Application of sum rules to the response of small metal particles

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Sum rules for the response of small spherical systems are derived and compared to the response calculated in the time-dependent local-density approximation by Ekardt. The ω^3 sum rule, which can be expressed in closed form, is useful as a supplement to the polarizability sum in locating the plasmon. Explicit formulas are obtained for the shifts in the plasmon frequency resulting from the diffusivity of the charge density and from the potential field of the ground state. We show on quite general grounds that the plasmon in a jellium model is red-shifted from the Mie frequency.

The electric response of small metal particles has been the object of recent experimental[1-3] and theoretical research.[4-7] The most complete theory available is the time-dependent local-density approximation (TDLDA), which we expect to be quite adequate for regions of frequency considered in this work. However, the theory requires large scale numerical calculations,[4,8,9] so it is of interest to see whether simpler approaches can reproduce the main physical results of the theory. In light of this, we investigate the application of sum rules to the determination of the response. This is partly motivated by the results in nuclear physics, where sum rules have proved to be very useful in treating the nuclear response.[10]

The sum rules are integrals over the response weighted with some power of the frequency. The easiest one to evaluate is the linear frequency-weighted sum, the well-known Thomas-Reiche-Kuhn (TRK) sum rule. Whenever two independent sum rules are available, an estimate for the plasmon frequency can be made by assuming that the state exhausts the sum rules. The polarizability sum, equivalent to the inverse frequency weighted response, has been shown to be useful in the description of the plasmon frequency. Unfortunately, there is no closed formula for the polarizability, and so one cannot see explicitly the dependence of the plasmon on the ground-state density distribution. In this work, we will concentrate on the rule weighted by the cube of the frequency. This sum has the advantage that it can be evaluated as an expectation value over the ground state, just like the linear sum rule.

We will apply the ω^3 sum rule to derive a formula for the plasmon in finite spherical metal particles. This sum rule has previously only been applied to dielectric properties of insulators.[11] Our main result is to exhibit deviations of the plasmon frequency from the Mie limit. We could also combine information from the three sums to estimate the sharpness of the plasmon as a function of multipolarity. However, in this work we will only study the long-wavelength plasmon in detail, deferring higher multipolarities to a later paper.

The formula for the plasmon will only involve integrals over ground-state quantities. This is possible because the TDLDA assumes that the same exchange-correlation functional that describes the ground state may be used for all frequencies. If the interaction were frequency dependent, no simple closed formula could be made. On the other hand, the result is nice from the point of view of density-functional theory, which provides a description of the many-particle system in terms of the ground-state density. On a rigorous level the theory only proves the existence of an interaction functional for the ground state. Practical theory extrapolates from the rigorous domain of the density-functional method by assuming locality and frequency independence in the exchange-correlation functional.

We first define some notation and derive the ω^3 sum. Let $f(r)$ be a function of position representing the external field acting on the system, and let ε_n be the energies of the eigenstates n. Then the sums are defined by

$$S_m=\sum_n \langle 0|f|n\rangle^2(\varepsilon_n-\varepsilon_0)^m . \tag{1}$$

The linear frequency-weighted sum rule is equal to the double-commutator expectation value,

$$S_1=\sum_n \langle 0|f|n\rangle^2(\varepsilon_n-\varepsilon_0)=\tfrac{1}{2}\langle 0|[f,[H,f]]|0\rangle = \frac{1}{2m}\langle 0|\,|\vec{\nabla} f|^2|0\rangle , \tag{2}$$

where H is the Hamiltonian of the system. The usual TRK expression is obtained with the field $f(r)=z$,

$$\sum_n \langle 0|z|n\rangle^2(\varepsilon_n-\varepsilon_0)=\frac{1}{2m}\langle 0|\hat{\mathbf{z}}\cdot\hat{\mathbf{z}}|0\rangle=\frac{N}{2m} , \tag{3}$$

with N being the number of particles in the system. We now consider the ω^3 sum, which is well defined in

TDLDA theory, although it may be divergent in general. The sum can be expressed in the quadruple commutator,

$$S_3^{\mathrm{LD}}=\tfrac{1}{2}\langle 0\,|\,[[H^{\mathrm{LD}},f],[H^{\mathrm{LD}},[H^{\mathrm{LD}},f]]]\,|\,0\rangle\ . \tag{4}$$

Here, the TDLDA Hamiltonian H^{LD} has the form of a density-dependent single-particle Hamiltonian,

$$H^{\mathrm{LD}}=\sum_{i=1}^{N}\left[-\frac{\vec{\nabla}_i^{\,2}}{2m}+V(r_i,\rho)\right]\ . \tag{5}$$

