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Surface modes in metal clusters and cavities

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Abstract. Solving the hydrodynamical equations by means of a variational principle, we obtain a simultaneous description of the surface and volume modes of the valence electrons in a metal. This variational scheme, which has been previously used in the context of nuclear fluid dynamics, is applied to describe the dynamics of the valence electrons in a spherical metal cluster and of the valence electrons in the metal surrounding a spherical cavity (void). The eigenmodes fulfil the linear energy-weighted sum rule (m_1), the inverse energy-weighted sum rule (m_{-1}) and orthogonality relations.

The surface modes predicted by Mie (in clusters) and by Natta (in cavities) appear in this model as natural solutions of the equations of motion and boundary conditions.

We have considered a stabilized spherical jellium model. The parameters of the effective interaction are obtained by means of a variational method taking into account the experimental values of the density, compressibility and bulk energy.

In the present model we have ignored the diffuseness of the equilibrium electron density, taking into account, however, the surface degrees of freedom of the valence electrons and thus allowing them to penetrate into the vacuum (outside of the jellium) when undergoing collective oscillations.

The spectra of the excitation energies, and the electronic transition currents and transition densities are obtained for spherical clusters and voids.

1. Introduction

The electrons in a metal are part of a complicated many-body system in which each electron interacts with all of the other electrons and the positive ions. For a review on metal clusters see the paper by Nesterenko [1]. A calculation, based on semiclassical methods, of the normal modes and of the electronic response to an applied static field is suggestive since it leads to considerable less complexity than a selfconsistent quantum mechanical calculation.

A simple and extensively exploited model amounts to representing the equilibrium electronic and ionic densities by step functions. With respect to the positive charge of the ions the well known jellium model is adopted, ignoring, therefore, the lattice structure of the positively charged ions and replacing it by a uniform rigid distribution with a sharp boundary. We assume that the equilibrium density of valence electrons is constant and has the bulk value; in particular, we assume the following universal shape for the equilibrium density of valence electrons of clusters (cavities): $n_0(r) = n_0(0)\Theta(R - r)$ ($n_0(r) = n_0(0)\Theta(r - R)$), $n_0(0)$ being the bulk equilibrium density of the valence electrons and also the density of the jellium.

In several quasiclassical and quantum mechanical treatments, referred to as ‘sharp-surface models’, the perturbed electron density is forced to vanish outside a suitably placed effective surface which has almost always been idealized as a sharp, mathematical boundary.

In fact in the framework of a sharp-surface model the total density fluctuation may include, in general, not only a bulk-charge fluctuation but also a surface-charge fluctuation which is located on the surface of the system. In the present calculation, the electrons are allowed to cross the frontier of the jellium, i.e. to penetrate into the vacuum.

2. The equilibrium state

We want to study the collective modes of the valence electrons in a metal cluster. Since we consider small-amplitude vibrations around the equilibrium state we have first to obtain the equilibrium state.

Our system is composed of the valence electrons plus the jellium. We consider a jellium stabilized by means of effective local short-range forces and we adjust their parameters in order to reproduce the equilibrium properties of a homogeneous system. We are considering the classical limit, which means that in a Wigner–Kirkwood expansion in powers of \hbar only the lowest-order terms are taken into account. To describe the equilibrium state of the gas of valence electrons in a spherical metal cluster we consider a Fermi-type distribution function:

$$f_0 = \Theta(R - r)\Theta\left(\mu_0 - \frac{p^2}{2m} - U_0\right) \quad (1)$$

where R is the radius, μ_0 is the chemical potential, and $U_0 = \sum_{v=1}^3 a_v v n_0^{v-1}$ is the equilibrium potential. Starting from the distribution function f_0 , the density n_0 and the kinetic energy density τ_0 are computed:

$$n_0 = g \int \frac{d^3 p}{(2\pi\hbar)^3} f_0 \quad \tau_0 = g \int \frac{d^3 p}{(2\pi\hbar)^3} f_0 \frac{p^2}{2m}$$

where $g = 2$ is the spin multiplicity. We find the following expression for the energy:

$$E[f_0] = V \left(\tau_0 + \sum_{v=1}^3 a_v n_0^v \right) \quad (2)$$

where V is the volume of the jellium. We have assumed a neutral metal cluster. As we have explained in reference [2], a_1 is connected to the pseudopotential, and a_2 and a_3 are respectively related to effective two-body and three-body interactions which we introduce in order to simulate the exchange and correlation contributions which otherwise would not have been included due to the semiclassical nature of the Vlasov equation.

The equilibrium state is obtained if the energy E is minimized. We constrain the equilibrium density of the valence electrons to be equal to the density of the jellium. The minimization takes into account the conservation of the number of valence electrons as a subsidiary condition. Allowing for a variation δn of the density, and also for a displacement δR of the surface (in the radial direction), we have

$$\begin{aligned} \delta(E - \mu_0 N) = & \int_V d^3 x \delta n \left[\frac{\hbar^2}{2m} (3\pi^2)^{2/3} n^{2/3} + \sum_{v=1}^3 a_v v n^{v-1} - \mu_0 \right] \\ & + \oint_{\Sigma} d\Sigma \delta R \left[\frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n^{5/3} + \sum_{v=1}^3 a_v n^v - \mu_0 n \right] = 0 \end{aligned} \quad (3)$$

where Σ is the boundary of V . The Lagrange multiplier μ_0 ensures the conservation of the particle number. Considering arbitrary variations δn and δR we obtain two equations:

$$\frac{\hbar^2}{2m} (3\pi^2)^{2/3} n_0^{2/3} + \sum_{v=1}^3 a_v v n_0^{v-1} - \mu_0 = 0 \quad (4)$$

$$\left[\frac{3\hbar^2}{10m} (3\pi^2)^{2/3} n_0^{5/3} + \sum_{v=1}^3 a_v n_0^v - \mu_0 n_0 \right]_{r=R} = 0. \quad (5)$$

From equations (4) and (5), and knowing some bulk equilibrium properties (n_0 , the bulk modulus \mathcal{B} , and E/N , where N is the total number of valence electrons, $\int_V d^3x n_0 = N$), we determine the chemical potential μ_0 and also the parameters a_1 , a_2 , and a_3 (see table II in reference [2]).

