Nonlocal exchange effects on the bulk plasmon dispersion relation

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Starting from the action principle, a bulk plasmon dispersion relation is obtained. We work with Slater determinants built of plane waves and consider a Hermitian generator of plasma oscillations (with well-defined $\mathbf{q}$ momentum) $S=\alpha Q-\beta P$, where $Q=\sum_j \cos(\mathbf{q}\cdot\mathbf{x}_j)$ is a time-even Hermitian generator, $P=\mathcal{B}\sum_j [\mathbf{p}_j\cdot\mathbf{q}\sin(\mathbf{q}\cdot\mathbf{x}_j)+\sin(\mathbf{q}\cdot\mathbf{x}_j)\mathbf{p}_j\cdot\mathbf{q}]$ is a time-odd Hermitian generator, $\alpha(t)$ and $\beta(t)$ are real time-dependent functions, and $\mathcal{B}$ is a real normalization constant. If the parameters α and β are small, the amplitude of the plasma oscillations generated by S is small. The quantum-mechanical action principle leads, in the harmonic approximation, to a quadratic Lagrangian $L^{(2)}(\alpha,\beta)$ from which the dispersion relation is obtained. The nonlocal expression of the exchange contribution is explicitly obtained. The resulting bulk plasmon dispersion relation is related to the energy-weighted and cubic-energy-weighted sum rules. Finally, we compare our results with the experimental data.

I. INTRODUCTION

A macroscopic description of the dynamics of a many-body system is physically appealing and transparent because it allows a clear identification of the mechanism responsible for the collective properties of the system. The standard fluid-dynamical approach[1-4] implicitly assumes a specific averaging process over the intrinsic degrees of freedom, which is achieved by focusing on the dynamics of the lowest momenta of the distribution function. This procedure leads, as is well known, to an intuitive dynamical description in terms of density, current, pressure tensor, etc.

It is the purpose of this paper to present an investigation of collective dynamics of the electron gas centered on the description of the time evolution of the collective degrees of freedom, which are characterized here by appropriate macroscopic collective variables. We follow a simple variational method[1,2] that has been developed and successfully used to study excited states of heavy nuclei. The method is based on the action principle applied to the determination of the optimal time evolution of appropriate generators of collective deviations from equilibrium.

A kind of averaging process over the dynamics of intrinsic degrees of freedom is implied by the use of restrictive operators that are constructed in such a way as to provide an adequate description of the collective, macroscopic degrees of freedom. The method preserves the important energy weighted sum rule, which is connected to the dielectric-function sum rule. Therefore, the asymptotic behavior of the response function is exactly reproduced for large frequencies.

Recent experimental information on the plasma excitations on nearly-free-electron-like materials[5,6] has been used to discuss different theoretical approaches that attempt to match their predictions against the experimental data within a few percent. It is especially convenient to obtain a manageable analytical expression of the dispersion relation for the collective modes of the system in order to use it in the usually involved calculations of several spectroscopies.

In a recent paper,[7] from an extended random-phase-approximation (ERPA) sum-rule technique, a compact expression for the dispersion relation of the electron-gas modes was obtained. It can incorporate in an easy and explicit way band-structure effects through a band effective mass and an ionic dielectric constant. Exchange and correlation effects were included through local expressions of Slater and Wigner types, respectively.

We assume the jellium model to represent the ionic positive background. Inclusion of band effects can be performed directly into our energy expansion (as was done in Ref. 7) in order to compare our results with experimental data.

This paper is organized as follows. In Sec. II we make a description of the method used and obtain the analytical expression for the dispersion relation. In Sec. III we compare our numerical results with experimental data and draw conclusions.

II. DESCRIPTION OF THE METHOD

We consider the quantum-mechanical Lagrangian

$$L=i\hbar\langle\phi|\dot{\phi}\rangle-\langle\phi|H|\phi\rangle\ , \tag{1}$$

where $|\phi\rangle$ is a Slater determinant that is related by means of a unitary transformation to the Slater determinant of plane waves $|\phi_0\rangle$, describing the ground state

$$|\phi\rangle=e^{(i/\hbar)S}|\phi_0\rangle\ . \tag{2}$$

For small-amplitude deviations from the equilibrium state, the Lagrangian L leads to the following harmonic expression:

$$L^{(2)}=\frac{i}{2\hbar}\langle\phi_0|[S,\dot{S}]|\phi_0\rangle-\frac{1}{2\hbar^2}\langle\phi_0|[S,[H,S]]|\phi_0\rangle \ . \quad (3)$$

We write the generator S as $S=\alpha(t)Q-\beta(t)P$, where P and Q are Hermitian operators of the type

$$Q=\sum_j \cos(\bar{q}\cdot\bar{x}_j) \ , \quad (4)$$

and

$$P=\mathcal{B}\sum_j [\bar{p}_j\cdot\bar{q}\sin(\bar{q}\cdot\bar{x}_j)+\sin(\bar{q}\cdot\bar{x}_j)\bar{p}_j\cdot\bar{q}] \ . \quad (5)$$

