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Abstract. Using realistic pseudoHamiltonians and pseudopotentials to describe ion–valence-electron interactions, we investigate the effects of non-locality of ion–electron interactions on the bulk plasmon energy in alkali metals. It is found that pseudoHamiltonians and pseudopotentials can lead to important effects on the optical mass and plasmon energies.

1. Introduction

The effect of core electrons on the Mie resonance in metal clusters has recently been investigated by several authors. In particular, realistic core potentials have been used in calculations of the dipole response of Li clusters within the self-consistent time-dependent local-density approximation (TDLDA) [1–3] and within the Hartree–Fock and random-phase approximations [4,5]. In these calculations it is found that the plasma resonance is red-shifted with respect to the classical formula by core effects, in better agreement with experiment. An important core effect is the modification of the effective mass due to the non-local components of the core potential [1,3]. The value of the effective mass is, however, found to depend on the particular model used for the core potential. In the case of Li clusters, where the observed red-shift is particularly large, this effective mass is in the range 1.15–1.53 [1,3,4]. Although the upper value 1.53 of the effective mass yields good agreement between the calculated [1] and experimental [6] position of the resonance, it seems to be in disagreement with the results from band structure calculations, which would imply lower values for the effective mass in spherically averaged models, as was pointed out in [2].

With the aim of investigating this point in more detail, we develop in this paper a pseudojellium model, which takes into account the non-local realistic core potentials available in the literature, and apply it to an electron gas. In a homogenous system it is possible to study in an analytical way the connections between the non-local components of the core potentials, the effective mass of valence electrons and their optical mass, which is the key quantity for the determination of the bulk plasmon energy, and hence to perfom a thorough comparison between the predictions of jellium and pseudojellium models where different pseudopotentials or pseudoHamiltonians are used.

The effects that we consider in this paper are the average effects of the electron-ion interaction sufficient to resolve the chemical difference between, say, two isovalent ions

belonging to the same group of the periodic table, but insensitive to the details of the crystalline geometry and of energy bands. Energy band effects have been treated, for example, in the case of alkali metals in [7].

The paper is organized as follows. In section 2 we define the pseudojellium model and discuss the associated Kohn–Sham description of the ground state and time-dependent linear response theory (TDLDA). In section 3 we analyse the prediction of the model for the bulk plasmon energy, its connection with the energy-weighted sum rule and the optical mass. The dispersion with momentum transfer of the plasmon energy is briefly considered in section 4. Finally, section 5 presents some conclusions.

2. The pseudojellium model for an electron gas

2.1. Definition and ground state

In the following we will define pseudojellium as a gas of N interacting valence electrons in an external ionic non-local potential given by the spatial average of an effective ion–electron interaction $\hat{v}$ with respect to the ionic coordinate r_I:

$$\bar{v} = \lim_{\Omega \to \infty} \frac{N}{\Omega} \int_\Omega \mathrm{d}r_\mathrm{I} \, \hat{v}. \tag{1}$$

The external potential $\hat{v}$ will be either the Bachelet, Hamann and Schluter (BHS) pseudopotential [8]

$$\hat{v}^{\mathrm{PP}} = v_{\mathrm{loc}}(r - r_\mathrm{I}) + \Delta \hat{v}(r - r_\mathrm{I} r' - r_\mathrm{I}) \tag{2}$$

with

$$\Delta \hat{v}(x, x') = \sum_\ell^{\ell_{\mathrm{max}}} \sum_m Y_{\ell,m}(\hat{x}) Y_{\ell,m}^*(\hat{x}') v_\ell(x) \frac{\delta(x - x')}{xx'} \tag{3}$$

or the Bachelet, Ceperley and Chiocchetti (BCC) pseudoHamiltonian [9]:

$$\hat{h} = h_{\mathrm{loc}}(r - r_\mathrm{I}) - \tfrac{1}{2}\nabla_{(r-r_\mathrm{I})} a(r - r_\mathrm{I}) \cdot \nabla_{(r-r_\mathrm{I})} + \tfrac{1}{2} L_{(r-r_\mathrm{I})} \frac{b(r - r_\mathrm{I})}{(r - r_\mathrm{I})^2} \cdot L_{(r-r_\mathrm{I})}. \tag{4}$$

