra}}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + j\omega\gamma},\tag{2}$$

where ω_p is the plasma frequency, *j* is the unit imaginary number and γ is the damping constant. The plasma frequency ω_p depends on the electron density n_e as,

$$\omega_p = \sqrt{rac{n_e q_e^2}{arepsilon_0 \mu}},$$



Fig. 1. Cross section of a spherical dome shell along the xz plane with the center on the origin. The axis of symmetry is along the z direction of a right-handed Cartesian coordinate system.

where μ , q_e and ε_0 denote the electron mass, electron charge, and permittivity of free space, respectively.

The value of γ for a bulk metal is influenced by several processes such as the Coulomb interaction, electron-phonon interaction, and electron scattering at interfaces. In the case of nanoparticles made of metals such as Ag and Au with sizes of 50 nm or less, the classical Drude model incorporates the quantum-confinement effects by phenomenologically modifying the damping constant as [29],

$$\gamma = \gamma_{\text{bulk}} + \frac{A v_f}{L_{\text{eff}}},$$

where γ_{bulk} is the damping factor measured for the bulk metal, A is a material interface and shape dependent factor, and v_f is the Fermi velocity. L_{eff} is the effective mean free path of an electron, taken to be the radius for a sphere and the thickness for a shell. When the nanoparticle dimensions are less than 10 nm, this size-dependent correction fails to describe the quantum effects properly. This is where the size-dependent quantum-mechanical contributions for the dielectric function enter the picture. Quantitative characterization of these effects for the spherical dome shells is the main focus of this paper.

3. Quantum mechanical dielectric function of a spherical dome shell

A spherical dome shell, as shown in Fig. 1, can be described by its inner radius *a*, outer radius *b* and the cut-off angle θ' . As our focus is on subwavelength spherical dome shells, we take the diameter of the spherical dome shell to be small compared to the wavelength λ of the incident electric field ($b \ll \lambda$). Therefore, we can assume that the incident electric field is uniform and does not vary spatially inside the particle [34]. In this quasi-static approximation, the response of the spherical dome shell to the electric field is given by a spatially invariant dielectric tensor of the general form

$$arepsilon = egin{bmatrix} arepsilon^{\mathrm{xx}} & arepsilon^{\mathrm{xy}} & arepsilon^{\mathrm{xz}} \ arepsilon^{\mathrm{yx}} & arepsilon^{\mathrm{yy}} & arepsilon^{\mathrm{yz}} \ arepsilon^{\mathrm{zx}} & arepsilon^{\mathrm{zz}} & arepsilon^{\mathrm{zz}} \end{bmatrix}$$

When the principle axes of the particle coincide with the Cartesian coordinate axes, all offdiagonal components of the dielectric tensor vanish. In addition, if we take the axis of rotational

symmetry of the spherical dome shell along the *z* axis, $\varepsilon^{xx} = \varepsilon^{yy}$, and we are left with only two independent components ε^{xx} and ε^{zz} . Without loss of generality, we assume that the electric field is linearly polarized along the *z* direction and write it in the form $\mathscr{E}(z,t) = \mathscr{E}_z \sin \omega t$. Noting that the polarizability $P^{zz}(\omega) \propto \mathscr{E}(z,t)$, ε^{zz} can be expressed in the form

$$\varepsilon^{zz}(\omega) = 1 + \frac{P^{zz}(\omega)}{\varepsilon_0 \mathscr{E}_z \sin \omega t}.$$
(3)

To calculate the polarizability $P^{zz}(\omega)$, we need to use quantum mechanics. We assume the system is in an unperturbed state for times t < 0 and its behaviour is governed by the time-independent Schrödinger equation wave function, obtained by solving [35],

$$H^0 \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}), \tag{4}$$

where H^0 is the unperturbed Hamiltonian and $\psi_i(\mathbf{r})$ is the wave function corresponding the initial state *i* of the system with the energy E_i . The unit $\mathbf{r} \equiv (\mathbf{x}, \mathbf{y}, \mathbf{z})$, is the position vector of a point inside the dome shell. When an electric field is applied at time t = 0, the wave function becomes time dependent, and electron transitions from the initial to final states take place owing to this perturbation. Let *f* represent the final state of the electron. The time-dependent wave function $\psi_f(\mathbf{r}, t)$ is obtained by solving

$$j\hbar \frac{\partial \psi_f(\mathbf{r},t)}{\partial t} = \left[H^0 + H'(t) \right] \psi_f(\mathbf{r},t), \tag{5}$$

where H'(t) is the time dependent perturbation,

$$H'(t) = q_e z \mathscr{E}_z \sin \omega t, \tag{6}$$

with \hbar denoting the reduced plank constant. Using the standard time dependent perturbation theory together with Eqs. (5) and (6), the solution is given by

$$\begin{split} \psi_f(\mathbf{r},t) &= \frac{1}{2} q_e \mathscr{E}_z \sum_i \langle \psi_i(\mathbf{r}) | z | \psi_f(\mathbf{r}) \rangle \psi_f(\mathbf{r}) \exp(\frac{-jE_f t}{\hbar}) \times \\ &\left\{ \frac{1 - \exp[j(\omega_{i,f} + \omega)t]}{\omega_{i,f} + \omega} + \frac{1 - \exp[j(\omega_{i,f} - \omega)t]}{\omega_{i,f} - \omega} \right\}, \end{split}$$

where

$$\omega_{i,f} = (E_f - E_i)/\hbar. \tag{7}$$

The dipole moment induced by the transitions to state f by the application of the electric field can be calculated using

$$\bar{p}_f^{\text{zz}}(\boldsymbol{\omega}) = \langle \psi_f(\mathbf{r},t) | - q_e z | \psi_f(\mathbf{r},t) \rangle.$$