3. The Lagrangian and the equations of motion

The time-dependent distribution function f describing some type of motion of the system is related to the equilibrium distribution function f_0 by means of a time-dependent canonical transformation:

$$f = f_0 + \{f_0, S\} + \frac{1}{2} \{\{f_0, S\}, S\} + \dots \quad (6)$$

where the curly brackets $\{, \}$ indicate Poisson brackets. The time-dependent generator S determines the type of motion that the system is undergoing. Such a generator appears as a solution of the Vlasov equation. Since we consider small-amplitude vibrations we will be concerned with the linearized Vlasov equation. The generator S may be decomposed into a time-even part Q and a time-odd part P :

$$S(\mathbf{x}, \mathbf{p}, t) = Q(\mathbf{x}, \mathbf{p}, t) + P(\mathbf{x}, \mathbf{p}, t). \quad (7)$$

The approximate procedure consists in considering a restricted variational space for the generator S and obtaining approximate solutions by means of the quantum mechanical variational principle. With respect to the generator Q ($Q(\mathbf{x}, -\mathbf{p}, t) = Q(\mathbf{x}, \mathbf{p}, t)$) one may consider a general expansion in powers of the momentum (which naturally includes only even powers of the momentum):

$$Q = \psi(\mathbf{x}, t) + \frac{1}{2} p_\alpha p_\beta \phi_{\alpha\beta}(\mathbf{x}, t) + \dots \quad (8)$$

and an explicit expression is given by truncating the expansion (8) at some point. For the generator P ($P(\mathbf{x}, -\mathbf{p}, t) = -P(\mathbf{x}, \mathbf{p}, t)$), instead of considering an analogous expansion in powers of the momentum [3–5] (involving only odd powers), as an alternative we define P implicitly as the generator of a canonical transformation such that the following equation is satisfied:

$$f_0 + \{f_0, P\} + \frac{1}{2} \{\{f_0, P\}, P\} + \dots = \Theta(R + R_1(\theta, \phi, t) - r) \Theta \times \left(\mu_0 - \frac{p^2}{2m} - U_0 - W(\mathbf{x}, t) - \frac{p_\alpha p_\beta}{2m} \chi_{\alpha\beta}(\mathbf{x}, t) - \dots \right). \quad (9)$$

The argument of the step function contains time-even fluctuations such as $W(\mathbf{x}, t)$ and $(p_\alpha p_\beta / 2m) \chi_{\alpha\beta}(\mathbf{x}, t)$. This method represents a possible way of defining the variational space and has been followed in several semiclassical models [6–8] used in nuclear physics. In the present note we restrict ourselves to the lowest-order truncation scheme within this

parametrization. Such a scheme, which has been previously considered for atomic nuclei in reference [9], implies

$$Q = \psi(\mathbf{x}, t) \quad (10)$$

and

$$f_0 + \{f_0, P\} + \frac{1}{2}\{\{f_0, P\}, P\} + \dots = \Theta(R + R_1(\theta, \phi, t) - r)\Theta \times \left(\mu_0 - \frac{p^2}{2m} - U_0 - W(\mathbf{x}, t) \right). \quad (11)$$

We consider the quantum mechanical Lagrangian

$$L = i\hbar \langle \dot{\phi} | \dot{\phi} \rangle - \langle \phi | H | \phi \rangle \quad (12)$$

and a time-dependent Slater determinant $|\phi\rangle$ which is related to the Slater determinant of $|\phi_0\rangle$ describing the g.s. by means of the unitary transformation

$$|\phi\rangle = \exp\left(\frac{i}{\hbar}\hat{S}\right)|\phi_0\rangle \quad (13)$$

where $\hat{S} = \hat{Q} + \hat{P}$ is a Hermitian time-dependent one-body operator. The variational approach allows for a systematic improvement of the approximation procedure, according to the variational choices for the generator S . On the other hand such a procedure may be controlled by relevant sum rules which are fulfilled by the approximate eigenmodes. The generators Q and P defined in equations (10) and (11) are the classical limits of the Wigner transforms of the Hermitian time-dependent operators \hat{Q} and \hat{P} . Here, and in the following equations, the dots over the dynamical fields indicate time derivatives. For small-amplitude deviations from the equilibrium state, one obtains up to second order in \hat{S} the following harmonic Lagrangian:

$$L^{(2)} = \frac{i}{2\hbar} \langle \phi_0 | [\hat{S}, \dot{\hat{S}}] | \phi_0 \rangle - \frac{1}{2\hbar^2} \langle \phi_0 | [\hat{S}, [H, \hat{S}]] | \phi_0 \rangle. \quad (14)$$

We consider the classical limit of the Lagrangian (14), retaining only the leading terms in a Wigner–Kirkwood expansion in powers of \hbar . We ensure that the particle number N is conserved by means of the Lagrange multiplier μ_0 . Considering the quantal Lagrangian (14) and taking into account the parametrization of S determined by the equations (10) and (11), we write the following semiclassical effective Lagrangian:

$$(L - \mu_0 N)^{(2)} = - \int_V d^3x (n_0 + n_1) \dot{\psi} - \oint_{\Sigma} d\Sigma R_1 n_0 \dot{\psi} - T^{(2)}[\psi] - E^{(2)}[n_1, R_1] \quad (15)$$

where

$$T^{(2)}[\psi] = \int_V d^3x \frac{n_0}{2m} (\nabla \psi) \cdot (\nabla \psi) \quad (16)$$

$$E^{(2)}[n_1, R_1] = \int_V d^3x \frac{\mathcal{B}}{2n_0^2} n_1^2 + \frac{e^2}{2} \int_V d^3x_1 d^3x_2 \frac{n_1(1)n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_1 d^3x_2 \frac{n_0(1)R_1(1)n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + \frac{e^2}{2} \oint_{\Sigma} d\Sigma_1 d\Sigma_2 \frac{n_0(1)R_1(1)n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|}. \quad (17)$$

The parameter \mathcal{B} stands for the bulk modulus and is equal to

$$\mathcal{B} = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} n_0^{5/3} + \sum_{\nu=1}^3 a_{\nu} \nu (\nu - 1) n_0^{\nu}. \quad (18)$$

The field n_1 is defined as the fluctuation of the density (inside the domain occupied by the jellium), $n_1 = n - n_0$. We assume that the dynamical variables (n_1, R_1, ψ) depart slightly from their equilibrium values $(0, 0, 0)$.

