

# Plasmonics

## Quantum mechanical model for plasmon excitations in nanostructures

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<b>Abstract:</b>	In this work we develop a theoretical quantum mechanical model for describing the plasmon excitations in nanostructures. This model is based in the electronic density according to the Density Functional Theory (DFT). We derive an expression for finding an approximation to the dispersion relation in a nanostructure from the complete Hamiltonian of the system. We apply this expression to an aluminium nano-ring showing how great, and not negligible, the ionic-interaction term is.

Plasmonics

Dear Editor:

Please find attached for your kind review, our manuscript entitled "Quantum mechanical model for plasmon excitations in nanostructures".

The study is a theoretical quantum mechanical model based on generation of plasmons in nanostructures, is based in the Density Functional Theory (DFT) and is able to take into account the electronic distribution due to the nanostructure shape. We also apply the model to the case of an aluminium nano-ring.

Look forward to your favorable consideration.

Most sincerely,

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# Quantum mechanical model for plasmon excitations in nanostructures

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**Abstract** In this work we develop a theoretical quantum mechanical model for describing the plasmon excitations in nanostructures. This model is based in the electronic density according to the Density Functional Theory (DFT). We derive an expression for finding an approximation to the dispersion relation in a nanostructure from the complete Hamiltonian of the system. We apply this expression to an aluminium nano-ring showing how great, and not negligible, the ionic-interaction term is.

**Keywords** plasmon · nano-structures · nano-ring · hamiltonian formalism

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## 1 Introduction

In recent years many novel nano-devices have been developed making necessary the study of nanostructures of different geometrical shape. In these nanostructures the plasmon generation and decay requires special attention due to their implication in the variation of the electrical and optical properties of the solid

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[1–5]. In addition, the study of creation and decay of plasmons is a very important field of research particularly in quantitative chemical analysis of surface and interface layers of solids [6–11] which revealed recently to be a useful tool for nanostructure characterization [12–15]. All these new developments require more accurate information on the process of plasmon generation and decay, and due to the very small dimension of the nanostructures, their shapes take on a very important role.

Usually, the study of plasmon excitations in solids is dealt by means of the *dielectric model* for which all the electrical properties of the material are contained in a function of the angular frequency  $\omega$  and the wave number  $k$ , known as the *dielectric function*  $\epsilon$ . This model is very appropriate and suitable when the number of atoms in the nanostructure is enough to make a clear distinction between the surface and the volume [16–20]. But it takes no account for the *local fields* resulting from the electronic density fluctuations and their interaction with the ionic lattice, phenomena which were advised earlier [21–30]. Such fluctuations are a very relevant issue in the case of very small nanostructures (i.e. with one or more dimensions in the order of one or two atoms) where the electronic charge distribution could change strongly along the space coordinates. Then, describing the electrical properties of these solids with a macroscopic magnitude may be inappropriate. Such is the case of fullerene and carbon nano-tubes [31–33].

In the late 60s and early 70s, Hohenberg, Kohn and Sham stated that the microscopic properties of a solid quantum system can be expressed in terms of its electronic charge density without lack of information [34,35]. These Hohenberg, Kohn and Sham's theorems gave rise the *Density Functional Theory* (DFT) [36–39] that allows to develop a model in which the nano-system properties are expressed in terms of the local electronic density, instead of the dielectric function.

In this work we develop a model based in the local charge density for describing the plasmon field. We derive a Hamiltonian expression for the plasmon field of a nanostructure. Then we use this model to study the dispersion relation of an one-atom-thick aluminium nanoring.

## 2 Theoretical Model

We develop the theoretical treatment in the frame of the *Hamiltonian formalism*, which describes the behaviour of the electronic density variations within a *plasmon field* by means of a quantum mechanical Hamiltonian [40,16,19,20]. According with it, the Hamiltonian per unit volume of the electronic gas has the form [40]:

$$h = \sum_{\mu,\nu} \frac{\rho_o^{(m)}}{2} \Upsilon_\mu \Upsilon_\nu + \frac{\alpha}{2} \frac{\partial R_\mu}{\partial x_\mu} \frac{\partial R_\nu}{\partial x_\nu} + \mathcal{V}(\mathbf{x}) \quad (1)$$

where  $\Upsilon_\mu$  and  $R_\mu$  are the momentum and coordinate conjugate quantities respectively,  $\rho_o^{(m)}(\mathbf{x})$  is the system initial mass density distribution,  $\alpha$  is the