Polarizability is the total dipole moment per unit volume. After considering all possible transitions, it can be written as,

$$P^{\rm zz}(\omega) = \frac{1}{V_p} \sum_f \bar{p}_f^{\rm zz}(\omega), \tag{8}$$

where V_p is the volume of the dome shell. We can now calculate the dielectric function $\varepsilon^{zz}(\omega)$. After including the damping effects and using Eqs. (3) and (8), it can be shown that

$$\varepsilon^{zz}(\omega) = 1 + \frac{2q_e^2}{\varepsilon_0 V_p \hbar} \sum_i \sum_f \frac{|\langle \psi_i(\mathbf{r}) | z | \psi_f(\mathbf{r}) \rangle|^2 \omega_{if}}{\omega_{i,f}^2 - \omega^2 - j\gamma \omega}.$$

After taking the interband effects into account, we can write the precding result in the form [23, 36],

$$\varepsilon^{zz}(\omega) = \varepsilon^{zz}_{inter}(\omega) + 1 + \omega_p^2 \sum_i \sum_f \frac{S_{i,f}^{zz}}{\omega_{i,f}^2 - \omega^2 - j\gamma\omega},$$
(9)

where we have introduced

$$S_{i,f}^{zz} = \frac{2\mu\omega_{i,f}}{\hbar N} |\langle \psi_f | z | \psi_i \rangle|^2, \tag{10}$$

and $N = n_e V_p$ stands for the total number of conduction electrons within the nanoparticle. All occupied states qualify as initial states and all unoccupied states qualify as final states. It is assumed that all states below the Fermi energy of the metal are occupied while the states above are unoccupied. The electron number N equals to twice the number of occupied states because of the spin degeneracy of electrons.

Equation (9) provides the general quantum-mechanical expression for the dielectric function of a spherical dome shell. However, The double sum in this equation is not easy to perform if we note that the sum over *i* and *f* is actually over all quantum numbers needed to specify the quantum state. Thus, we adopt the following strategy. Rather than calculating the complex quantity $\varepsilon^{zz}(\omega)$, we focus on its imaginary part responsible to absorption. From Eq. (9) it can be written as,

$$[\varepsilon^{zz}(\omega)]_{\rm im} = [\varepsilon^{zz}_{\rm inter}(\omega)]_{\rm im} + \omega_p^2 \sum_i \sum_f \frac{S_{i,f}^{zz} \gamma \omega}{(\omega_{i,f}^2 - \omega^2)^2 + \gamma^2 \omega^2}.$$
(11)

The real part of the dielectric function can then be calculated using the Kramers–Kronig relation [37]

$$[\boldsymbol{\varepsilon}^{zz}(\boldsymbol{\omega})]_{re} = \frac{2\omega}{\pi} P \int_0^\infty \frac{[\boldsymbol{\varepsilon}^{zz}(\boldsymbol{\omega}')]_{im} - 1}{\boldsymbol{\omega}'^2 - \boldsymbol{\omega}^2} d\boldsymbol{\omega}',$$

where P denotes the Cauchy principal value.

We now focus on how to perform the double sum in Eq. (11). It is known that he resonances of $[\varepsilon^{zz}(\omega)]_{im}$ occur in groups corresponding to changes in the value of the quantum number for which the energy dependence is the greatest [23, 36]. Let us call this quantum number v and let the difference of this quantum number between the final and initial states be Δv . A Lorenzian profile can be fitted to $[\varepsilon^{zz}(\omega)]_{im}$ by writing $S_{i,f}^{zz}$ as a function of Δv and introducing the group frequency $\Omega_{\Delta v}^{zz}$ as,

$$[\varepsilon^{zz}(\omega)]_{\rm im} = [\varepsilon^{zz}_{\rm inter}(\omega)]_{\rm im} + \omega_p^2 \sum_{\Delta\nu} \frac{S^{zz}_{\Delta\nu} \gamma \omega}{(\Omega^{zz}_{\Delta\nu}{}^2 - \omega^2)^2 + \gamma^2 \omega^2},$$

where

$$S_{\Delta v}^{zz} = \sum_{i} \sum_{f} S_{i,f}^{zz}, \qquad (12)$$

$$\Omega_{\Delta \nu}^{zz} = \frac{1}{S_{\Delta \nu}^{zz}} \sum_{\substack{i \ f}} \sum_{f} S_{i,f}^{zz} \omega_{i,f}.$$
(13)

The summation is restricted to all other quantum numbers and their differences between initial and final states except Δv . This model has proven to match well with the experimental data and the extrapolated values derived from the density functional theory approach for nanospheres of diameters in the 2–10 nm range, as presented in Ref. [17]. In this paper, it is reported that there is a substantial blue shift of resonance peaks in the experimental data and the density-functional results when the diameter of nanospheres is reduced to below 10 nm. This cannot be explained by the modified Drude model but agrees well with the results derived from the analytical model based on Eq. (12).

3.1. Wave function of a spherical dome shell

In order to calculate $S_{\Delta V}^{zz}$ we have to derive expressions for the wave functions and corresponding eigenenergies for electrons inside the spherical dome shell by solving the Schrödinger equation (4).

In Ag and Au nano structures with non ultra small dimensions, the behavior of conduction electrons can be closely approximated as a free-electron gas constrained by infinite potential barriers at the boundaries of the particle.

This enables us to describe the electronic properties of the particle in terms of a singleelectron wave function that extends over the entire particle and vanishes at the boundaries. Considering the symmetry of our system, it is convenient to use the spherical coordinates (r, θ, ϕ) . For a spherical dome shell, the wave function $\psi(r, \theta, \phi)$ is obtained by solving

$$\frac{-\hbar^2}{2\mu} \frac{1}{r^2 \sin \theta} \left[\sin \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + V(r)\psi = E\psi, \quad (14)$$

with the potential energy V(r) given by

$$V(r) = \begin{cases} 0 & \text{if } a \le r \le b \\ \infty & \text{otherwise} \end{cases}$$

We also need to remember that for a spherical dome shell with the cut-off angle θ' (see Fig. 1), the angle θ is restricted to lie in the range $\theta' \le \theta \le \pi$. Also note that all wave functions must be orthonormal, i.e.,

$$\int \psi_{\kappa}(r,\theta,\phi) [\psi_{\rho}(r,\theta,\phi)]^* d^3 V_p = \delta_{\kappa,\rho}, \qquad (15)$$

where κ and ρ are labels of the quantum states, $\delta_{\kappa,\rho}$ is the Kronecker's delta function and the integration is over the entire volume of the dome shell.

