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Optical sum rules for inhomogeneous electron systems

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Optical properties can be determined by either the transverse dielectric function $\epsilon_\perp(\mathbf{q},\omega)$ or the longitudinal dielectric function $\epsilon_\parallel(\mathbf{q},\omega)$ in the long-wavelength limit, i.e., $\mathbf{q}\to\mathbf{0}$. By expressing $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ in terms of density response functions, we calculate the third, fifth, and seventh frequency moments of $\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ in addition to the first frequency moment, the well-known conductivity sum rule. While the third and fifth moments reflect the inhomogeneity of the system, correlation effects contribute explicitly to the seventh moment. In addition, the frequency moments of $\mathrm{Im}[-1/\epsilon_\parallel(\mathbf{q}\to\mathbf{0},\omega)]$ can be constructed from these moments. The dielectric functions evaluated in a self-consistent field (SCF) approximation, such as the random phase approximation (RPA) or the adiabatic local density approximation (ALDA), satisfy the first three odd frequency moments provided the single particle states on which the SCF calculation is based are calculated in the corresponding SCF approximation. The seventh frequency moment constitutes a severe requirement that $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ evaluated in the RPA or the ALDA cannot satisfy. This is demonstrated for nearly free electron systems.

I. INTRODUCTION

Sum rules are defined as frequency moments of the dissipative part of response functions. Both the transverse and longitudinal dielectric functions are defined by response functions. The transverse dielectric function $\epsilon_\perp(\mathbf{q},\omega)$ is related to the current-current response function, while the longitudinal dielectric function $\epsilon_\parallel(\mathbf{q},\omega)$ can be expressed by the density-density response function. As shown for isotropic systems by Ambegaokar and Kohn[1] in the long wavelength or optical limit, i.e., $\mathbf{q}\to\mathbf{0}$, $\epsilon_\perp(\mathbf{q},\omega)=\epsilon_\parallel(\mathbf{q},\omega)$. We make use of this property when we evaluate sum rules for the energy loss function $\mathrm{Im}[-1/\epsilon_\parallel(\mathbf{q},\omega)]$ for $\mathbf{q}\to\mathbf{0}$.

Sum rules are useful properties of response functions from both the experimental and the theoretical points of view. They determine the high frequency behavior or, more precisely, the frequency moments are the expansion coefficients of the asymptotic high frequency expansion.

In principle, the evaluation of response functions of a system requires knowledge of the exact eigenstates of the unperturbed system. In most cases, these cannot be calculated and approximations are unavoidable. On the other hand, sum rules can be evaluated exactly in some cases. They can be used not only as a testing ground for the quality of approximations involved in calculations of response function, but are also used as guides for the construction of approximations.

Most microscopic calculations are performed with one of the variants of the self-consistent field (SCF) approximations, such as the random phase approximation (RPA) or the adiabatic local density approximation (ALDA) of density functional theory. In these calculations, self-consistency enters at two levels. First of all, the SCF approximation is based on the response function of (seemingly) independent particles, and the effective potential that determines the independent particle states must be determined self-consistently. Second, the effective dynamical potential to which the independent particles respond has to be determined self-consistently. Sum rules demonstrate that the two self-consistency procedures are not independent of each other. Past RPA type calculations of the dielectric function were often based inconsistently on band structure calculations (LDA), such as the $X\alpha$ method. We show that sum rules are violated in this case. A consistent RPA calculation must be based on single particle states evaluated in the Hartree approximation.

Approximations affect different properties in different ways. For example, we show that a consistent ALDA calculation of the optical properties, i.e., $1/\epsilon_\parallel(\mathbf{q}\to\mathbf{0},\omega)$, satisfies the first, third, and fifth frequency moment sum rules, whereas for $\mathbf{q}\neq\mathbf{0}$ the third frequency moment is violated and thus an accurate determination of the plasmon dispersion cannot be expected within the ALDA even for small q.

The different behavior can be understood as follows. If a weak external periodic perturbation with wave vector $\mathbf{q}$ acts on the system, the response will depend on correlations over distances equal to or larger than the wavelengths $\lambda=2\pi/q$ with $q=|\mathbf{q}|$. In the optical limit ($\lambda\to\infty$), correlations are expected to vanish. However, this is true only if the system is homogeneous. In inhomogeneous systems, regions of different density respond differently to a long-wavelength perturbation, such as visible light invoking ultimately short-wavelength fluctuations and correlations. As a result, we are able to evaluate the third and fifth frequency moments in terms of the inhomogeneous electron density and of the external potential that causes the inhomogeneity. The seventh frequency moment, however, explicitly involves correlations.

As expected from the above discussion for the jellium model, all frequency moments of $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ and of

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$\mathrm{Im}[-1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)]$ are known, as we briefly indicate. For sufficiently high frequencies, we have

$$\epsilon_{\perp}(\omega)\equiv\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)=\mathrm{Re}\,\epsilon_{\perp}(\omega)=1-\frac{\omega_p^{0^2}}{\omega^2}\quad,\tag{1}$$

where $\omega_p^{0^2}=4\pi n_0e^2/m$ is determined by n_0, the density of the electrons. Because $\epsilon_{\perp}(\omega)$ satisfies Kramers-Kronig relations, we have for large ω,

$$\begin{aligned}\mathrm{Re}\,\epsilon_{\perp}(\omega)&=1+P\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{\mathrm{Im}\epsilon_{\perp}(\omega')}{\omega'-\omega}\\&=1-\sum_{n=1}^{\infty}\frac{1}{\omega^{2n}}I^{(2n-1)}\quad,\end{aligned}\tag{2}$$

where P denotes the principal value. $I^{(2n-1)}$ is the frequency moment of order $(2n-1)$ of $\mathrm{Im}\,\epsilon_{\perp}(\omega)$, i.e.,

$$I^{(2n-1)}=P\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^{2n-1}\mathrm{Im}\,\epsilon_{\perp}(\omega)\quad.\tag{3}$$

Only odd moments contribute, because $\mathrm{Im}\,\epsilon_{\perp}(\omega)$ is an odd function of ω. By comparison with (1), we see that

$$\begin{aligned}I^{(1)}&=\omega_p^{0^2}\ ,\\I^{(2n-1)}&=0\quad\text{for}\quad n>1.\end{aligned}\tag{4}$$

This result (4) is also obtained by inserting

$$\mathrm{Im}\,\epsilon_{\perp}(\omega)=\pi\omega_p^{0^2}\frac{\delta(\omega)}{\omega}\tag{5}$$

into (3). We make use of $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)=\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$ and have for high frequencies

$$\frac{1}{\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)}=\frac{1}{1-\omega_p^{0^2}/\omega^2}=1+\sum_{n=1}^{\infty}\frac{\omega_p^{0^{2n}}}{\omega^{2n}}\ ,\tag{6}$$

and because of the Kramers-Kronig relations,

$$\begin{aligned}\frac{1}{\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)}&=1-P\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{1}{\omega'-\omega}\\&\quad\times\mathrm{Im}\Big[-\frac{1}{\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega')}\Big]\\&\equiv1+\sum_{n=1}^{\infty}\frac{1}{\omega^{2n}}F^{(2n-1)}\quad.\end{aligned}\tag{7}$$

We find by comparison with (6)

$$F^{(2n-1)}=\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^{2n-1}\mathrm{Im}\Big[-\frac{1}{\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)}\Big]=\omega_p^{0^{2n}}\tag{8}$$

for $n=1,2,3,\ldots$, which also follows when

$$\mathrm{Im}\left[-\frac{1}{\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)}\right]=\frac{\pi}{2}\omega_p^0[\delta(\omega-\omega_p^0)-\delta(\omega+\omega_p^0)]\tag{9}$$

is inserted into (8).

These simple results are valuable as limiting cases for inhomogeneous systems when the external (crystal) potential becomes constant. Of course, the third frequency moment sum rule for $\mathbf{q}\neq\mathbf{0}$ for the jellium model

$$F^{(3)}(\mathbf{q})=\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^3\mathrm{Im}\left[-\frac{1}{\epsilon_{\|}(\mathbf{q},\omega)}\right],\tag{10}$$

which is known in the literature,[2] reduces to $\omega_p^{0^4}$ for $\mathbf{q}\to\mathbf{0}$.

An outline of the paper follows. In Sec. II, $\epsilon_{\perp}(\mathbf{q},\omega)$ and $\epsilon_{\|}(\mathbf{q},\omega)$ are defined in terms of current-current and density-density response functions, respectively. We then express $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)$ in terms of density-density response functions and evaluate the third, fifth, and seventh frequency moments of $\mathrm{Im}\,\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)$ for inhomogeneous systems. For simplicity, we consider ideal crystals of cubic symmetry and neglect lattice dynamical effects. Finally, by using $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)=\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$, we obtain a high frequency expansion of $1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$ by inverting the high frequency expansion of $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)$. The expansion coefficients that we obtain in this way are the first four odd frequency moments of $\mathrm{Im}[-1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)]$.

The seventh moment is very complicated. For nearly free electron systems, however, the seventh moment can be expressed to second order in the weak (local) pseudopotential in terms of third moments of the jellium density response function $\chi''(G,\omega)$, where $\chi(G,\omega)=\chi'(G,\omega)+i\chi''(G,\omega)$ and $\mathbf{G}$ are reciprocal lattice vectors with $G=|\mathbf{G}|$. The third frequency moment of $\chi''(G,\omega)$ is very well known[2] and, to the extent that many ground state properties of the jellium model have been determined in recent years with increasing accuracy by Monte Carlo (MC) simulations,[3–6] their numerical values are accurately known.

We use extensive literature on the theory of the density response function of the jellium model, discussing (Sec. III) various approximate forms for $\chi(G,\omega)$. This section is devoted to a study of the extent to which $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)$, evaluated in a SCF approximation, satisfies the exact sum rules.

Furthermore, in the SCF approximation, the dielectric function of inhomogeneous systems can be decomposed into two contributions, a term accounting for direct interband and intraband transitions and a term that arises from the coupling of long- and short-wavelength fluctuations, as a consequence of the inhomogeneity. This term is known as local field corrections (lfc). Its evaluation is very cumbersome and the neglect of this term is known as the Ehrenreich-Cohen[7] approximation. For quasihomogeneous systems, such as simple metals, its contribution is expected to be small. In any case, it is desirable to have some *a priori* means to judge their importance and we show that sum rules for the lfc provide such an estimate. A summary and conclusion are presented in Sec. IV.