The action integral should be stationary if we allow for arbitrary variations of the collective coordinates ψ , n_1 and R_1 :

$$\delta \int_{t_1}^{t_2} dt (L - \mu_0 N)^{(2)} = 0. \quad (19)$$

The variation with respect to ψ leads to

$$\int_V d^3x \delta\psi \left[\dot{n}_1 + \nabla \cdot \left(\frac{n_0}{m} \nabla \psi \right) \right] + \oint_{\Sigma} d\Sigma \delta\psi \dot{R}_1 n_0 = 0 \quad (20)$$

and the variation with respect to n_1 leads to the equation

$$\int_V d^3x_1 \delta n_1 \left[\dot{\psi}(1) + \frac{\mathcal{B}}{n_0^2} n_1(1) + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right] = 0 \quad (21)$$

and also the variation with respect to R_1 leads to the equation

$$\oint_{\Sigma} d\Sigma_1 \delta R_1 \left[\dot{\psi}(1) + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right] = 0. \quad (22)$$

Since the variations $\delta\psi$, δn_1 and δR_1 are arbitrary, the equations of motion of the system follow:

$$\dot{n}_1 + \frac{n_0}{m} \nabla^2 \psi = 0 \quad (23)$$

$$\dot{R}_1 - \frac{1}{m} (\hat{\mathbf{n}} \cdot \nabla \psi)_{r=R} = 0 \quad (24)$$

$$-\dot{\psi}(1) = \frac{\mathcal{B}}{n_0^2} n_1(1) + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \quad (25)$$

$$\left\{ n_0 \dot{\psi}(1) + e^2 \int_V d^3x_2 \frac{n_0(1)n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(1)n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right\}_{|\mathbf{x}_1|=R} = 0. \quad (26)$$

In equation (24), $\hat{\mathbf{n}}$ represents the outward normal. These equations of motion are similar to the equations (31)–(34) of reference [9]. The basic difference is that now instead of an atomic nucleus we have another system (valence electrons plus jellium) and thus we are now including the Coulomb interaction.

4. Orthogonality relations and sum rules

We seek solutions of the form

$$A(\mathbf{x}, t) = \sum_j \bar{A}^{(j)}(\mathbf{x}) \sin(\omega_j t + \gamma_j) \quad (27)$$

for the fields n_1 and R_1 and of the form

$$B(\mathbf{x}, t) = \sum_j \bar{B}^{(j)}(\mathbf{x}) \cos(\omega_j t + \gamma_j) \quad (28)$$

for the velocity potential ψ .

Making use of equation (20) and replacing $\delta\psi$ by $\psi^{(i)}$, it is easy to show that

$$\int_V d^3x \frac{n_0}{2m} (\nabla\psi^{(i)}) \cdot (\nabla\psi^{(j)}) = \frac{1}{2} \int_V d^3x \psi^{(i)} \dot{n}_1^{(j)} + \frac{1}{2} \oint_\Sigma d\Sigma n_0 \psi^{(i)} \dot{R}_1^{(j)}. \quad (29)$$

Using equations (21) and (22) it may be seen that

$$\begin{aligned} & \int_V d^3x \frac{\mathcal{B}}{2n_0^2} \dot{n}_1^{(i)} \dot{n}_1^{(j)} + \frac{e^2}{2} \int_V d^3x_1 d^3x_2 \frac{\dot{n}_1^{(i)}(1) \dot{n}_1^{(j)}(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \\ & + \frac{e^2}{2} \oint_\Sigma d\Sigma_1 d^3x_2 \frac{n_0(1) \dot{R}_1^{(i)}(1) \dot{n}_1^{(j)}(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \\ & + \frac{e^2}{2} \oint_\Sigma d\Sigma_1 d^3x_2 \frac{n_0(1) \dot{R}_1^{(j)}(1) \dot{n}_1^{(i)}(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \\ & + \frac{e^2}{2} \oint_\Sigma d\Sigma_1 d\Sigma_2 \frac{n_0(1) \dot{R}_1^{(i)}(1) n_0(2) \dot{R}_1^{(j)}(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \\ & = -\frac{1}{2} \int_V d^3x \dot{n}_1^{(i)} \ddot{\psi}^{(j)} - \frac{1}{2} \oint_\Sigma d\Sigma \dot{R}_1^{(i)} n_0 \ddot{\psi}^{(j)} \\ & = \omega_j^2 \left(\frac{1}{2} \int_V d^3x \dot{n}_1^{(i)} \psi^{(j)} + \frac{1}{2} \oint_\Sigma d\Sigma \dot{R}_1^{(i)} n_0 \psi^{(j)} \right). \end{aligned} \quad (30)$$

From equations (29) and (30), the orthogonality relations follow. We write $n_1^{(j)}(\mathbf{x}, t) = \bar{n}_1^{(j)}(\mathbf{x})\alpha_j(t)$, $R_1^{(j)}(\theta, \phi, t) = \bar{R}_1^{(j)}(\theta, \phi)\alpha_j(t)$ and $\psi^{(j)}(\mathbf{x}, t) = \bar{\psi}^{(j)}(\mathbf{x})\beta_j(t)$, where $\alpha_j \propto \sin(\omega_j t + \gamma_j)$ and $\beta_j \propto \cos(\omega_j t + \gamma_j)$. If $\omega_i^2 \neq \omega_j^2$ the orthogonality relation may then be written as follows:

$$\frac{1}{2} \left(\int_V d^3x \bar{n}_1^{(i)} \bar{\psi}^{(j)} + \oint_\Sigma d\Sigma \bar{R}_1^{(i)} n_0 \bar{\psi}^{(j)} \right) = \delta_{ij}. \quad (31)$$

We will show that this model satisfies the energy weighted sum rule (m_1) as well as the inverse energy-weighted sum rule (m_{-1}). Let $\hat{D} = \sum_{i=1}^N D(\mathbf{x}_i)$ be an excitation operator. We expand $D(\mathbf{x})$ in the basis of the eigenfunctions $\bar{\psi}^{(j)}$, $D(\mathbf{x}) = \sum_j c_j \bar{\psi}^{(j)}(\mathbf{x}) = \sum_j c_j \psi^{(j)}(\mathbf{x}, 0)$, where in equations (27) and (28) all of the γ_n were taken to be zero. From the orthogonality relation it follows that

$$c_j = \frac{1}{2} \left(\int_V d^3x D \bar{n}_1^{(j)} + \oint_\Sigma d\Sigma D n_0 \bar{R}_1^{(j)} \right). \quad (32)$$

If we consider $\psi(\mathbf{x}, 0) = D(\mathbf{x})$ and if we replace $\delta\psi$ by D we find from equation (20)

$$T^{(2)}[D] = \frac{1}{2} \left(\int_V d^3x D \dot{n}_1 + \oint_\Sigma d\Sigma D n_0 \dot{R}_1 \right)_{t=0} \quad (33)$$

where $n_1 = \sum_j c_j n_1^{(j)}$ and $R_1 = \sum_j c_j R_1^{(j)}$. Finally, using the expansion $D(\mathbf{x}) = \sum_j c_j \bar{\psi}^{(j)}(\mathbf{x})$ and the orthogonality relation (31) we have the following equation:

$$T^{(2)}[D] = \sum_{ij} c_i c_j \frac{1}{2} \left(\int_V d^3x \bar{\psi}^{(i)} \dot{n}_1^{(j)} + \oint_\Sigma d\Sigma n_0 \bar{\psi}^{(i)} \dot{R}_1^{(j)} \right)_{t=0} = \sum_j \omega_j c_j^2 \equiv m_1. \quad (34)$$

which corresponds to the energy-weighted sum rule m_1 .

