This is to certify that the

dissertation entitled

LINEAR RESPONSE FUNCTIONS OF AN INTERACTING
FERMI GAS AT $T = 0$

presented by

Rajasinghe Nimalakirthi

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date March 30, 1993

LINEAR RESPONSE FUNCTIONS OF AN INTERACTING FERMI GAS AT T=0

By

Rajasinghe Nimalakirthi

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1993

ABSTRACT

LINEAR RESPONSE FUNCTIONS OF AN INTERACTING FERMI GAS AT T = 0

By

R. Nimalakirthi

The response of an interacting Fermi gas in its ground state to weak external electromagnetic fields is analyzed in this thesis. The system's response to arbitrary scalar and vector potentials has been studied within the random phase approximation.

The electrical response is characterized via the nonlocal polarizability density denoted by $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$, which gives the polarization $\mathbf{P}(\mathbf{r}, \omega)$ induced at point $\mathbf{r}$ in a system by a perturbing electric field $\mathbf{E}(\mathbf{r}', \omega)$ acting at the point $\mathbf{r}'$, within linear response. A homogeneous electron gas at zero temperature is selected as a well characterized system, for the purpose of determining the nonlocal polarizability density and thus gaining information about the nature and functional form of $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$. The longitudinal component (in $\mathbf{k}$ space) of the nonlocal polarizability density $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ is connected to the dielectric function $\varepsilon(\mathbf{k},\omega)$, and this connection is used to obtain results at two levels of approximation. Results from the Thomas-Fermi (TF) form and the random phase approximation (RPA) for $\varepsilon(\mathbf{k},\omega)$ are compared. At TF level, the nonlocal polarizability density is evaluated analytically, while within the RPA asymptotic analytical results are obtained. The RPA results are qualitatively distinct from the TF results, which diverge as

$|\mathbf{r} - \mathbf{r}'|$ approaches zero. Within the RPA, there are two long-range components in $\boldsymbol{\alpha}^{L}(\mathbf{r}, \mathbf{r}'; 0)$: the first is a monotonically decreasing component that arises from the net charge screening in the electron gas, and varies as $|\mathbf{r} - \mathbf{r}'|^{-3}$. The second is an oscillatory component with terms of order $|\mathbf{r} - \mathbf{r}'|^{-n}$ $(n \geq 3)$. The latter is associated with Friedel oscillations in the electron density as found in Langer and Vosoko's study of the screening of an impurity charge. The results indicate the possibility of long-range, intramolecular terms in the nonlocal polarizability densities of individual molecules.

For molecular systems, it is shown that the change in nonlocal polarizability density due to an infinitesimal shift in nuclear position is determined by the hyperpolarizability density. The same hyperpolarizability density describes the electronic charge distribution's nonlinear response to external fields.

A method is provided to obtain the asymptotic form of the dynamic charge density susceptibility, as a function of space and time variables, for a homogeneous electron gas treated within the RPA. It is shown that the calculation reduces to a single quadrature over frequency.

Explicit expressions for current density susceptibilities as a function of transferred momentum and frequency are obtained within the RPA in a gauge in which the scalar potential is zero.

TO MY PARENTS

ACKNOWLEDGMENTS

My sincere thanks go to Professor Katharine C. Hunt for her guidance, encouragement and support throughout this study. I would also like to thank to my committee members Professor R. I. Cukier, Professor S. D. Mahanti and Professor P. M. Duxbury for their valuable suggestions.

TABLE OF CONTENTS

LIST OF FIGURES

1. INTRODUCTION

Within linear response theory [1, 2], the properties of a perturbed system are expressed in terms of its equilibrium properties. References 1 and 2 treat the response of a system to an external force by a simple perturbation method, assuming that the external perturbation can be expressed as an additional term in the Hamiltonian and that it does not drive the system far from equilibrium. Kubo [2] has shown that the complex susceptibility and complex conductivity, and hence the electric polarization and induced currents, can be rigorously expressed in terms of equilibrium time correlation functions of the associated dynamical variables. For example, it was shown by Kubo that the conductivity tensor for a given frequency of the applied field can be rigorously expressed in terms of electric current components fluctuating spontaneously in the equilibrium state. There has been considerable interest in evaluating transport coefficients given by Kubo's formulas.

One of the important tools of quantum field theory is the Green function, which is convenient for the study of the properties of interacting quantized fields. These tools turn out to be useful also in statistical mechanics, in cases where one can sum the same type of perturbation theory diagrams. The application of Green functions is fruitful in the quantum theory of fields when combined with spectral representations. Spectral representations for the time-correlation functions and for retarded Green functions were first established and used in statistical mechanics in the theory of fluctuations and in the statistical mechanics of irreversible processes, beginning with a paper by Callen and Welton [1]. Retarded and advanced Green functions, and their simplest applications to the theory of irreversible processes are discussed at greater length in Zubarev's paper [4]. They are very convenient for application in statistical mechanics as they can be analytically continued in the complex plane. Linear response functions are most simply expressed in terms of retarded double time Green functions.

Because of the long range of the Coulomb force, the interactions in a collection of electrons involve many particles simultaneously. It is well known that an electron gas of high density can undergo organized oscillations resembling sound waves. These oscillations, the so-called ''plasma oscillations'' represent the effect of the long-range correlations of electron positions brought about by Coulomb interactions. A description in terms of these organized oscillations therefore provides a natural way of treating the long-range electron interactions, and leads to greater insight into the dynamical behavior of the electron gas. We can distinguish between two kinds of response of the electrons to the field. In one of these, the phase difference between the particle response and the field producing it is independent of the position of the particle. This is the response which contributes to the organized behavior of the system. In the other the phase difference between the field and the response depends on the position of the particle. Because of the general random location of the particles, this second response tends to average out to zero when we consider a large number of electrons, and we can neglect the contribution arising from this. This procedure is the ''random phase approximation'' (RPA). The collective description is similar to a complete perturbation theory treatment in that the perturbation is applied to the collective particle motion.

The behavior of the electrons in a dense electron gas can be analyzed in terms of their density fluctuations. These density fluctuations may be split into two components. One component is associated with the organized oscillations of the system as a whole. The other is associated with the random thermal motion of the individual electrons and shows no collective behavior. This split up of the density fluctuations corresponds to an effective separation of the Coulomb interaction into long-range and short-range parts; the separation occurs at roughly the Debye length. Bohm and Pines [5] used the above split-up of the density fluctuations to study the collective response of the electron gas to the field of an individual charged particle moving with a specified velocity v_0. When v_0 is less than the mean thermal speed of the gas, they found that the collective response is just such as to screen out the field of the specified particle within a distance of order of the Debye length.