II. SUM RULES AND ASYMPTOTIC EXPANSIONS FOR $\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ AND $\mathrm{Im}[-1/\epsilon_\parallel(\mathbf{q}\to\mathbf{0},\omega)]$

A. Definitions of $\epsilon_\perp(\mathbf{q},\omega)$ and $\epsilon_\parallel(\mathbf{q},\omega)$

Consistent with their use in macroscopic Maxwell's equations, $\epsilon_\perp(\mathbf{q},\omega)$ and $\epsilon_\parallel(\mathbf{q},\omega)$ are defined[8] by

$$\epsilon_\perp(\mathbf{q},\omega) = 1 - \frac{\omega_p^{0^2}}{\omega^2} + \frac{4\pi e^2}{\omega^2}\boldsymbol{\eta}\cdot\chi_{\mathbf{jj}}(\mathbf{q},\mathbf{q};\omega)\cdot\boldsymbol{\eta} \qquad (11)$$

and

$$\frac{1}{\epsilon_\parallel(\mathbf{q},\omega)} = 1 - \frac{4\pi e^2}{q^2}\chi_{nn}(\mathbf{q},\mathbf{q};\omega) \quad . \qquad (12)$$

In (11), $\boldsymbol{\eta}$ is the polarization vector of the transverse field, so that $\boldsymbol{\eta}\cdot\mathbf{q} = 0$. $\chi_{\mathbf{jj}}(\mathbf{q},\mathbf{q};\omega)$ and $\chi_{nn}(\mathbf{q},\mathbf{q};\omega)$ are the current-current and density-density response functions defined in linear response theory at $T = 0$ K by

$$\chi_{\mathbf{jj}}(\mathbf{q},\mathbf{q}';\omega) = \frac{1}{\Omega}\sum_\nu\left\{\frac{\langle 0|\hat{\mathbf{j}}_{\mathbf{q}}|\nu\rangle\langle\nu|\hat{\mathbf{j}}_{-\mathbf{q}'}|0\rangle}{E_\nu - E_0 - \hbar\omega - i\delta} - \frac{\langle 0|\hat{\mathbf{j}}_{-\mathbf{q}'}|\nu\rangle\langle\nu|\hat{\mathbf{j}}_{\mathbf{q}}|0\rangle}{E_0 - E_\nu - \hbar\omega - i\delta}\right\}. \qquad (13)$$

Ω is the volume of the system and

$$\hat{\mathbf{j}}_{\mathbf{q}} = \frac{1}{2m}\sum_\alpha\{\mathbf{p}_\alpha e^{-i\mathbf{q}\cdot\mathbf{r}_\alpha} + e^{-i\mathbf{q}\cdot\mathbf{r}_\alpha}\mathbf{p}_\alpha\} \qquad (14)$$

is the Fourier transform of the current operator. $\chi_{nn}(\mathbf{q},\mathbf{q};\omega)$ is obtained by replacing the current operators in (13) by the density operators $\hat{n}_{\mathbf{q}}$, $\hat{n}_{-\mathbf{q}'}$. They are defined by

$$\hat{n}_{\mathbf{q}} = \sum_\alpha e^{-i\mathbf{q}\cdot\mathbf{r}_\alpha}. \qquad (15)$$

$E_\nu, |\nu\rangle$ are the eigenstates of the unperturbed system, i.e.,

$$\mathcal{H}_0|\nu\rangle = E_\nu|\nu\rangle \ , \qquad (16)$$

with

$$\mathcal{H}_0 = \sum_\alpha\left(\frac{\mathbf{p}_\alpha^2}{2m} + V(\mathbf{r}_\alpha)\right) + \frac{e^2}{2}\sum_{\substack{\alpha,\alpha'\\(\alpha\neq\alpha')}}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_{\alpha'}|}. \qquad (17)$$

$E_0, |0\rangle$ denotes the ground state of the system. In general,

$$\chi_{AA}(\mathbf{q},\mathbf{q}';\omega) = \chi'_{AA}(\mathbf{q},\mathbf{q}';\omega) + i\chi''_{AA}(\mathbf{q},\mathbf{q}';\omega) \quad , \qquad (18)$$

where A can be either n or $\mathbf{j}$. The reactive part $\chi'_{AA}(\mathbf{q},\mathbf{q}';\omega)$ and the dissipative part $\chi''_{AA}(\mathbf{q},\mathbf{q}';\omega)$ are related by Kramers-Kronig relations and, as a consequence, the dissipative part satisfies the relation

$$\frac{1}{\Omega}\langle 0|[A_{\mathbf{q}}(t), A_{-\mathbf{q}'}(t')]|0\rangle = \hbar\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\chi''_{AA}(\mathbf{q},\mathbf{q}';\omega)e^{-i\omega(t-t')}. \qquad (19)$$

Sum rules as frequency moments of order n are obtained by differentiating (19) n-p times with respect to t, p times with respect to t' and taking the limit $t\to t'$ at the end, i.e.,

$$\frac{1}{\Omega}\lim_{t\to t'}\left\langle 0\left|\left[\left(i\hbar\frac{\partial}{\partial t}\right)^{n-p}A_{\mathbf{q}}(t), \left(-i\hbar\frac{\partial}{\partial t'}\right)^{p}A_{-\mathbf{q}'}(t')\right]\right|0\right\rangle = \hbar^{n+1}\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^n\chi''_{AA}(\mathbf{q},\mathbf{q}';\omega), \qquad (20)$$

where $p\leq n$ and for two operators A,B $[A,B] = AB - BA$. These sum rules connect the dynamical behavior of the system described by $\chi''_{AA}(\mathbf{q},\mathbf{q}';\omega)$ with ground state properties. This is obvious by the inspection of the left-hand side of (20), and sum rules are useful if the latter can be evaluated in terms of some known quantities.

It follows from (11) and (12) that sum rules can be formulated for $\epsilon_\perp(\mathbf{q},\omega)$ and $1/\epsilon_\parallel(\mathbf{q},\omega)$. Very well known examples are the conductivity and f sum rules, which are the first frequency moments,

$$I^{(1)} \equiv \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega\,\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega) = \omega_p^{0^2}, \qquad (21)$$

$$F^{(1)} \equiv \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega\,\mathrm{Im}\left[\frac{-1}{\epsilon_\parallel(\mathbf{q},\omega)}\right] = \omega_p^{0^2}. \qquad (22)$$

Here, the average electron density n_0 determines $\omega_p^{0^2} = 4\pi e^2 n_0/m$.

B. $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ in terms of density response functions

In order to obtain higher order frequency moment sum rules for $\epsilon_\perp(\mathbf{q},\omega)$ and for $1/\epsilon_\parallel(\mathbf{q},\omega)$ in the optical limit $\mathbf{q}\to\mathbf{0}$, we rewrite $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ in terms of density response functions. Because of the transversality condition $\boldsymbol{\eta}\cdot\mathbf{q} = 0$, $\boldsymbol{\eta}\cdot\hat{\mathbf{j}}_{\mathbf{q}}$ commutes with the Coulomb interaction of the electrons in $\mathcal{H}_0$ [last term in (17)] and thus

$$\begin{aligned}\lim_{\mathbf{q}\to 0}(E_0 - E_\nu)\langle 0|\boldsymbol{\eta}\hat{\mathbf{j}}_{\mathbf{q}}|\nu\rangle &= \lim_{q\to 0}\langle 0|[\mathcal{H}_0, \boldsymbol{\eta}\hat{\mathbf{j}}_{\mathbf{q}}]|\nu\rangle \\ &= \langle 0|[\mathcal{H}_0, \boldsymbol{\eta}\cdot\hat{\mathbf{j}}_{\mathbf{0}}]|\nu\rangle \\ &= -\frac{\hbar}{im}\left\langle 0\left|\sum_\alpha\boldsymbol{\eta}\nabla_\alpha V(\mathbf{r}_\alpha)\right|\nu\right\rangle \\ &= \sum_{\mathbf{G}\neq\mathbf{0}}\frac{\hbar(\boldsymbol{\eta}\cdot\mathbf{G})}{m}V_{-\mathbf{G}}\langle 0|\hat{n}_{\mathbf{G}}|\nu\rangle, \end{aligned} \qquad (23)$$

where in the last step an ideal crystal is assumed. Then $V(\mathbf{r}) = \sum_{\mathbf{G}}V_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{r}}$ is periodic and $\mathbf{G}$ are reciprocal lattice vectors.

The existence of a gap in insulators means that electronic excitations are not possible for $\omega \to 0$. Then, using (23), $\mathrm{Im}\epsilon_\perp(\omega) \equiv \mathrm{Im}\epsilon_\perp(\mathbf{q} \to \mathbf{0}, \omega)$ can be rewritten in the form

$$\begin{aligned}\mathrm{Im}\epsilon_\perp(\omega) &= \frac{4\pi^2 e^2}{\omega^2}\frac{1}{\Omega}\sum_\nu |\langle 0|\boldsymbol{\eta}\hat{\mathbf{j}}_0|\nu\rangle|^2 \delta(E_\nu - E_0 - \hbar\omega)\\ &= \frac{4\pi e^2}{m^2\omega^4}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\cdot\mathbf{G})(\mathbf{G}'\cdot\boldsymbol{\eta})V_{-\mathbf{G}}V_{\mathbf{G}'}\chi''\\ &\quad\times(\mathbf{G},\mathbf{G}';\omega) \quad . \end{aligned} \tag{24}$$

Here and in the remainder of the paper, we drop the indices nn, which denote the density-density response function, i.e., $\chi_{nn}(\mathbf{G},\mathbf{G}';\omega) \equiv \chi(\mathbf{G},\mathbf{G}';\omega)$. The conductivity sum rule (21) and application of Kramers-Kronig relations yield

$$\begin{aligned}\omega_p^{0^2} &= \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega\mathrm{Im}\epsilon_\perp(\omega)\\ &= \frac{4\pi e^2}{m}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}V_{\mathbf{G}'}\frac{1}{2}\frac{\partial^2}{\partial\omega^2}\\ &\quad\times\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}\end{aligned} \tag{25}$$

and

$$\begin{aligned}\mathrm{Re}\epsilon_\perp(\omega) &= 1 - \frac{\omega_p^{0^2}}{\omega^2}\\ &\quad+\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}V_{\mathbf{G}'}[\chi'(\mathbf{G},\mathbf{G}';\omega)\\ &\quad-\chi'(\mathbf{G},\mathbf{G}';0)].\end{aligned} \tag{26}$$

At first sight, the form of $\mathrm{Re}\epsilon_\perp(\omega)$ is surprising for an insulator considering the small ω behavior. However, expanding $\chi'(\mathbf{G},\mathbf{G}';\omega)$ in a Taylor series for small ω

$$\begin{aligned}\chi'(\mathbf{G},\mathbf{G}';\omega) &= \chi'(G,G';0) + \frac{\omega^2}{2!}\frac{\partial^2}{\partial\omega^2}\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}\\ &\quad+\frac{\omega^4}{4!}\frac{\partial^4}{\partial\omega^4}\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}+\cdots\end{aligned} \tag{27}$$

proves that $\epsilon_\perp(\omega)$ exhibits the appropriate behaviour of an insulator, namely for $\omega \to 0$

$$\begin{aligned}\epsilon_\perp(\omega) &= 1 + \frac{4\pi e^2}{m^2}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}\\ &\quad\times V_{\mathbf{G}'}\frac{1}{4!}\frac{\partial^4}{\partial\omega^4}\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}+\cdots\\ &= 1 + P\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\frac{1}{\omega}\mathrm{Im}\epsilon_\perp(\omega)+\cdots\\ &= \epsilon_\perp(0)+\cdots .\end{aligned} \tag{28}$$

For an insulator, therefore, we have

$$\begin{aligned}\epsilon_\perp(\omega) &= 1 - \frac{\omega_p^{0^2}}{\omega^2} + \frac{4\pi e^2}{\omega^4 m^2}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}\\ &\quad\times V_{\mathbf{G}'}[\chi(\mathbf{G},\mathbf{G}';\omega)-\chi(\mathbf{G},\mathbf{G}';0)] \quad .\end{aligned} \tag{29}$$

A form very similar to (29) can be derived for metals, with an important modification. For the jellium model of a metal,

$$\mathrm{Im}\epsilon_\perp(\omega) = \pi\frac{\omega_p^2}{\omega}\delta(\omega) \tag{30}$$

exhausts the conductivity sum rule, where $\omega_p^2 = 4\pi n_v e^2/m$ is determined by the valence electron density n_v. In a real crystalline metal, there is a contribution from interband transitions in addition to the intraband term (30). The latter must be reduced appropriately to allow for the additional contribution in the conductivity sum rule. As we shall show below, the reduction factor is m/m_{opt}, where m_{opt} is the optical mass. Writing $\omega_p^2 = \omega_p^{0^2} n_v/n_0$, we have for a metal

$$\begin{aligned}\mathrm{Im}\epsilon_\perp(\omega) &= \pi\omega_p^{0^2}\frac{n_v}{n_0}\frac{m}{m_{\mathrm{opt}}}\frac{\delta(\omega)}{\omega}\\ &\quad+\frac{4\pi e^2}{m^2\omega^4}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}V_{\mathbf{G}'}\chi''\\ &\quad\times(\mathbf{G},\mathbf{G}';\omega).\end{aligned} \tag{31}$$