We use the standard method of separation of variables and assume that the wave function $\psi(r, \theta, \phi)$ can be separated into radial[R(r)], azimuthal[$F(\phi)$] and polar[$Q(\theta)$] components as,

$$\psi(r,\theta,\phi) = R(r)Q(\theta)F(\phi). \tag{16}$$

Substitution of Eq. (16) into Eq. (15) leads to the expressions:

$$\int_{a}^{b} R_{\kappa}(r) R_{\rho}^{*}(r) r^{2} dr = \delta_{\kappa,\rho}$$
$$\int_{0}^{2\pi} \int_{\theta'}^{\pi} F_{\kappa}(\phi) F_{\rho}^{*} Q_{\kappa}(\theta) Q_{\rho}^{*}(\theta) \sin \theta \, d\theta d\phi = \delta_{\kappa,\rho}$$

Next step is to find solutions for the radial, polar and azimuthal components of Eq. (14).

3.1.1. Radial component

We can separate the radial part from the Eq. (14) as,

$$\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} + \left[\frac{2mE}{\hbar^2} - \frac{l(l+1)}{r^2}\right] R(r) = 0,$$

where $a \le r \le b$ and *l* is the azimuthal quantum number. For a thin shell we can make the assumption (b-a) << a. The solutions of this equation involve the Bessel and Neumann functions. Using their asymptotic approximations and applying the boundary and normalization

conditions, we find the radial part [36],

$$R(r) = \frac{1}{r} \sqrt{\frac{2}{b-a}} \sin\left[\frac{n\pi}{b-a}(r-a)\right]$$
(17)

and the allowed electron energy E to be

$$E_{n,l} = \frac{h^2}{2\mu} \left[\frac{n^2 \pi^2}{(b-a)^2} + \frac{l^2}{a^2} \right],$$
(18)

with $n \ge 1$ and $l \ge 0$. From this equation it is clear that the main quantum number over which energy changes rapidly is *n* because $(b - a) \ll a$. Therefore we can associate Δv in Eq. (12) with Δn .

3.1.2. Azimuthal component

The azimuthal component of the Eq. (14) can be separated as,

$$\frac{d^2 F(\phi)}{d\phi^2} + m^2 F(\phi) = 0,$$
(19)

where m is the magnetic quantum number. After considering the boundary condition

$$F(\phi) = F(\phi + 2\pi).$$

and the normalization condition, the solution to Eq. (19) is given by

$$F(\phi) = \frac{1}{\sqrt{2\pi}} \exp\left(jm\phi\right),\tag{20}$$

where $m = \{\dots -2, -1, 0, 1, 2, \dots\}.$

3.1.3. Polar component

The polar component of the Eq. (14) can be separated as,

$$\sin\theta \frac{d}{d\theta} \left[\sin\theta \frac{dQ}{d\theta} \right] + \left[l(l+1)\sin^2\theta - m^2 \right] Q = 0, \tag{21}$$

where $\theta' \leq \theta \leq \pi$ and $Q(\theta') = 0$. Introducing $x = \cos \theta$ we can write it in the form

$$(1-x^2)\frac{d^2Q}{dx^2} - 2x\frac{dQ}{dx} + \left[l(l+1) - \frac{m^2}{1-x^2}\right]Q = 0,$$

where we introduce the boundary point $\zeta = \cos \theta'$ such that

$$-1 \le x \le \zeta, \qquad Q(\zeta) = 0. \tag{22}$$

Solutions of Eq. (21) are known when the shell is complete so that $\theta' = 0$ and x = 1. They are known as the associated Legendre polynomials defined by [35];

$$P_l^m(x) = \frac{(-1)^l}{2^l l!} (1 - x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (1 - x^2)^l.$$
(23)

Associated Legendre polynomials have following properties that are important for our derivation:

$$\int_{-1}^{1} P_{l}^{m}(x) P_{l'}^{m}(x) dx = \frac{2(m+l)!}{(2l+1)(l-m)!} \,\delta_{l,l'},\tag{24}$$

$$(l-m)P_l^m(x) = x(2l-1)P_{l-1}^m(x) - (l+m-1)P_{l-2}^m(x),$$
(25)

$$P_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x).$$
(26)

After normalization using Eq. (24), Q(x) for a complete shell is given by

$$Q(x) = \sqrt{\frac{(2l+1)(l-m)!}{2(m+l)!}} P_l^m(x),$$

 $l > 0, \quad -l \le m \le l.$

This solution is unusable for spherical dome shells for which $\theta' \neq 0$. However, for sufficiently small θ' , we can define a new set of linearly shifted Associated Legendre polynomials (shifted ALP) as,

$$\widetilde{P}_{l}^{m}(x) = P_{l}^{m}(k_{1}x + k_{2}), \qquad (27)$$

where,

$$k_1 = \frac{2}{\zeta + 1}, \qquad k_2 = \frac{1 - \zeta}{\zeta + 1}.$$
 (28)

These shifted ALPs enable us to write Q(x) after normalization as,

$$Q(x) = \sqrt{k_1 \frac{(2l+1)(l-m)!}{2(m+l)!}} \widetilde{P}_l^m(x), \qquad l > 0, \quad -l \le m \le l.$$
⁽²⁹⁾

As shown in Appendix 5, this function is orthogonal over the interval [ζ ,-1] while satisfying the boundary condition given in Eq. (22).

$$\int_{-1}^{\zeta} \widetilde{Q}_l^m(x) \widetilde{Q}_{l'}^m(x) dx = 1.$$

From Eqs. (23), (26), (27), and (28) we can see that $\widetilde{P}_l^m(\zeta) = P_l^m(1) = 0$ when $m \neq 0$. This satisfies the boundary condition in Eq. (22). It also sets the lower limit of *l* as 1 because m = 0 is not allowed. Further, $\widetilde{P}_l^m(x)$ obeys the recurrence relation derived in Appendix 5.