elasticity factor [40] and the electrostatic energy  $\mathcal{V}(\mathbf{x})$  is given by

$$\mathcal{V}(\mathbf{x}) = \frac{1}{2} \phi(\mathbf{x}) \rho(\mathbf{x}) \quad (2)$$

being  $\phi(\mathbf{x})$  and  $\rho(\mathbf{x})$  the electrostatic potential and the charge density of the system, respectively, as a function of the coordinate position vector  $\mathbf{x}$ . We assume that the ionic charge density  $\rho_o^+(\mathbf{x})$  remains static and the system performs small oscillations:  $\delta\rho = -\rho_o^-(\mathbf{x})\Delta(\mathbf{x})$ , where  $\rho_o^-(\mathbf{x})$  is the initial electronic charge density, and  $\Delta(\mathbf{x}) = \sum_\mu \partial R_\mu / \partial x_\mu$  the elastic deformation of the electronic gas. We get

$$\rho(\mathbf{x}) = \rho_o^+(\mathbf{x}) - \rho_o^-(\mathbf{x}) \left[ 1 + \sum_\mu \frac{\partial R_\mu}{\partial x_\mu} \right] \quad (3)$$

As we are interested in collective oscillation phenomena, we work these expressions in the momentum space with the transformations:

$$\Upsilon_\mu(\mathbf{x}) = \sum_k V_k^\mu e^{-i\mathbf{k}\cdot\mathbf{x}} \quad (4)$$

$$R_\mu(\mathbf{x}) = \sum_k Q_k^\mu e^{i\mathbf{k}\cdot\mathbf{x}} \quad (5)$$

The potential energy of the system is related with the electric potential, thus we need to make also the transformation  $\phi(\mathbf{x}) = \sum_k \phi_k e^{i\mathbf{k}\cdot\mathbf{x}}$ , where we assumed that the plasma waves are all longitudinal (i.e.  $Q_k \parallel \mathbf{k}$ ) [41], and write the equation 2 in the form:

$$\begin{aligned} \mathcal{V}(\mathbf{x}) = & 2\pi \sum_k \left( \frac{1}{k^2 N} \right) [\rho_o^+(\mathbf{x}) - \rho_o^-(\mathbf{x})]^2 - 2\pi \sum_{k,k'} e^{i\mathbf{k}\cdot\mathbf{x}} Q_k Q_{k'} \\ & - 2\pi i \left( \frac{1}{k} + k \sum_q \frac{1}{qN} \right) \sum_k Q_k \rho_o^-(\mathbf{x}) [\rho_o^+(\mathbf{x}) - \rho_o^-(\mathbf{x})] e^{i\mathbf{k}\cdot\mathbf{x}} \end{aligned} \quad (6)$$

Taking into account eqs. 4, 5 and 6 we write eq. 1 in the form:

$$\begin{aligned} H = & \frac{1}{2} \sum_{k,k'} V_k V_{k'} \chi(k, k') - \frac{1}{2} \sum_k Q_k Q_{k'} k k' \delta_{k,-k'} \\ & - 2\pi \sum_{k,k'} Q_k Q_{k'} \xi(k, k') - 2\pi i \sum_k Q_k \nu(k) + \epsilon_o \end{aligned} \quad (7)$$

with

$$\chi(k, k') = \int \rho_o^{(m)}(\mathbf{x}) e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}} d^3\mathbf{x} \quad (8)$$

$$\xi(k, k') = \frac{k'}{k} \int [\rho_o^-(\mathbf{x})]^2 e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{x}} d^3\mathbf{x} \quad (9)$$

$$\nu(k) = \left( \frac{1}{k} + k \frac{h_N^{(2)}}{N} \right) \int \rho_o^-(\mathbf{x}) [\rho_o^+(\mathbf{x}) - \rho_o^-(\mathbf{x})] e^{i\mathbf{k}\cdot\mathbf{x}} d^3\mathbf{x} \quad (10)$$

and

$$\epsilon_o = 2\pi \frac{h_N^{(2)}}{N} \int [\rho_o^+(\mathbf{x}) - \rho_o^-(\mathbf{x})] d^3\mathbf{x} \quad (11)$$