The conductivity sum rule then provides a general definition of m_{opt}

$$\begin{aligned}1 - \frac{n_v}{n_0}\frac{m}{m_{\mathrm{opt}}} &= \frac{1}{n_0 m}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}\\ &\quad\times V_{\mathbf{G}'}\frac{1}{2}\frac{\partial^2}{\partial\omega^2}\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}.\end{aligned} \tag{32}$$

Using (31), $\mathrm{Re}\epsilon_\perp(\omega)$ as obtained by Kramers-Kronig is identical in form to (26). For the small ω behavior, we find with the help of (32) typical metallic behavior

$$\begin{aligned}\mathrm{Re}\epsilon_\perp(\omega) &= -\frac{\omega_p^{0^2}}{\omega^2}\frac{m}{m_{\mathrm{opt}}}\frac{n_v}{n_0}\\ &\quad+\frac{4\pi e^2}{m^2}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}\\ &\quad\times V_{\mathbf{G}'}\frac{1}{4!}\frac{\partial^4}{\partial\omega^4}\chi'(\mathbf{G},\mathbf{G}';\omega)|_{\omega=0}\\ &= -\frac{a}{\omega^2}+b.\end{aligned} \tag{33}$$

In summary, for a metal, we have

$$\begin{aligned}\epsilon_\perp(\omega) &= 1 - \frac{\omega_p^{0^2}}{\omega^2} + i\pi\omega_p^{0^2}\frac{m}{m_{\mathrm{opt}}}\frac{n_v}{n_0}\frac{\delta(\omega)}{\omega}\\ &\quad+\frac{4\pi e^2}{m^2\omega^4}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta})V_{-\mathbf{G}}V_{\mathbf{G}'}\\ &\quad\times[\chi(\mathbf{G},\mathbf{G}';\omega)-\chi(\mathbf{G},\mathbf{G}';0)].\end{aligned} \tag{34}$$

Parts of the results presented in this subsection were derived by various authors.[9–11]

C. The third and fifth frequency moment sum rules

We are now in a position to obtain some additional sum rules for $\epsilon_\perp(\omega)$. The third frequency moment sum rule can be calculated either from the original definition of $\epsilon_\perp(\omega)$ or from (29) or (34), respectively. Following Hopfield,[12] we obtain

$$I^{(3)} \equiv \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega^3 \mathrm{Im}\epsilon_\perp(\omega) = \frac{4\pi e^2}{\hbar^2} \frac{1}{\Omega} \times \langle 0|[\boldsymbol{\eta}\hat{\mathbf{j}}_0, [\mathcal{H}_0, \hat{\mathbf{j}}_0 \boldsymbol{\eta}]]|0\rangle = -\frac{4\pi e^2}{m^2} \sum_{\mathbf{G}\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})^2 V_{-\mathbf{G}} n_{\mathbf{G}}, \tag{35}$$

where $n_{\mathbf{G}} = \langle 0|\hat{n}_{\mathbf{G}}|0\rangle/\Omega$. Using (29) and (34), we obtain

$$I^{(3)} = \frac{4\pi e^2}{m^2} \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\mathbf{G}'\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta}) V_{-\mathbf{G}} V_{\mathbf{G}'} P \times \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \frac{1}{\omega} \chi''(\mathbf{G}, \mathbf{G}'; \omega) = \frac{4\pi e^2}{m^2} \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\mathbf{G}'\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta}) V_{-\mathbf{G}} V_{\mathbf{G}'} \chi'(\mathbf{G}, \mathbf{G}'; 0). \tag{36}$$

It follows from (35) and (36) that

$$(\boldsymbol{\eta}\mathbf{G}) n_{\mathbf{G}} = -\sum_{\mathbf{G}'\neq\mathbf{0}} \chi(\mathbf{G}, \mathbf{G}'; 0)(\boldsymbol{\eta}\mathbf{G}') V_{\mathbf{G}'} \quad . \tag{37}$$

In this way, $n_{\mathbf{G}}$ is uniquely determined by the crystal potential and the static density response function. Although the important result (37) has some similarity to a linear response relation, this is not the case, because $\chi(\mathbf{G}, \mathbf{G}'; 0)$ itself depends in general on $V(\mathbf{r})$. It reduces to a linear response relation in the weak pseudopotential limit when $\chi(\mathbf{G}, \mathbf{G}'; \omega)$ can be replaced by $\delta_{\mathbf{G}\mathbf{G}'} \chi(G, \omega)$, where $\chi(G, \omega)$ is the density response function of the jellium model.

With the aid of (37), we rewrite (34) and obtain

$$\epsilon_\perp(\omega) = 1 - \frac{{\omega_p^0}^2}{\omega^2} + i\pi {\omega_p^0}^2 \frac{m}{m_{\mathrm{opt}}} \frac{n_v}{n_0} \frac{\delta(\omega)}{\omega} + \frac{4\pi e^2}{m^2 \omega^4} \sum_{\mathbf{G}\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})^2 V_{-\mathbf{G}} n_{\mathbf{G}} + \frac{4\pi e^2}{m^2 \omega^4} \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\mathbf{G}'\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta}) V_{-\mathbf{G}} V_{\mathbf{G}'} \chi \times (\mathbf{G}, \mathbf{G}'; \omega), \tag{38}$$

which includes the insulator (29) for $m/m_{\mathrm{opt}} = 0$.

The fifth frequency moment of $\mathrm{Im}\epsilon_\perp(\omega)$ is derived using the f sum rule for $\chi(\mathbf{G}, \mathbf{G}'; \omega)$, i.e.,

$$M^{(1)}(\mathbf{G}, \mathbf{G}') \equiv \int_{\infty}^{+\infty} \frac{d\omega}{\pi} \omega \chi''(\mathbf{G}, \mathbf{G}'; \omega) = \frac{1}{\hbar^2} \frac{1}{\Omega} \langle 0|[[\hat{n}_{\mathbf{G}}, \mathcal{H}_0], \hat{n}_{-\mathbf{G}'}]|0\rangle = \frac{\mathbf{G} \cdot \mathbf{G}'}{m} n_{\mathbf{G}-\mathbf{G}'} \ , \tag{39}$$

and we find

$$I^{(5)} = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega^5 \epsilon_\perp(\omega) = \frac{4\pi e^2}{m^3} \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\mathbf{G}'\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})(\mathbf{G} \cdot \mathbf{G}')(\mathbf{G}'\boldsymbol{\eta}) V_{-\mathbf{G}} V_{\mathbf{G}'} n_{\mathbf{G}-\mathbf{G}'}. \tag{40}$$

The third and fifth frequency moments are measures of the inhomogeneity of the system and vanish as expected if $V_{\mathbf{G}} \to 0$.

D. The seventh frequency moment sum rule

According to (31), we have

$$I^{(7)} \equiv \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega^7 \mathrm{Im}\epsilon_\perp(\omega) = \frac{4\pi e^2}{m^2} \sum_{\mathbf{G}\neq\mathbf{0}} \sum_{\mathbf{G}'\neq\mathbf{0}} (\boldsymbol{\eta}\mathbf{G})(\mathbf{G}'\boldsymbol{\eta}) V_{-\mathbf{G}} V_{\mathbf{G}'} M^{(3)}(\mathbf{G}, \mathbf{G}'), \tag{41}$$

where $M^{(3)}(\mathbf{G}, \mathbf{G}')$ is the third frequency moment of $\chi''(\mathbf{G}, \mathbf{G}'; \omega)$.

$$M^{(3)}(\mathbf{G}, \mathbf{G}') \equiv \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} \omega^3 \chi''(\mathbf{G}, \mathbf{G}'; \omega) = \frac{1}{\hbar^4} \frac{1}{\Omega} \langle 0|[[\hbar\mathbf{G} \cdot \hat{\mathbf{j}}_{\mathbf{G}} \, , \mathcal{H}_0], \hbar\mathbf{G}' \hat{\mathbf{j}}_{-\mathbf{G}'}]|0\rangle. \tag{42}$$

Formally, it is not difficult to evaluate the commutators in (42), but its numerical evaluation for arbitrary crystals is presently very difficult. The formal result is presented in Appendix A. Here, we restrict ourselves to nearly free electron (NFE) systems and replace $M^{(3)}(\mathbf{G}, \mathbf{G}')$ by $\delta_{\mathbf{G},\mathbf{G}'} \cdot M^{(3)}(G)$, where $M^{(3)}(G)$ is the third frequency moment[2] of $\chi''(G, \omega)$, the dissipative part of the density response function $\chi(G, \omega)$ of the jellium model.

$$M^{(3)}(G) = \frac{n_0 G^2}{m} \left\{ \left(\frac{\hbar G^2}{2m}\right)^2 + 4\left(\frac{G^2}{2m}\right) \langle E_{\mathrm{kin}} \rangle + \omega_p^2 [1 - I(G)] \right\}. \tag{43}$$

$\langle E_{\mathrm{kin}} \rangle = \langle 0| \sum_j (\mathbf{P}_j^2/2m)|0\rangle/N$ is the average kinetic energy per electron, when N is the number of electrons. It consists of the kinetic energy of independent electrons and of a correlation contribution,

$$\langle E_{\mathrm{kin}} \rangle = \langle E_{\mathrm{kin}} \rangle_0 - \frac{\partial}{\partial r_s} [r_s \varepsilon_c(r_s)] \quad , \tag{44}$$

where $\langle E_{\mathrm{kin}} \rangle_0 = 3\varepsilon_F^0/5$. ε_F^0 is the free electron Fermi energy and $\varepsilon_c(r_s)$ is the correlation energy per particle as a function of the density parameter r_s [$4\pi(r_s a_0)^3/3 = n_0^{-1}$, a_0: Bohr radius]. $\varepsilon_c(r_s)$ is known in the metallic regime from MC simulations.[3–5] Correlation effects including exchange arising from the Coulomb interaction are accounted for by

$$I(G) = -\frac{1}{N} \sum_{\mathbf{k}\neq 0, \mathbf{k}\neq \mathbf{G}} \frac{\mathbf{k}\cdot\mathbf{G}}{G^2} K(\mathbf{G},\mathbf{k})[S(|\mathbf{G}-\mathbf{k}|)-1] \quad , \tag{45}$$

with

$$K(\mathbf{G},\mathbf{k}) = \frac{\mathbf{k}\cdot\mathbf{G}}{k^2} + \frac{\mathbf{G}(\mathbf{G}-\mathbf{k})}{|\mathbf{G}-\mathbf{k}|^2} \tag{46}$$

and the static structure factor

$$S(q) = \frac{1}{N}\langle 0|\hat{n}_{\mathbf{q}}\hat{n}_{-\mathbf{q}}|0\rangle. \tag{47}$$

$S(q)$ is known from MC simulations[5] and $I(G)$ was first calculated by Iwamoto *et al.*[13]