The self consistent field (SCF) method, in which a many-electron system is described by a time-dependent interaction of a single electron with a self-consistent electromagnetic field, has been shown to be equivalent to the dielectric approach of Nozières and Pines [9] to the many electron problem, in work by Ehrenreich and Cohen [10]. Ehrenreich and Cohen's paper establishes the relationship among the equation of motion approach, the quantum kinetic equations, the calculation of the dielectric function, and Landau's Fermi liquid theory. The simplicity and ease of interpretation of the SCF method commends it for problems such as the calculation of the dielectric constant and the response of the system to a general external perturbation. By studying the system's response to an arbitrary scalar potential and a vector potential we can evaluate the induced particle density and current density respectively. By using the facts that the transverse vector potential excites only a transverse current and is not screened by the longitudinal Coulomb interaction we separate the vector equation into its transverse and longitudinal parts. By using the equation of continuity, we obtain a result for the longitudinal current self-consistently.

A knowledge of the RPA dielectric constant at arbitrary frequency enables one to calculate a number of interesting properties of the electron gas. It also predicts correctly a number of properties of the electron gas such as the plasmon frequency. In the RPA, since Im $\underline{\varepsilon}_{RPA}(q,\omega)$ vanishes for the plasmon modes, there will be no damping of the plasmons. The plasmon frequency is determined by the dispersion relation Re $\underline{\varepsilon}_{RPA}(q,\omega) = 0$ [11]. At small values of q, Im $\underline{\varepsilon}_{RPA}(q,\omega)$ is proportional to ω at small values of ω. The proportionality to ω is an important feature of Im $\underline{\varepsilon}_{RPA}(q,\omega)$. The long-wavelength plasmon will now be damped. The linear dependence of Im $\underline{\varepsilon}_{RPA}(q,\omega)$ on ω must also occur for the exact dielectric function. The physical property under consideration is the rate at which electron-hole pairs are made in the electron gas [12]. A hole is a state which has an electron removed from the filled Fermi sea. An initial electron of momentum **p** and energy $\varepsilon_{\mathbf{p}}$ is excited by a perturbation with (**q**,ω). Thus it is excited to a new state with momentum **p**+ **q** and energy $\varepsilon_{\mathbf{p+q}} = \varepsilon_{\mathbf{p}} + \omega$. The electron can only be scattered into states which are previously unoccupied, so $\varepsilon_{\mathbf{p+q}}$ must be above the occupied Fermi sea. Thus the basic process takes an electron from below to above the Fermi level. Thus the excitation processes make electron-hole pairs. By simple arguments, it can be shown that the rate of making electron-hole pairs is proportional to ω, at small values of ω. At small values of ω we can expect damping to be small.

The calculation of the induced screening charge density (about an impurity) in the RPA has been carried out by Langer and Vosko [13]. In contrast to the Thomas-Fermi calculation, the screening density at the origin is finite in the RPA. In the RPA, the screening density does not go to zero exponentially, but rather oscillates at large values of r. The second feature had appeared in earlier calculations of Friedel [15]. These oscillations come about as a result of a logarithmic singularity in $\underline{\varepsilon}_{RPA}(q,0)$. At $q = 2p_F$ its first derivative becomes infinite. The physical origin of the singularity is not difficult to trace. When $q < 2p_F$, one may excite an electron from one part of the Fermi surface to the another; the electron hole excitation spectrum begins at zero energy. When $q > 2p_F$, one must instead supply energy to excite an electron; the corresponding excitation spectrum begins at some finite energy. Friedel oscillations are an exact microscopic property of normal electron liquids; they may be considered as a direct reflection of the sharpness of the Fermi surface [11, 16].

This thesis focuses on susceptibilities of the electron gas and molecular systems, specifically the charge-density susceptibility, the current-density susceptibility, the nonlocal polarizability density, and the hyperpolarizability density.

The nonlocal polarizability density is a linear response tensor that gives the polarization $\mathbf{P}(\mathbf{r}, \omega)$ induced at a point $\mathbf{r}$ in a molecule by a perturbing electric field $\mathbf{E}(\mathbf{r}', \omega)$ that acts at the point $\mathbf{r}'$ [18-23]: The nonlocal polarizability density was introduced by Maaskant and Oosterhoff in a study of optical rotation in condensed media [18]. In their work, $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ is expressed as a difference of two components that are individually divergent as $\omega \rightarrow 0$, and each transition matrix element in the expression involves an operator specified only as an infinite series [8]. For response to fields that are derivable from a scalar potential, $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ can be recast in a computationally tractable form, via a connection [22] between its spatial Fourier transform and that of the charge-density susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ [24-29]. The function $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ determines the change in charge density at point $\mathbf{r}$ in response to a perturbing scalar potential acting at $\mathbf{r}'$, within linear response. This connection gives the *longitudinal* component of the polarizability density $\boldsymbol{\alpha}^{L}(\mathbf{r}, \mathbf{r}'; \omega)$ [22].

In chapter 2, we briefly review the general theory of linear response. Collective oscillations and the RPA are discussed in chapter 3. Chapter 4 contains a discussion of the linear response to scalar and vector potentials acting as perturbations. There we obtain the transverse and longitudinal current density susceptibilities within the RPA in gauge-nvariant form. It is shown that the longitudinal current density is screened within the RPA. The new results of this thesis are contained in chapters 5, 6, and 7.

In chapter 5 we give a generalization of the Langer and Vosko result by evaluating the charge density susceptibility and the nonlocal polarizability density, for a scalar potential of arbitrary spatial variation. We establish a connection between the static, longitudinal component of the nonlocal polarizability density in position space and the dielectric function $\varepsilon(\mathbf{k}, 0)$, and then use the connection to obtain results at two levels of approximation to $\varepsilon(\mathbf{k}, 0)$: we compare the results from the Thomas-Fermi (TF) [11,12] and the RPA approximation. Within the TF approximation, we obtain analytical results, while within the RPA, we obtain asymptotic analytical results.

In chapter 5 we also describe the extension of the approach used in previous sections to evaluate the dynamic charge-density susceptibility. We develop a method to evaluate the asymptotic form of dynamic charge density susceptibility within the RPA.

In chapter 6 we study the response to a field of arbitrary polarization. It is most convenient to choose a gauge such that the vector potential alone represents the applied electromagnetic fields, and study the induced current. A given longitudinal electric field produces the same current, whether it is by a vector potential or by a scalar potential; thus the induced polarization current is gauge invariant. Explicit expressions for transverse and longitudinal current density susceptibilities are obtained in (q,ω) space within the RPA.