where  $h_N^{(2)}$  is the  $N$ -th order *generalized harmonic number* of 2, defined by  $h_N^{(2)} = \sum_k^N 1/k^2$ . Each of the first and third terms in eq. 7 can be separated into two sums with terms with  $k = -k'$  and terms with  $k \neq -k'$ , taking into account the factors

$$\chi(k, -k) = \int \rho_o^{(m)}(\mathbf{x}) d^3\mathbf{x}$$

$$\xi(k, -k) = \int [\rho_o^-(\mathbf{x})]^2 d^3\mathbf{x}$$

to write the Hamiltonian in eq. 7 as a sum of two terms,  $H = H_o + H_I$ , where

$$H_o = \frac{\mu}{2} \sum_k V_k V_{-k} + \left[ 4\pi \int [\rho_o^-(\mathbf{x})]^2 d^3\mathbf{x} + \alpha k^2 \right] Q_k Q_{k'} + \epsilon_o \quad (12)$$

and

$$H_I = \sum_{k, k'; k' \neq -k} \left\{ \frac{1}{2} P_k P_{k'} \chi(k, k') - 2\pi Q_k Q_{k'} \xi(k, k') \right\} \quad (13)$$

with  $\mu = \int \rho_o^{(m)}(\mathbf{x}) d^3\mathbf{x}$ , the total electronic mass. The expression 12 indicates that  $H_o$  is the Hamiltonian of an harmonic oscillator [42,43,40], from which we obtain the dispersion relation  $\omega(k)$ :

$$\omega_k^2 = \left\{ 4\pi \int [\rho_o^-(\mathbf{x})]^2 d^3\mathbf{x} + \alpha k^2 \right\} \mu^{-1} \quad (14)$$

Now we apply the second quantization, defining the operators  $V_k$  and  $Q_k$ :

$$V_k = i \sqrt{\frac{\omega_k}{2\mu}} (a_k^\dagger + a_{-k})$$

$$Q_k = \frac{1}{\sqrt{2\omega_k\mu}} (a_k + a_{-k}^\dagger)$$

where  $a_k^\dagger$  and  $a_k$  are the  $k$ -mode plasmon creation and absorption operators respectively. Then,  $H_o$  takes the form:

$$H_o = \frac{1}{2} \sum \omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right) + \epsilon_o$$

and we also write  $H_I$ :

$$\begin{aligned} H_I = & -\frac{1}{4\mu} \sum_{k,k';k' \neq -k} \sqrt{\omega_k \omega_{k'}} \chi(k, k') \left[ a_k^\dagger a_{k'}^\dagger - a_k^\dagger a_{-k'} - a_{-k} a_{k'}^\dagger + a_{-k} a_{-k'} \right] \\ & -\frac{\pi}{\mu} \sum_{k,k';k' \neq -k} \frac{1}{\sqrt{\omega_k \omega_{k'}}} \xi(k, k') \left[ a_k a_{k'} + a_k a_{-k'}^\dagger + a_{-k}^\dagger a_{k'} + a_{-k}^\dagger a_{-k'}^\dagger \right] \\ & -\frac{2\pi i}{\sqrt{2\omega_k \mu}} \sum_k \nu(k) \left[ a_k + a_{-k}^\dagger \right] \end{aligned} \quad (15)$$

The first and second terms in the equation 15 are extra-diagonal elements of the Hamiltonian matrix and the third one is a *dispersive* term [41] due to the interaction between the electron and the ionic core.

In order to solve this Hamiltonian, we have to find out a way to diagonalize it, i.e. by means of a canonical transformation of the creation ( $a^\dagger$ ) and absorption ( $a$ ) operators, that will convert the total Hamiltonian to a diagonal form. Nevertheless, due to the extremely dense-matrix form of the interaction term  $H_I$ , the task of diagonalizing  $H$  is very difficult. We note however, that the whole expression for  $H$  is a *one-body* Hamiltonian anyway.

### 3 Application and results

When studying the plasmon generation and decay in macroscopic systems, we usually refer to surface and volume as two very distinguishable qualities of the solid, making the difference between *surface plasmons* and *bulk plasmons*, as the electron oscillations occur in the surface of the material, or as they occur *inside* the material, respectively. The case of an object formed by a one-atom thick linear array is different, because it is difficult to define a surface that separates the *bulk* from the *external media*. Therefore, we can not distinguish between surface and bulk plasmons. The electronic gas oscillations generates *linear plasmon* because they move along a single dimension.