The pseudoHamiltonian (4) can be derived from the pseudopotential (3) by imposing the condition that the eigenvalues and eigenfunctions of the Kohn–Sham equations for the atom coincide in the two cases [9], or can be built directly starting from a full core atom calculation [10]. It has recently been used for studying the static and dynamic properties of clusters of alkali metals [1,5]. In this case, the spatial average of (1) is made inside a sphere of radius $R = r_s N_\mathrm{I}^{1/3}$, where r_s is the Wigner–Seitz radius $r_s = (3/4\pi\rho_0)^{1/3}$ and ρ_0 is the static bulk density. In the bulk limit of (1) we have $N/\Omega = \rho_0$.

The Kohn–Sham equations for the pseudojellium take the form

$$\left(-\tfrac{1}{2}\nabla_r^2 + \int \mathrm{d}r' \frac{\rho(r')}{|r - r'|} + \bar{v} + v_{\mathrm{xc}}(\rho(r)) \right) \phi_i(r) = \epsilon_i \phi_i(r) \tag{5}$$

where $\rho(r)$ is the density of the valence electrons and v_{xc} is the usual exchange-correlation term within the LDA. In the pseudopotential case, the non-local part of the external ionic potential acts on the single-particle wavefunction $\phi_i(r)$ as an integral kernel:

$$\overline{\Delta\hat{v}}\phi_i(r) \equiv \int dr' \, \overline{\Delta\hat{v}}(r, r')\phi_i(r') \tag{6}$$

whereas in the pseudoHamiltonian case it acts as a differential operator, like the kinetic energy operator. A self-consistent solution of these equations has been investigated in [11] for the bulk, where $\phi_i = e^{ik\cdot r}/\sqrt{\Omega}$, and for metal clusters in [1, 3]. In particular, it has been found that, in the case of the BCC pseudoHamiltonian, in the bulk the effective mass

$$m^*(k) = \left(\frac{\partial^2\epsilon_k}{\partial k^2}\right)^{-1} \tag{7}$$

is constant with k, and is given by

$$\frac{1}{m^*} = 1 + \rho_0 \int dr\left(a(r) + \tfrac{2}{3}b(r)\right) \tag{8}$$

where $a(r)$ and $b(r)$ are the functions entering (4). On the other hand, for the BHS pseudopotential the effective mass is strongly momentum dependent.

2.2. The TDLDA response theory

In this work we investigate the effects of the non-local component of the pseudopotential and pseudoHamiltonian on the dispersion of the bulk plasmon by use of the TDLDA. In this approach the time-dependent solutions of the system coupled with an external oscillating field with which it interacts through a field $\lambda(G^\dagger e^{-i\omega t} + Ge^{+i\omega t})$ are given by

$$i\frac{\partial}{\partial t}\phi_i(r, t) = \left(-\tfrac{1}{2}\nabla_r^2 + \int dr'\frac{\rho(r', t)}{|r - r'|} + \bar{\hat{v}} + v_{xc}(\rho(r, t)) + \lambda(G^\dagger e^{-i\omega t} + Ge^{+i\omega t})\right)\phi_i(r, t) \tag{9}$$

where

$$\rho(r, t) = \sum_{i=1}^{N} |\phi_i(r, t)|^2. \tag{10}$$

In the infinite system, due to translational invariance, one has $G = e^{-iq\cdot r}$ and (9) gives rise to solutions of the form

$$\rho(r, t) = \rho_0 + \delta\rho\left(e^{i(q\cdot r - \omega t)} + e^{-i(q\cdot r - \omega t)}\right) \tag{11}$$

where $\delta\rho$ is a constant to be determined and ρ_0 is the static bulk density. The dynamic polarizability relative to the excitation operator $F = \sum_i^N e^{iq\cdot r_i}$ is given by [12]

$$\chi(F, G, \omega)_{\text{TDLDA}} = \frac{F_+(\omega)}{\lambda} \tag{12}$$

where $F_+(\omega)$ is defined by

$$\delta F(t) \equiv \int dr\, e^{iq\cdot r}\delta\rho(r,t) = F_+ e^{i\omega t} + F_- e^{-i\omega t} \tag{13}$$

where $\delta\rho(r,t) = \rho(r,t) - \rho_0$. Using (11) one then gets

$$\chi(F,G,\omega)_{\text{TDLDA}} = \frac{1}{\lambda}\int dr\, e^{iq\cdot r}\delta\rho e^{-iq\cdot r} = \frac{1}{\lambda}\Omega\delta\rho. \tag{14}$$