In Eq. (5), $\mathcal{B}$ stands for a normalization constant, which we choose in such a way that

$$\langle\phi_0|[P,Q]|\phi_0\rangle=-i\hbar \ . \quad (6)$$

Equation (6) implies that $\mathcal{B}=1/(Nq^2)$, where N is the number of free electrons. With this choice for $\mathcal{B}$ the variables α and β behave as canonical variables [see Eq. (14)]. An analogous approach has been followed in other fields of physics with good results (see, for example, Refs. 1–4).

The operator $H=T+V$ stands for the Hamiltonian of an electron gas in a uniform positive background (jellium model), and T and V are, respectively,

$$T=\sum_j \frac{p_j^2}{2m} \ , \quad (7)$$

$$V=\sum_{i<j}\frac{e^2}{|\bar{x}_i-\bar{x}_j|}+\sum_j U(\bar{x}_j)+W \ , \quad (8)$$

where $U(\bar{x})$ is the potential due to the uniform positive density distribution and W is the electrostatic energy of the positive background (e being the electronic charge). The term W plays no role in the Lagrangian (3), and $\sum_j U(\bar{x}_j)$ is canceled with the zero-momentum scattering component of the first term in the right-hand side (rhs) of Eq. (8).

We find the following expressions (from now on, we use atomic units: $e^2=m=\hbar=1$). For the kinetic contribution, the nonzero terms are

$$\langle\phi_0|[P,[T,P]]|\phi_0\rangle=\frac{2}{N}\left[\frac{3}{5}k_F^2+\frac{q^2}{4}\right] \quad (9)$$

and

$$\langle\phi_0|[Q,[T,Q]]|\phi_0\rangle=\frac{N}{2}q^2 \ , \quad (10)$$

where $k_F=(3\pi^2 n_0)^{1/3}$ is the Fermi momentum and n_0 is the constant ground-state electronic density. For the Coulomb contribution, the direct term (D) is

$$\langle\phi_0|[P,[V,P]]|\phi_0\rangle_D=\frac{8\pi n_0}{Nq^2} \ , \quad (11)$$

and the exchange term (E) is

$$\langle\phi_0|[P,[V,P]]\phi_0\rangle_E=\frac{9\pi n_0}{Nq^2}\zeta(x) \ , \quad (12)$$

where $x=q/k_F$ and

$$\zeta(x)=\frac{4}{189}\left[-\frac{76}{15}+\frac{4}{x^2}-\frac{71}{20}x^2-\frac{x^4}{20}+\left[\frac{36}{80}x^4-\frac{x^6}{80}\right]\ln\left|1-\frac{4}{x^2}\right|\right]+\left[-\frac{16}{189x^3}+\frac{4}{35x}-\frac{x}{15}+\frac{x^2}{36}\right]\ln\left|\frac{x+2}{x-2}\right| \ . \quad (13)$$

We remark that the calculation of the exchange term is lengthy but analytical. We note that the expression $\zeta(x)$ has already been presented in the literature in Ref. 8 in the context of the asymptotic behavior of the response function in the high-frequency limit. As we will see later, it is related to the cubic energy weighted sum rule computed with the operator Q. Therefore, the Lagrangian (3) may be written as follows:

$$L^{(2)}=\tfrac{1}{2}(\dot{\beta}\alpha-\beta\dot{\alpha})-\frac{\alpha^2}{2M}-\frac{\beta^2 K}{2} \ , \quad (14)$$

where

$$K=\langle\phi_0|[P,[H,P]]|\phi_0\rangle \ , \quad (15)$$

and

$$\frac{1}{M}=\langle\phi_0|[Q[H,Q]]|\phi_0\rangle \ . \quad (16)$$

Arbitrary variations of α and β lead, respectively, to the following equations:

$$\dot{\beta}=\alpha/M \quad (17)$$

and

$$\dot{\alpha}=-\beta K \ , \quad (18)$$

or, equivalently,

$$\ddot{\beta}+\frac{K}{M}\beta=0 \ , \quad (19)$$

for which the harmonic frequency oscillation is

$$\omega_q=\sqrt{K/M} \ , \quad (20)$$

or, explicitly,

$$\omega_q^2=\omega_p^2+\tfrac{3}{5}k_F^2q^2+\tfrac{1}{4}q_4+\frac{3}{2\pi}k_F^3\zeta(x) \ , \quad (21)$$

where $\omega_p^2=4\pi n_0$ is the plasma frequency. Equation (21) is the main result in this paper. In order to allow for comparison with other results in the literature, we consider the expansion of the exchange contribution only up to q^2 order, obtaining for ω_q^2 the following expression:

$$\omega_q^2=\omega_p^2+\frac{3}{5}\left[k_F^2-\frac{1}{3}\frac{k_F}{\pi}\right]q^2+\tfrac{1}{4}q_4 \ , \quad (22)$$

which agrees up to the order q^2 with the result presented in Eq. (3.19) of Ref. 9. Our result for the plasmon dispersion relation differs from the result of Ferrell[10] based on the many-body theory. The magnitude of the coefficient

of q^4 of the noninteracting contribution is not reproduced, although the correct sign is obtained. The discrepancy is due to the fact that our approach does not take into account the dynamics of the intrinsic degrees of freedom. It is, however, remarkable that the coefficient of q^2 is correctly reproduced on the basis of the collective dynamics. We also observed that the exchange contribution to the q^2 coefficient in Eq. (22) is less negative than that obtained using a local-density approximation for the exchange.[7]

III. DISCUSSION AND CONCLUSION

Sum rules[11] are useful tools to investigate collective dynamical properties of many-body systems. The present model satisfies the m_1 sum rule for the operators Q and P. Since P is proportional to $[H,Q]$, the model also satisfies the sum rule m_3 for the operator Q, so that the high-frequency asymptotic behavior of the response function is exactly reproduced.[8] Therefore (see Ref. 12),

$$m_3/m_1=\omega_q^2 , \tag{23}$$

with

$$m_1=\omega_q|\langle q|Q|0\rangle|^2=\frac{Nq^2}{4} , \tag{24}$$

and

$$m_3=\omega_q^3|\langle q|Q|0\rangle|^2 = \frac{N_q^2}{4}\left[\tfrac{3}{5}q^2k_F^2+\tfrac{1}{4}q^4+\omega_p^2+\frac{3}{2\pi}k_F^3\zeta(x)\right] , \tag{25}$$

where $\langle q|Q|0\rangle$ is the transition matrix element of Q between the ground state $|0\rangle$ and the plasmon state $|q\rangle$.

In Fig. 1, to compare with available experimental data for aluminum,[6] we have used a modified dispersion relation equation, given by

$$\omega_q^2=\frac{3}{5}\left[\frac{k_F}{m^*}\right]^2 q^2+\frac{q^4}{4m^{*2}}+\frac{1}{m^*\epsilon}\left[\omega_p^2+\frac{3}{2\pi}k_F^3\zeta(x)\right] , \tag{26}$$

where band effects are included through a band-effective electronic mass m^* and a dielectric constant ϵ that models the polarizability of the ionic positive background under the assumption that the inner-shell energies of the positive ions are far from the energy values of the plasma oscillations, which is the case for aluminum. We use

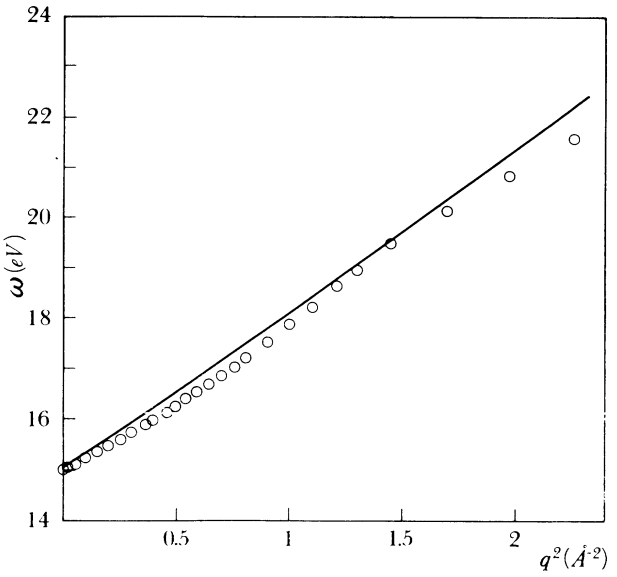

FIG. 1. Bulk dispersion relation for aluminum ($r_s=2.07$) obtained from Eq. (26) compared with experimental data from Ref. 6.

$\epsilon=1.05$ and $m^*=1.045$ a.u., obtained from the calculated shifts of the plasmon energies at $q=0$ due to the inhomogeneity and core polarization effects, made by Sturm in Ref. 13. There is good agreement with experimental value (differences of less than 4%) even for values of q higher than the cutoff value $q_c^2=1.4$ Å^{-2} ($q_c=\omega_p/k_F$), over which Landau damping takes place and the plasma oscillations degenerate into electron-hole excitations.

We conclude that the nonlocality in the exchange interaction can be adequately included in the dispersion relation of plasma oscillations for nearly-free-electron metals within a still manageable expression that can incorporate in an easy way band-structure effects and that reproduces experimental data quite well for small values of r_s (the radius of the sphere that includes a unit electronic charge).

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