By substituting the radial, azimuthal and polar components, given by Eqs. (17), (20), (29) respectively, in Eq. (16) we obtain the wave function in the form

$$\psi_{n,l,m}(r,\theta,\phi) = \sqrt{\frac{k_1(2l+1)(l-m)!}{2\pi(b-a)(m+l)!}} \frac{1}{r} \sin\left[\frac{n\pi}{b-a}(r-a)\right] \widetilde{P}_l^m(\cos\theta) \exp(jm\phi),$$

where the three quantum numbers satisfy $n \ge 1$, $l \ge 1$, and $1 \le |m| \le l$.

3.2. Calculation of $S_{i,f}^{zz}$

To obtain the dielectric function, we need to find $S_{i,f}^{zz}$ given in Eq. (11) by calculating the matrix element $\langle \Psi_i | z | \Psi_f \rangle$, the total number of electrons N, and the frequency difference term $\omega_{i,f}$. Also we have to find the valid ranges for n, l, and m to carry out the double sum indicated in Eq. (11).

The initial state wave function $\psi_i = \psi_{n,l,m}$ depends on the three quantum numbers n, l, and m. We take the final wave function to be $\psi_f = \psi_{n+\Delta n,l+\Delta l,m+\Delta m}$ by changing these quantum numbers to $n + \Delta n$, $l + \Delta l$ and $m + \Delta m$. Using $z = r \cos(\theta)$, the matrix element $M_{if} = \langle \psi_i | z | \psi_f \rangle$ is calculated as,

$$M_{if} = \int_0^{2\pi} d\phi \int_{\theta'}^{\pi} \sin\theta d\theta \int_a^b r^2 dr \, \psi(r,\theta,\phi)_{n,l,m} r \cos\theta \left[\psi(r,\theta,\phi)_{n+\Delta n,l+\Delta l,m+\Delta m}\right]^* \tag{30}$$

The triple integral is calculated in Appendix 5 and the final result is found to be

$$\begin{split} M_{if} &= \delta_{\Delta m,0} \Big[\sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} \frac{\delta_{\Delta l,1}}{k_1} + \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}} \frac{\delta_{\Delta l,-1}}{k_1} - \frac{k_2}{k_1} \delta_{\Delta l,0} \Big] \times \\ & \left\{ \frac{4(b-a)[(-1)^{\Delta n}-1]n(n+\Delta n)}{\pi^2(2n+\Delta n)^2 \Delta n^2} + b \delta_{\Delta n,0} \right\}. \end{split}$$

To calculate $\omega_{i,f}$ we use its definition in Eq. (7). The initial energy $E_i = E_{n,l}$ is given in Eq. (18), and the final energy is given by $E_f = E_{n+\Delta n, l+\Delta l}$. Thus,

$$\omega_{i,f} = \frac{\hbar}{2\mu} \left[\frac{\Delta n(2n+\Delta n)\pi^2}{(b-a)^2} + \frac{\Delta l(2l+\Delta l+1)}{a^2} \right].$$
(31)

To calculate total number of electrons, let n_f be the value of n at the Fermi level when l = 1, which is the minimum value that l can have. From Eq. (18) we can write Fermi energy E_{Fermi} as,

$$E_{\text{Fermi}} = \frac{\hbar^2}{2\mu} \left[\frac{n_f^2 \pi^2}{(b-a)^2} + \frac{1}{a^2} \right] \approx \frac{\hbar^2}{2\mu} \left[\frac{n_f^2 \pi^2}{(b-a)^2} \right],$$

where we neglected the second term by noting that $(b-a) \ll a$ for a thin shell. Since all initial states should lie below the Fermi energy level, Using $E_i \leq E_{\text{Fermi}}$, we obtain the condition following upper bound for *l*:

$$l \le l_{\max} = \operatorname{Int}\left[\sqrt{(n_f^2 - n^2)} \frac{\pi a}{(b - a)}\right],$$

where Int(x) denotes the integer part of x. The total number of electrons N can now be found by summing over all occupied states such that $n \le n_f$ and $l \le l_{max}$. After considering the spin degeneracy, we find

$$N = \sum_{n=1}^{n_f} \sum_{l=1}^{l_{\max}} \sum_{\substack{-l \le m \le l \\ m \ne 0}}^{2} 2$$
$$= 2 \sum_{n=1}^{n_f} l_{\max}(l_{\max} + 1) \approx \frac{4\pi^2 a^2 n_f^3}{3(b-a)^2}$$

By substituting the expressions for M_{if} , $\omega_{i,f}$, and N in (10), we finally obtain

$$\begin{split} S_{l,f}^{zz} &= S_{n,\Delta n,l,\Delta l,m,\Delta m}^{zz} \frac{3(b-a)^2}{4\pi^2 a^2 n_f^3} \left[\frac{\Delta n(2n+\Delta n)\pi^2}{(b-a)^2} + \frac{\Delta l(2l+\Delta l+1)}{a^2} \right] \times \\ &\delta_{\Delta m,0} \Big[\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)} \frac{\delta_{\Delta l,1}}{k_1^2} + \frac{(l+m)(l-m)}{(2l-1)(2l+1)} \frac{\delta_{\Delta l,-1}}{k_1^2} + \frac{k_2^2}{k_1^2} \delta_{\Delta l,0} \Big] \times \\ &\left\{ \frac{16(b-a)^2[(-1)^{\Delta n}-1]^2 n^2(n+\Delta n)^2}{\pi^4 (2n+\Delta n)^4 \Delta n^4} + b^2 \delta_{\Delta n,0} \right\}. \end{split}$$

The appearance of several Kronecker delta functions in this equations helps us in identifying the range of Δm and Δl . Clearly, their only allowed values are $\Delta m = 0$ and $\Delta l = -1, 0, 1$. In addition, the values of n and l are limited such that $n \leq \text{Int}(n_f)$ and $l \leq l_{\text{max}}$. One more requirement is that $E_f > E_{\text{Fermi}}$. From Eq. (18), we obtain

$$l > g = \operatorname{ceil} \Big[\frac{\pi a}{(b-a)} \sqrt{n_f^2 - (n + \Delta n)^2} - \Delta l \Big],$$

where ceil stands for the integer obtained by rounding upward. Since the minimum value *l* has to be ≥ 1 , we set l_{\min} as max $\{1, g\}$.