We first evaluate the innermost commutator, which only has a contribution from the kinetic energy operator in H^{LD},

$$[H^{\mathrm{LD}},f]=\sum_{i=1}^{N}F_i=-\frac{1}{m}\sum_{i=1}^{N}\left[\frac{\vec{\nabla}\cdot\vec{u}_i}{2}+\vec{u}_i\cdot\vec{\nabla}\right]\ , \tag{6}$$

where $\vec{u}_i=\vec{\nabla}f(r_i)$. Physically, the vector field $\vec{u}_i$ represents a displacement field associated with the impulsive perturbation potential f. The operator F_i then gives the effect of the field on the ground-state density,

$$\begin{aligned}\langle i\,|\,[\hat{\rho}(r),F_i]\,|\,i\rangle&=-\frac{1}{m}[\,\vec{\nabla}\cdot\vec{u}\,|\,\phi_i(r)\,|^2+\vec{u}\cdot\vec{\nabla}\,|\,\phi_i(r)\,|^2]\\&=-\frac{1}{m}\,\vec{\nabla}\cdot(\vec{u}\rho_i)\ .\end{aligned} \tag{7}$$

Our next task is to evaluate the commutator of H^{LD} with F_i. We first derive the contribution from the potential field V and then consider the more cumbersome kinetic contribution. The commutator of the potential of particle j with F_i is

$$[V(r_j,\rho),F_i]=\frac{1}{m}\vec{u}_i\cdot\vec{\nabla}\,V(r_j,\rho)\ . \tag{8}$$

The potential field depends on particle i explicitly when $i=j$ and implicitly through the ρ dependence on particle i, whether or not $i=j$. In the first case, the commutator is a single-particle operator on particle i, involving the gradient of the LDA static potential. The remaining commutator in Eq. (4) is nonzero only for the operator F_i, and the expectation value is

$$\begin{aligned}&\langle i\,|\,[F_i,m^{-1}\vec{u}_i\cdot\vec{\nabla}\,V]\,|\,i\rangle\\&\qquad=m^{-2}\int d^3r\,[\,\vec{\nabla}\cdot(\vec{u}\rho_i)]\,\vec{u}\cdot\vec{\nabla}\,V\ .\end{aligned} \tag{9}$$

When $i\neq j$ the expression in Eq. (8) is a two-body operator and the final commutator is nonzero only for F_j. The expectation of this may be expressed as

$$\begin{aligned}&\langle ij\,|\,[F_j,[V(r_j,\rho),F_i]]\,|\,ij\rangle\\&\qquad=\frac{1}{m^2}\int d^3r\int d^3r'[\,\vec{\nabla}\cdot(\vec{u}\rho_j)]_{r'}\frac{\delta V(r')}{\delta\rho(r)}(\vec{u}\cdot\vec{\nabla}\rho_i)_r\ .\end{aligned} \tag{10}$$

The functional derivative of the potential with respect to density in the above equation is nothing more than the two-particle interaction, which will have a Coulomb part and a zero range LDA part to account for exchange and correlations,

$$\frac{\delta V(r')}{\delta\rho(r)}=\frac{e^2}{|\,r-r'\,|}+v_{\mathrm{xc}}(\rho)\delta^{(3)}(\vec{r}-\vec{r}\,')\ . \tag{11}$$

The general formula for the kinetic contribution to the ω^3 sum may be found in Ref. 12. It is rather cumbersome so we shall not display it in full here but only for the restricted cases of pure multipole fields,

$$f_L(r)=r^L Y_{LM}(\hat{r})\ . \tag{12}$$

The Laplacian of the multipole field vanishes, eliminating many terms in the commutators. The first commutator of the kinetic energy with F_i is

$$[-\tfrac{1}{2}m^{-1}\vec{\nabla}_i^{\,2},F_i]=\frac{1}{m}\sum_{\mu,\nu}(\nabla_\mu u_\nu)\nabla_\mu\nabla_\nu\ . \tag{13}$$

The expectation value of the final commutator can then be expressed in the form

$$\begin{aligned}&\langle i\,|\,[F_i,[-\tfrac{1}{2}m^{-1}\vec{\nabla}_i^{\,2},F_i]]\,|\,i\rangle\\&\qquad=\frac{1}{m^2}\int d^3r\sum_{\mu,\nu,\lambda}(\nabla_\mu u_\lambda)(\nabla_\nu u_\lambda)\tau_{\mu\nu}\ ,\end{aligned} \tag{14}$$

where

$$\tau_{\mu\nu}=\frac{1}{m}\phi_i(r)(\overleftarrow{\nabla}-\vec{\nabla})_\mu(\overleftarrow{\nabla}-\vec{\nabla})_\nu\phi_i(r) \tag{15}$$

is the momentum flux tensor associated with the state i.