Such plasmons were studied with the theoretical model of the *uni-dimensional electron gas* conforming the so-called *uni-dimensional plasmons* [44,45] (as an idealized form of linear plasmons). In spite of the few theoretical studies on this kind of plasmons, they were observed experimentally by inelastic scattering of slow electrons across metallic nanowires of atomic thickness [46].

We must be aware of really dealing with one-dimensional plasmons because our electron-gas is three-dimensional, even though the oscillations that it generate move in one dimension [46].

### 3.1 The aluminium nano-ring

Our purpose is to apply our theoretical model to an one-atom-thick aluminium nano-ring, according to real geometrical dimensions [47]. The advantages of the ring geometry are the symmetry and periodicity. In an array forming a *collar* made of equal and equidistant atoms, each of them is completely equivalent to any other, there are no borders neither bounds and if the number of atoms is large enough, we neglect locally the curvature of the array (then  $\mathbf{a} = a\hat{\mathbf{z}}$ ), and the *collar* seems to be a linear array of atoms:  $R_\mu(\mathbf{x} + \mathbf{a}) = R_\mu(\mathbf{x})$  ( see figure 1) from which we get the periodicity condition

$$k = 2\pi n/a \quad (16)$$

with  $a$  the distance between two consecutive atoms and  $n$  an integer. From an experimental point of view, is possible to obtain nanorings made of carbon [48], zinc oxide from magnetic-field-curved nano-ribbons [49],  $Zn_2SnO_4$  from an evaporation method [50], and aluminium by using carbon nano-tubes as *mould* [47]. These latter are unstable, because as they separate from the mould, they dismantle or fold into a *zigzag* [51].

As another consequence of the periodicity, we need to integrate the expressions 8, 9, 10 and 11 just in one *cell* (which is the portion of ring containing an atom) and then multiplying by the number of atoms  $n_a$ , instead of integrating in all the space occupied by the ring:  $\int_{ring} \dots = n_a \int_{cell} \dots$ ; therefore from now on, we suppress the subindex *cell*, and we assume that all the integrations are restricted to one cell.

The unperturbed Hamiltonian does not change, but the expression 14 is now:

$$\omega_k^2 = \left\{ 4\pi \int [\rho_o^-(\mathbf{x})]^2 d^3\mathbf{x} + \alpha k^2/n_a \right\} \mu^{-1} \quad (17)$$

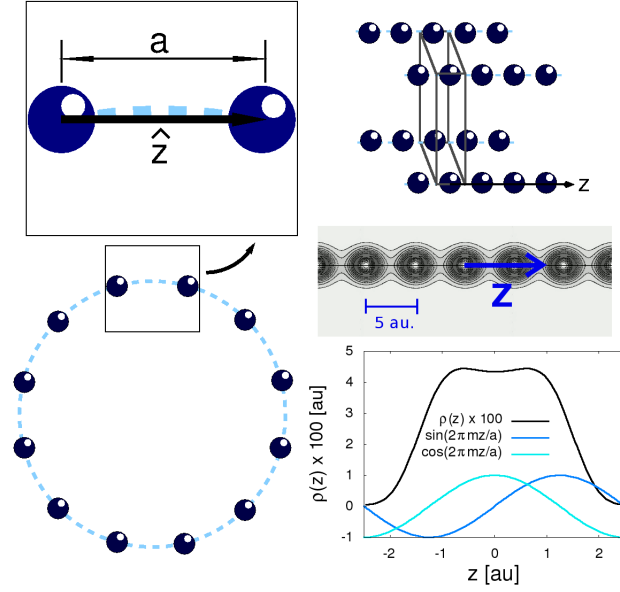
and the last contribution of the perturbed term  $H_I$  is:

$$-2\pi i n_a \sum_k \left( a_k + a_{-k}^\dagger \right) \nu(k)$$

In addition, the factors  $\chi$ ,  $\xi$  and  $\nu$  in equations 8, 9 and 10 have complex exponents of the form  $e^{i2\pi m z/a}$ , being  $m$  an integer, and can be written as the sum of two terms  $e^{i2\pi m z/a} = i \sin(2\pi m z/a) + \cos(2\pi m z/a)$ . However, the electronic charge density, has the profile of a pair function, as we see in the bottom-right corner of figure 1, therefore, the *sine* part vanishes when integrated with integer powers of the density, remaining just the *cosine* component.