3.3. Calculation of $S_{\Lambda n}^{zz}$ and $\Omega_{\Lambda n}^{zz}$

The final step is to calculate $S_{\Delta n}^{zz}$ and $\Omega_{\Delta n}^{zz}$ as defined in Eq. (12). Recalling that $\Delta v = \Delta n$ and that each sum involves all three quantum numbers, we can write $S_{\Delta n}^{zz}$ as,

$$S_{\Delta n}^{zz} = \sum_{n=1}^{n_{\max}} \sum_{\Delta l=-1}^{1} \sum_{\substack{l=l_{\min}\\m\neq 0}}^{l_{\max}} \sum_{\substack{l\leq m\\m\neq 0}} \sum_{\Delta m} S_{n,\Delta n,l,\Delta l,m,\Delta m}^{zz}.$$

The five-fold term can not be done analytically. However, we can reduce it to a double sum over n and l by performing the sums over m and Δm analytically. Further, terms with $\delta_{\Delta n,0} \delta_{\Delta l,0}$ and $\delta_{\Delta n,0} \delta_{\Delta l,-1}$, that imply no change in energy level and energy emission respectively are neglected since we are considering transitions that result only in absorption. The result is found to be

$$S_{\Delta n}^{zz} = \sum_{n=1}^{n_{\max}} \sum_{\Delta l=-1}^{1} \sum_{l=l_{\min}}^{l_{\max}} \frac{3(b-a)^2}{4\pi^2 k_1^2 a^2 n_f^3} \Big\{ \frac{l(5+9l+4l^2)}{3(3+8l+4l^2)} \Big[H + \frac{2(l+1)(b-a)^2 H}{\pi^2 a^2(2n+\Delta n)\Delta n} + 2(l+1)\frac{b^2}{a^2} \delta_{\Delta n,0} \Big] \delta_{\Delta l,1} + \frac{l(1+3l-4l^2)}{3(1-4l^2)} \Big[H - \frac{2l(b-a)^2 H}{\pi^2 a^2(2n+\Delta n)\Delta n} \Big] \delta_{\Delta l,-1} + 2lk_2^2 H \delta_{\Delta l,0} \Big\},$$
(32)

where,

$$H(n,\Delta n) = \frac{16[(-1)^{\Delta n} - 1]^2 n^2 (n + \Delta n)^2}{\pi^2 (2n + \Delta n)^3 \Delta n^3}$$

Similarly, we can calculate $\Omega_{\Delta n}^{zz}$ using Eq. (31) and (13). The result is found to be

$$\Omega_{\Delta n}^{zz} = \frac{1}{S_{\Delta n}^{zz}} \sum_{n=1}^{n_{\text{max}}} \sum_{\Delta l=-1}^{1} \sum_{l=l_{\text{min}}}^{l_{\text{max}}} S_{\Delta n}^{zz} \frac{\hbar}{2\mu} \left[\frac{\Delta n (2n+\Delta n)\pi^2}{(b-a)^2} + \frac{\Delta l (2l+\Delta l+1)}{a^2} \right].$$
(33)

The dielectric function for the spherical dome shell can now be calculated by substituting Eq. (32) and (33) in Eq. (12).

4. Results and discussion

In this section we calculate the real and imaginary parts of the dielectric function as a function of wavelength for a practical configuration of a metallic dome shell. We choose silver (Ag) as the shell material owing to the availability of a wide range of data for this metal. Using Eq. (32) and (33) we calculate the dielectric functions of a dome with a fixed cut-off angle and compared it to that of a complete shell (Appendix 5). We also compare it to the Drude model with size-dependent correction as given in Eqs. (1) and (2). Since the cut-off angle we consider are relatively small, we assume that the effective mean free path of the electron can be approximated by its value for a complete shell [29], i.e., $L_{\text{eff}} = (b - a)$. For similar reasons, we used A = 1 in the calculations [34]. Values of ω_p and γ_{bulk} were taken as 8.97 eV and 0.016 eV, respectively [17]. Fermi energy of the metal was calculated using $E_{\text{Fermi}} = \frac{1}{2}\mu v_f^2$, and Fermi velocity was taken as $v_f = 1.39 \times 10^6 \text{ ms}^{-1}$ for Ag [17].

The wavelength range we are interested in corresponds to 300 to 1200 nm. Interband component (ε_{inter}) of the dielectric function for Ag does not have a significant variation with size when dimensions are above 2 nm [30]. This allows us to use the following size-independent



Fig. 2. Imaginary (a) and real (b) parts of the dielectric functions of spherical dome shells of varying thickness calculated with the quantum mechanical model are shown by solid lines. Cut-off angle is 25.8° ($\zeta = 0.9$) for the spherical dome shells. Empirical values obtained from Drude model with size dependent correction for a shell with a = 40 nm and b = 45 nm is shown by the dotted-dashed line. a and b values given in the figure are in nanometers. The dashed line and dotted line shows the experimental bulk dielectric values taken from Refs. [27] and [38] respectively.

interband term in our permittivity model, which matches with the experimental bulk data for this frequency range [17],;

$$\varepsilon_{\text{inter}}(\omega) = \frac{3.66}{1 - \exp(4.08 - \hbar\omega/q_e)} - 1$$

Calculated dielectric functions of spherical Ag dome shells of four different thickness (2 to 5 nm) are shown in Fig. 2. It can be seen that oscillatory behaviour of the dielectric function is highly dependent on the thickness of the spherical dome shell. The dot-dashed line shows the results of the Drude model with size dependent correction for a shell with a = 40 nm and b = 45 nm. It provides a reasonable approximation to the blue curve obtained numerically but

fails to reproduce oscillations seen there. Also when the thickness is increased, the quantummechanical dielectric function of the spherical dome shell gets closer to the experimental bulk data values.