E. Sum rules for $\mathrm{Im}[-1/\epsilon_{\|}(\mathbf{q}\to \mathbf{0},\omega)]$

The asymptotic high frequency expansion of $\epsilon_{\perp}(\omega)$ is given by

$$\epsilon_{\perp}(\omega) = 1 - \frac{I^{(1)}}{\omega^2} - \frac{I^{(3)}}{\omega^4} - \frac{I^{(5)}}{\omega^6} - \frac{I^{(7)}}{\omega^8} - \dots, \tag{48}$$

where for $n = 1,2,3,4$ the moments $I^{(2n-1)}$ are given by (21), (35) or (36), (40), and (41). Using[1] $\epsilon_{\perp}(\omega) = \epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$, the asymptotic expansion of $1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$ is obtained by inverting (48),

$$1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega) = 1 + \frac{F^{(1)}}{\omega^2} + \frac{F^{(3)}}{\omega^4} + \frac{F^{(5)}}{\omega^6} + \frac{F^{(7)}}{\omega^8} + \cdots. \tag{49}$$

$F^{(2n-1)}$ are the frequency moments of $\mathrm{Im}[-1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)]$ expressed in terms of $I^{(2n-1)}$.

$$F^{(1)} = I^{(1)}, \tag{50a}$$

$$F^{(3)} = [I^{(1)}]^2 + I^{(3)}, \tag{50b}$$

$$F^{(5)} = [I^{(1)}]^3 + 2I^{(1)}I^{(3)} + I^{(5)}, \tag{50c}$$

$$F^{(7)} = [I^{(1)}]^4 + 3[I^{(1)}]^2 I^{(3)} + 2I^{(1)}I^{(5)} + I^{(7)}. \tag{50d}$$

For $V_{\mathbf{G}} \to 0$, the jellium results of Sec. I are recovered. $F^{(3)}$ was previously derived by Taut[14] in a different way. The above results can be generalized to arbitrarily inhomogeneous systems by replacing $\mathbf{q}+\mathbf{G}$, $\mathbf{q}+\mathbf{G}'$ by $\mathbf{q}$, $\mathbf{q}'$. Then there is no Brillouin zone that restricts $\mathbf{q}$ and $\mathbf{q}'$.

Finally, some comments on the external potential $V(\mathbf{r})$ are necessary. If we wish to include the response of all the core electrons, $V(\mathbf{r})$ is the superposition of the potentials of the nuclei. Representing the nuclei as point charges, $V(\mathbf{r})$ is singular at the nuclei with the consequence that the moments $I^{(2n-1)}$, $F^{(2n-1)}$ diverge for $n > 1$. To avoid this, one must introduce a cutoff in the $\mathbf{G}$ summation related to the finite spatial extent of the nuclei. It was pointed out by Hopfield[12] in connection with $I^{(3)}$ that this sum rule makes sense when smooth pseudopotentials are used. Smooth pseudopotentials have been designed for all elements of the periodic table, but they are, in general, nonlocal.

In general, response functions and thus dielectric functions cannot be calculated exactly. In the next section, we will examine the most common approximations with respect to their ability or inability to satisfy the sum rules that have been derived in this section.

III. SUM RULES AND SELF-CONSISTENT FIELD APPROXIMATIONS FOR THE DIELECTRIC FUNCTION

Microscopic calculations of the dielectric function are usually carried out in one of the variants of the self-consistent field approximations such as the RPA, the ALDA, or time dependent local density approximation (TDLDA) of density functional theory.[15] As pointed out in the Introduction, self-consistency enters at two levels: first in the calculation of single particle states on which the independent particle response function is based, and second in the calculation of the effective dynamical field to which the supposedly independent particle responds. Sum rules tie these two self-consistency conditions together. We now pose the question: To what extent do SCF approximations satisfy the sum rules we derived above?

Before we go into the details of the investigation, we summarize the results. The first, third, and fifth frequency moments are satisfied in a SCF calculation, provided the effective single particle potential that determines the single particle states for the independent particle density response function are calculated using the same self-consistency condition as imposed on the calculation of the effective dynamical potential. This means that Hartree type single particle states must be used when the response is calculated in the time dependent Hartree approximation (commonly known as RPA) or LDA type single particle states for the response in the ALDA or TDLDA of density functional theory.

Past calculations of the dielectric function within the RPA were often based on single particle states calculated by the $X\alpha$ method, a particular form of the LDA. In this way, sum rules are violated as will be shown explicitly. Violations of sum rules are also likely to occur when exchange correlation effects are taken into account differently in the effective single particle potential and in the effective dynamical potential.

To satisfy the seventh frequency moment sum rule is much more difficult, because it involves exchange-correlation (xc) effects via the correlation contributions to the kinetic energy and to the Coulomb interaction. The investigation within the NFE approximation illustrates that calculations carried out consistently in the sense that the first, third, and fifth frequency moments are satisfied, and do not necessarily satisfy the seventh moment sum rule. In fact, the RPA and the ALDA violate the seventh moment sum rule. For the RPA, this is not surprising, because xc effects are neglected at both levels, but even the ALDA violates this sum rule. First attempts to overcome this problem were made by Gross and Kohn,[16] Iwamoto and Gross,[17] and Dabrowski.[18]

A. Self-consistent field approximations and the third and fifth frequency moments

We first demonstrate that a consistent ALDA calculation of $\epsilon(\mathbf{q}\rightarrow\mathbf{0},\omega)$ satisfies the first, third, and fifth frequency moment sum rules. This includes the RPA if on both levels xc effects are neglected. The proof is very simple if the starting point is the form of $\epsilon_\perp(\omega)$ displayed in (38). The first and third frequency moments are already built in, but the density $n_\mathbf{G}$ has to be calculated from the solutions of Kohn-Sham equations. Thus, we have to consider the fifth frequency moment. This is obtained from the last term in (38), which depends on $\chi(G,G';\omega)$.

In the ALDA, we have

$$\chi^{\mathrm{ALDA}}(\mathbf{G},\mathbf{G}';\omega)=\sum_{G''}\chi^0(\mathbf{G},\mathbf{G}'';\omega)\tilde{\epsilon}^{-1}_{\mathbf{G}''\mathbf{G}'}(\mathbf{q}\rightarrow\mathbf{0},\omega). \tag{51}$$

Here, $\chi^0(\mathbf{G},\mathbf{G}'';\omega)$ is the independent particle response function, denoted by an upper index 0, which is calculated using the (self-consistent) solutions of the Kohn-Sham equations. $\tilde{\epsilon}^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\rightarrow\mathbf{0},\omega)$ is an element of the inverse of the microscopic dielectric matrix $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\rightarrow\mathbf{0},\omega)$, which is related to $\chi^0(\mathbf{G},\mathbf{G}';\omega)$. Its precise form will be given later. It is sufficient to note here that $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\rightarrow\mathbf{0},\omega)=\delta_{\mathbf{G}\mathbf{G}'}+\cdots$ and $\tilde{\epsilon}^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\rightarrow\mathbf{0},\omega)=\delta_{\mathbf{G}\mathbf{G}'}-\cdots$. Now, the independent particle response function $\chi^0(\mathbf{G},\mathbf{G}';\omega)$ has the high frequency behavior,

$$\chi^0(\mathbf{G},\mathbf{G}';\omega)=-\frac{1}{\omega^2}\frac{\mathbf{G}\cdot\mathbf{G}'}{m}n_{\mathbf{G}-\mathbf{G}'} \tag{52}$$

and, for large ω, we have

$$\begin{aligned}\epsilon_\perp(\omega)=1&-\frac{\omega_p^{0^2}}{\omega^2}+\frac{\omega_p^{0^2}}{\omega^4}\sum_{\mathbf{G}\neq0}\frac{(\eta\mathbf{G})^2}{m}V_{-\mathbf{G}}\frac{n_\mathbf{G}}{n_0}\\&-\frac{\omega_p^{0^2}}{\omega^6}\sum_{\mathbf{G}\neq0}\sum_{\mathbf{G}'\neq0}\frac{(\eta\cdot\mathbf{G})(\mathbf{G}\cdot\mathbf{G}')(\mathbf{G}'\cdot\eta)}{m^2}\\&\times V_{-\mathbf{G}}V_{\mathbf{G}'}\frac{n_{\mathbf{G}-\mathbf{G}'}}{n_0}+\cdots.\end{aligned} \tag{53}$$

This is formally identical with the exact result (48) when only the first three odd moments are considered, but the density $n_\mathbf{G}$ is obtained from the solutions of the Kohn-Sham equations (or from the Hartree equations for the RPA). Note that $V_\mathbf{G}$ is the bare crystal potential. We see that the use of (38) as the starting point to calculate the optical properties avoids automatically inconsistencies with respect to the first, third, and fifth frequency moment sum rules. However, most SCF calculations derive $\epsilon_\parallel(\mathbf{q},\omega)$ and obtain the optical properties in the limit $\mathbf{q}\rightarrow\mathbf{0}$.

In the ALDA, we have, with $v_\mathbf{q}=4\pi e^2/q^2$,

$$\begin{aligned}\frac{1}{\epsilon_\parallel(\mathbf{q},\omega)}&=1-v_\mathbf{q}\chi^{\mathrm{ALDA}}(\mathbf{q},\mathbf{q}';\omega)\\&=1-v_\mathbf{q}\sum_\mathbf{G}\chi^0(\mathbf{q},\mathbf{q}+\mathbf{G};\omega)\tilde{\epsilon}^{-1}_{\mathbf{G}\mathbf{0}}(\mathbf{q},\omega)\quad,\end{aligned} \tag{54}$$

where $\tilde{\epsilon}^{-1}_{\mathbf{G}\mathbf{G}'}$ is the inverse of the matrix $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}$ defined by

$$\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)+\Xi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)\ , \tag{55}$$

with

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=\delta_{\mathbf{G}\mathbf{G}'}+v_{\mathbf{q}+\mathbf{G}}\chi^0(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}';\omega) \tag{56}$$

and

$$\Xi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)=\sum_{\mathbf{G}''}K^{\mathrm{xc}}(\mathbf{G}-\mathbf{G}'')\chi^0(\mathbf{q}+\mathbf{G}'',\mathbf{q}+\mathbf{G}';\omega). \tag{57}$$

$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ is formally identical to the microscopic dielectric matrix introduced by Adler[19] and Wiser[20] in the RPA. The matrix $\Xi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ accounts for dynamical exchange-correlation effects and, in the ALDA, we have

$$K^{\mathrm{xc}}(\mathbf{r})=\frac{d}{dn}V^{\mathrm{xc}}|_{n=n(\mathbf{r})}=\sum_\mathbf{G}K^{\mathrm{xc}}(\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}}\ , \tag{58}$$

with

$$V^{\mathrm{xc}}(\mathbf{r})=\frac{d}{dn}[n\varepsilon_{\mathrm{xc}}(n)]|_{n=n(\mathbf{r})}=\sum_\mathbf{G}V^{\mathrm{xc}}_\mathbf{G}e^{i\mathbf{G}\cdot\mathbf{r}}\quad. \tag{59}$$

It follows from (58) and (59) that

$$\mathbf{G}\,V^{\mathrm{xc}}_\mathbf{G}=\sum_{\mathbf{G}'}K^{\mathrm{xc}}(\mathbf{G}-\mathbf{G}')\mathbf{G}'n_{\mathbf{G}'}\quad. \tag{60}$$

Whereas $V^{\mathrm{xc}}(\mathbf{r})$ enters the Kohn-Sham equations, which provide the single particle states to calculate χ^0, $K^{\mathrm{xc}}(\mathbf{r})$ contributes to the self-consistent dynamical potential. $\varepsilon_{\mathrm{xc}}(n)$ is the exchange-correlation energy per electron in the jellium model of density n. Equation (60) will be important in checking the fulfilment of the sum rules in the ALDA.