Now we consider the system perturbed by an external potential $D(\mathbf{x})$. The perturbed energy of the system is

$$E' = E + \int_V d^3x D(\mathbf{x})(n_0 + n_1) + \oint_\Sigma d\Sigma R_1 n_0 D(\mathbf{x}). \quad (35)$$

Within the present semiclassical approach it is easy to obtain the perturbed state. In order to determine the fields n_1 and R_1 , associated with the polarization produced by the external potential D , we minimize $E' - \mu N$. Taking into account equation (3) and considering $\mu = \mu_0 + \mu_1$, we have

$$\delta \left\{ \int_V d^3x n_1(D - \mu_1) + \oint_{\Sigma} d\Sigma R_1 n_0(D - \mu_1) + E^{(2)}[n_1, R_1] \right\} = 0. \quad (36)$$

Allowing for arbitrary variations of n_1 , we find

$$-(D(1) - \mu_1) = \frac{\mathcal{B}}{n_0^2} n_1(1) + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \quad (37)$$

and considering arbitrary variations of R_1 it follows that

$$\left[D(1) - \mu_1 + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right]_{|\mathbf{x}_1|=R} = 0. \quad (38)$$

If the external field $D(\mathbf{x})$ satisfies the Laplace equation, $\nabla^2 D = 0$, it is clear from equations (37) and (38) that $n_1 = 0$; therefore, for such an operator, the polarization density is characterized by a pure surface displacement (represented by R_1) of the valence electrons at the surface. Taking into account equations (21) and (22) we write

$$-\frac{1}{2} \left(\int_V d^3x n_1 \dot{\psi} + \oint_{\Sigma} d\Sigma R_1 n_0 \dot{\psi} \right) = E^{(2)}[n_1, R_1]. \quad (39)$$

We consider the polarization density as given by n_1 and R_1 taken from equations (37) and (38), and we consider the following expansions: $n_1 = \sum_j g_j n_1^{(j)}(\mathbf{x}, 0)$, $\dot{\psi} = \sum_j g_j \dot{\psi}^{(j)}(\mathbf{x}, 0)$, $R_1 = \sum_j g_j R_1^{(j)}(\mathbf{x}, 0)$, where in equations (27) and (28) all of the $\gamma_n = \pi/2$. The coefficients g_j are determined by the orthogonality relations (31):

$$g_j = \frac{1}{2} \left(\int_V d^3x \bar{\psi}^{(j)} n_1 + \oint_{\Sigma} d\Sigma n_0 \bar{\psi}^{(j)} R_1 \right). \quad (40)$$

Using the expansions of n_1 , ψ and R_1 , it follows that

$$E^{(2)}[n_1, R_1] = - \sum_{ij} g_i g_j \frac{1}{2} \left(\int_V d^3x n_1^{(i)} \dot{\psi}^{(j)} + \oint_{\Sigma} d\Sigma R_1^{(i)} n_0 \dot{\psi}^{(j)} \right)_{t=0} = \sum_j \omega_j g_j^2. \quad (41)$$

We now determine the relation between the coefficients c_j and g_j . Using equations (32), (37) and (38), we may write

$$\begin{aligned} c_j &= \frac{1}{2} \left(\int_V d^3x \bar{n}_1^{(j)} D + \oint_{\Sigma} d\Sigma \bar{R}_1^{(j)} n_0 D \right) \\ &= -\frac{1}{2} \int_V d^3x \bar{n}_1^{(j)} \left[\frac{\mathcal{B}}{n_0^2} n_1(1) + e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right. \\ &\quad \left. + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right] \\ &\quad - \frac{1}{2} \oint_{\Sigma} d\Sigma \bar{R}_1^{(j)} n_0(1) \left[e^2 \int_V d^3x_2 \frac{n_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} + e^2 \oint_{\Sigma} d\Sigma_2 \frac{n_0(2)R_1(2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \right] \\ &= \sum_j g_i \left[\frac{1}{2} \int_V d^3x \bar{n}_1^{(j)} \dot{\psi}^{(i)} + \frac{1}{2} \oint_{\Sigma} d\Sigma \bar{R}_1^{(j)} n_0 \dot{\psi}^{(i)} \right]_{t=0} = -\omega_j g_j \end{aligned} \quad (42)$$

where equations (25) and (26) were also taken into account. From equations (41) and (42) the m_{-1} sum rule may be written as follows:

$$m_{-1} \equiv \sum_j \frac{c_j^2}{\omega_j} = E^{(2)}[n_1, R_1]. \quad (43)$$

The Lagrange multiplier μ_1 applies only to $\ell = 0$, and in this case it is evaluated with the help of the subsidiary condition

$$\int_V d^3x n_1 + \oint_{\Sigma} d\Sigma R_1 n_0 = 0. \quad (44)$$

It is convenient to note that m_{-1} defined in equation (43) is related to the static polarizability α , defined as

$$\alpha = \int_V d^3x n_1 D + \oint_{\Sigma} d\Sigma R_1 n_0 D. \quad (45)$$

In fact it is clear from equations (37), (38) and (43)–(45) that $\alpha = 2m_{-1}$.

5. Polynomial approximation

Due to the Coulomb interaction, instead of solving exactly the equations of motion (23)–(26) it is more convenient to look for approximate solutions using a variational method. We make an expansion of the dynamical fields ψ and n_1 in multipoles and, for each multipolarity, we express the radial dependence by a polynomial in (r/R) :

$$\psi = \sum_{k=k_{min}}^{k_{max}} a_k(t)(r/R)^k Y_{\ell 0} \quad (46)$$

$$n_1 = n_0 \sum_{k=q_{min}}^{q_{max}-1} b_k(t)(r/R)^k Y_{\ell 0} \quad (47)$$

and we consider

$$R_1(t) = b_{q_{max}}(t) Y_{\ell 0} \quad (48)$$

where $q_{max} = q_{min} + n_{dim} - 1$ and $k_{max} = k_{min} + n_{dim} - 1$. We have associated the same number n_{dim} of variational parameters with both fields ψ and (n_1, R_1) . We see that the polynomial for n_1 has one power less than the polynomial which describes ψ , since we are keeping one parameter ($b_{q_{max}}$) to describe R_1 . For metal clusters we choose $k_{min} \geq 0$ and $q_{min} \geq 0$ (so that the fluctuations n_1 and ψ do not diverge when $r \rightarrow 0$). The value of n_{dim} depends on the truncation scheme that we choose for the numerical calculations. In principle we would have the exact solutions of equations (23)–(26) when $k_{min} = 0$, $q_{min} = 0$ and $n_{dim} \rightarrow \infty$. Actually since we are considering a limited number of polynomials, we consider $k_{min} = 0$ for $\ell = 0$, $k_{min} = 1$ for $\ell \geq 1$, $q_{min} = 0$ for $\ell = 0$, $q_{min} = 1$ for $\ell = 1$, $q_{min} = 2$ for $\ell = 2$, and $q_{min} = 3$ for $\ell \geq 3$. Inserting expressions (46)–(48) into equations (15)–(17), we obtain the Lagrangian