We can now construct an estimate for a collective oscillation such as the plasmon by the ratio of sum rules,

$$\omega_{\mathrm{sud}}^2=\frac{S_3}{S_1}=\frac{\langle 0\,|\,[[H^{\mathrm{LD}},f],[H^{\mathrm{LD}},[H^{\mathrm{LD}},f]]]\,|\,0\rangle}{\langle 0\,|\,[f,[H^{\mathrm{LD}},f]]\,|\,0\rangle}\ . \tag{16}$$

This estimate may be interpreted as a sudden limit because the frequency is that associated with the short-time restoring force following an impulsive perturbation. This is in contrast to the formula based on the polarizability sum,

$$\omega_{\mathrm{ad}}^2=\frac{S_1}{S_{-1}}\ , \tag{17}$$

which is an adiabatic estimate in the sense that the long-time behavior of the system governs the restoring force. As is clear from the derivation, the commutator ratio Eq. (16) must equal the ratio of integrals over the TDLDA response function if appropriate self-consistent potentials and densities are used to evaluate the ground-state expectation values. Equation (16) will be a good estimate of the plasmon peak frequency if the sum rules are exhausted at frequencies near the peak. We will now examine how well this is fulfilled in the case of the long-wavelength plasmon, where we set $f=z$. Then the kinetic contribution to S_3 vanishes completely. Physically, the oscillation is a pure translation of the electrons, which does not change their kinetic energy. From Eqs. (3), (4), (9), (10), and (16), we obtain the following formula for the plasmon:

$$\omega_{\mathrm{sud}}^2=\frac{4\pi}{3mN}(I_c+I_{\mathrm{xc}}+I_v)\ , \tag{18a}$$

where

$$I_c=\frac{4\pi}{3}e^2\int_0^\infty dr\,r^2\int_0^\infty dr'(r')^2\frac{d\rho}{dr}\left|_r\frac{r_<}{r_>^2}\frac{d\rho}{dr}\right|_{r'}, \tag{18b}$$

$$I_{xc}=\int_0^\infty dr\,r^2\left[\frac{d\rho}{dr}\right]^2 v_{xc}(\rho), \tag{18c}$$

$$I_v=-\int_0^\infty dr\,r^2\frac{d\rho}{dr}\frac{dV}{dr}. \tag{18d}$$

The first thing to check with Eq. (18) is that the Mie formula emerges when we neglect all terms except for the Coulomb interaction, and approximate the density distribution by that of a uniform sphere. We define the radius of the sphere as R, and the electron density as n_0. Then the transition density is

$$\frac{d\rho}{dr}=n_0\delta(r-R)=\frac{3N}{4\pi R^3}\delta(r-R) \tag{19}$$

and the Coulomb contribution to Eq. (18a) is evaluated as

$$I_c=I_0=\frac{4\pi}{3}e^2n_0^2R^3 \tag{20}$$

to obtain the Mie formula for the surface plasmon,

$$\omega^2=\frac{4\pi}{3mN}I_0=\frac{4\pi n_0e^2}{3m}. \tag{21}$$

In more realistic models there are three corrections to the Mie formula, arising from the two integrals that were neglected and from the smoothing out of the sharp density distribution in the Coulomb integral. From the general structure of the integrals we can infer that the jellium model will predict a red-shift of the plasmon frequency. To see this, we separate the self-consistent potential into an electronic part and the remainder from the background charge. The derivative of the electronic potential is evaluated by functional differention

$$\frac{dV}{dr}=\frac{\delta V}{\delta\rho}\frac{d\rho}{dr}.$$

We obtain two terms, arising from the Coulomb interaction and the LDA exchange interaction, which contribute to I_v to just cancel the integrals I_c and I_{xc}. The net contribution is just the force from the background charge. Since this is the field of a uniformly charged sphere, the maximum force is at $r=R$, and the integral is largest if $d\rho/dr$ is concentrated at R, as in the classical case. In the realistic case the average force weighted by $d\rho/dr$ will be lower.