In chapter 7, we develop a general result for another linear response tensor, the polarizability density. The results are obtained for an isolated molecule in its ground electronic state. We prove by direct perturbation theory that when a nucleus in a molecule shifts infinitesimally, the resulting change in polarizability density is determined by the same hyperpolarizability density that fixes the response to external fields. This is a general quantum mechanical result. It is rather straightforward, but previously unanticipated. It has applications in the analysis of interpretation of intensities of vibrational Raman bands.

Chapter 8 contains a brief summary and conclusions. Mathematical identities needed in the calculations are presented in two appendices.

2. THE GENERAL THEORY OF LINEAR RESPONSE

The formalism of linear response theory is straightforward. We consider a system that in the distant past ($t \to -\infty$) was prepared in a state of equilibrium. Let us suppose that in the distant past an external force was switched on adiabatically. As a result, the system is no longer in stable equilibrium. On the other hand, internal affairs in the system should not be much affected by a small force, and the lowest-order response that moves the system to a new stable state compatible with the imposed constraints can be connected to local equilibrium fluctuations. We must, first of all, estimate when an external force can be considered small. In the most general case, we can argue that the energy transmitted to a particle by the external force over a characteristic distance in the system has to be small compared to its average energy in local equilibrium [1a].

This criterion is, in fact, very conservative in a situation where the external force is switched on adiabatically. "Adiabatically" here means slow on the time scale of the regression of local fluctuations. In this case the system only has to adjust at any instant of time by an infinitesimal amount to the new external constraints. If we follow the time evolution of the system via the statistical operator, this implies that first-order, time-dependent perturbation theory should be adequate [1a]. Such an approach leads to constitutive relations that are linear in the applied external forces [1a]. It has therefore received the name "linear response theory". The use of first-order time dependent perturbation theory in the study of transport phenomena in many-body systems was advocated in an early paper by Callen and Welton [1].

The following review is patterned on a paper of Kubo [2], where a rather general framework was laid out for the calculation of the systems response to mechanical forces within a Hamiltonian formalism [1a].

Linear response theory makes an assumption that the applied external force must be such that it can be incorporated as part of the total Hamiltonian of the system. This, of course, means that the results of linear response theory are as general as can be, and are, as with most general results in physics, not directly useful for practical calculations [1a]. However, linear response theory is eminently suited to prove general features of nonequilibrium physics, such as positivity of transport coefficients, validity of the Onsager reciprocity [3] relations, sum rules, and dispersion relations. To do practical calculations based on linear response theory, one can either employ equilibrium Greens function techniques, use kinetic equations, or resort to semi-empirical models with experimental data as partial input. The latter approach is often rewarding since linear response theory expresses transport coefficients in terms of time-dependent correlation functions, which are quite often available from experiments [1a]. However in the work presented in this thesis, the former method is followed.

a. Quantum Mechanical Response Theory

Let us consider an isolated system, the Hamiltonian of which is denoted by H. The dynamical motion of the system determined by H is called the ''natural motion'' of the system. We suppose that an external field F(t) is applied to the system, the effect of which is represented by the perturbation term,

$$H'(t) = -AF(t) \tag{2.1}$$

The motion of the system is perturbed by the external force, but the perturbation is small if the force is weak. The response is observed through the change $\Delta B(t)$ of a physical quantity B. The problem is now to express $\Delta B(t)$ in terms of the natural motion of the system.

The initial ensemble which represents statistically the initial state of the system is specified by the density matrix ρ satisfying $[H, \rho] = 0$ [2]. The motion of the ensemble under the perturbation (2.1) is represented by $\rho'(t)$, which obeys the equation,

$$\partial\rho'(t)/\partial t = 1/\, i\hbar\, [H + H'(t), \rho'(t)] \tag{2.2}$$

With the initial condition $\rho'(-\infty) = \rho$, we expand $\rho'(t)$ as

$$\rho'(t) = \rho + \Delta\rho(t) \tag{2.3}$$

In the linear approximation, the solution for $\Delta\rho(t)$ is [2]

$$\Delta\rho(t) = -1/i\hbar \int_{-\infty}^{t} \exp(-i(t-t')H/\hbar)\, [A, \rho]\, \exp(i(t-t')H/\hbar)\, F(t')dt'. \tag{2.4}$$

It is convenient to introduce the operator $a^{\times}$ operating on another operator b by the following definition

$$a^{\times}b = [a, b]\,, \tag{2.5}$$

for which one finds the rule [2]

$$e^{a^{\times}} b = e^{a}\, b\, e^{-a}\,. \tag{2.6}$$

With this notation, equations (2.2) and (2.4) can be written as [2]

$$\partial\rho'(t)/\partial t = 1/i\hbar\, (H^{\times} + H'^{\times}(t))\, \rho'(t) \tag{2.7}$$

$\Delta\rho(t) = -1/i\hbar \int^{t}_{-\infty} \exp(-i(t-t')H^{\times}/\hbar)\,[A, \rho]\,F(t')\,dt'.$ (2.8)

The response $\Delta B(t)$ of the quantity B is statistically [2]

$\Delta B(t) = \mathrm{Tr}\, \Delta\rho(t)B$

$= -1/i\hbar\, \mathrm{Tr} \int^{t}_{-\infty} [A, \rho]\, B(t-t')\, F(t')dt'$ (2.9)

where B(t) is the Heisenberg representation of B following the equation

$dB(t)/dt = 1/i\hbar[B(t), H]\,.$ (2.10)

The response function is now [2]

$\psi_{BA}(t) = -1/i\hbar\, \mathrm{Tr}\, [A, \rho]B(t)$

$= 1/i\hbar\, \mathrm{Tr}\; \rho\, [A, B(t)].$ (2.11)

The above Kubo formula [2] is valid at finite temperatures, because a trace over the thermal distribution is taken. At zero temperature this is equivalent to taking the expectation value in the ground state.

b. Double-Time Green Functions and Time Correlation Functions

The Green functions in statistical mechanics are the appropriate generalization of the concept of correlation functions. They are just as intimately connected with the evaluation of observed quantities, and they have well-known advantages when equations are formulated and solved [4].

Following Zubarev [4] we define double-time retarded and advanced Green functions Gr(t, t′) and Ga(t, t′) as follows:

$Gr(t, t') = -i\, \theta(t-t')\langle[A(t), B(t')]\rangle$ (2.12)

$Ga(t, t') = +i\, \theta(t'-t)\langle[A(t), B(t')]\rangle$ (2.13) where <.....> indicates that one should average over a thermal ensemble at finite temperature, and at zero temperature it simply means averaging over the Heisenberg ground state of the interacting system. A(t) and B(t) are the Heisenberg representation of the operators A and B, expressed in terms of a product of particle creation and annihilation operators (or a product of quantized field functions). The theta function is defined by $\theta(t) = \begin{matrix} 1 & t>0 \\ 0 & t<0 \end{matrix}$

(For convenience, a system of units in which h=1 is used from here onward.)