For $q\rightarrow0$, (54) reduces to $1/\epsilon_\parallel(\mathbf{q}\rightarrow\mathbf{0},\omega)=\tilde{\epsilon}^{-1}_{\mathbf{00}}(\mathbf{q}\rightarrow\mathbf{0},\omega)$, or

$$\begin{aligned}\epsilon_\parallel(\mathbf{q}\rightarrow\mathbf{0},\omega)&=1/\tilde{\epsilon}^{-1}_{\mathbf{00}}(\mathbf{q}\rightarrow\mathbf{0};\omega)\\&=\tilde{\epsilon}_{\mathbf{00}}(\mathbf{q}\rightarrow\mathbf{0},\omega)-\sum_{\mathbf{G}\neq0}\sum_{\mathbf{G}'\neq0}\tilde{\epsilon}_{\mathbf{0G}}(\mathbf{q}\rightarrow\mathbf{0},\omega)\\&\quad\times M^{-1}_{\mathbf{G}\mathbf{G}'}(\omega)\tilde{\epsilon}_{\mathbf{G}'\mathbf{0}}(\mathbf{q}\rightarrow\mathbf{0},\omega),\end{aligned} \tag{61}$$

where $M^{-1}_{\mathbf{G}\mathbf{G}'}(\omega)$ is the inverse of the submatrix or minor $M_{\mathbf{G}\mathbf{G}'}(\omega)$, which is the microscopic dielectric matrix $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}$ without the first row and first column. To see whether or not (61) satisfies the first three sum rules, we consider the high frequency expansions of the elements of the microscopic dielectric matrix that constitute the right-hand side of (61). Specifically, we need

$$\tilde{\epsilon}_{\mathbf{00}}(\mathbf{q}\to\mathbf{0},\omega)=1-\frac{I^{(1)}_{\mathbf{00}}}{\omega^2}-\frac{I^{(3)}_{\mathbf{00}}}{\omega^4}-\frac{I^{(5)}_{\mathbf{00}}}{\omega^6}-\cdots. \tag{62a}$$

For $\mathbf{G}\neq\mathbf{0}$,

$$\tilde{\epsilon}_{\mathbf{0G}}(\mathbf{q}\to\mathbf{0},\omega)=-\frac{I^{(1)}_{\mathbf{0G}}}{\omega^2}-\frac{I^{(3)}_{\mathbf{0G}}}{\omega^4}-\cdots, \tag{62b}$$

$$\tilde{\epsilon}_{\mathbf{G0}}(q\to 0,\omega)=-\frac{I^{(1)}_{\mathbf{G0}}}{\omega^2}-\frac{I^{(3)}_{\mathbf{G0}}}{\omega^4}-\cdots, \tag{62c}$$

and for $\mathbf{G}\neq\mathbf{0}$, $\mathbf{G}'\neq\mathbf{0}$

$$M^{(-1)}_{\mathbf{GG}'}(\omega)=\frac{1}{\tilde{\epsilon}_{\mathbf{GG}'}(\mathbf{0},\omega)}=\delta_{\mathbf{GG}'}+\frac{I^{(1)}_{\mathbf{GG}'}}{\omega^2}+\cdots. \tag{62d}$$

For any $\mathbf{G}$ and $\mathbf{G}'$, $I^{(2n-1)}_{\mathbf{GG}'}$ is defined by

$$I^{(2n-1)}_{\mathbf{GG}'}=\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^{2n-1}\tilde{\epsilon}''_{\mathbf{GG}'}(\mathbf{q}\to\mathbf{0},\omega). \tag{63}$$

Inserting (62) in (61), we obtain the asymptotic expansion of $\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$. The expansion coefficients are then the sum rules $I^{(2n-1}_{\mathrm{ALDA}}$ for $\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$ in terms of the sum rules $I^{(2n-1)}_{\mathbf{GG}'}$,

$$I^{(1)}_{\mathrm{ALDA}}=I^{(1)}_{\mathbf{00}}, \tag{64a}$$

$$I^{(3)}_{\mathrm{ALDA}}=I^{(3)}_{\mathbf{00}}+\sum_{\mathbf{G}\neq\mathbf{0}}I^{(1)}_{\mathbf{0G}}I^{(1)}_{\mathbf{G0}}, \tag{64b}$$

$$I^{(5)}_{\mathrm{ALDA}}=I^{(5)}_{\mathbf{00}}+\sum_{\mathbf{G}\neq\mathbf{0}}(I^{(1)}_{\mathbf{0G}}I^{(3)}_{\mathbf{G0}}+I^{(3)}_{\mathbf{0G}}I^{(1)}_{\mathbf{G0}})+\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}I^{(1)}_{\mathbf{0G}}I^{(1)}_{\mathbf{GG}'}I^{(1)}_{\mathbf{G}'\mathbf{0}}, \tag{64c}$$

and for $1/\epsilon_{\|}(\mathbf{q}\to\mathbf{0},\omega)$

$$F^{(1)}_{\mathrm{ALDA}}=I^{(1)}_{\mathbf{00}}, \tag{65a}$$

$$F^{(3)}_{\mathrm{ALDA}}=I^{(3)}_{\mathbf{00}}+\sum_{\mathbf{G}}I^{(1)}_{\mathbf{0G}}I^{(1)}_{\mathbf{G0}}, \tag{65b}$$

$$F^{(5)}_{\mathrm{ALDA}}=I^{(5)}_{\mathbf{00}}+\sum_{\mathbf{G}}(I^{(1)}_{\mathbf{0G}}I^{(3)}_{\mathbf{G0}}+I^{(3)}_{\mathbf{0G}}I^{(1)}_{\mathbf{G0}})+\sum_{\mathbf{G}}\sum_{\mathbf{G}'}I^{(1)}_{\mathbf{0G}}I^{(1)}_{\mathbf{GG}'}I^{(1)}_{\mathbf{G}'\mathbf{0}}. \tag{65c}$$

To prove that $I^{(2n-1)}_{\mathrm{ALDA}}$ is formally identical with $I^{(2n-1)}$ and $F^{(2n-1)}_{\mathrm{ALDA}}$ with $F^{(2n-1)}$ as derived in Sec. II, we need to evaluate the appropriate elements $I^{(2n-1)}_{\mathbf{GG}'}$. For any $\mathbf{G}$ and $\mathbf{G}'$, we find

$$I^{(1)}_{\mathbf{GG}'}=\lim_{\mathbf{q}\to\mathbf{0}}\left\{v_{\mathbf{q}+\mathbf{G}}\frac{(\mathbf{q}+\mathbf{G})(\mathbf{q}+\mathbf{G}')}{m}n_{\mathbf{G}-\mathbf{G}'}+\sum_{\mathbf{G}''}K^{\mathrm{xc}}(\mathbf{G}-\mathbf{G}'')\frac{(\mathbf{G}''+\mathbf{q})(\mathbf{G}'+\mathbf{q})}{m}n_{\mathbf{G}''-\mathbf{G}'}\right\} \tag{66}$$

and, in particular,

$$I^{(3)}_{\mathbf{00}}=-v_{\mathbf{q}}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{(\mathbf{qG})^2}{m}\tilde{V}_{\mathbf{G}}n_{\mathbf{G}}, \tag{67}$$

$$I^{(5)}_{\mathbf{00}}=v_{\mathbf{q}}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}\frac{(\mathbf{qG})(\mathbf{G}\cdot\mathbf{G}')(\mathbf{G}'\mathbf{q})}{m^3}\tilde{V}_{-\mathbf{G}}\tilde{V}_{\mathbf{G}'}n_{\mathbf{G}-\mathbf{G}'}, \tag{68}$$

$$I^{(3)}_{\mathbf{0G}}=-v_{\mathbf{q}}\sum_{\mathbf{G}'}\frac{(\mathbf{qG}')(\mathbf{G}'\mathbf{G})}{m^2}\tilde{V}_{-\mathbf{G}'}n_{\mathbf{G}'-\mathbf{G}}+\sum_{\mathbf{G}'}K^{\mathrm{xc}}(-\mathbf{G}')\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^2\chi^0_{\mathbf{GG}'}(\mathbf{q}\to\mathbf{0},\omega), \tag{69}$$

$$I^{(3)}_{\mathbf{G0}}=-v_{\mathbf{G}}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{(\mathbf{qG}')(\mathbf{G}'\mathbf{G})}{m^2}\tilde{V}_{-\mathbf{G}'}n_{\mathbf{G}'-\mathbf{G}}+\sum_{\mathbf{G}'}\sum_{\mathbf{G}''\neq\mathbf{0}}K^{\mathrm{xc}}(\mathbf{G}-\mathbf{G}')\frac{(\mathbf{qG}'')(\mathbf{G}''\mathbf{G})}{m^2}\times\tilde{V}_{G''}n_{G'-G''}, \tag{70}$$

where the single particle potential $\tilde{V}_G$ that enters the Kohn-Sham equations is defined by

$$\tilde{V}_{\mathbf{G}}=V_{\mathbf{G}}+v_{\mathbf{G}}n_{\mathbf{G}}+V^{\mathrm{xc}}_{\mathbf{G}}. \tag{71}$$

Inserting (66)–(70) into (64) and (65) and using (75) and (60) one finds that the first, third, and fifth frequency moment sum rules are satisfied in the ALDA. If, however, the solutions of the Kohn-Sham equations are used to calculate the dielectric function in the RPA, i.e., neglecting $K^{\mathrm{xc}}(\mathbf{r})$, then (for example)

$$I^{(3)}\neq-\frac{4\pi e^2}{m^2}\sum_{\mathbf{G}\neq\mathbf{0}}\frac{(\mathbf{qG})^2}{q^2}n_{\mathbf{G}}\{V_{-\mathbf{G}}+V^{\mathrm{xc}}_{-\mathbf{G}}\}. \tag{72}$$

The additional term $\sim V^{\mathrm{xc}}_{-\mathbf{G}}$ is responsible for the violation of $I^{(3)}$ given by (35).

Finally, we point out that the general definition of the optical mass given in (32) and evaluated in the SCF approximation is equivalent to the well-known determination of m_{opt} from the band structure directly. This is outlined briefly in Appendix B.