We now proceed to write down the explicit expression of the dynamic polarizability. Let us define the density-dependent potential $V_{\text{TDLDA}}(r,\rho(r,t))$ of (9):

$$V_{\text{TDLDA}}\big(r,\rho(r,t)\big) = \int dr'\frac{\rho(r',t)}{|r-r'|} + v_{\text{xc}}\big(\rho(r,t)\big). \tag{15}$$

Inserting solution (11) in (15), one gets terms linear in $\delta\rho(r,t) = \rho(r,t) - \rho_0$:

$$V_{\text{TDLDA}}\big(r,\rho(r,t)\big) = V_{\text{LDA}}(\rho_0) + \left(\frac{\partial V_{\text{TDLDA}}}{\partial\rho}\right)_{\rho=\rho_0}\delta\rho(r,t) \tag{16}$$

where $\rho_0 = 3/4\pi r_s^3$ and $V_{\text{LDA}}(\rho_0)$ are the static density and potential, respectively. From (16) and (11) one gets

$$V_{\text{TDLDA}}\big(r,\rho(r,t)\big) = V_{\text{LDA}}(\rho_0) + \left[\int dr'\frac{e^{iq\cdot(r'-r)}}{|r-r'|} + \left(\frac{\partial v_{\text{xc}}}{\partial\rho}\right)_{\rho=\rho_0}\right]\delta\rho(e^{i(q\cdot r-\omega t)} + \text{CC})$$

$$= V_{\text{LDA}}(\rho_0) + \left[\frac{4\pi}{q^2} + \left(\frac{\partial v_{\text{xc}}}{\partial\rho}\right)_{\rho=\rho_0}\right]\delta\rho(e^{i(q\cdot r-\omega t)} + \text{CC}). \tag{17}$$

The TDLDA equations now assume the following form:

$$i\frac{\partial}{\partial t}\phi_i(r,t) = [\![-\tfrac{1}{2}\nabla_r^2 + V_{\text{LDA}}(\rho_0) + \bar{v} + \{[(4\pi/q^2) + (\partial v_{\text{xc}}/\partial\rho)_{\rho=\rho_0}]\delta\rho + \lambda\}$$

$$\times (e^{i(q\cdot r-\omega t)} + \text{CC})]\!]\phi_i(r,t)$$

$$= \big[-\tfrac{1}{2}\nabla_r^2 + V_{\text{LDA}}(\rho_0) + \bar{v} + \lambda'(q)\big(e^{i(q\cdot r-\omega t)} + \text{CC}\big)\big]\phi_i(r,t) \tag{18}$$

where we have defined

$$\lambda'(q) = \lambda + \left[\frac{4\pi}{q^2} + \left(\frac{\partial v_{\text{xc}}}{\partial\rho}\right)_{\rho=\rho_0}\right]\delta\rho. \tag{19}$$

Equations (18) are now TDLDA equations for a non-interacting (single-particle) gas of electrons in a static field $V_{\text{LDA}}(\rho_0)+\bar{v}$ and submitted to a new external field $\lambda'(q)(e^{i(q\cdot r-\omega t)}+\text{CC})$ with coupling constant $\lambda'(q)$ given by (19). The dynamic polarizability corresponding to these equations is the single-particle response function:

$$\chi^0(q,\omega) = 2\sum_{m,i}\epsilon_{m,i}\frac{|\langle m|e^{iq\cdot r}|i\rangle|^2}{(\omega+i\eta)^2 - \epsilon_{m,i}^2}. \tag{20}$$