$$L^{(2)} = \sum_{kq} \left[C_{kq} a_k \dot{b}_q - \frac{1}{2m} A_{kq} a_k a_q - \frac{1}{2} B_{kq} b_k b_q \right] \quad (49)$$

where

$$A_{kq} = \frac{n_0(0)R[kq + \ell(\ell + 1)]}{k + q + 1} \quad \text{for } k_{min} \leq k \leq k_{max} \text{ and } k_{min} \leq q \leq k_{max} \quad (50)$$

$$C_{kq} = \frac{n_0(0)R^3}{k + q + 3} \quad \text{for } k_{min} \leq k \leq k_{max} \text{ and } q_{min} \leq q < q_{max} \quad (51)$$

$$C_{kq_{max}} = n_0(0)R^2 \quad \text{for } k_{min} \leq k \leq k_{max} \quad (52)$$

$$B_{kq} = \frac{BR^3}{k + q + 3} + \frac{\omega_p^2 n_0(0)mR^5}{(2\ell + 1)(k + q + 5)} \left(\frac{1}{q + \ell + 3} + \frac{1}{k + \ell + 3} \right) \quad \text{for } q_{min} \leq k < q_{max} \text{ and } q_{min} \leq q < q_{max} \quad (53)$$

$$B_{kq_{max}} = B_{q_{max}k} = \frac{\omega_p^2 n_0(0)mR^4}{(2\ell + 1)(q + \ell + 3)} \quad \text{for } q_{min} \leq k < q_{max} \quad (54)$$

and

$$B_{q_{max}q_{max}} = \frac{\omega_p^2 n_0(0)mR^3}{2\ell + 1}. \quad (55)$$

Here ω_p is the plasma frequency, or bulk volume plasmon ($\omega_p^2 = 4\pi n_0(0)e^2/m$). Requiring the action integral to be stationary for arbitrary variations of the variables a_q and b_q , the following equations are obtained:

$$\sum_q \left(C_{kq} \dot{b}_q - \frac{1}{m} A_{kq} a_q \right) = 0 \quad (56)$$

and

$$\sum_k (-C_{kq} \dot{a}_k - B_{kq} b_q) = 0. \quad (57)$$

We assume harmonic time dependence for the variables a_k and b_k ($\ddot{a}_k = -\omega^2 a_k$), so from equations (56) and (57) we obtain the following eigenvalue equation:

$$m\omega^2 [a] = ([C]^T)^{-1} [B] [C]^{-1} [A] [a] \quad (58)$$

where $[a]$ and $[b]$ are the vectors with components a_k and b_k , and $[A]$, $[B]$, and $[C]$ are the matrices with components A_{ik} , B_{ik} , and C_{ik} . Solving the eigenvalue equation (58), we obtain the normal modes which are characterized by the eigenfrequencies ω_j and the eigenvectors $[a]^{(j)}$. The vectors $[b]^{(j)}$ are then easily obtained.

Considering an external potential $D(r) = g(r)Y_{\ell 0}$, instead of obtaining the exact values of the polarization density (n_1, R_1) given by equations (37) and (38), we also follow the polynomial approach based on equations (47) and (48) and on a variation of $E' - \mu N$ with respect to the parameters b_k . For $k < q_{max}$, we find

$$\sum_q B_{kq} b_q = - \int_V d^3x n_0 \left[Y_{\ell 0} \left(\frac{r}{R} \right)^k (D - \mu_1) \right] \quad (59)$$

and for $k = q_{max}$, we obtain

$$\sum_k B_{q_{max}k} b_k = - \oint_{\Sigma} d\Sigma Y_{\ell 0} n_0 (D - \mu_1). \quad (60)$$

The eigenmodes fulfil the orthogonality relations (31), and additionally they satisfy the m_1 and m_{-1} sum rules.

We can easily apply the present method to study the collective modes of the valence electrons around a spherical cavity (void) in a metal. The equilibrium distribution function is

$$f_0 = \Theta(r - R)\Theta\left(\mu_0 - \frac{p^2}{2m} - U_0\right) \quad (61)$$

where R is the radius of the cavity. The same equations of motion, (23)–(26), are obtained. We consider again polynomial expansions of the fields ψ and n_1 . In equation (46) we set $k_{max} = -1$. In equation (47) we set $q_{max} = -2$ for $\ell \neq 0$, and $q_{max} = -3$ for $\ell = 0$. Following the same method we obtain again a Lagrangian of the form given by equation (49), where the matrices now have the following expression:

$$A_{kq} = -\frac{n_0(0)R[kq + \ell(\ell + 1)]}{k + q + 1} \quad \text{for } k_{min} \leq k \leq k_{max} \text{ and } k_{min} \leq q \leq k_{max} \quad (62)$$

$$C_{kq} = -\frac{n_0(0)R^3}{k + q + 3} \quad \text{for } k_{min} \leq k \leq k_{max} \text{ and } q_{min} \leq q < q_{max} \quad (63)$$

and $C_{qk_{max}}$ is again given by equation (52),

$$B_{kq} = -\frac{\mathcal{B}R^3}{k + q + 3} + \frac{\omega_p^2 n_0(0)mR^5}{(2\ell + 1)} \left\{ (\delta_{\ell+3+q} + \delta_{\ell+3+k}) \frac{1}{(k + q + 5)^2} + \frac{1 - \delta_{\ell+3+q}}{\ell + 3 + q} \left(\frac{-1}{k + q + 5} + \frac{1}{2 - \ell + k} \right) + \frac{1 - \delta_{\ell+3+k}}{\ell + 3 + k} \left(\frac{-1}{k + q + 5} + \frac{1}{2 - \ell + q} \right) \right\} \quad \text{for } q_{min} \leq k < q_{max} \text{ and } q_{min} \leq q < q_{max} \quad (64)$$

$$B_{qk_{max}} = B_{q_{max}q} = -\frac{\omega_p^2 n_0(0)mR^4}{(2\ell + 1)(2 - \ell + q)} \quad \text{for } q_{min} \leq q < q_{max} \quad (65)$$

and $B_{q_{max}q_{max}}$ is again given by equation (55). We arrive at the same eigenvalue problem as is represented by equations (56) and (57).