B. Sum rules for local field corrections

Before we consider the seventh frequency moment sum rule, we consider once more (61). As the right-hand side of (61) shows, two contributions to $\epsilon_{\parallel}(\mathbf{q}\to\mathbf{0},\omega)$ can be distinguished. The first term, $\tilde{\epsilon}_{\mathbf{00}}$, can be interpreted as arising from direct interband and intraband transitions, whereas in the second term, the off-diagonal element $\tilde{\epsilon}_{\mathbf{0G}}$ and $\tilde{\epsilon}_{\mathbf{G0}}$ describe the coupling of long-wavelength and short-wavelength fluctuations. This term is denoted local field corrections (lfc) and originates from the microscopic inhomogeneity of the system. Obviously, its calculation increases the computational work considerably and one is naturally interested to find arguments for neglecting lfc as the Ehrenreich-Cohen[7] approximation suggests. Here sum rules can provide some useful information. We define for the lfc

$$\begin{aligned}\Delta I^{(2n-1)} &= -\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^{2n-1}\mathrm{Im}\Big\{\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}\tilde{\epsilon}_{\mathbf{0G}}\\ &\qquad\times(\mathbf{q}\to\mathbf{0},\omega)M^{-1}_{\mathbf{GG}'}(\omega)\tilde{\epsilon}_{\mathbf{G}'\mathbf{0}}(\mathbf{q}\to\mathbf{0},\omega)\Big\}\\ &= \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\omega^{2n-1}\mathrm{Im}\Big\{\epsilon_{\parallel}(\mathbf{q}\to\mathbf{0},\omega)\\ &\qquad-\tilde{\epsilon}_{00}(\mathbf{q}\to\mathbf{0},\omega)\Big\}\end{aligned}\tag{73}$$

and find that

$$\Delta I^{(1)} = 0,\tag{74a}$$

$$\begin{aligned}\Delta I^{(3)} &= -\frac{4\pi e^2}{m^2}\sum_{\mathbf{G}\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})^2 n_{-\mathbf{G}}\{V_{\mathbf{G}}-\tilde{V}_{\mathbf{G}}\}\\ &= \frac{4\pi e^2}{m^2}\sum_{\mathbf{G}\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})^2 n_{-\mathbf{G}}\{n_{\mathbf{G}}v_{\mathbf{G}}+V^{\mathrm{xc}}_{\mathbf{G}}\},\end{aligned}\tag{74b}$$

where the last step reqires (71).

$$\begin{aligned}\Delta I^{(5)} &= \frac{4\pi e^2}{m^3}\sum_{\mathbf{G}\neq\mathbf{0}}\sum_{\mathbf{G}'\neq\mathbf{0}}(\boldsymbol{\eta}\mathbf{G})(\mathbf{GG}')\\ &\qquad\times(\mathbf{G}'\boldsymbol{\eta})n_{\mathbf{G}-\mathbf{G}'}\{V_{-\mathbf{G}}V_{\mathbf{G}'}-\tilde{V}_{-\mathbf{G}}\tilde{V}_{\mathbf{G}'}\}.\end{aligned}\tag{74c}$$

It is interesting to note that local field corrections do not contribute to the f sum rule, so that lfc lead only to a redistribution of oscillator strengths. The enhancement in one part of the spectrum must necessarily be accompanied by the reduction in some other part of the spectrum. It appears that lfc tend to enhance the oscillator strength in the high frequency spectrum and to suppress the low frequency part, and this can be shown explicitly in the NFE approximation.

$\Delta I^{(3)}$ provides us with an overall estimate of the error that is made in the Ehrenreich-Cohen approximation when $\mathrm{Im}\epsilon_{\parallel}(\mathbf{q}\to\mathbf{0},\omega)\approx\mathrm{Im}\tilde{\epsilon}_{\mathbf{00}}(\mathbf{q}\to\mathbf{0},\omega)$. Since the two terms in (74b) tend to cancel, the Ehrenreich-Cohen approximation appears to be more reasonable than a (inconsistent) RPA calculation using LDA single particle states [see (72) or (67) with (71)]. If $|\Delta I^{(2n-1)}/I^{(2n-1)}|\ll 1$ for $n=3$ and $n=5$, one has some indications that lfc might be unimportant, but if $|\Delta I^{(2n-1)}/I^{(2n-1)}|\sim 1$ then lfc are definitely important. Whether or not lfc are important will of course depend on the system in question.

C. Violation of the seventh frequency moment sum rule by RPA and ALDA

It is appealing that a consistent RPA/Hartree or ALDA/LDA calculation satisfies the first three sum rules. This, however, is not true for the seventh frequency moment sum rule, as we shall demonstrate for NFE systems. As pointed out in Sec. II, working to second order in the weak pseudopotential $\epsilon_{\perp}(\mathbf{q}\to\mathbf{0},\omega)$ can be expressed in terms of the density response function $\chi(q,\omega)$ of the jellium model taken at $q=G=|\mathbf{G}|$, where $\mathbf{G}$ are reciprocal lattice vectors. The third moment of $\chi''(G,\omega)$ is needed, which evaluated in the RPA yields

$$M^{(3)}_{\mathrm{RPA}}(G) = \frac{n_0G^2}{m}\left\{\left(\frac{\hbar G^2}{2m}\right)^2+4\left(\frac{G^2}{2m}\right)\langle E_{\mathrm{kin}}\rangle_0+\omega_p^2\right\}.\tag{75}$$

It differs from the exact result $M^{(3)}(G)$ [Eq. (43)], by the neglect of all terms that account for exchange and correlation effects. The ALDA yields

$$\begin{aligned}M^{(3)}_{\mathrm{ALDA}}(G) &= \frac{n_0G^2}{m}\left\{\left(\frac{\hbar G^2}{2m}\right)^2+4\left(\frac{G^2}{2m}\right)\langle E_{\mathrm{kin}}\rangle_0\right.\\ &\qquad\left.+\omega_p^2(1-\mathcal{G}_{\mathrm{ALDA}}(G)\right\},\end{aligned}\tag{76}$$

with ($k_F^3=3\pi^2n_0$)

$$\mathcal{G}_{\mathrm{ALDA}}(q) = \gamma_0\left(\frac{q}{k_F}\right)^2\tag{77}$$

and

$$\begin{aligned}\gamma_0 &= -\frac{1}{v_{k_F}}\frac{d^2}{dn^2}\{n[\varepsilon_x(n)+\varepsilon_c(n)]\}|_{n=n_0}\\ &= \frac{1}{4}+\frac{\pi}{6}\alpha r_s^2\frac{d\varepsilon_c}{dr_s}-\frac{\pi}{12}\alpha r_s^3\frac{d^2\varepsilon_c}{dr_s^2},\end{aligned}\tag{78}$$

where $\alpha=(4/9\pi)^{1/3}$ and $v_{k_F}=v_{q=k_F}$, $\varepsilon_x=-(3/4\pi\alpha)r_s^{-1}$, and ε_c are in atomic units. In order to agree with the exact moment $M^{(3)}(q)$ [see Eq. (43)], $\mathcal{G}_{\mathrm{ALDA}}(q)$ would have to be equal to

$$\begin{aligned}\mathcal{G}_3(q) &= I(q)-\frac{4}{\omega_p^2}\left(\frac{q^2}{2m}\right)[\langle E_{\mathrm{kin}}\rangle-\langle E_{\mathrm{kin}}\rangle_0]\\ &= I(q)+\frac{4}{\omega_p^2}\left(\frac{q^2}{2m}\right)\frac{d}{dr_s}[r_s\varepsilon_c(r_s)].\end{aligned}\tag{79}$$

$\mathcal{G}_{\mathrm{ALDA}}(q)$, however, is completely different from $\mathcal{G}_3(q)$, as we show for $r_s=2$ in Fig. 1. This failure of the ALDA to account properly for dynamic correlation effects sheds some light on the limitations of both the ALDA and the LDA, since the ground state theorem[8] relates the exchange-correlation energy ε_c via

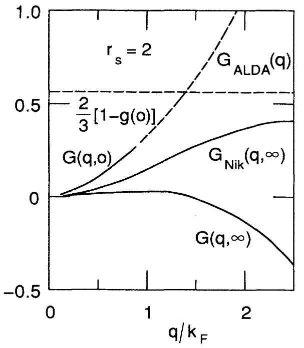

FIG. 1. Limiting forms of $\mathcal{G}(q,\omega)$ for $r_s = 2$. Notice $\mathcal{G}_3(q) = \mathcal{G}(q,\infty)$. Partially redrawn from Fig. 4(b) of Ref. 13.

frequency-, momentum-, and coupling-constant integrations of $\chi''(\mathbf{q},\omega;r_s)$. This violation of the seventh moment sum rule by $\epsilon_\perp(\omega)$ evaluated in the RPA and in the ALDA is of course not limited to NFE systems, but applies also to the general case, when the crystal potential is not weak and $M^{(3)}(G)$ has to be replaced by $M^{(3)}(\mathbf{G},\mathbf{G}')$ derived in Appendix A.

D. Sum rules and the "generalized mean field approximation"

A method to overcome these problems, in principle, is provided by the so-called generalized mean field approximation.[21] Following a many-body analysis by Hubbard,[22] a so-called local field factor $\mathcal{G}(q,\omega)$ is introduced to account for dynamical exchange-correlation effects within the jellium model (not to be confused with local field effects arising from inhomogeneity). In this approximation, the density response function (indexed by H for Hubbard) is given by

$$\chi_H(q,\omega) = \frac{\chi^0(q,\omega)}{1+v_q[1-\mathcal{G}(q,\omega)]\chi^0(q,\omega)}. \tag{80}$$

Again, $\mathcal{G}(q,\omega)$ cannot be calculated exactly. In most cases, phenomenological forms are designed by fitting them to exact constraints arising from sum rules, asymptotic limits, and the fluctuation-dissipation (FD) theorem. Of course, a $\mathcal{G}(q,\omega)$ obtained in this way depends crucially on the choice of $\chi^0(q,\omega)$ used in (80). In most cases, the independent particle response function $\chi^0(q,\omega)$ is the well-known Lindhard function. Considerable confusion has been caused by a definition used by Niklasson,[23] where the Fermi function in the definition of the Lindhard function is replaced by the true momentum distribution of the interacting electrons. This has important consequences when the third frequency moment of $\chi''_H(q,\omega)$ is evaluated, and this has been overlooked many times in the literature,[15] as will be discussed below. If $\chi^0(q,\omega)$ is the Lindhard function, then $\chi_H(q,\omega)$ goes over into the RPA result when $\mathcal{G}(q,\omega) \equiv 0$.

Practically all forms used in applications are "static" approximation, i.e., $\mathcal{G}(q,\omega) = \mathcal{G}(q)$. They are not only used in calculations of static or low frequency properties, but also to study dynamical properties such as the plasmon dispersion. We shall show that the meaning of "static" here is not unique.

An important constraint (for $\omega = 0$) on $\mathcal{G}(q,0)$ comes from the requirement that $\chi(q,\omega)$ must satisfy the compressibility sum rule[24] in the limit $q \to 0$. Applied to $\chi_H(q,\omega)$ gives

$$\lim_{q\to 0} \mathcal{G}(q,0) = \gamma_0 \left(\frac{q}{k_F}\right)^2. \tag{81}$$

γ_0 was defined in (78) and can be calculated using results from MC calculations.[3–5] The ALDA obviously satisfies this constraint, but there it is assumed to be valid for arbitrary q. To go beyond the ALDA, Utsumi and Ichimaru[25] designed a form of $\mathcal{G}(q)$ by interpolating between the limit (81) and a large q limit derived by Kimball,[26]

$$\lim_{q\to\infty} \mathcal{G}(q) = [1-g(0)] \quad , \tag{82}$$

where $g(0)$ is the pair distribution function at $r = 0$. But $\mathcal{G}(q)$ defined by (82) has nothing to do with $\mathcal{G}(q,0)$ because, (82) follows from the fluctuation-dissipation (FD) theorem with the assumption that $\mathcal{G}(q)$ is independent of ω, i.e.,

$$S(q) = \frac{\hbar}{n_0}\int_0^\infty \frac{d\omega}{\pi} \frac{\mathrm{Im}\chi^0(q,\omega)}{|1+v_q[1-\mathcal{G}(q)]\chi^0(q,\omega)|^2}. \tag{83}$$

The physical meaning of $\mathcal{G}(q)$ that interpolates between (81) and (82) is not clear because, in principle, (83) determines $\mathcal{G}(q)$ for arbitrary q, when $S(q)$ is known from MC simulations.