Finally, [A, B] indicates the commutator or anti-commutator:

$$[A, B] = AB - \eta BA\ , \eta = \begin{matrix} -1 \text{ Fermion} \\ +1 \text{ Boson} \end{matrix}$$

The sign of η is determined by the problem. Generally speaking, A and B are neither Bose nor Fermi operators [4].

When the time arguments are the same, $t = t'$, the Green functions are not defined, because of the discontinuous factor $\theta(t-t')$. We note that in the case of statistical equilibrium the Green functions $Gr(t, t')$ and $Ga(t, t')$ depend on t and t' only through $(t-t')$ [4].

For the time being we have introduced the Green functions purely formally, by analogy with the quantum theory of fields. We shall satisfy ourselves now by concrete examples that they are very conveniently applied in quantum statistics to problems concerning a system of a large number of interacting particles. One can choose for A and B operators of different kinds: for instance, Fermi or Bose operators and their products, density operators or current operators. The choice of the operators A and B is determined by the conditions of the problem [4].

The time correlation funtions used in statistical mechanics are averages over the statistical ensemble of the product of operators in the Heisenberg representation of the kind

$$\varphi_{BA}(t, t') = <B(t')\ A(t)> \text{ and } \varphi_{AB}(t, t') = <A(t)\ B(t')> \tag{2.14}$$

In the case of statistical equilibrium the time correlation functions depend, as do the Green functions, only on t - t′. But they are defined also when the times are the same, t = t′. In quantum mechanics we need to take the symmetrized product of operators.

In subsequent work we restrict our attention to the zero temperature problem, and we are interested in two types of external perturbations, namely those due to scalar potentials and those due to vector potentials.

We can write down the perturbing Hamiltonians for electrons exposed to a scalar potential perturbation or a vector potential perturbation respectively as

$$H'(t) = -e \int d^3r\ \rho(r,t)\ \varphi(r,t) \tag{2.15}$$

$$H'(t) = -1/c \int d^3r\ \mathbf{J}(r,t) \cdot A(r,t). \tag{2.16}$$

The induced particle density and paramagnetic term in the induced current density in the linear approximation are

$$\delta< \rho(r,t)> = ie \int^{t}_{-\infty} dt' \int d^3r' <[\rho(r,t), \rho(r',t')] > \varphi(r',t') \tag{2.17}$$

$$\delta< \mathbf{J}(r,t)> = i/c \int^{t}_{-\infty} dt' \int d^3r' <[\mathbf{J}(r,t), \mathbf{J}(r',t')]> \cdot A(r',t') \tag{2.18}$$

Now in analogy with Eq. (1.11) we define retarded density and current correlation functions as

$$\alpha(r\,t, r'\,t') = -i\,\theta(t-t') <[\rho(r,t), \rho(r',t')]> \tag{2.19}$$

$$\chi(r\,t, r'\,t') = -i\,\theta(t-t') <[J(r,t), J(r',t')]>. \tag{2.20}$$

Then Eq. (2.17) and Eq. (2.18) may be written as

$$\delta< \rho(r,t)> = -e \int_{-\infty}^{+\infty} dt' \int d^3r'\, \alpha(r\,t, r'\,t')\, \varphi(r',t') \tag{2.21}$$

$$\delta< J(r,t)> = -1/c \int_{-\infty}^{+\infty} dt' \int d^3r'\, \chi(r\,t, r'\,t') \cdot A(r',t'). \tag{2.22}$$

where causal behavior is enforced by the retarded nature of α and χ respectively. Eq. (2.21) and Eq. (2.22) typify a general result that the linear response of an operator to an external perturbation is expressible as the space-time integral of a suitable retarded correlation function. [Note: Eq. (2.18) does not give us the total current, as there is an additional term proportional to $-e^2/mc\ A(r,t)$; see reference 11, Eq. (52.12).]

In subsequent work we wish to evaluate α and χ for a specific model system, namely the interacting electron gas with a uniform and exactly opposite charged background, so that the whole system is neutral.

3. COLLECTIVE OSCILLATIONS AND THE RANDOM PHASE APPROXIMATION

In this section we give a short review of Pines and Bohm [5] theory of plasma oscillations, and wish to develop a detailed physical picture of the behavior of the electrons in a dense electron gas. We are concerned with the organization produced by the Coulomb interactions. From the work of Pines and Bohm: ''In a dense electron gas, the particles interact strongly because of the long range of the Coulomb force; in fact each particle interacts simultaneously with all the other particles. As a result the equations of motion become extremely difficult to solve. The usual perturbation based on the assumption of interaction between particles breaks down.... A collective description provides a far better starting point for a solution than a description in terms of individual particles [5]''.

''Instead of following the motion of the individual particles, we describe the gas in terms of the Fourier components of the electron density at each point in space. These Fourier components are proportional to the density fluctuations in the electron gas. We find that the density fluctuations can be split into two parts. One part represents an organized oscillation with the characteristic plasma frequency, and is clearly associated with the collective behavior of the system. The other part is associated with the motion of the individual particles.... For wavelengths greater than a certain critical length λ_D (the Debye length), the fluctuations are primarily collective... For wavelengths smaller than λ_D, however, the fluctuations are primarily associated with individual particle motion [5]''.

''As any electron moves through the assembly, the other electrons are pushed away from it by the Coulomb repulsion. Each particle is thus surrounded by a cloud of extent λ_D, in which there is a deficiency of electrons, which is responsible for screening the field of the particle in question [5]''.

''The splitup of the density fluctuation into collective and individual-particle components may be viewed in the following way. The collective part includes the effects of the long range of the Coulomb force which lead to the simultaneous interactions of many particles. The individual-particle component represents the density fluctuations arising from the randomly moving individual particles plus their, comoving electron clouds, and thus includes the effects of the residual short-range screened Coulomb force [5]''.

''Certain examples of collective behavior in an electron gas are well known from the study of gaseous discharges. These are the organized oscillations of the system as a whole, the plasma oscillations. The ions in a metal are also susceptible to a collective description, and, in interaction with electrons, they give rise to sound waves, whose properties canbe calculated with the collective method. In this way, one can obtain an improved treatment of the so-called lattice-electron interaction, which is important in the theory of electrical conductivity [5]''.

''We begin by a study of the way in which the interactions in an assembly of electrons bring about organized behavior and collective oscillations. We shall consider an aggregate of approximately free electrons embedded in a medium of fixed positive charges whose average density is equal to that of the electrons [5]''. For the purpose of these calculations this distribution of charge can be regarded as uniformly smeared out, throughout the entire system. Hence, it merely serves to neutralize the net electron charge.