Therefore, taking into account the eq. 16, all these factors become:

$$\chi_{n,n'} = \int [\rho_o^{(m)}(\mathbf{x})] \cos[(2\pi(n+n')\frac{z}{a})] d^3\mathbf{x} \quad (18)$$



**Fig. 1** A one-atom thick aluminium nano-ring, and its treatment as a nano-wire in Quantum Espresso. The schematic representation of a generic twelve-atoms nano-ring (bottom left corner). The local curvature of the nano-ring is neglected and it locally seems to be a linear array of atoms called *nano-wire* (upper left corner). In order to calculate the electronic density of the system, the DFT pack *Quantum Espresso* (QE) allow us to represent the nano-wires as a periodic succession of special user-customized dimension cells called *supercells* (upper right corner). The electronic density distribution in an aluminium nano-wire where atoms are separated at  $a = 5.0$  au. is computed by QE and is plotted on grayscale showing different density areas (centre right). The electronic charge density profile along  $z$ -axis in a single supercell is a pair function of  $z$  (bottom right).

$$\xi_{n,n'} = 2\pi \frac{n'}{n} \int [\rho_o^-(\mathbf{x})]^2 \cos\left[(2\pi(n+n')\frac{z}{a})\right] d^3\mathbf{x} \quad (19)$$

$$\nu_n = \frac{an_a}{2\pi} \left( \frac{1}{n} + \frac{nh_N^{(2)}}{N} \right) \int \rho_o^-(x)(\rho_o^+(x) - \rho_o^-(x)) \cos\left[\frac{2\pi n z}{a}\right] d^3\mathbf{x} \quad (20)$$

And from eq. 15 we can write down  $H_I$  in the form:

$$\begin{aligned} H_I = & I_1 \left( a_k^\dagger a_{k'}^\dagger - a_k^\dagger a_{-k'} - a_{-k} a_{k'}^\dagger + a_{-k} a_{-k'} \right) \\ & + I_2 \left( a_k a_{k'} + a_k a_{-k'}^\dagger + a_{-k}^\dagger a_{k'} + a_{-k}^\dagger a_{-k'}^\dagger \right) \\ & + iI_3 \left( a_k + a_{-k}^\dagger \right) \end{aligned} \quad (21)$$

where, the *c-numbers*  $I_1$ ,  $I_2$  and  $I_3$  are:

$$I_1(n, n') = -\frac{\sqrt{\omega_n \omega_{n'}}}{4\mu} \int \rho_o^{(m)}(\mathbf{x}) \cos \left[ 2\pi(n + n') \frac{z}{a} \right] d^3\mathbf{x} \quad (22)$$

$$I_2(n, n') = -\frac{2\pi^2}{\mu \sqrt{\omega_n \omega_{n'}}} \frac{n'}{n} \int (\rho_o^-(\mathbf{x}))^2 \cos \left[ 2\pi(n + n') \frac{z}{a} \right] d^3\mathbf{x} \quad (23)$$

$$I_3(n) = -\frac{an_a}{\sqrt{2\omega_n \mu n_a}} \left( \frac{1}{n} + n \frac{h_N^{(2)}}{N} \right) \times \int \rho^-(\mathbf{x}) [\rho^+(\mathbf{x}) - \rho^-(\mathbf{x})] \cos \left[ 2\pi n \frac{z}{a} \right] d^3\mathbf{x} \quad (24)$$

From the eq. 17 we obtain the available modes  $\omega_n$ :

$$\omega_n^2 = \frac{4\pi \int [\rho_o^-(\mathbf{x})]^2 d^3\mathbf{x} + 4\pi^2 \alpha n^2 / a^2 n_a}{\int \rho_o^{(m)}(\mathbf{x}) d^3\mathbf{x}} \quad (25)$$

In order to find the plasma oscillation frequencies for the nanoring, we need to find an approximate value for the electronic charge and mass densities  $\rho_o^-$  and  $\rho_o^{(m)}$ , as a function of the spatial coordinates. These two densities are related via

$$\frac{\rho_o^-(\mathbf{x})}{\rho_o^{(m)}(\mathbf{x})} = \frac{q_e}{m_e}$$

being  $q_e$  and  $m_e$  the electron charge and mass respectively.