The single-particle (-hole) states $|m\rangle$ ($|i\rangle$) and excitation energies $\epsilon_{m,i}$ are built with the solutions of the static Kohn–Sham equations (5). From (14), the result for the TDLDA polarizability, and the analogous relation for χ^0:

$$\chi^0(q,\omega) = \frac{1}{\lambda'(q)}\Omega\delta\rho \tag{21}$$

one then gets

$$\lambda\chi_{\text{TDLDA}} = \lambda'(q)\chi^0 = \Omega\delta\rho \tag{22}$$

and therefore

$$\chi(q,\omega)_{\text{TDLDA}} = \chi^0(q,\omega)\left[1 - \frac{1}{\Omega}\left(\frac{4\pi}{q^2} + \frac{\partial v_{\text{xc}}}{\partial\rho}\bigg|_{\rho=\rho_0}\right)\chi^0(q,\omega)\right]^{-1}. \tag{23}$$

3. Bulk plasmon energy and energy-weighted sum rule

The energy of the bulk plasmon can be derived by solving the equation

$$\chi^0(q,\omega) = \Omega\left(\frac{4\pi}{q^2} + \frac{\partial v_{\text{xc}}}{\partial\rho}\bigg|_{\rho=\rho_0}\right)^{-1} \tag{24}$$

which gives the poles of $\chi(q,\omega)_{\text{TDLDA}}$. In the following we will focus on the $q \to 0$ limit of (24). In this limit one can neglect in (24) the exchange-correlation term with respect to the Coulomb term, and consider the limiting case $\omega \gg \epsilon_{m,i}$ in the evaluation of $\chi^0(q,\omega)$ since only this part of $\chi^0(q,\omega)$ becomes relevant for the collective solution of (24), as is apparent from the graphical solution of (24). From (20), for $\omega \gg \epsilon_{m,i}$ one gets

$$\chi^0(q,\omega) \simeq \frac{2}{\omega^2}m_1^{\text{sp}}(q) \tag{25}$$

where m_1^{sp} is the energy-weighted sum rule

$$m_1^{\text{sp}} \equiv \sum_{m,i}\epsilon_{m,i}|\langle m|e^{iq\cdot r}|i\rangle|^2 = \tfrac{1}{2}\left\langle 0\left|\left[\sum_i e^{-iq\cdot r_i},\left[H_0,\sum_i e^{iq\cdot r_i}\right]\right]\right|0\right\rangle \tag{26}$$

and H_0 is the single-particle Hamiltonian generating the single-particle basis with which one builds $\chi^0(q,\omega)$ and the ground state $|0\rangle$ of (26). From (24), (25) one finally gets

$$\frac{2}{\omega^2}m_1^{\text{sp}}(q) = \frac{\Omega}{4\pi}q^2. \tag{27}$$

Equation (27) is a general result valid in the $q \to 0$ limit. Evaluation of m_1^{sp} in different models yields different predictions for the energy of the bulk plasmon. In the usual jellium model one has the well known result

$$m_1^{\text{jm}} = \tfrac{1}{2}Nq^2 \tag{28}$$

which follows immediately from the fact that in the jellium model the only term of H_0 contributing to the commutator (26) is the kinetic energy term. In the pseudojellium model the non-local terms of the electron–ion potential give rise, for both pseudopotential and pseudoHamiltonian cases, to corrections to the result (28). At first sight these corrections might appear surprising since the true Hamiltonian has no momentum dependence and satisfies the energy-weighted sum rule. However, the number of electrons entering in the sum rule is in principle the total number (valence plus core) of electrons, and not only the number N of valence electrons as in (28). In the pseudojellium model one takes into account only the valence electrons, as in the jellium model, but unlike the jellium model the core electrons are simulated with an effective valence-electron–ion interaction. Inside the ionic core the effective interaction between valence electrons and ions must now incorporate a short-range repulsive term to mimic the orthogonality to the occupied core states, and it then cannot be the local Coulomb interaction as in the jellium model. We expect that pseudojellium will correctly describe the excitation strength, and then the energy-weighted sum rule, in the low-energy region. At energies much higher than the plasmon, there would be an additional excitation strength not contained in the pseudojellium model, restoring the sum rule result with the true Hamiltonian.