Each electron in the assembly is acted on by the sum of the forces arising from all of the other electrons plus that resulting from the smeared-out positive charge [5]. The potential energy of interaction between the ith and jth electrons, $e^2/|\mathbf{x}_i - \mathbf{x}_j|$, may be expanded as a Fourier series in a box of unit volume with periodic boundary conditions, which gives [5]

$$e^2/|\mathbf{x}_i - \mathbf{x}_j| = 4\pi e^2 \sum_{\mathbf{k}} (1/k^2)\exp[i\mathbf{k}\cdot(\mathbf{x}_i - \mathbf{x}_j)]. \tag{3.1}$$

The equation of motion of the ith electron is given by [5]

$$d^2\mathbf{x}_i/dt^2 = -(4\pi e^2 i/m) \sum_{j,\mathbf{k}}{}' (\mathbf{k}/k^2)\exp[i\mathbf{k}\cdot(\mathbf{x}_i - \mathbf{x}_j)] \tag{3.2}$$

where the prime denotes a sum in which $\mathbf{k} = 0$ is excluded. (The term with $k = 0$ takes into account the uniform background of positive charge, and hence the overall charge neutrality of the system.)

"The range of the Coulomb potential is so great that many-body collisions are important.... Under these conditions, the electrons move together in organized fashion, and one finds the well-known phenomenon of "plasma" oscillations of the system as a whole [5].

The particle density in our box of unit volume is given by

$$\rho(\mathbf{x}) = \sum_i \delta(\mathbf{x} - \mathbf{x}_i). \tag{3.3}$$

The Fourier components $\rho_{\mathbf{k}}$ of the density are given by

$$\rho_{\mathbf{k}} = \int d\mathbf{x}\, \rho(\mathbf{x}) \exp(-i\mathbf{k}\cdot\mathbf{x}) = \sum_i \exp(-i\mathbf{k}\cdot\mathbf{x}_i) \tag{3.4}$$

and $\rho(\mathbf{x}) = \Sigma_{i,\mathbf{k}} \exp[i\mathbf{k}\cdot(\mathbf{x} - \mathbf{x}_i)]$. (3.5)

We note that ρ_0 represents the mean electron density, n, and the $\rho_\mathbf{k}$ with $\mathbf{k} \neq 0$ describe fluctuations about that mean density [5]. Furthermore, we note that the expectation value of $\rho_\mathbf{k}$ with $\mathbf{k} \neq 0$ is equal to zero because of the translational invariance of the system. "It is readily verified that the equation of motion (3.2) may be re-expressed as [5]

$$d^2\mathbf{x}_i/dt^2 = -(4\pi e^2 i/m)\Sigma'_\mathbf{k} (\mathbf{k}/k^2)\ \rho_\mathbf{k} \exp(i\mathbf{k}\cdot\mathbf{x}_i). \tag{3.6}$$

The $\rho_\mathbf{k}$ thus determine the force acting on each particle."

We now obtain the equations describing the time behavior of the $\rho_\mathbf{k}$. On differentiating (3.4), we have [5]

$$d\rho_\mathbf{k}/dt = -i\, \Sigma_i\, (\mathbf{k}\cdot\mathbf{v}_i) \exp(-i\mathbf{k}\cdot\mathbf{x}_i) \tag{3.7}$$

$$d^2\rho_\mathbf{k}/dt^2 = -\, \Sigma_i\, [(\mathbf{k}\cdot\mathbf{v}_i)^2 + i(\mathbf{k}\cdot d\mathbf{v}_i/dt)] \exp(-i\mathbf{k}\cdot\mathbf{x}_i). \tag{3.8}$$

We obtain $d\mathbf{v}_i/dt$ from the equations of motion (3.2), and $d^2\rho_\mathbf{k}/dt^2$ becomes [5]

$$d^2\rho_\mathbf{k}/dt^2 = -\Sigma_i(\mathbf{k}\cdot\mathbf{v}_i)^2 \exp(-i\mathbf{k}\cdot\mathbf{x}_i) - \Sigma_{\substack{ij \\ \mathbf{k}' \neq 0}} [4\pi e^2/mk'^2]\, \mathbf{k}\cdot\mathbf{k}'\, \{\exp[i(\mathbf{k}' - \mathbf{k})\cdot\mathbf{x}_i]\}\exp(-i\mathbf{k}'\cdot\mathbf{x}_j) \tag{3.9}$$

In the second term we split the sum over $\mathbf{k}'$ into two parts. The first part, with $\mathbf{k}' = \mathbf{k}$, is independent of the coordinate, $\mathbf{x}_i$, so that the sum over i yields n, the total number of particles [5]. The terms with $\mathbf{k}' \neq \mathbf{k}$ contain the phase factor $\exp[i(\mathbf{k}' - \mathbf{k}).\mathbf{x}_i]$ which depends on the position of the particles. These terms tend to average out to zero, since there are a very large number of particles distributed very nearly in random positions [5]. As a first approximation, we neglect such terms. This procedure we call the random phase approximation [5]. Using the above approximation we then obtain

$$d^2\rho_k/dt^2 = - \Sigma_i (\mathbf{k}\cdot\mathbf{v}_i)^2 \exp(-i\mathbf{k}\cdot\mathbf{x}_i) \; -(4\pi ne^2/m) \Sigma_i \exp(-i\mathbf{k}\cdot\mathbf{x}_i). \tag{3.10}$$

The first term arises from the motion of the individual particles. For sufficiently small **k** it is clear that the first term can be neglected. Under these conditions, Eq. (3.10) becomes [5]

$$d^2\rho_k/dt^2 + (4\pi ne^2/m)\rho_k = 0. \tag{3.11}$$

Thus, as a result of the Coulomb interaction, the electron density oscillates with the well-known ''plasma'' frequency, $\omega_p = (4\pi ne^2/m)^{1/2}$. The excitation of a particular ρ_k corresponds to a wave-like density fluctuation, analogous to a sound wave [5].

a. Equivalence of the Self-Consistent Field Approach and the Collective Approach Based on the RPA

''The electromagnetic properties of crystals have long been studied by considering the time-dependent interaction of a single particle with a self-consistent electromagnetic field. This procedure seems plausible for studying the response of electrons to any external perturbation, and Bardeen [6], Ferrel [7] and Lindhard [8]... have used this ...approach ...in discussing such phenomena as the frequency and wave-number dependence of the dielectric constant, plasma oscillations, and characteristic energy losses in solids [10]''. These and similar phenomena have also been studied on the basis of a dielectric formulation of the many-body problem by Nozières and Pines [9]. The explicit relationship of the self-consistent field approach (Lindhard) to the collective approach (Nozières and Pines) has been studied by Ehrenreich and Cohen [10]. Here we give a short review closely following their work.