The charge density  $\rho_o^+(\mathbf{x})$  in eq. 20, represents the atomic ionic cores. The aluminium atom has thirteen electrons, from these, just the  $3s^2$  and  $3p^1$  are in the conduction band. The atomic nucleus, of charge  $+13q_e$ , is then screened by ten electrons, remaining the *core* with a net charge  $+3q_e$ . The ionic string inside the electronic cloud can suffer length variations, but these variations are in any case very small and we can neglect them, thus we consider the ionic cores as fixed points:

$$\rho_o^+(\mathbf{x}) = 3q_e \sum_j^{ring} \delta(\mathbf{x} - \mathbf{x}_j)$$

where  $\mathbf{x}_j$  is the coordinate vector of the  $j$ -th core. As before, integrating in a cell this expression becomes:

$$\rho_o^+(\mathbf{x}) = 3q_e \delta(\mathbf{x} - \mathbf{x}_o) \quad (26)$$

where  $\mathbf{x}_o$  is the coordinate of the core in the cell.

Another subject we must deal with, is the number  $N$  of modes we should consider in the above sums. According to the *Pines criterion* [41] all the sums

should be limited up to  $k$ , where  $k \ll k_c$ , and the critic value  $k_c$  is given by  $k_c = \omega_p/v_F$ , with  $v_F$ , the Fermi velocity of the solid. The justification of this criterion is based in the fact that for  $k$  greater than the critic value, there are no collective modes of the electron gas, but individual collisions with the electrons of the conduction band [41,52]. Such criterion can be used just in an approximated way, until we calculate the numerical value of the modes:

$$k_c = \frac{\omega_p m_e}{k_F \hbar}$$

In atomic units, this gives  $k_c = \omega_p/k_F$ . Using our data for the aluminium  $k_F = 0.92$  au.,  $\omega_p = 15.3$ , we get  $k_c \approx 16.6$ ; this is, the value of  $n_c$  coming from the periodicity of the ring geometry:

$$2\pi n_c/a \approx 16.6 \Rightarrow n_c \approx 13$$

where we used  $a = 5$  au. , therefore, we limit the sums just to a few modes, say  $n = 0, \dots, 5$ .

### 3.2 Density calculation for an aluminium nanoring

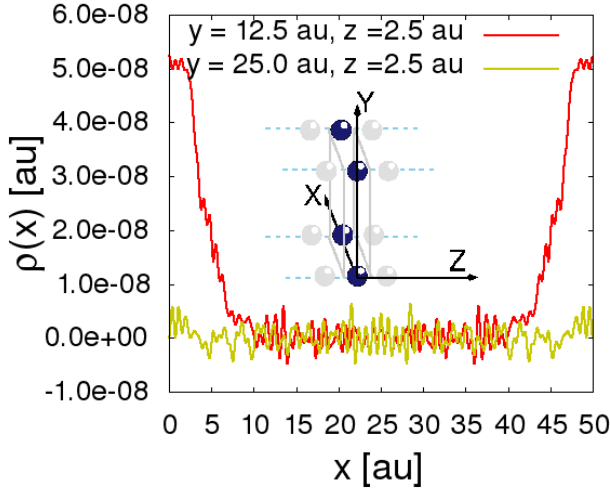
The calculation of the electronic charge and mass densities starting from the atomic orbitals is a very complex task, even for an 1-dimensional array. However, it is possible to perform a numerical approximation with computer techniques implementing DFT. In this work we use the *Quantum Espresso* (QE) pack for DFT calculations [53]. We recall that in our approximation, the ring locally is approached to a linear array, which is very useful because rings are not allowed in QE, but periodical structures are. These periodical structures can be real crystalline lattices or user-defined non conventional cells known in the QE jargon as *supercells*.

We calculate the electron density of an orthogonal square base supercell with a side of 50 au. to keep the wires away enough each other, to avoid mixing of electrons from different wires, and 5 au. height, according to the dimensions of the real nanorings obtained experimentally [47] (see figure 1).

The Quantum Espresso `pw.x` tool is able to calculate a 3-dimensional matrix with the electronic density values as a function of the coordinates, and as expected, as bigger the matrix, accurate the density [54]. This QE density matrix provides data for numerically integrate the density.

The centre-right of figure 1 shows the electron density of a nanowire segment as obtained by Quantum Espresso, the darker the colour, the higher the density; the white spots in the centre depict the atom ionic cores.