Furthermore, the third frequency moment $M^{(3)}(q)$ again fixes a different static $\mathcal{G}(q) = \mathcal{G}_3(q)$ for any q, where $\mathcal{G}_3(q)$ was defined by (79). In the small q limit, $\mathcal{G}_3(q)$ reduces to

$$\lim_{q\to 0} \mathcal{G}_3(q) = \gamma_3 \left(\frac{q}{k_F}\right)^2 \tag{84}$$

with

$$\begin{aligned}\gamma_3 &= \frac{1}{v_{k_F}}\left\{\frac{4}{5}n^{2/3}\frac{d}{dn}\{n^{-2/3}[\varepsilon_x(n)+\varepsilon_c(n)]\}\right.\\ &\qquad \left.\left. -6n^{1/3}\frac{d}{dn}[n^{-1/3}\varepsilon_c(n)]\right\}\right|_{n=n_0}\\ &= \frac{3}{20} + \frac{11}{10}\pi\alpha r_s\varepsilon_c + \frac{13}{10}\pi\alpha r_s^2\frac{d\varepsilon_c}{dr_s}.\end{aligned} \tag{85}$$

In Fig. 2, $\gamma_0(r_s)$ and $\gamma_3(r_s)$ are plotted as functions of r_s, together with $g(0,r_s)$. Obviously $\gamma_3(r_s) \neq \gamma_0(r_s)$. The rather different behavior of $\mathcal{G}_{\mathrm{ALDA}}(q)$, which coincides for small q with $\mathcal{G}(q,0)$ and which is plotted together with $\mathcal{G}_3(q)$ in Fig. 1, demonstrates the incompatibility of the static local field factors $\mathcal{G}(q)$ satisfying different exact requirements, as pointed out previously by Iwamoto.[2]

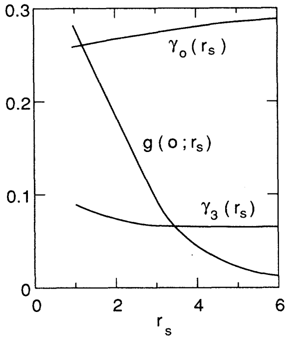

FIG. 2. Parameters $\gamma_0(r_s)$, $\gamma_3(r_s)$, and $g(0;r_s)$ that determine limiting forms of $\mathcal{G}(q,\omega)$ in the small and large q limits.

From a fundamental point of view, a frequency independent local field factor is an ill-defined concept.

Nevertheless, in dealing with small ω and small q properties, it appears that the ALDA, which satisfies the compressibility sum rule, is a reasonable approximation. Even the small q plasmon dispersion constant α is much better described by $\mathcal{G}(q,0)=\mathcal{G}_{\mathrm{ALDA}}(q)$ than by $\mathcal{G}_3(q)$. The latter one hardly changes the RPA value of α. Whereas in the small q regime $\mathcal{G}(q)$ is important, for very large q ($q \gg 2k_F$) the screening denominator in (80) becomes ineffective because it tends to unity. The importance of $\mathcal{G}(q)$, therefore, diminishes. This might explain the success of LDA calculations. The largest uncertainty prevails in the intermediate q region for $k_F < q < 3k_F$, which affects the optical properties, because the small and most important reciprocal lattice vectors $\mathbf{G}$ related to the potential coefficient $V_{\mathbf{G}}$ are located in this region.

In order to satisfy all known requirements, it is crucial to keep the frequency dependence of $\mathcal{G}(q,\omega)$. In fact, $\mathcal{G}(q,\omega)$ is a complex function of ω,

$$\mathcal{G}(q,\omega)=\mathcal{G}'(q,\omega)+i\mathcal{G}''(q,\omega)\ , \tag{86}$$

and satisfies Kramers-Kronig relations,[21] for example,

$$\mathcal{G}'(q,\omega)-\mathcal{G}_3(q)=P\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{\mathcal{G}''(q,\omega')}{\omega'-\omega}. \tag{87}$$

For $\omega=0$, we obtain an important sum rule for $\mathcal{G}(q,\omega)$,

$$\mathcal{G}(q,0)-\mathcal{G}_3(q)=P\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{\mathcal{G}''(q,\omega')}{\omega'}, \tag{88}$$

when $\mathcal{G}_3(q)$ and $\mathcal{G}(q,0)$ are known, where $\mathcal{G}_3(q)$ is given by (79) and $\mathcal{G}(q,0)$ satisfies the compressibility sum rule. We observe that dynamical processes that constitute $\mathcal{G}''(q,\omega)$ are responsible for the difference between $\mathcal{G}(q,0)$ and $\mathcal{G}_3(q)=\mathcal{G}(q,\infty)$, where the last equality follows from (87). Such dynamical correlation processes are, for example, multiple particle-hole pair excitations, multiple plasmon excitations, and combined plasmon particle-hole pair excitations. For small q, these were studied by Dubois and Kivelson,[27] Hasegawa and Watabe,[28] and Glick and Long[29] in the high density limit. In the large ω limit, when dynamical screening becomes inefficient, the approximations become equivalent and yield for any q (in atomic units),

$$\lim_{\omega\to\infty}\mathcal{G}''(q,\omega)=\frac{1}{v_{k_F}}\frac{c}{\omega^{3/2}}\left(\frac{q}{k_F}\right)^2 \tag{89a}$$

with $c=46\pi/15$. (Glick and Long find $c=23\pi/15$.) Using (87), one finds for large frequencies

$$\lim_{\omega\to\infty}\mathcal{G}'(q,\omega)=\mathcal{G}(q,\infty)-\frac{1}{v_{k_F}}\frac{c}{\omega^{3/2}}\left(\frac{q}{k_F}\right)^2. \tag{89b}$$

As noted above, there is considerable confusion in the literature about the large q limit of $\mathcal{G}(q,\infty)=\mathcal{G}_3(q)$. If we adopt for $\chi^0(q,\omega)$ in (80) the form that Niklasson[23] uses in his derivation, the third frequency moment gives

$$M^{(3)}_{\mathrm{Nik}}(q)=\frac{n_0q^2}{m}\left\{\left(\frac{\hbar q^2}{2m}\right)^2+4\left(\frac{q^2}{2m}\right)\langle E_{\mathrm{kin}}\rangle\right.$$
$$\left.+\omega_p^2[1-\mathcal{G}_{\mathrm{Nik}}(q,\infty)]\right\}, \tag{90}$$

which on comparing with the exact result (43) gives

$$\mathcal{G}_{\mathrm{Nik}}(q,\infty)=I(q)\ , \tag{91}$$

with the large q limit

$$\lim_{q\to\infty}\mathcal{G}_{\mathrm{Nik}}(q,\infty)=\frac{2}{3}[1-g(0)]. \tag{92}$$

However, adopting the Lindhard function for $\chi^0(q,\omega)$ and using (79) and (82) leads to

$$\lim_{q\to\infty}\mathcal{G}(q,\infty)=\lim_{q\to\infty}\mathcal{G}_3(q)$$
$$=\frac{2}{3}[1-g(0)]+\frac{4}{\omega_p^2}\left(\frac{q^2}{2m}\right)\frac{\partial}{\partial r_s}[r_s\varepsilon_c(r_s)], \tag{93}$$

which goes to $(-\infty)$ as q^2. The q^2 divergence is known in the literature[21] and the completely different behavior is illustrated in Fig. 1. Pathak and Vashishta[30] also point out that working with the Lindhard function, they arrive at $\mathcal{G}_3(q)=I(q)$ when they neglect the difference between $\langle E_{\mathrm{kin}}\rangle$ and $\langle E_{\mathrm{kin}}\rangle_0$.

Apart from the constraints on $\mathcal{G}(q,\omega)$ discussed above, very little is known for arbitrary q and ω. Based on the knowledge of $\mathcal{G}(q,0)$, $\mathcal{G}(q,\infty)$ for small q and on (89a), Gross and Kohn[16] and Iwamoto and Gross[17] designed a Padé like interpolation formula for $\mathcal{G}(q,\omega)$. Dabrowski[18] tried to extend this interpolation scheme to arbitrary q adopting various approximate forms of $\mathcal{G}(q)$ for $\mathcal{G}(q,0)$ available in the literature. This would be relevant for application to the optical properties in the NFE approximation, for example. Further work along these lines is needed.

IV. CONCLUSION

The optical constants can be evaluated equally well from the transverse dielectric function $\epsilon_\perp(\mathbf{q},\omega)$ or the longitudinal dielectric function $\epsilon_\|(\mathbf{q},\omega)$ in the limit of $\mathbf{q}\to\mathbf{0}$. Since the calculation of the macroscopic dielectric function from the microscopic structure constitutes a complicated many-body problem, one must depend on approximations. Sum rules provide general criteria to examine the quality of the involved approximations. We have shown that in the optical limit the first four odd frequency moments of both $\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ and $\mathrm{Im}-1/\epsilon_\|(\mathbf{q}\to\mathbf{0},\omega)$ can be evaluated. With increasing order, the general information that is contained in the moments becomes increasingly detailed. While the first moment depends on the number density of the electrons, the third and fifth moments reflect the inhomogeneity of the electronic system determined by the external potential $V(\mathbf{r})$ that causes the inhomogeneous distribution of the electron density $n(\mathbf{r})$. Correlation contributions to the kinetic energy and exchange-correlation effects arising from the Coulomb interaction give important contributions to the seventh moment.

The moments are obtained by first rewriting $\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ in terms of density response functions. The fifth and seventh frequency moments of $\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ are related to the first and third frequency moments of the density response functions. The moments of $\mathrm{Im}-1/\epsilon_\|(\mathbf{q}\to\mathbf{0},\omega)$ can then be expressed in terms of the frequency moments of $\mathrm{Im}\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$.

$\epsilon_\perp(\mathbf{q}\to\mathbf{0},\omega)$ evaluated in the RPA or ALDA satisfies the first, third, and fifth moments, provided the band structure is evaluated in the Hartree approximation or LDA, respectively. Many RPA calculations are based on LDA band structure calculations, such as the $X\alpha$ method, and this leads to violations of sum rules. To satisfy in this case the first three odd moments, the dielectric function must be calculated in the ALDA using the same approximation for xc effects as in the LDA band structure calculation.

In SCF approximations, such as the RPA or the ALDA, sum rules for local field effects arising from the inhomogeneity of the system can be defined and the first few moments can be calculated. In this way, one can estimate the overall error which is made when local field effects are neglected.[7] This is important information, since the evaluation of the local field effects increases the computational effort substantially. A comparison of approximate forms of the third frequency moment shows that the neglect of local fields appears to be more reasonable than an RPA calculation inconsistently based on a band structure calculation in the LDA.

Although the seventh frequency moment can be formally derived for arbitrary crystals, its numerical evaluation is presently possible only for NFE systems, in which case the third moment of the density response function of the jellium model is required. Numerical estimates can be obtained from computer simulations of the ground state properties of the jellium model.

Both the RPA and the ALDA lead to a violation of the seventh moment sum rule. The RPA by definition neglects xc effects altogether, whereas the ALDA cannot properly account for dynamic exchange-correlation effects. In principle, these deficiencies can be overcome within the "generalized mean field theory" of the jellium model. In this approach, exchange-correlation effects in the density response are expressed in term of a local field factor $\mathcal{G}(q,\omega)$. As is clear from (80), it influences decisively the response at small and intermediate q values up to about three k_F, whereas for very large q, the screening denominator approaches unity and the specific form of $\mathcal{G}(q,\omega)$ becomes less important. In most applications, a "static" approximation $\mathcal{G}(q,\omega)\equiv\mathcal{G}(q)$ is used. Such an approximation cannot be valid, in general. As pointed out by Iwamoto,[2] a $\mathcal{G}(q)=\mathcal{G}(q,0)$ that is compatible with the compressibility sum rule as derived, for example, in the ALDA is incompatible with a $\mathcal{G}(q)=\mathcal{G}_3(q)$ derived from the third frequency moment. Both forms are incompatible with a $\mathcal{G}(q)=\mathcal{G}_{\mathrm{FD}}(q)$ that is fitted to $S(q)$ obtained by computer simulation using the FD theorem. $\mathcal{G}(q)=\mathcal{G}_{\mathrm{UI}}(q)$ as designed by Utsumi and Ichimaru[25] satisfies the compressibility sum rule for small q and the large q limit obtained by Kimball,[26] using the FD theorem. Whether such a procedure yields any improvement over the ALDA is doubtful. For small q and frequencies up to the plasma frequency ω_p, the ALDA appears to be a reasonable approximation.