We consider the single-particle Liouville equation

$$i\,\partial\rho(t)/\partial t = [H, \rho(t)] \tag{3.12}$$

as describing the response of any particle of the system to the self-consistent potential $V(x,t)$, where ρ is the single-particle density matrix. The single particle Hamiltonian in Eq. (3.12) is

$$H = H_0 + V(x,t)\,, \tag{3.13}$$

where $H_0 = p^2/2m$ is the Hamiltonian of a free electron satisfying Schrödinger's equation $H_0|\mathbf{p}\rangle = \varepsilon_{\mathbf{p}}|\mathbf{p}\rangle$, and $|\mathbf{p}\rangle = \exp i\mathbf{p}\cdot\mathbf{x}$, in a system of unit volume. We expand the operator ρ in the form $\rho = \rho^{(0)} + \rho^{(1)}$. The unperturbed density matrix has the property $\rho^{(0)}|\mathbf{p}\rangle = n(\mathbf{p})|\mathbf{p}\rangle$, where $n(\mathbf{p})$ is the distribution function. We now Fourier analyze $V(x,t)$ in the form

$$V(x,t) = \Sigma_{\mathbf{q}} V(q,t) \exp -i\mathbf{q}\cdot\mathbf{x} \tag{3.14}$$

and linearize Eq. (3.12) by neglecting products of the type $V\rho^{(1)}$. This approximation is equivalent to first-order self-consistent perturbation theory [10]. Taking matrix elements between states $\mathbf{p}$ and $\mathbf{p+q}$, we thus obtain [10]

$$i\,\partial\langle\mathbf{p}|\,\rho^{(1)}|\mathbf{p+q}\rangle/\partial t = \langle\mathbf{p}|[H_0, \rho^{(1)}]|\mathbf{p+q}\rangle + \langle\mathbf{p}|[V, \rho^{(0)}]|\mathbf{p+q}\rangle$$

$$= (\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p+q}})\,\langle\mathbf{p}|\rho^{(1)}|\mathbf{p+q}\rangle + [\,n(\mathbf{p} + \mathbf{q}) - n(\mathbf{p})\,]V(q,t), \tag{3.15}$$

where $\langle \mathbf{p}|V|\mathbf{p+q}\rangle = V(\mathbf{q},t)$. The potential V consists of an external potential V_0 plus the screening potential V_s, which is related to the induced change in electron density [10],

$$\Delta n = \mathrm{Tr}\,\{\delta(\mathbf{x}_e - \mathbf{x})\rho^{(1)}\} = \Sigma_{\mathbf{q}} \exp -i\mathbf{q}\cdot\mathbf{x}\ \Sigma_{\mathbf{p}'}\ \langle \mathbf{p}'|\rho^{(1)}|\mathbf{p}'+\mathbf{q}\rangle \tag{3.16}$$

by Poisson's equation:

$$\nabla^2 V_s = -4\pi\,\Delta n\, e^2. \tag{3.17}$$

Here $\delta(\mathbf{x}_e - \mathbf{x})$ is the charge density operator, $\mathbf{x}_e$ being the position operator and $\mathbf{x}$ referring to a specific point in space [10]. We thus find [10]

$$V_s(\mathbf{q},t) = v_{\mathbf{q}}\, \Sigma_{\mathbf{p}'}\ \langle \mathbf{p}'|\rho^{(1)}|\mathbf{p}'+\mathbf{q}\rangle, \tag{3.18}$$

where $v_q = 4\pi e^2/q^2$. By substituting the above expression giving V_s for V in Eq. (3.15), we obtain the Liouville-Poisson equation determining $\langle \mathbf{p}|\rho^{(1)}|\mathbf{p+q}\rangle$ in the absence of an external perturbation:

$$\begin{aligned} i\ \partial\langle \mathbf{p}|\ \rho^{(1)}|\mathbf{p+q}\rangle/\partial t &= (\varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p+q}})\,\langle \mathbf{p}|\rho^{(1)}|\mathbf{p+q}\rangle \\ &\quad + v_{\mathbf{q}}[\,n(\mathbf{p}+\mathbf{q}) - n(\mathbf{p})\,]\,\Sigma_{\mathbf{p}'}\ \langle \mathbf{p}'|\rho^{(1)}|\mathbf{p}'+\mathbf{q}\rangle. \end{aligned} \tag{3.19}$$

"In solving problems by the SCF method, however, one can usually avoid the explicit expression of V_s in terms of $\rho^{(1)}$ within the equation of motion by means of an assumption about the time dependence of $V(\mathbf{q},t)$. To illustrate this point, we calculate the frequency and wave-number dependence of the longitudinal dielectric constant $\underline{\varepsilon}(\mathbf{q},\omega)$. We imagine that the external potential $V_0(\mathbf{q},t)$ acts on the system with time dependence $\exp(i\omega t+\eta t)$, where $\eta \rightarrow 0^+$ corresponds to an adiabatic turning on of the perturbation. This potential polarizes the system [10]". From electrodynamics we have the relation

$$P(q, t) = (1/4\pi)\,[\,\underline{\varepsilon}(q,\omega) - 1]\,E(q,t). \tag{3.20}$$

The polarization P(q,t) is related to the induced change in electron density by

$\nabla\cdot\mathbf{P} = e\Delta n$ or

$$-iqP(q,t) = e\Delta n(q,t) \tag{3.21}$$

and the electric field E(q,t) is given by

$$eE(q,t) = -iqV(q,t). \tag{3.22}$$

"Equation (3.15) is readily solved for $\langle \mathbf{p} | \rho^{(1)} | \mathbf{p+q} \rangle$ by assuming that $\langle \mathbf{p} | \rho^{(1)} | \mathbf{p+q} \rangle$ and $V_s(q,t)$ have the same time dependence as $V_0(q,t)$. The induced change in electron density $\Delta n(q,t)$ may then be calculated from Eq. (3.16) and $\underline{\varepsilon}(q,\omega)$ deduced from the field equations (3.20, 21, 22). We find [10]"

$$\underline{\varepsilon}(\mathbf{q},\omega) = 1 - \lim_{\eta\to 0^+} v_q \sum_{\mathbf{p}} \left[\frac{n(\mathbf{p} + \mathbf{q}) - n(\mathbf{p})}{\varepsilon_{\mathbf{p+q}} - \varepsilon_{\mathbf{p}} - \omega + i\eta} \right] \tag{3.23}$$

"This result was first obtained by Lindhard [8], with the SCF method and later by Nozières and Pines [9] using a many-particle approach based on the random phase approximation for a Fermi gas at zero temperature [10]". The equivalence of the SCF approach and the collective approach based on the RPA is clearly demonstrated in Section 2 of Ehrenreich and Cohen's paper. In the next chapter we follow a closely related analysis to find the response of a many-electron system.