6. Numerical results

We focus on sodium. The set of parameters used is $a_1 = -5.8348 \text{ \AA}^{-3}$, $a_2 = -133.17 \text{ \AA}^{-6}$, and $a_3 = 1642.9 \text{ \AA}^{-9}$, and this leads to the following equilibrium properties: $n_0 = 2.5435 \times 10^{-2} \text{ \AA}^{-3}$, $\mathcal{B} = 4.3372 \times 10^{-2} \text{ eV \AA}^{-3}$, $E/N = -6.2670 \text{ eV}$ and $\hbar\omega_p = 5.9221 \text{ eV}$.

Table 1. For the multipolarity $\ell = 2$ we give the energies of the eigenmodes of a sodium cluster for different truncation schemes ($2 \leq n_{dim} \leq 7$) in order to study the convergence of the present model. For the test we have considered a sodium cluster having 92 atoms.

$n_{dim} = 2$	3.745 441	6.503 286				
$n_{dim} = 3$	3.745 441	6.315 491	7.690 505			
$n_{dim} = 4$	3.745 441	6.312 949	6.879 498	9.608 027		
$n_{dim} = 5$	3.745 441	6.311 168	6.871 213	7.645 409	12.228 73	
$n_{dim} = 6$	3.745 441	6.311 156	6.850 521	7.628 119	8.613 972	15.489 44
$n_{dim} = 7$	3.745 441	6.311 155	6.850 316	7.542 108	8.584 155	9.788 481 19.337 09

We have carried out semiclassical calculations for metal clusters and voids in the spherical jellium approximation. We found that typical results for the lowest modes

Table 2. For the multipolarity $\ell = 2$ we give the energies of the cavity eigenmodes of the valence electrons of a homogeneous medium of Na for different truncation schemes ($2 \leq n_{dim} \leq 7$) in order to study the convergence of the present model. We have considered a cavity with 92 missing atoms.

$n_{dim} = 2$	4.689 293	6.075 170					
$n_{dim} = 3$	4.587 210	5.928 334	6.087 684				
$n_{dim} = 4$	4.587 210	5.926 024	5.972 964	6.517 200			
$n_{dim} = 5$	4.587 210	5.924 326	5.953 581	6.109 137	7.424 019		
$n_{dim} = 6$	4.587 210	5.923 249	5.939 419	6.024 705	6.353 680	8.922 477	
$n_{dim} = 7$	4.587 210	5.922 721	5.931 967	5.976 698	6.165 982	6.706 386	11.074 90

Table 3. For each multipolarity (first column), we list the excitation energies (second column), the exhausted percentage of the m_1 sum rule (third column), and the exhausted percentage of the m_{-1} sum rule (fourth column), for a sodium cluster of 92 atoms. An equilibrium distribution function of the Fermi type (equation (1)) was considered. We also list the excitation energies (fifth column), the exhausted percentage of the m_1 sum rule (sixth column), and the exhausted percentage of the m_{-1} sum rule (seventh column) for a spherical cavity in a homogeneous medium of Na with 92 missing atoms. An equilibrium distribution function of the Fermi type (equation (61)) was assumed. We have considered $n_{dim} = 7$.

ℓ_i^π	$\hbar\omega_i$ (eV)	m_1 (%)	m_{-1} (%)	$\hbar\omega_i$ (eV)	m_1 (%)	m_{-1} (%)
0_1^+	6.0403	92.394	93.517	5.9221	74.999	75.138
0_2^+	6.3818	5.7757	5.2369	5.9222	7.9846	7.9990
0_3^+	6.9142	1.1417	0.8819	5.9251	9.3382	9.3460
1_1^-	3.4191	100	100	4.8353	100	100
1_2^-	6.1615	0.0	0.0	5.9225	0.0	0.0
1_3^-	6.6048	0.0	0.0	5.9290	0.0	0.0
2_1^+	3.7454	100	100	4.5872	100	100
2_2^+	6.3112	0.0	0.0	5.9227	0.0	0.0
2_3^+	6.8503	0.0	0.0	5.9320	0.0	0.0
3_1^-	3.8769	100	100	4.4767	100	100
3_2^-	6.4860	0.0	0.0	5.9230	0.0	0.0
3_3^-	7.1144	0.0	0.0	5.9346	0.0	0.0
4_1^+	3.9480	100	100	4.4140	100	100
4_2^+	6.6831	0.0	0.0	5.9231	0.0	0.0
4_3^+	7.3968	0.0	0.0	5.9355	0.0	0.0

converged with a small number of terms in the polynomials in equations (46) and (47). We present for different values of n_{dim} the energies of the eigenmodes appearing for $\ell = 1$ for a cluster (table 1) and for a void (table 2). Each time that we increase n_{dim} by one unit, we are adding a term in the expansions (46) and (47), and as a consequence a new normal mode appears which has the particularity of being the eigenmode with the highest energy. The energies of the lower eigenmodes show up as being very stable with respect to the values that they had in the previous truncation scheme. We can also conclude that the convergence is faster for the lower modes, which are, therefore, especially stable, being independent of the particular truncation scheme.

For metal clusters we consider the excitation operators

$$\begin{aligned}
 D(\mathbf{x}) &= r^2 & \text{for } \ell = 0 \\
 D(\mathbf{x}) &= r^\ell Y_{\ell 0} & \text{for } \ell > 0.
 \end{aligned}
 \tag{66}$$

Then, for $D(\mathbf{x}) = r^2$, we have

$$m_1 = \frac{8\pi n_0(0)R^5}{5m} \tag{67}$$

and for $D(\mathbf{x}) = r^\ell Y_{\ell 0}$, we have

$$m_1 = \frac{n_0(0)}{2m} \ell R^{2\ell+1}. \tag{68}$$

In order to determine the polarization density we have followed the polynomial approach. Considering a spherical metal cluster and an excitation operator of the form $D(\mathbf{x}) = r^\ell Y_{\ell 0}$, it may be easily seen from equations (59) and (60) that $b_k = 0$ if $k < q_{max}$ and

$$b_{q_{max}} = -\frac{(2\ell + 1)R^{\ell-1}}{\omega_p^2 m}. \tag{69}$$

Since $n_1 = 0$, a pure surface polarization (represented by R_1) is obtained. Inserting $n_1 = 0$ and R_1 , determined by equation (69), we obtain from equation (43) the value of m_{-1} for an operator of the type $r^\ell Y_{\ell 0}$:

$$m_{-1} = \frac{n_0(0)(2\ell + 1)R^{2\ell+1}}{2\omega_p^2 m}. \tag{70}$$

For metal voids, in particular, we consider the excitation operators

$$\begin{aligned} D(\mathbf{x}) &= r^{-2} && \text{for } \ell = 0 \\ D(\mathbf{x}) &= r^{-\ell-1} Y_{\ell 0} && \text{for } \ell > 0. \end{aligned} \tag{71}$$