Behaviour of the dielectric function as we change the cut-off angle is shown by Fig. 3. It can be seen that the imaginary part of the dielectric function increases slightly with a decreasing cut-off angle. Also we can see that the quantum mechanical dielectric function of the spherical shell begins approaching that of a spherical dome shell for the smallest cut-off angle. When the cut-off angle is reduced to zero, dielectric function of the spherical dome shell we have derived should match that of the spherical shell. For this, we have to include the l = 0 and m = 0 terms we discarded in the calculations while calculating $S_{\Delta n}^{ZZ}$ and $\Omega_{\Delta n}^{ZZ}$ since the boundary condition for a spherical dome shell given in given in Eq. (22) is not relevant for a complete shell.

It is evident from the Figs. 2 and 3 that the influence of varying the shell thickness is much stronger than varying the cut-off angle on the dielectric function of spherical dome shells. This is because the quantum confinement is much stronger in the radial direction than in the polar direction for the spherical dome shells we have considered here.

Also, it is apparent from Figs. 2 and 3 that the quantum-mechanical dielectric function can exhibit oscillatory behavior for some parameter values, a feature absent from the Drude model even when size dependent corrections are included. The origin of oscillation lies in the quantization of the energy levels, which clearly cannot be included within the framework of the Drude model. It can be seen from the expression for the energy levels of an electron [Eq. (18)] that, because of the term $(b-a)^2$ in the denominator of the first term, for thin spherical dome shells energy difference between different states with different *n* values is large and therefore cannot be ignored, as is done in classical models by replacing the sum by an integral. In other words, when the oscillator strength weighted average transition frequency, $\Omega_{\Delta v}^{zz}$, is close to the frequency of the incident electric field, the polarizability of the particle increases substantially and results in distinctive peaks in the dielectric function.

Similar oscillatory behavior due to quantum confinement has been experimentally observed for material properties such as conductivity in literature [20,21].

Calculated extinction cross section of a spherical dome shell using our model and the Drude model with size dependant correction are shown in Fig. 4. It can be seen that the oscillations in the quantum mechanically derived dielectric function will create variations in the extinction spectrum as well. The position of oscillations in the dielectric function and therefore, the corresponding variations in the extinction spectrum depends on the thickness, aspect ratio and cut off angle of the spherical dome shell. In Fig. 4, such variations can be seen in the wavelength range 500 - 600 nm and 900 - 1100 nm. Based on these geometric parameters, if dominant oscillations occur close to the plasmon resonance frequency, it can shift or broaden the plasmon resonance in the extinction spectrum. Knowledge of such variations become important for sensitive sensing applications such as SERS.

In addition to quantum size effects, interband effects and surface scattering we have discussed here, dielectric functions of nano particles exhibit nonlocal effects related to in-homogeneous distribution of surface electrons and electron spill-outs.

In Ref. [17], experimental EELS data for Ag nanospheres with dimensions in 1–10 nm range has been well matched by a theoretical model which was developed by considering contributions to the dielectric function from screening effects due to d-electrons (inter band contributions), surface scattering and discretization electronic energy levels (quantum size effects). This model is very much similar to the model we have developed here. In the Ref. [39], in addition to contributions from inter band effects and quantum size effects, nonlocal effects including electron spill-outs are considered to exlain experimental data of Ref. [17] for Ag spheres. However, in Ref. [39] they employ a much simpler model, that does not reflect energy gap differ-



Fig. 3. Imaginary (a) and real (b) parts of the dielectric function of spherical dome shells for four different cut-off angles (solid lines). The dielectric function of a complete shell $(\theta' = 0)$ calculated with the quantum-mechanical model is shown by a dashed line, while values obtained from the Drude model with size dependent corrections area shown by a dotted dash line. In all calculations a = 40 nm and b = 43 nm.

ences between different electronic levels, to obtain the quantum size effects. The calculations in Ref. [17] seem to show strong agreement with experimental data, even without nonlocal effects including electron spill-outs. Electron spill-outs result in red shifts in resonance energy. Also, it has been shown that nonlocal effects [40, 41] on the dielectric function can become significant for nanoshells [42] when the outer radius of the shells becomes very small (10 nm) or when the shell thickness becomes very small (1 nm). They become less significant with the increasing shell radius, even though the thickness is small. Since the dome shell diameter we are considering is much greater than 10 nm and thickness is >1 nm, we do not consider the these effects on the dielectric function in our analysis.



Fig. 4. Extinction cross section and the imaginary part of the dielectric functions of a spherical dome shell calculated using our model and the Drude model with size dependent correction. The dimensions are a = 40 nm, b = 45 nm and cut-off angle $= 25.8^{\circ}$ ($\zeta = 0.9$). For extinction cross section calculations, the core of the spherical dome shell was taken as Si ($\varepsilon = 2.04$) and the surrounding as air ($\varepsilon = 1$).

5. Conclusions

We have obtained the quantized energy levels and the corresponding wave functions of a free electron inside a spherical dome shell. We used them to calculate the dielectric function of such a dome shell with the assumption of a small cut-off angle using shifted associated Legendre polynomials. We have compared our results with the classical Drude model, modified to include size-dependent corrections, and also with the experimental bulk permittivity data. We have also compared the spherical dome shell with its spherical shell counterpart using a fully quantum-mechanical analysis to study how much the removal of a small part of the shell effects the results.