As is explicitly shown in the appendix, we get the following expressions for the m_1^{sp} sum rule in pseudojellium with the pseudoHamiltonian and pseudopotential, respectively:

$$m_1^{PH} = \frac{Nq^2}{2}\left(1 + \rho_0 \int \left(a(r) + \tfrac{2}{3}b(r)\right)dr\right) \tag{29}$$

and

$$m_1^{PP} = \frac{Nq^2}{2}\left(1 - \frac{4}{3\pi}k_F^2 \int \overline{\Delta v}(x)x^3 j_1(k_F x)dx\right) \tag{30}$$

where

$$\overline{\Delta v}(x) = \frac{2}{\pi}\sum_{\ell}^{\ell_{max}}(2\ell + 1)\int q^2 dq\, x'^2 dx'\, j_0(qx)\left(j_\ell(qx')\right)^2 v_\ell(x') \tag{31}$$

and the $j_l(qx)$ are spherical Bessel functions. From (27)–(31) one gets for the energy of the bulk plasmon, ω_p, the result

$$\omega_p = \sqrt{\frac{4\pi\rho_0}{m_{opt}}} \tag{32}$$

where the inverse optical mass $1/m_{opt}$ is equal to 1 in the jellium model and given by

$$\frac{1}{m_{opt}^{PH}} = 1 + \rho_0 \int dr\left(a(r) + \tfrac{2}{3}b(r)\right) \tag{33}$$

and

$$\frac{1}{m_{opt}^{PP}} = 1 - \frac{4}{3\pi}k_F^2 \int \overline{\Delta v}(x)x^3 j_1(k_F x)dx \tag{34}$$

for the pseudoHamiltonian and pseudopotential, respectively.

Table 1. Optical masses and bulk plasmon energies (in eV) of alkali metals in the pseudojellium model with pseudopotentials (PP) and pseudoHamiltonians (PH). Experimental values for Li are from [22, 23]; for the rest of alkalis see [14]. We used r_s values of 3.25, 3.93, 4.86, 5.20 and 5.62 for the alkalis from Li to Cs, respectively [13].

	m_{opt}^{PP}	m_{opt}^{PH}	ω_p^{PP}	ω_p^{PH}	ω_p^{exp}
Li	1.155	1.526	7.48	6.51	6.7
Na	1.051	1.040	5.90	5.93	5.72
K	1.017	0.983	4.36	4.44	3.72
Rb	0.980	0.909	4.01	4.17	3.41
Cs	1.015	0.872	3.51	3.79	2.99

From (32)–(34) one can see how the non-local parts of the pseudoHamiltonians and pseudopotentials correct the bulk plasmon energy with respect to the jellium prediction. One can also notice that, in the case of the pseudoHamiltonian, $1/m_{opt}$ coincides with $1/m^*$ of (8) due to the fact that in this case $1/m^*$ is constant. This is not the case for the pseudopotential, due to the k-dependence of the effective mass. The connection between $1/m_{opt}^{PP}$ and $1/m_{PP}^*$ passes through the evaluation of the energy-weighted sum rule (26).

In table 1 we report the predictions of the different models for the optical mass and for the bulk plasmon energy of alkali metals together with the experimental results. From the table one can see that the predictions of the pseudoHamiltonians and pseudopotentials do not coincide, and are particularly different in the case of lithium where non-local effects are more important. One way to obtain an improved pseudoHamiltonian, giving bulk plasmon properties closer to the predictions of the pseudopotential, would be to impose the same local part for both pseudopotential and pseudoHamiltonian while treating the non-local parts differently in each case. Table 1 shows that the predicted plasmon energies are systematically higher than the experimental values. A simple estimate of core polarization effects can be done by taking into account the fact that the dielectric function $\epsilon(q, \omega)$ would be shifted to $\epsilon(q, \omega) + \Delta\epsilon$ by these effects. Using the values of $\Delta\epsilon$ given in [13] one finds that plasmon energies are redshifted by about 1% in Li up to 13% in Cs, thus leaving a large discrepancy in Li. On the other hand, it is known [7] that a lowering of calculated plasmon energies in the series Na to Cs originates from band structure effects, which are not accounted for in the present approach.