Before displaying the results of numerical evaluation of the above integrals it is useful to derive analytic approximations to see the functional dependencies of the corrections. For this purpose the error function provides a convenient parametrization of the ground-state density, because ρ' is then a Gaussian. Specifically, we choose ρ and ρ' to be

$$\rho(r)=n_0\,\mathrm{erf}\left[\frac{R-r}{a}\right], \tag{22}$$

$$\frac{d\rho}{dr}=\frac{n_0}{a\sqrt{\pi}}\exp\left[-\frac{(r-R)^2}{a^2}\right], \tag{23}$$

where a is our surface thickness parameter. It is only necessary to expand all integrals in powers of $1/R$, keeping the lowest term.

For example, the integral over the Coulomb field is

$$I_c=\int_0^\infty dr\,r^2\int_0^\infty dr'(r')^2\frac{n_0^2}{a^2\pi}\exp\left[-\frac{(r-R)^2+(r'-R)^2}{a^2}\right]\frac{r_<}{r_>^2}\frac{4\pi}{3}e^2$$

$$=2\int_0^\infty dr\int_0^\infty dr'(r')^3\frac{n_0^2}{a^2\pi}\exp\left[-\frac{(r-R)^2+(r'-R)^2}{a^2}\right]\frac{4\pi}{3}e^2. \tag{24}$$

This integral may be approximately evaluated by transforming variables to $x=(1/\sqrt{2})(r-r')$ and $y=(1/\sqrt{2})(r+r'-2R)$ and extending the limits of integration to infinity,

$$I_c\approx 2\int_{-\infty}^{+\infty}dy\int_0^\infty dx\left[R+\frac{1}{\sqrt{2}}(y-x)\right]^3\frac{n_0^2}{a^2\pi}\exp\left[-\frac{x^2+y^2}{a^2}\right]\frac{4\pi}{3}e^2$$

$$=n_0^2\left[R^3-\frac{3R^2a}{\sqrt{2\pi}}+O(R)\right]\frac{4\pi}{3}e^2. \tag{25}$$

Thus, the finite surface thickness lowers the Coulomb integral by the following amount:

$$\frac{I_c}{I_0}\simeq 1-\frac{3a}{\sqrt{2\pi}R}. \tag{26}$$

We next consider the exchange integral, which is surface peaked due to the presence of $(d\rho/dr)^2$ in the integrand. The function $v_{xc}(\rho)$ is slowly varying so we may replace it by $v_{xc}(n_0/2)$ without serious error. The integral is then evaluated to give

$$I_{xc} \simeq \int_0^\infty dr\, r^2 \frac{n_0^2}{a^2\pi} \exp\left[-\frac{2(r-R)^2}{a^2}\right] v_{xc}(n_0/2)$$
$$= \frac{n_0^2 R^2}{a\sqrt{2\pi}} v_{xc}(n_0/2)\ . \tag{27}$$

The ratio of the exchange integral to the Coulomb is given by the following expression to lowest order in $1/R$:

$$\frac{I_{xc}}{I_0} \simeq \frac{3v_{xc}(n_0/2)}{4\pi\sqrt{2\pi}aR}\ . \tag{28}$$

This also produces a red-shift of the plasmon, because the exchange interaction is attractive. Notice that the correction increases with the sharpness of the surface and in fact diverges for an infinitely sharp surface. This may seem unphysical, but it must be remembered that the sum rule is based on a self-consistent ground state as an input density. If such a density becomes very sharp, it must be as a consequence of the potential becoming singular, and then the contribution (28) may not be evaluated separately from the contribution due to the static potential.

The last term in (18), the potential contribution, is proportional to the overlap of the transition density and the gradient of the static potential. We can estimate this using the same kind of parametrization for dV/dr that we used for $d\rho/dr$. We define a new surface thickness parameter a', and a parameter Δ for the displacement of the half-potential radius from the half-density radius. Then the potential integral is

$$I_v \approx n_0 R^2 V(0) \left[\frac{1}{\pi(a^2+a'^2)}\right]^{1/2} \exp\left[-\frac{\Delta^2}{a^2+a'^2}\right] \tag{29}$$

and the ratio to the Coulomb integral is

$$\frac{I_v}{I_0} \simeq \frac{3V(0)}{4\pi n_0 R e^2} \left[\frac{1}{\pi(a^2+a'^2)}\right]^{1/2} \exp\left[-\frac{\Delta^2}{a^2+a'^2}\right]\ . \tag{30}$$

Note that this contribution always results in a blue-shift to the plasmon. Also, we see that all three corrections to the Mie formula are proportional to $1/R$. The Mie formula will become exact for large spherical clusters.