Oscillatory behaviour seen in the dielectric function is due to the presence of discreet energy levels in our calculations, which cannot be ignored for small dimensions. When the diameter of the spherical dome shell is large while the cut-off angle is small, the quantum confinement is much higher in the radial direction than in the polar direction, and the quantum-mechanical dielectric function of the shell can be taken as a close approximation to that of a spherical dome shell. The Drude model including the size dependent correction also provides a close approximation in the frequency range we have considered, particularly when the oscillations become negligible as the thickness of the spherical dome shell is increased.

Oscillatory behavior seen in the dielectric function will cause variations in the extinction spectrum in the corresponding wavelength range.

The quantum mechanical dielectric function derived in this paper is based on the behaviour of a non-interacting electron gas confined within a thin spherical-shape dome shell. Our results provide an insight into how the quantum effects introduce the geometric parameters into the dielectric function of thin spherical dome shells, at a tolerable computational cost. Study of

such quantum effects for particles of different shapes are extremely useful for engineering real world applications such as quantum cryptography, energy harvesters, transistor, lasers, quantum computers, quantum communication systems etc. Spherical dome shells with their unique optical properties can offer new opportunities in the design of these applications.

Appendix A: properties of $\widetilde{P}_{l}^{m}(x)$

We can prove the orthogonality of the shifted associated Legendre polynomials, $\widetilde{Q}_l^m(x)$, as follows. Let $\dot{x} = k_1 x + k_2$. From Eq. (29) and (24) we can write

$$\begin{split} \int_{-1}^{\zeta} \widetilde{\mathcal{Q}}_{l}^{m}(x) \widetilde{\mathcal{Q}}_{l'}^{m}(x) dx &= \int_{-1}^{\zeta} \sqrt{k_{1} \frac{(2l+1)(l-m)!}{2(m+l)!}} \widetilde{P}_{l}^{m}(x) \sqrt{k_{1} \frac{(2l'+1)(l'-m)!}{2(m+l')!}} \widetilde{P}_{l'}^{m}(x) dx \\ &= \sqrt{k_{1} \frac{(2l+1)(l-m)!}{2(m+l)!}} \sqrt{k_{1} \frac{(2l'+1)(l'-m)!}{2(m+l')!}} \frac{1}{k_{1}} \int_{-1}^{1} P_{l}^{m}(x) P_{l'}^{m}(x) dx \\ &= \sqrt{k_{1} \frac{(2l+1)(l-m)!}{2(m+l)!}} \sqrt{k_{1} \frac{(2l'+1)(l'-m)!}{2(m+l')!}} \frac{1}{k_{1}} \frac{2(m+l)!}{(2l+1)(l-m)!} \delta_{l,l'} \\ &= k_{1} \frac{(2l+1)(l-m)!}{2(m+l)!} \frac{1}{k_{1}} \frac{2(m+l)!}{(2l+1)(l-m)!} \delta_{l,l'} \\ &= 1. \end{split}$$

We can also obtain a recurrence relation for the shifted associated Legendre polynomials. From Eq. (25), (27) and (28), we obtain

$$(l-m)P_{l}^{m}(k_{1}x+k_{2}) = (k_{1}x+k_{2})(2l-1)P_{l-1}^{m}(k_{1}x+k_{2}) - (l+m-1)P_{l-2}^{m}(k_{1}x+k_{2}) (l-m)\widetilde{P}_{l}^{m}(x) = (k_{1}x+k_{2})(2l-1)\widetilde{P}_{l-1}^{m}(x) - (l+m-1)\widetilde{P}_{l-2}^{m}(x) (k_{1}x+k_{2})(2l-1)\widetilde{P}_{l-1}^{m}(x) = \frac{(l-m)\widetilde{P}_{l}^{m}(x) + (l+m-1)\widetilde{P}_{l-2}^{m}(x) - k_{2}(2l-1)\widetilde{P}_{l-1}^{m}(x)}{k_{1}(2l-1)}.$$
 (34)

Appendix B: calculation of the matrix element M_{if}

The matrix element in Eq. (30) can be written explicitly as,

$$M_{if} = \int_{0}^{2\pi} \int_{\theta'}^{\pi} \left\{ \sin \theta \cos \theta Q(\theta)_{l,m} [Q(\theta)_{l+\Delta l,m+\Delta m}]^* F(\phi)_m [F(\phi)_{m+\Delta m}]^* \, d\theta d\phi \right\} \times \int_{a}^{b} r^3 R(r)_{n,l} [R(r)_{n+\Delta n,l+\Delta l}]^* \, dr.$$
(35)

The integration involving the radial part is the same as for a spherical shell and can be performed as [36],

$$\int_{a}^{b} r^{3} R(r)_{n,l} [R(r)_{n+\Delta n,l+\Delta l}]^{*} dr = \frac{4(b-a)[(-1)^{\Delta n}-1]n(n+\Delta n)}{\pi^{2}(2n+\Delta n)^{2}\Delta n^{2}} + b\delta_{\Delta n,0}.$$

The remaining part of the integration, which involves the polar and azimuthal components is different from a spherical shell. It can be calculated using expressions derived for $F(\phi)$ and

 $Q(\theta)$ in Eq. (29) and (20) as follows.