4. The plasmon dispersion coefficient

In the pseudojellium model it is possible to study in an analytical way the plasmon dispersion up to q^2 terms. To do that, it is sufficient to take into account the exchange-correlation contribution in (24) and at the same time to keep the next term in the expansion (25) of the single-particle response function (20):

$$\chi^0(q, \omega)\bigg|_{\omega \gg \epsilon_{m,i}} \simeq \frac{2}{\omega^2}\left(m_1^{sp}(q) + \frac{1}{\omega^2}m_3^{sp}(q)\right) \tag{35}$$

where m_3^{sp} is the cubic energy-weighted sum rule

$$m_3^{sp} \equiv \sum_{m,i} \epsilon_{m,i}^3 |\langle m|e^{iq\cdot r}|i\rangle|^2 = \frac{1}{2}\left\langle 0\left|\left[\left[\sum_i e^{-iq\cdot r_i}, H_0\right], \left[H_0, \left[H_0, \sum_i e^{iq\cdot r_i}\right]\right]\right]\right|0\right\rangle. \tag{36}$$

In the case of the pseudoHamiltonian one can easily evaluate m_3^{sp} (see the appendix) to obtain

$$m_3^{PH} = \frac{3k_F^2}{10m_{opt}^3} N q^4. \tag{37}$$

The calculation with the pseudopotential is much more involved, and will not be presented here. Using (24) and the results (29), (37) one readily gets the plasmon dispersion up to q^2 terms:

$$\omega^2 = \omega_p^2 + \left(\frac{3}{5} \frac{k_F^2}{m_{opt}^2} + \frac{\rho_0}{m_{opt}} \frac{\partial v_{xc}}{\partial \rho} \Big|_{\rho=\rho_0} \right) q^2. \tag{38}$$

From this result one sees that the optical mass generated by the non-local part of the ionic potential significantly affects the plasmon coefficient:

$$\alpha = \frac{3}{5} \frac{k_F^2}{m_{opt}^2} + \frac{\rho_0}{m_{opt}} \frac{\partial v_{xc}}{\partial \rho} \Big|_{\rho=\rho_0}. \tag{39}$$

In contrast, this coefficient is not affected by the core polarizability, at least in the way in which this effect was taken into account in the preceding section.

Table 2. Plasmon dispersion coefficient normalized to the RPA value for different alkali metals as predicted by the pseudojellium model with pseudoHamiltonians. Experimental values are from [14].

	α/α_{RPA} (PH)	α/α_{RPA} (Jellium)	α/α_{RPA} (Exp.)
Li	0.21	0.67	—
Na	0.53	0.59	0.62
K	0.51	0.49	0.30
Rb	0.60	0.45	0.03
Cs	0.63	0.40	−0.80

In table 2 we report the predictions of (39) for α/α_{RPA} ($\alpha_{RPA} = \frac{3}{5}k_F^2$) together with the experimental results of [14]. To perform the derivative of the exchange-correlation potential entering (39) we have used the Perdew–Zunger [15] correlation potential. The numerical values of α/α_{RPA} obtained with this procedure and with $m_{opt} = m^*$ are very close to the predictions of the local field theory of Vashishta and Singwi [16], as reported in [14].

As one can see from table 2, the pseudoHamiltonian prediction for m_{opt} gives a decreasing ratio α/α_{RPA} with respect to the jellium model result for Li and Na, but an increasing ratio in the case of K, Rb and Cs; this is in strong disagreement with experiments. Nevertheless, this influence of core electrons on the plasmon dispersion coefficient is in agreement with the result of [7]. From K to Cs core electrons tend to produce positive dispersion, increasing the value of α. We note, however, that the density dependence of the dispersion coefficient cannot be explained by local field theory with inclusion of core effects; it is due to other effects. Regarding this point, we comment on the two commonly accepted viewpoints. The first viewpoint [17–21] assumes that band structure effects are small in alkali metals [14], and that the observed dispersion is due to a large q- and ω-dependent exchange correlation term, which is not included in the LDA. In fact, the LDA approximation simply gives the $q, \omega \rightarrow 0$ limit of this term. The second viewpoint assigns the dispersion