We now apply these estimates to the plasmon in small sodium clusters. The self-consistent LDA theory of spherical sodium clusters with a jellium Hamiltonian is given in Ref. 13. We shall follow that work, using densities and potentials shown in Fig. 3 of Ref. 13. The jellium Hamiltonian is chosen with a background charge parameter $r_s=4$, which corresponds to an asymptotic electron density $n_0=0.003\,73$ in units of inverse Bohr radius cubed, i.e., $(0.0529\ \text{nm})^{-3}$. At this density the classical Mie resonance occurs at a frequency $\omega_p/3=0.2497$ Ry$=3.398$ eV. The TDLDA theory of the response for this Hamiltonian is reported in Ref. 4. In general, the TDLDA response shows a strong peak in the vicinity of the Mie frequency, but somewhat red-shifted from it. We quote in Table I the numerical values of the peak frequency for clusters of 20, 92, and 198 atoms. In the second and third columns of the table are given the sum-rule ratios calculated directly from the TDLDA response curves. The adiabatic frequency is necessarily lower than the sudden frequency, *but both are quite close together.* This shows that the dipolar surface plasmon is rather well localized in frequency. Although the sudden frequency is higher than the adiabatic, it still is red-shifted from the Mie frequency, as required by our earlier argument. The adiabatic frequency is the closer of the two estimates. The TDLDA response also shows a broad hump around the position of the volume plasmon in the larger systems, which can only acquire transition strength by coupling to the surface plasmon. The sudden estimate is much more sensitive to this higher frequency component, and thus produces a less accurate estimate of the surface-plasmon peak. It should be possible within the sum-rule approach to explicitly derive the coupling between the plasmons, but we shall not attempt that here.

We next evaluate the various integrals over the ground-state densities to calculate the sudden frequency. Using the ground-state data from Ref. 12, we evaluated Eqs. (18a)—(18c) for the same clusters. The results are shown in Table II. It may be seen that the corrections are largest for the smallest cluster, and scale approximately as $1/R$. Also note that there is a strong cancellation between the potential contribution and the finite surface thickness correction to the Coulomb integral. At a qualitative level, it may be said that the corrections are of opposite sign in the jellium model, leaving only a small residual effect. For a detailed discussion of the various competing effects in locating the surface plasmon the interested reader is referred to Ref. 4. It should also be noted as a consistency check on all of the computations, that the sudden frequency as calculated explicitly from the response agrees with the integral formula to 1%, which is the limit of our numerical accuracy.[14]

Finally, we shall apply the error-function approximation to the density to make approximate estimates of the

TABLE I. Surface-plasmon frequency in sodium clusters ($r_s=4$), extracted from the TDLDA response for various particle numbers N. Frequencies are given as a fraction of the Mie value, $\omega_p/3=0.2497$ Ry$=3.4$ eV.

N	ω (peak)	ω (adiabatic)	ω (sudden)
20	0.885	0.877	0.940
92	0.893	0.922	0.964
198	0.893	0.915	0.951

TABLE II. Contributions to the shift in surface-plasmon frequency. The integrals in Eqs. (18a)—(18c) are given for various size clusters, expressed as a percentage of the classical Coulomb integral, Eq. (20). The values obtained from the analytic expressions Eqs. (26), (28), and (30) for $N=198$ are shown in the last row in parentheses.

N	$\frac{I_c-I_0}{I_0}$	$\frac{I_{xc}}{I_0}$	$\frac{I_v}{I_0}$
20	−18%	−15%	+18%
92	−10	−9	+11
198	−9	−7	+8
	(−11)	(−5)	(+9)

integrals. A good fit $d\rho/dr$ for $N=198$ is obtained with the function Eq. (20) having a surface thickness $a=2.14$ a.u. For the potential, we fit the peak region of dV/dr, using the following parameters in Eq. (30): $V=0.29$ Ry, $a'=1.66$ a.u. and $\Delta=1.2$ a.u. Finally, we mention that the value of the LDA interaction to be used in Eq. (28) is $v_{xc}(n_0/2)=52$ Ry/a.u.[3] The analytic approximations Eqs. (26), (28), and (30) then give values for the integrals quoted in parentheses in Table II. We see that the estimates are quite close, so it should be possible to treat the dipolar collective features of other systems (other particle numbers and r_s values; ellipsoidal distortions, etc.) just using simple properties of the density and potential that can be subsumed in a few parameters.

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