For $D(\mathbf{x}) = r^{-2}$, we have

$$m_1 = \frac{8\pi n_0(0)}{3mR^3} \tag{72}$$

and for $D(\mathbf{x}) = r^{-\ell-1} Y_{\ell 0}$, we have

$$m_1 = \frac{n_0(0)(\ell + 1)}{2mR^{2\ell+1}}. \tag{73}$$

For a spherical cavity a surface mode is excited by the operator $r^{-\ell-1} Y_{\ell 0}$. In an analogous way we find that, for such an operator, the polarization density is characterized by $n_1 = 0$, the displacement of the surface R_1 is determined by

$$b_{q_{max}} = -\frac{(2\ell + 1)R^{-\ell-2}}{\omega_p^2 m} \tag{74}$$

and the value of m_{-1} is

$$m_{-1} = \frac{n_0(0)(2\ell + 1)R^{-2\ell-1}}{2\omega_p^2 m}. \tag{75}$$

We consider a spherical cluster with 92 atoms and also a spherical void with 92 missing atoms. In table 3 we present the energies of the three lowest eigenmodes, for different values of ℓ , together with the percentages of m_1 and m_{-1} sum rules exhausted by each state for a cluster, and we also present the same results for a void. The lowest eigenmode appearing for each multipolarity $\ell > 0$ is a surface mode and has energy which is independent of N and is equal to

$$\hbar\omega_\ell^{\text{Mie}} = \hbar\sqrt{m_1/m_{-1}} = \hbar\omega_p\sqrt{\frac{\ell}{2\ell + 1}}$$

for clusters, in agreement with Mie [10], and

$$\hbar\sqrt{m_1/m_{-1}} = \hbar\omega_p\sqrt{\frac{\ell+1}{2\ell+1}}$$

for cavities, in agreement with Natta [11].

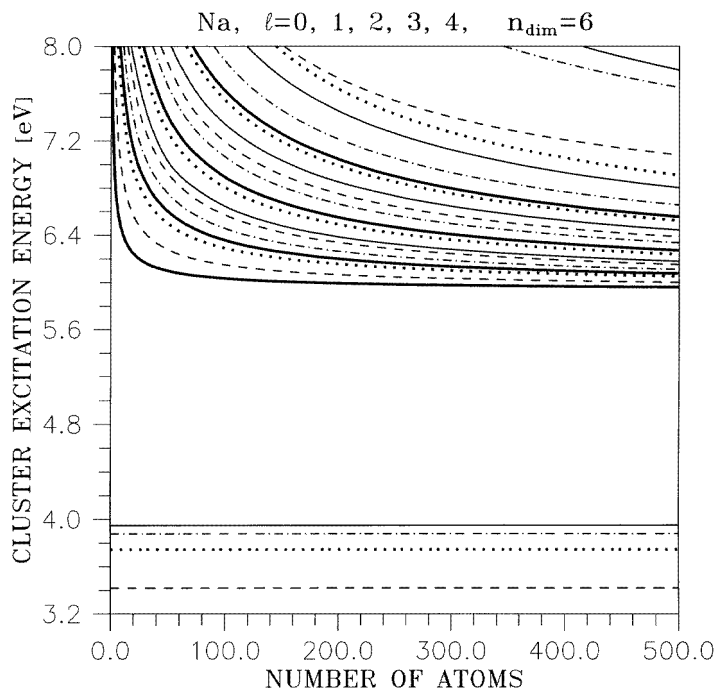


Figure 1. The cluster excitation energy versus the number of atoms of the cluster, for sodium, for angular momenta $0 \leq \ell \leq 4$ for the lowest eigenstates. The thick full curves refer to $\ell = 0$ normal modes, the dashed curves refer to $\ell = 1$ normal modes, the dotted curves refer to $\ell = 2$ normal modes, the chain curves refer to $\ell = 3$ normal modes, and the thin full curves refer to $\ell = 4$ normal modes. The horizontal lines at the bottom represent the surface modes.

Experimentally [12], the optical spectra of small isolated sodium clusters are dominated by the dipole resonance of the surface collective mode of the sodium valence electrons, and the resonance frequency shifts from 2.4 eV to near the bulk value of $\omega_p/\sqrt{3} = 3.4$ eV as cluster size increases. The classical Mie limit ($\omega_1^{\text{Mie}} = \omega_p/\sqrt{3}$) is approached for clusters as small as $\langle N \rangle \sim 125$ atoms, where $\langle N \rangle$ stands for the average number of atoms in the cluster. In figure 1 we represent the energies of the lowest eigenmodes as functions of the number of atoms of the cluster, and in figure 2 we represent the energies of the lowest eigenmodes as functions of the number of missing atoms of the cavity (the surface modes are not included in figure 2).

In figure 3 we present the flow field corresponding to the eigenmode 0_1^+ (for a metal cluster with $N = 92$) in terms of radial functions j_{\pm} defined by

$$\mathbf{j}(\mathbf{x}) = j_+(r)\mathbf{Y}_{\ell\ell+10} + j_-(r)\mathbf{Y}_{\ell\ell-10} \quad (76)$$

where $\mathbf{Y}_{\ell\ell\pm 10}$ stand for the vector spherical harmonics. The velocity field of the surface modes in metal clusters is proportional to $\nabla(r^{\ell}Y_{\ell 0})$, and the velocity field of the surface modes in voids is proportional to $\nabla(r^{-\ell-1}Y_{\ell 0})$.

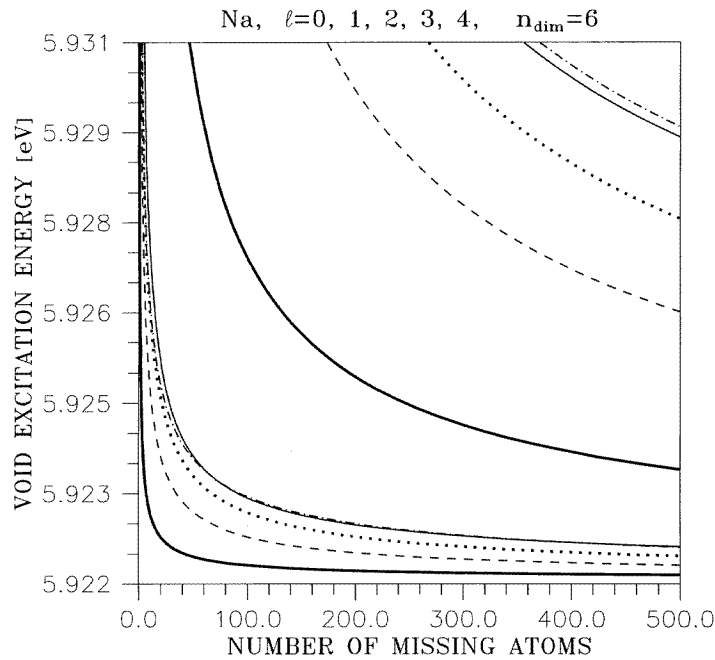


Figure 2. Excitation spectra of voids in sodium versus the number of missing atoms in the cavity for the lowest normal modes for angular momenta $0 \leq \ell \leq 4$. The thick full curves refer to $\ell = 0$ normal modes, the dashed curves refer to $\ell = 1$ normal modes, the dotted curves refer to $\ell = 2$ normal modes, the chain curves refer to $\ell = 3$ normal modes, and the thin full curves refer to $\ell = 4$ normal modes. The surface modes which appear for $\ell > 0$ and which have constant energies equal to $\hbar\omega_p\sqrt{(\ell+1)/(2\ell+1)}$ are not included in the figure since their energies are lower than the energies represented on the ordinate axis.