to band structure effects [7]. When going from Na to Cs, the d band approaches the Fermi level and becomes narrower. Since the plasmon energies lie in these interband transitions, the d band may be responsible for the observed behaviour. In this work we have not considered these two possible effects, and we simply investigated average effects of the non-local part of the electron–ion interaction. These latter effects are particularly important in Li, whereas the other effects are probably not so important.

5. Conclusions

We have used ionic pseudopotentials and pseudoHamiltonians, which replace core electrons in atomic calculations, to build a pseudojellium model with the aim of describing static and dynamic properties of quantum electron fluids in an external ionic field. As an application, we have studied the dispersion of the bulk plasmon in alkali metals. We have stressed the role of the optical mass due to non-local components of the ionic potential. The optical mass has been obtained by means of the relation of the dynamic polarizability and the energy-weighted sum rule in the $q \to 0$ limit. An analytic expression of the energy-weighted sum rule in terms of the non-local components of the ionic potential has been found.

The value of the optical mass depends on the particular model (pseudopotential or pseudoHamiltonian) used for the core potential when non-local effects are important and the optical mass deviates from the bare mass. As a consequence, we have found that, in the case of lithium, the predicted value for the energy of the bulk plasmon varies considerably from one model to another. This result seems to be a feature only of infinite systems, while in (small) finite-size systems, such as clusters of alkali metals, different models still give quite similar predictions for the position of the plasma resonance [3]. This is due to the fact that, unlike the bulk case, in finite systems the local parts of the pseudopotential and pseudoHamiltonian play a crucial role and cancel differences between the two models originating from the different non-local components.

Appendix A. The energy-weighted sum rule

In this appendix we evaluate the energy-weighted sum rule (26) in the different models discussed in this work. For all these models the Hamiltonian H_0 entering (26) can be written as (see (5))

$$H_0 = \sum_{j=1}^{N} \left(-\tfrac{1}{2}\nabla_r^2 + \int dr' \frac{\rho(r')}{|r - r'|} + \bar{\bar{v}} + v_{xc}(\rho(r)) \right)_j . \tag{A1}$$

In the jellium model $\bar{v}$ is a local operator as well as $v_{xc}(\rho(r))$, and the only term of H_0 contributing to the commutator in (26) is the kinetic energy term. From the following properties:

$$[\nabla^2, e^{iq \cdot r_i}] = e^{iq \cdot r_i}(-q^2 + 2iq \cdot \nabla) \qquad [e^{-iq \cdot r_i}, [\nabla^2, e^{iq \cdot r_i}]] = -2q^2 \quad (A2)$$

one immediately gets the jellium result (28).

In the pseudojellium case, we have firstly to perform the spatial average of (1). For the pseudoHamiltonian (4), defining $x = r - r_I$, one has

$$\hat{h} = h_{loc}(x) - \tfrac{1}{2}\nabla_x a(x) \cdot \nabla_x + \tfrac{1}{2}L_x \frac{b(x)}{x^2} \cdot L_x. \qquad (A3)$$

The spatial average of the first term of (A3) gives

$$\bar{h}_{loc} = \rho_0 \int d^3x \, h_{loc}(x) \equiv \rho_0 \langle h_{loc} \rangle \qquad (A4)$$

where $\rho_0 = N/\Omega$ is the bulk density. For the second term one has $(\nabla_x = \nabla_r)$

$$-\tfrac{1}{2}\rho_0 \int \nabla_r a(x)\nabla_r \, d^3x = -\tfrac{1}{2}\langle a \rangle \rho_0 \nabla_r^2 \qquad \langle a \rangle \equiv \int a(x)d^3x. \qquad (A5)$$