4. THE LINEAR RESPONSE TO SCALAR AND VECTOR POTENTIALS IN THE RPA

There are many methods of deriving the RPA equations. In this work the equation of motion method is followed, because of its simplicity. The derivation by use of equations of motion is also called the self-consistent field method [10].

The Hamiltonian of the system (H_0) consists of the kinetic energy term and the electron-electron interaction term. To this we add the external interaction term. We can express H_0 in terms of second-quantized particle creation c_p^+ and annihilation c_p operators [12]

$$H_0 = \sum_p \varepsilon_p c^+{}_p c_p + 1/2 \sum_{q,p,k} v_q c^+{}_{p+q} c^+{}_{k-q} c_k c_p \tag{4.1}$$

where v_q is the Fourier transform of the Coulomb potential. Spin indices are omitted and a factor of two is introduced in the final expressions to account for the spin summation.

For scalar potential and vector potential perturbations, we express the external interactions as

$$H_S'(t) = -e\Sigma_q \rho(-q,t)\varphi(q,t) \tag{4.2}$$

$$H_V'(t) = -1/c\Sigma_q J(-q,t) \cdot A(q,t) \tag{4.3}$$

where the particle density operator and the current density operator have the forms

$$\rho(q,t) = \Sigma_p c^+{}_{p+q}(t)\, c_p(t) \tag{4.4}$$

$$J(q,t) = (-e/m)\Sigma_p (p + q/2)\, c^+{}_{p+q}(t) c_p(t). \tag{4.5}$$

It should be noted that the diamagnetic current, proportional to $\rho(\mathbf{r},t)\,\mathbf{A}(\mathbf{r},t)$ in $\mathbf{r}$ space, is not included in Eq. (4.5).

In the homogeneous electron gas, the particle density operator ($\mathbf{q} \neq 0$) has an expectation value of zero unless there is a perturbation of the system. A perturbation on the system of character $(\mathbf{q},\omega)$ will polarize the electron system. The effect of such a polarization of the system is to screen out the external potential at large distances. In the linear screening model, the average of the particle density operator is proportional to the potential causing the perturbation [12].

The equations of motion to be solved are

$$i\, dc^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}}/dt = [H, c^{+}_{\mathbf{p+q}} c_{\mathbf{p}}] \tag{4.6}$$

$$(-ie/\mathrm{m})d(\mathbf{p} + \mathbf{q}/2)\, c^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}}/dt = (-e/\mathrm{m})(\mathbf{p} + \mathbf{q}/2)\, [H, c^{+}_{\mathbf{p+q}} c_{\mathbf{p}}]. \tag{4.7}$$

The four terms in H give four terms in the commutator with $c^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}}$. The kinetic energy operator leads to the terms

$$[\sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}\, c^{+}_{\mathbf{k}} c_{\mathbf{k}}, c^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}}] = (\varepsilon_{\mathbf{p+q}} - \varepsilon_{\mathbf{p}})\, c^{+}_{\mathbf{p+q}} c_{\mathbf{p}} \tag{4.8}$$

$$(-e/\mathrm{m})(\mathbf{p} + \mathbf{q}/2)[\sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}\, c^{+}_{\mathbf{k}} c_{\mathbf{k}}\, , c^{+}_{\mathbf{p+q}} c_{\mathbf{p}}] = (-e/\mathrm{m})(\varepsilon_{\mathbf{p+q}} - \varepsilon_{\mathbf{p}})(\mathbf{p} + \mathbf{q}/2)\, c^{+}_{\mathbf{p+q}} c_{\mathbf{p}} \tag{4.9}$$

for density and current respectively.

The external perturbations give the terms

$$-e\sum_{\mathbf{q}'\mathbf{k}} \varphi(\mathbf{q}', t)\, [c^{+}_{\mathbf{k-q}'}\, c_{\mathbf{k}}, c^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}}] = -e\sum_{\mathbf{q}'} \varphi(\mathbf{q}', t)\, [c^{+}_{\mathbf{p+q-q}'}\, c_{\mathbf{p}} - c^{+}_{\mathbf{p+q}} c_{\mathbf{p+q}'}]$$

$$\approx -e\varphi(\mathbf{q},t)[c^{+}_{\mathbf{p}} c_{\mathbf{p}} - c^{+}_{\mathbf{p+q}} c_{\mathbf{p+q}}] \tag{4.10a}$$

$$-e\sum_{\mathbf{q}'\mathbf{k}} \varphi(\mathbf{q}',t)\,(-e/m)\,(\mathbf{p}+\mathbf{q}/2)[c^{+}_{\mathbf{k}-\mathbf{q}'}c_{\mathbf{k}}, c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}}]$$

$$= -e\,(-e/m)\,(\mathbf{p}+\mathbf{q}/2)\sum_{\mathbf{q}'}\varphi(\mathbf{q}',t)\,[c^{+}_{\mathbf{p}+\mathbf{q}-\mathbf{q}'}c_{\mathbf{p}} - c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}'}]$$

$$\approx -e\,(-e/m)\,(\mathbf{p}+\mathbf{q}/2)\,\varphi(\mathbf{q},t)[c^{+}_{\mathbf{p}}c_{\mathbf{p}} - c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}}] \qquad (4.10b)$$

and similarly,

$$-1/c\,(-e/m)\sum_{\mathbf{k}'\mathbf{q}'}(\mathbf{k}'+\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,[c^{+}_{\mathbf{k}'}c_{\mathbf{k}'+\mathbf{q}'}, c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}}]$$

$$= -1/c\,(-e/m)\sum_{\mathbf{q}'}(\mathbf{p}+\mathbf{q}-\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,c^{+}_{\mathbf{p}+\mathbf{q}-\mathbf{q}'}c_{\mathbf{p}} - (\mathbf{p}+\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}'}$$

$$\approx -1/c\,(-e/m)\,(\mathbf{p}+\mathbf{q}/2)\cdot\mathbf{A}_{\mathbf{q}}\,[c^{+}_{\mathbf{p}}c_{\mathbf{p}} - c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}}]. \qquad (4.11a)$$

$$-1/c(e/m)^2(\mathbf{p}+\mathbf{q}/2)\sum_{\mathbf{k}'\mathbf{q}'}(\mathbf{k}'+\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,[c^{+}_{\mathbf{k}'}c_{\mathbf{k}'+\mathbf{q}'}, c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}}]$$

$$= -1/c(e/m)^2(\mathbf{p}+\mathbf{q}/2)\sum_{\mathbf{q}'}(\mathbf{p}+\mathbf{q}-\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,c^{+}_{\mathbf{p}+\mathbf{q}-\mathbf{q}'}c_{\mathbf{p}} - (\mathbf{p}+\mathbf{q}'/2)\cdot\mathbf{A}_{\mathbf{q}'}\,c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}'}$$

$$\approx -1/c(e/m)^2(\mathbf{p}+\mathbf{q}/2)(\mathbf{p}+\mathbf{q}/2)\cdot\mathbf{A}_{\mathbf{q}}\,[c^{+}_{\mathbf{p}}c_{\mathbf{p}} - c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}+\mathbf{q}}]. \qquad (4.11b)$$

The summation over **q**′ is approximated by taking only the term **q** = **q**′ in Eqs. (4.10) and (4.11). The terms with other values of **q**′ are neglected. It is assumed that they average to zero within the random phase approximation.