In our numerical QE matrix we expect the electron density tends smoothly to zero as the integration element goes away from the nanowire. Nevertheless, this is not true: the numerical values of the electron density oscillate around zero in these regions. This is a lack of precision in QE, and is due to the plane wave decomposition of the electronic eigenstates, that does not compensate completely in the low-density region (See figure 2). Anyway, the value of the



**Fig. 2** Electronic density oscillation along supercell x-axis inter-wire space, where it expected to vanish softly.

**Table 1** Calculated values of  $\omega_n$  from the integration of a  $1200 \times 1200 \times 120$  matrix density.

$n$	$\omega_n [au]$	$\omega_n [eV]$	$I_3(n)$
0	0.4736686	12.84116	-
1	0.4736686	12.84116	1.91614
2	0.4736686	12.84116	0.77654
3	0.4736687	12.84116	1.27174
4	0.4736687	12.84116	1.77312
5	0.4736687	12.84116	2.27869

integral of the electronic density  $q = \int \rho_o^-(\mathbf{x}) dxdydz$  is useful to control the quality of the QE matrix. The value of this integral extended to a cell must be approximately equal to 3 au., ie. the total value of the charge of the free electrons for an atom of aluminium.

The Table 1, shows the obtained results for a ring made of  $n_a = 16$  atoms and a cell divided into  $1200 \times 1200 \times 120$  matrix elements. The plasma frequency (2nd column) is  $\omega_o = 12.8 eV$ , which lays between the values of the bulk plasmon  $\omega_p = 15.3 eV$  and surface plasmon  $\omega_s = 11.1 eV$  frequencies for the aluminium. As seen in the table, the term proportional to  $n^2$  makes no a significant contribution to the values of  $\omega_n$ . In addition, the integral value of the charge give us  $q = 2.95$  au.

The factor  $I_3(n)$  (last column), is obtained from the integration of eq. 24 and shows clearly that this term is *not negligible*, which means that the interaction between the ionic network of the ring and the free electrons is very strong. Due to their values, not even a perturbation analysis is applicable [42, 43].

**Table 2** Factors  $I_1(n, n')$  and  $I_2(n, n')$  multiplied by  $10^3$ , for values  $n, n'$  such as  $n + n' = 1, \dots, 5$ . For a density matrix of dimension  $1200 \times 1200 \times 120$ .

$n$	$n'$	$I_1(n, n') \times 10^3$	$I_2(n, n') \times 10^3$
0	1	3.24694	0.00000
0	2	-0.16748	0.00000
0	3	0.00785	0.00000
1	1	-0.16748	-4.49818
1	2	0.00785	0.00000
1	3	0.00259	0.00000
2	1	0.00785	8.17224
2	2	0.00259	0.00607
2	3	0.00159	0.00000

In the Table 2, we list the factors  $I_1(n, n')$  and  $I_2(n, n')$  obtained by the integrals in eqs. 22 and 23 respectively. The values  $I_1$  and  $I_2$  are very small compared with  $\omega$  (first column in table 1), and that is the reason of being neglected.

#### 4 Concluding remarks

We developed a method that is suitable for the study of plasmon phenomena in nanostructures with strong electronic density variations or whether the interaction between the electrons and the ionic core is relevant.

With this method we find a first approximate value for the oscillation modes of the plasma, which is between the values for bulk and surface plasmons. We also found, that the ionic arrangement behind the electronic cloud interacts strongly with it. The significance of this interaction was predicted in the past [24, 22]. Unfortunately, there were no experiments of plasmon excitations in nanowires reported until the date to compare our theoretical values.

A good numerical approximation to the matrix density is required and QE is not suitable due to its slowness; the time for the calculations to perform increases linearly with each dimension, ie. it increases *cubically* with the increase of the three dimensions [54].

In addition, we remark that we have chose an appropriate geometry where the integral factors  $I_1$  and  $I_2$  are negligible. This could not be true for any other geometric arrangement, then, the complete Hamiltonian  $H = H_o + H_I$  should be considered, which implies to take into account extra-diagonal elements of a highly dense matrix.

Finally, the factor  $\alpha$  that we have used here, corresponds to the *bulk* or macroscopic aluminium. Its contribution is not appreciable in this nano-ring but in order to improve precision we should take into account the *scale effects* that acts on it [55].

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