Finally, for the third term one has

$$\int d^3x \, (x \wedge p) \cdot \frac{b(x)}{x^2}(x \wedge p) = \int d^3x \left(b(x)p^2 - (x \cdot p)^2 \frac{b(x)}{x^2} \right) \qquad (A6)$$

and using

$$\int d\Omega_x \, (x \cdot p)^2 = \tfrac{4}{3}\pi x^2 p^2$$

one finally gets

$$\rho_0 \int d^3x \, (x \wedge p) \cdot \frac{b(x)}{x^2}(x \wedge p) = -\tfrac{2}{3}\langle b \rangle \rho_0 \nabla_r^2 \qquad \langle b \rangle \equiv \int b(x) \, d^3x. \qquad (A7)$$

Gathering all terms we have

$$\bar{v}_{PH} = \rho_0 \left[-\tfrac{1}{2}(\langle a \rangle + \tfrac{2}{3}\langle b \rangle)\nabla_r^2 + \langle h_{loc} \rangle \right]. \qquad (A8)$$

The sum rule calculation then proceeds as in the jellium case, giving the result (29).

In the case of the pseudopotential (3), to calculate the spatial average

$$\overline{\Delta v}(r, r') = \rho_0 \int dr_I \, \Delta v(r - r_I, r' - r_I) \qquad (A9)$$

one uses

$$\Delta v(r - r_I, r' - r_I) = \frac{1}{(2\pi)^6} \int d^3q \, d^3q' \, e^{iq \cdot (r - r_I)} e^{-iq' \cdot (r' - r_I)} \Delta v(q, q') \quad (A10)$$

where $\Delta v(q, q')$ is the Fourier transform of $\Delta v(x, x')$. A straightforward calculation then gives

$$\overline{\Delta v}(y) = \frac{2}{\pi} \sum_{\ell}^{\ell_{max}} (2\ell + 1) \int dq \, dy' \, q^2 y'^2 j_0(qy)[j_\ell(qy')]^2 v_\ell(y') \tag{A11}$$

where $y = r - r'$. Using the commutators

$$\langle r|[\,\overline{\Delta v}(r - r'), e^{iq \cdot r}\,]|r'\rangle = \overline{\Delta v}(r - r')(e^{iq \cdot r'} - e^{iq \cdot r})$$

$$\langle r|[e^{-iq \cdot r}, [\,\overline{\Delta v}(r - r'), e^{iq \cdot r}\,]]|r'\rangle = \overline{\Delta v}(r - r')(e^{iq \cdot (r-r')} + e^{-iq \cdot (r-r')} - 2) \tag{A12}$$

one finally finds the following contribution to the energy-weighted sum rule:

$$\Delta m_1^{PP} = N\frac{4k_F^2}{\pi} \int_0^\infty \overline{\Delta v}(x)[j_0(qx) - 1]j_1(k_F x)x \, dx. \tag{A13}$$

In the $q \to 0$ limit one then gets

$$\Delta m_1^{PP} = -N\frac{4k_F^2}{\pi}\frac{1}{6}q^2 \int_0^\infty \overline{\Delta v}(x)j_1(k_F x)x^3 \, dx. \tag{A14}$$

Adding this contribution to the kinetic energy contribution ($\frac{1}{2}Nq^2$), finally one gets the result (31).

We finally note that, in the case of the pseudoHamiltonian for which the effective mass is constant, it is possible to evaluate very easily the cubic energy-weighted sum rule:

$$m_3^{PH} \equiv \sum_{m,i} \epsilon_{m,i}^3 |\langle m|e^{iq \cdot r}|i\rangle|^2 = \frac{1}{2}\left\langle 0\left|\left[\left[\sum_i e^{-iq \cdot r_i}, H_0^{PH}\right], \left[H_0^{PH}, \left[H_0^{PH}, \sum_i e^{iq \cdot r_i}\right]\right]\right]\right|0\right\rangle \tag{A15}$$

in the single-particle approximation. This sum rule is relevant for the evaluation of the plasmon dispersion coefficient. Using results (A2), (A8) one gets

$$m_3^{PH} = \frac{3k_F^2}{10m_{opt}^3}Nq^4. \tag{A16}$$

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