7. Conclusion

The present model is based on the Thomas–Fermi approximation. It gives a reasonable description of the general tendencies, of the orders of magnitude, and also of their numerical values at large N , but cannot provide a quantitative description of small clusters in which the quantum effects are important. Using the equations of motion and boundary conditions directly obtained from the action principle, we have shown that the normal modes fulfil the energy-weighted sum rule (m_1), the inverse energy-weighted sum rule (m_{-1}), and orthogonality relations.

In our model we have introduced collective variables related to the hydrodynamical equations, and as a consequence it may be proved, and also numerically checked, that the linear and the inverse energy-weighted sum rules are fulfilled. In the present approach as well as in the model of reference [2], we have considered an equilibrium state which has the drawback of not taking into account the spill-out of the valence electrons in the equilibrium state. However, this equilibrium state is selfconsistent within our semiclassical approach based on an equilibrium energy functional given by equation (2) and leads to a very good convergence of the lowest eigenmodes, already with a small number of polynomials, as may be seen in the tables 1 and 2.

We obtain several eigenmodes for the model, and for each multipolarity $\ell > 0$ one of these modes is a pure surface oscillation, and the other eigenmodes are volume modes. We

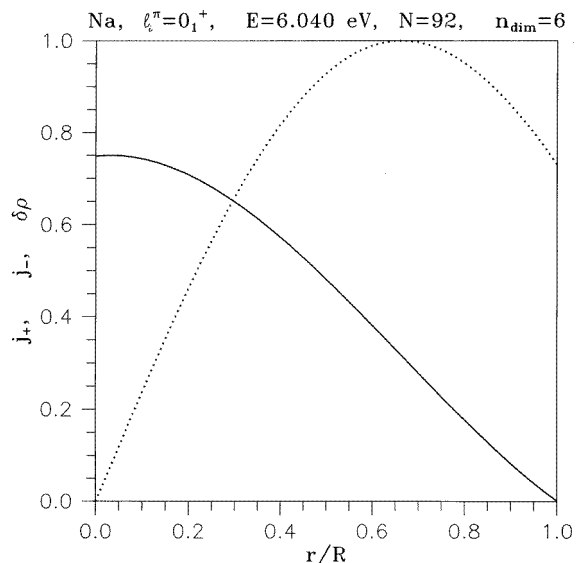


Figure 3. For a sodium cluster of 92 atoms (radius $R = 6.328 \text{ \AA}$), we show the radial functions of \mathbf{j} for the eigenmode 0_1^+ . The full curve refers to the function $j_+(r)$ and the dotted curve refers to $-j_{div}(r)$ where $j_+(r)$ is defined by equation (76) and $-j_{div}(r)$ is defined by the equation $\nabla \cdot \mathbf{j} = j_{div}(r)Y_{\ell 0}$.

have recovered for spherical metal clusters the well known classical Mie [10] expression for the energies of the surface modes, and we have shown that it is equal to $\hbar\sqrt{m_1/m_{-1}}$. The present model also predicts volume modes. All of the modes with $\ell = 0$ and, for every multipolarity $\ell > 0$, all of the modes except the lowest mode (which is a surface mode), are volume modes and may be interpreted as the remainder of a strongly fragmented volume plasmon. In analogy with the behaviour presented in reference [2], the energies of these modes approach the energy of the volume plasmon when the cluster size increases.

We have also applied our model to a void, a system which is essentially the complement of a metallic sphere embedded in medium of permittivity ϵ_0 . We have assumed that the material inside the void is a vacuum, so $\epsilon_0 = 1$.

The $\ell = 0$ modes around a void correspond to spherically symmetrical oscillations of the electron gas and may conveniently be called ‘breathing’ modes. These modes as well as the other modes are localized oscillations since the fields and currents decay away from the surface, and the density fluctuations occur only at the surface and close to it (in the non-retarded limit). The volume modes have energies very close to the volume plasmon as may be seen in figure 2. Also as the size of the cavity increases, the energies of the volume modes approach $\hbar\omega_p$.

The response of the metal in which the void is located was modelled by the free-electron gas described by a semiclassical approach. In the present model the eigenfrequencies of the surface plasmon modes are in agreement with the prediction of surface-charge-density oscillations associated with a spherical cavity in a metallic medium which has been made by Natta [11]:

$$\omega_{\ell}^{\text{Natta}} = \omega_p \sqrt{\frac{\ell + 1}{\ell(\epsilon_m + 1) + 1}} \quad (77)$$

where ϵ_m is the permittivity of the medium inside the cavity.

The surface plasmon modes of spherical metal clusters and of spherical voids in metals were calculated within a hydrodynamic formulation (see reference [13]). Since the model is semiclassical we are allowed not to consider the spill-out (for metal clusters) or the spill-in (for voids) of the valence electrons. Although we have assumed that during the vibrations the valence electrons could penetrate into the vacuum, we have considered that in the equilibrium state the densities of the jellium and of the valence electrons were equal, and therefore in the present model the spill-out or the spill-in of the valence electrons was not considered. The consideration of these quantum effects should improve the description of the collective surface modes, in particular for small clusters and small voids. The fact that larger Na clusters [14] show a surface plasma peak which approaches the classical value seems to indicate that the relative effect of the electron spill-out decreases with increasing cluster size. Therefore, the consideration of the effect of the spill-out of the valence electrons in the equilibrium density is expected to provide a better description of the collective modes of the valence electrons in small clusters and voids.

The time-dependent Thomas–Fermi method is suitable for a good description of surface modes, providing that the cluster is large enough. In references [6–8] this method has been used to describe successfully surface modes in large atomic nuclei. However, it appears that the determination of the exact threshold corresponding to the crossover between ‘few-body’ and ‘many-body’ behaviours requires the consideration of quantal corrections which were neglected in the present treatment.

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