To satisfy all the known requirements, one has to keep the frequency dependence of $\mathcal{G}(q,\omega)$. In fact, $\mathcal{G}(q,\omega)$ is complex and can be chosen to satisfy Kramers-Kronig relations and all known constraints. Using $\mathcal{G}(q,0)$ and $\mathcal{G}(q,\infty)=\mathcal{G}_3(q)$, a sum rule for $\mathrm{Im}\,\mathcal{G}(q,\omega)$ can be derived from Kramers-Kronig relations. In addition, for large ω, $\mathrm{Im}\,\mathcal{G}(q,\omega)\sim\omega^{-3/2}$ is known from a high density expansion.[29]

Some confusion exists in the literature about $G(q,\infty)$. This can be traced to different definitions of $\mathcal{G}(q,\omega)$ as defined, for example, by Niklasson[23] and by many other workers in the field. Due to the fact that Niklasson defines an independent particle response function, where the Fermi function that is used in the Lindhard function is replaced by the true momentum distribution, we have $\mathcal{G}_{\mathrm{Nik}}(q,\infty)=I(q)$ and $\lim_{q\to\infty}I(q)=\frac{2}{3}[1-g(0)]$, whereas the definition through the Lindhard function leads to an additional term to $\mathcal{G}(q,\infty)$ that diverges as $(-q^2)$ for $q\to\infty$.

Very little is known for arbitrary values of q and ω. For small q, Gross, Kohn, and Iwamoto (GKI) designed a Padé like interpolation formula that by construction satisfies appropriate requirements, i.e., $\mathcal{G}(q,0)$, $\mathcal{G}(q,\infty)$, and $\lim_{\omega\to\infty}\mathrm{Im}\,\mathcal{G}(q,\omega)$. Dubois and Kivelson[27] and Hasegawa and Watabe[28] calculated $\mathrm{Im}\,\epsilon(q,\omega)$ as arising from dynamical correlation processes called multipair excitations such as pair-pair excitation, plasmon-plasmon excitations, and plasmon-pair excitations. It is based on a decoupling of a four body correlation function by a product of two body correlation functions. A numerical evaluation[31] leads to a form of $\mathrm{Im}\,\mathcal{G}(q,\omega)$ that differs substantially from the GKI form in the small and intermediate ω regimes, but approaches the same limit for $\omega\to\infty$. $\mathcal{G}(q,\omega)$ can be used to determine small q plasmon dispersion and damping. Details will be published elsewhere.[31]

A different, momentum conserving decoupling scheme was used by Toigo and Woodruff.[32] Kugler demonstrated that this is an example of a general scheme proposed by Tahir-Kehli and Jarrett.[33] Although, in principle, applicable for arbitrary q and ω, it has a number of disadvantages. (See review article by Kugler.[21]) For the evaluation of optical properties in the NFE approximation, $\mathcal{G}(q,\omega)$ is required for $q = G$ with $k_F \leq G \leq 3k_F$ and $\frac{1}{10}\omega_p \leq \omega \leq 2\omega_p$. In this intermediate q and ω regime, $\mathcal{G}(q,\omega)$ is very uncertain. More work is needed to understand the rather complicated dynamical correlation processes in this (q,ω) regime.

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APPENDIX A

Here we present the result of a straightforward but lengthy evaluation of the commutators that lead to $M^{(3)}(\mathbf{q},\mathbf{q}')$ needed for the evaluation of the seventh frequency moment sum rule in (41) in the general case. We obtain

$$M^{(3)}(\mathbf{q},\mathbf{q}') = \frac{n_{\mathbf{q}-\mathbf{q}'}}{m}(\mathbf{q}\cdot\mathbf{q}')\{R(\mathbf{q},\mathbf{q}') + T(\mathbf{q},\mathbf{q}') + W(\mathbf{q},\mathbf{q}') + \omega_p^{0^2}[1 - I(\mathbf{q},\mathbf{q}')]\}\,, \qquad \text{(A1)}$$

where

$$\hbar^2 R(\mathbf{q},\mathbf{q}') = \frac{3}{2}\frac{\hbar^4(\mathbf{q}\cdot\mathbf{q}')^2}{m^2} + 2\varepsilon_{\mathbf{q}}\varepsilon_{\mathbf{q}'} - \varepsilon_{\mathbf{q}}^2 - \frac{\hbar^2(\mathbf{q}\cdot\mathbf{q}')}{m}\varepsilon_{\mathbf{q}} - 2\frac{\hbar^2(\mathbf{q}\cdot\mathbf{q}')}{m}\varepsilon_{\mathbf{q}'}\,, \qquad \text{(A2)}$$

$$T(\mathbf{q}\cdot\mathbf{q}') = \frac{1}{n_{\mathbf{q}-\mathbf{q}'}}\frac{1}{\Omega}\left\langle 0\left|\sum_j \frac{1}{m^2}e^{i(\mathbf{q}-\mathbf{q}')\mathbf{r}_j}[(\mathbf{q}\cdot\mathbf{p}_j)^2 + 2(\mathbf{q}\cdot\mathbf{p}_j)(\mathbf{q}'\cdot\mathbf{p}_j)(\mathbf{q}'\cdot\mathbf{p}_j)]\right|0\right\rangle\,, \qquad \text{(A3)}$$

$$W(\mathbf{q},\mathbf{q}') = \frac{1}{n_{\mathbf{q}-\mathbf{q}'}}\frac{1}{(\mathbf{q}\cdot\mathbf{q}')}\sum_{\mathbf{q}''\neq 0}\frac{(\mathbf{q}''\cdot\mathbf{q})(\mathbf{q}-\mathbf{q}'')\cdot\mathbf{q}'}{m^2}V_{\mathbf{q}''}n_{\mathbf{q}-\mathbf{q}'-\mathbf{q}''} \qquad \text{(A4)}$$

and

$$I(\mathbf{q},\mathbf{q}') = -\frac{1}{N}\sum_{\mathbf{k}\neq 0,\mathbf{q}}\frac{(\mathbf{k}\cdot\mathbf{q})}{(\mathbf{q}'\cdot\mathbf{q})}K(\mathbf{q},\mathbf{k}) \times[S(\mathbf{q}-\mathbf{k},\mathbf{q}'-\mathbf{k}) - 1]\,, \qquad \text{(A5)}$$

with

$$K(\mathbf{q},\mathbf{k}) = \frac{(\mathbf{k}\cdot\mathbf{q})}{k^2} + \frac{\mathbf{q}\cdot(\mathbf{q}-\mathbf{k})}{|\mathbf{q}-\mathbf{k}|^2} \qquad \text{(A6)}$$

and

$$S(\mathbf{q},\mathbf{q}') = \frac{1}{\Omega}\frac{1}{n_{\mathbf{q}-\mathbf{q}'}}\langle 0|\hat{n}_{\mathbf{q}}\hat{n}_{-\mathbf{q}'}|0\rangle\,. \qquad \text{(A7)}$$

For $\mathbf{q} = \mathbf{q}'$ and systems of cubic symmetry, (A1) reduces to

$$M^{(3)}(\mathbf{q},\mathbf{q}) = \frac{n_0 q^2}{m}\left\{\left(\frac{\hbar q^2}{2m}\right)^2 + 4\left(\frac{q^2}{2m}\right)\langle E_{\text{kin}}\rangle + \frac{1}{n_0}\frac{1}{q^2}\sum_{\mathbf{q}\neq 0}\frac{(\mathbf{q}\cdot\mathbf{q})(\mathbf{q}-\mathbf{q})\cdot\mathbf{q}}{m^2}V_{\mathbf{q}}n_{-\mathbf{q}} + \omega_p^{0^2}[1 - I(\mathbf{q},\mathbf{q})]\right\}. \qquad \text{(A8)}$$

For a homogeneous system, i.e., $V_{\mathbf{q}} = 0$, (A8) reduces to (43).

APPENDIX B

In Sec. II, we gave a general definition of the optical mass in terms of density response functions [see Eq. (32)]. In Sec. III, we saw that lfc do not contribute to the f sum rule. Thus, within the SCF approximation, m_{opt} can be determined by the f sum rule for $\text{Im}\tilde{\epsilon}_{00}(\mathbf{q}\to\mathbf{0},\omega)$. Furthermore, for $\mathbf{q}\to\mathbf{0}$, $\tilde{\epsilon}_{00}(\mathbf{q}\to\mathbf{0},\omega) = \epsilon_{00}(q\to 0,\omega)$, which is given explicitly by

$$\text{Im}\epsilon_{00}(q\to 0,\omega) = \pi\frac{\omega_p^{0^2}}{\omega}\frac{n_v}{n_0}\frac{m}{m_{\text{opt}}}\delta(\omega) + \frac{4\pi e^2}{m^2\omega^4}\sum_{\mathbf{G}\neq 0}\sum_{\mathbf{G}'\neq 0}(\eta\mathbf{G}) \times(\mathbf{G}'\eta)\tilde{V}_{-\mathbf{G}}\tilde{V}_{\mathbf{G}'}\chi''^0(\mathbf{G},\mathbf{G}';\omega)\,. \qquad \text{(B1)}$$

The f sum rule yields

$$1 - \frac{n_v}{n_0}\frac{m}{m_{\text{opt}}} = \frac{1}{mn_0}\sum_{\mathbf{G}\neq 0}\sum_{\mathbf{G}'\neq 0}(\eta\mathbf{G})(\mathbf{G}'\eta)V_{-\mathbf{G}} \times V_{\mathbf{G}'}\frac{1}{2}\frac{\partial^2}{\partial\omega^2}\chi'^0(\mathbf{G},\mathbf{G}':\omega)\Big|_{\omega=0}\,. \qquad \text{(B2)}$$

On the other hand, it is very well known[34] that the optical mass can be calculated directly from the band structure according to

$$\frac{n_v}{m_{\mathrm{opt}}} = \frac{1}{4\pi^3}\frac{1}{\hbar^2}\sum_{\ell}\int d^3k\; f(\varepsilon_{\ell\mathbf{k}})\;(\eta\vec{\nabla}_k)^2\varepsilon_{\ell\mathbf{k}}. \tag{B3}$$

Here, ℓ are band indices and $\varepsilon_{\ell\mathbf{k}}$, $|\ell\mathbf{k}\rangle$ are the eigenstates of the Kohn-Sham equations. The integral in (B3) extends over the first Brillouin zone. Note that occupied bands do not contribute to the right-hand side of (B3).

At first sight, the two definitions of m_{opt} (B2) and (B3) look rather different. The equivalence of the two definitions follows from the effective mass theorem[35] and the identity $\ell \neq \ell'$,

$$(\varepsilon_{\ell\mathbf{k}} - \varepsilon_{\ell'\mathbf{k}})\langle \ell\mathbf{k}|\eta\mathbf{p}|\ell'\mathbf{k}\rangle = \sum_{\mathbf{G}\neq 0} \hbar(\eta\mathbf{G})\tilde{V}_{-\mathbf{G}}\langle \ell\mathbf{k}|e^{-i\mathbf{G}\cdot\mathbf{r}}|\ell'\mathbf{k}\rangle. \tag{B4}$$

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