$$\int_{0}^{2\pi} \int_{\theta'}^{\pi} \sin\theta \cos\theta Q(\theta)_{l,m} [Q(\theta)_{l+\Delta l,m+\Delta m}]^{*} F(\phi)_{m} [F(\phi)_{m+\Delta m}]^{*} d\theta d\phi
= \sqrt{k_{1}} \frac{(2l+1)(l-m)!}{2(m+l)!} \sqrt{k_{1}} \frac{[2(l+\Delta l)+1][(l+\Delta l)-(m+\Delta m)]!}{2[(m+\Delta m)+(l+\Delta l)]!}
\int_{0}^{2\pi} \frac{1}{\sqrt{2\pi}} \exp(jm\phi) \frac{1}{\sqrt{2\pi}} \exp[-i(m+\Delta m)\phi] d\phi
\int_{\theta'}^{\pi} \sin\theta \cos\theta \widetilde{P}_{l}^{m}(\cos\theta) \widetilde{P}_{l+\Delta l}^{m+\Delta m}(\cos\theta) d\theta
= \delta_{\Delta m,0} \sqrt{k_{1}} \frac{(2l+1)(l-m)!}{2(m+l)!} \sqrt{k_{1}} \frac{[2(l+\Delta l)+1][(l+\Delta l)-m]!}{2[m+(l+\Delta l)]!}
\int_{\theta'}^{\pi} \sin\theta \cos\theta \widetilde{P}_{l}^{m}(\cos\theta) \widetilde{P}_{l+\Delta l}^{m}(\cos\theta) d\theta
= \delta_{\Delta m,0} \sqrt{k_{1}} \frac{(2l+1)(l-m)!}{2(m+l)!} \sqrt{k_{1}} \frac{[2(l+\Delta l)+1][(l+\Delta l)-m]!}{2[m+(l+\Delta l)]!} \int_{-1}^{\zeta} x \widetilde{P}_{l}^{m}(x) \widetilde{P}_{l+\Delta l}^{m}(x) dx.$$
(36)

After substituting the recurrence relation given by Eq. (34) in (36), this can be further simplified as,

$$\begin{split} &\int_{0}^{2\pi} \int_{\theta'}^{\pi} \sin\theta \cos\theta Q(\theta)_{l,m} [Q(\theta)_{l+\Delta l,m+\Delta m}]^* F(\phi)_m [F(\phi)_{m+\Delta m}]^* \, d\theta d\phi \\ &= \delta_{\Delta m,0} \sqrt{k_1 \frac{(2l+1)(l-m)!}{2(m+l)!}} \sqrt{k_1 \frac{[2(l+\Delta l)+1][(l+\Delta l)-m]!}{2[m+(l+\Delta l)]!}} \times \\ &\int_{-1}^{\zeta} \left\{ \frac{[(l+1)-m] \widetilde{P}_{l+1}^m(x) + [(l+1)+m-1] \widetilde{P}_{(l+1)-2}^m(x) - k_2 [2(l+1)-1] \widetilde{P}_{(l+1)-1}^m(x)}{k_1 [2(l+1)-1]} \times \right. \\ &\left. \left. \tilde{P}_{l+\Delta l}^m(x) \right\} dx \\ &= \delta_{\Delta m,0} \Big[\sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} \frac{\delta_{\Delta l,1}}{k_1} + \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}} \frac{\delta_{\Delta l,-1}}{k_1} - \frac{k_2}{k_1} \delta_{\Delta l,0} \Big]. \end{split}$$

Therefore, we can write M_{if} as,

$$M_{if} = \left\{ \frac{4(b-a)[(-1)^{\Delta n}-1]n(n+\Delta n)}{\pi^2(2n+\Delta n)^2\Delta n^2} + b\delta_{\Delta n,0} \right\} \times \\ \delta_{\Delta m,0} \left[\sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} \frac{\delta_{\Delta l,1}}{k_1} + \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}} \frac{\delta_{\Delta l,-1}}{k_1} - \frac{k_2}{k_1} \delta_{\Delta l,0} \right]$$

Appendix C: quantum mechanical dielectric function for shell

The terms $S_{\Delta n}^{zz}$ and $\Omega_{\Delta n}^{zz}$ for a spherical shell of small thickness can be given as [36],

$$\begin{split} S_{\Delta n}^{zz} &= \sum_{n=1}^{n_{\max}} \sum_{l=l_{\min}}^{l_{\max}} \sum_{\Delta l=-1}^{1} \left(\left\{ \frac{4(b-a)^{2}[(-1)^{\Delta n}-1]^{2}n^{2}(n+\Delta n)^{2}(l+1)}{\pi^{4}a^{2}n_{f}^{3}(2n+\Delta n)^{3}\Delta n^{3}} \right. \\ &+ \frac{8(b-a)^{4}[(-1)^{\Delta n}-1]^{2}n^{2}(n+\Delta n)^{2}(l+1)^{2}}{\pi^{6}a^{4}n_{f}^{3}(2n+\Delta n)^{4}\Delta n^{4}} + \frac{(b-a)^{2}(l+1)^{2}}{a^{2}\pi^{2}n_{f}^{3}}\delta_{\Delta n,0} \right\} \delta_{\Delta l,+1} \\ &+ \left\{ \frac{4(b-a)^{2}[(-1)^{\Delta n}-1]^{2}n^{2}(n+\Delta n)^{2}l}{\pi^{4}a^{2}n_{f}^{3}(2n+\Delta n)^{3}\Delta n^{3}} - \frac{8(b-a)^{4}[(-1)^{\Delta n}-1]^{2}n^{2}(n+\Delta n)^{2}l^{2}}{\pi^{6}a^{4}n_{f}^{3}(2n+\Delta n)^{4}\Delta n^{4}} \right\} \delta_{\Delta l,-1} \right) \\ \Omega_{\Delta n}^{zz} &= \frac{1}{S_{\Delta n}^{zz}} \sum_{n=1}^{n_{\max}} \sum_{l=l_{\min}}^{l} \sum_{\Delta l=-1}^{1} S_{\Delta n}^{zz} \frac{\hbar}{2\mu} \left[\frac{\Delta n(2n+\Delta n)\pi^{2}}{(b-a)^{2}} + \frac{\Delta l(2l+\Delta l+1)}{a^{2}} \right]. \end{split}$$

where,

$$n_{\max} = \left[\left[\sqrt{\frac{2\mu}{\hbar^2}} \left[\frac{(b-a)^2 E_{\text{Fermi}}}{\pi^2} \right] \right] \right],$$

$$l_{\max} = \left[\frac{\pi a}{(b-a)} \sqrt{(n_f^2 - n^2)} \right],$$

$$l_{\min} = \max\{0, \left[\frac{a\pi}{(b-a)} \sqrt{n_f^2 - (n+\Delta n)^2} - \Delta l \right] \}.$$

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