The commutator with the electron interaction term leads to two terms, each with four operators [12]:

$$[H_{ee}, c^{+}_{\mathbf{p}+\mathbf{q}}c_{\mathbf{p}}] = \Sigma_{\mathbf{k}'\mathbf{q}'}\, v_{\mathbf{q}'}\,[c^{+}_{\mathbf{p}+\mathbf{q}+\mathbf{q}'}c^{+}_{\mathbf{k}'}c_{\mathbf{k}'+\mathbf{q}'}c_{\mathbf{p}} - c^{+}_{\mathbf{p}+\mathbf{q}}c^{+}_{\mathbf{k}'-\mathbf{q}'}c_{\mathbf{k}'}c_{\mathbf{p}-\mathbf{q}'}] \qquad (4.12)$$

"The result is approximated by pairing up the operators. We select values of the summation variables which produce operators of the type we are seeking. These are either combinations such as $c^+_{\mathbf{p}} c_{\mathbf{p}}$ or $c^+_{\mathbf{p+q}}\, c_{\mathbf{p}}$. There are three combinations which are interesting: $\mathbf{q}' = -\mathbf{q}$; $\mathbf{k}' = \mathbf{p}$; $\mathbf{k}' = \mathbf{p+q}$ [12]". These give the combinations, in the case of the density [12]:

$$[H_{ee}, c^+_{\mathbf{p+q}}\, c_{\mathbf{p}}] = [c^+_{\mathbf{p}} c_{\mathbf{p}} - c^+_{\mathbf{p+q}}\, c_{\mathbf{p+q}}]\{ v_{\mathbf{q}} \sum_{\mathbf{k}'} c^+_{\mathbf{k}'+\mathbf{q}}\, c_{\mathbf{k}'} - \sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q+q}'}\, c_{\mathbf{p+q}'}\}$$

$$- c^+_{\mathbf{p+q}}\, c_{\mathbf{p}} [\sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q+q}'}\, c_{\mathbf{p+q+q}'} - \sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q}'}\, c_{\mathbf{p+q}'}], \qquad (4.13)$$

and in the case of the current:

$$(-e/m)(\mathbf{p} + \mathbf{q}/2)[H_{ee}, c^+_{\mathbf{p+q}}\, c_{\mathbf{p}}] = (-e/m)(\mathbf{p} + \mathbf{q}/2)[c^+_{\mathbf{p}} c_{\mathbf{p}} - c^+_{\mathbf{p+q}}\, c_{\mathbf{p+q}}]\{ v_{\mathbf{q}} \sum_{\mathbf{k}'} c^+_{\mathbf{k}'+\mathbf{q}}\, c_{\mathbf{k}'}$$

$$- \sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q+q}'}\, c_{\mathbf{p+q}'}\}$$

$$-(-e/m)(\mathbf{p} + \mathbf{q}/2)\, c^+_{\mathbf{p+q}}\, c_{\mathbf{p}} [\sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q+q}'}\, c_{\mathbf{p+q+q}'}$$

$$- \sum_{\mathbf{q}'} v_{\mathbf{q}'}\, c^+_{\mathbf{p+q}'}\, c_{\mathbf{p+q}'}]. \qquad (4.14)$$

(We note that the commutator with the Coulomb interaction term remains the same in both cases. When spin indices are included explicitly, the term $v_{\mathbf{q}} \sum_{\mathbf{k}'} c^+_{\mathbf{k}'+\mathbf{q}}\, c_{\mathbf{k}'}$ includes a sum over spin states, while the remaining terms have a single associated spin index identical to that for $c^+_{\mathbf{p+q}}\, c_{\mathbf{p}}$.)

Now we take the ground state average of Eqs. (4.8, 10a, 11a, 13) and Eqs. (4.9, 10b, 11b, 14). In addition, the number operators $c^+_{\mathbf{p}} c_{\mathbf{p}}$ and $c^+_{\mathbf{p+q}}\, c_{\mathbf{p+q}}$ are replaced by their averages $n(\mathbf{p})$ and $n(\mathbf{p} + \mathbf{q})$ to obtain the result, in the case of the density:

$$\begin{aligned} \langle [H,\ c^{+}_{p+q}\, c_p] \rangle = {} & (\varepsilon_{p+q} - \varepsilon_p)\langle c^{+}_{p+q}\, c_p \rangle + [\, \Sigma(p+q) - \Sigma(p)]\langle c^{+}_{p+q}\, c_p \rangle \\ & + [\, n(p) - n(p+q)\,][v_q \langle \rho(q,t) \rangle \{1-G(q)\} - e\, \varphi(q,t) \\ & + (e/mc)\,(p + q/2)\cdot A(q,t)], \end{aligned} \qquad (4.15)$$

and in the case of the current:

$$\begin{aligned} \langle [H, (-e/m)(p+q/2)\, c^{+}_{p+q}\, c_p] \rangle = {} & (\varepsilon_{p+q} - \varepsilon_p)\, (-e/m)(p+q/2)\, \langle c^{+}_{p+q}\, c_p \rangle \\ & + [\, \Sigma(p+q) - \Sigma(p)]\, (-e/m)(p+q/2)\, \langle c^{+}_{p+q}\, c_p \rangle \\ & + [\, n(p) - n(p+q)\,][v_q\, (-e/m)(p+q/2) \langle \rho(q,t) \rangle \{1-G(q)\} \\ & - 1/c\, (e/m)^2 (p+q/2)(p+q/2)\cdot A(q,t) \\ & + (e/m)\, e\, (p+q/2)\ \ \varphi(q,t)]\ . \end{aligned} \qquad (4.16)$$

where $\Sigma(p) = -\Sigma_q v_q\, n(p+q)$ is the exchange energy and the Hubbard approximation as defined in Ref. (12) has been used to introduce the function G(q).

Since the density and current respectively satisfy the equations of motion:

$$i\, d\langle c^{+}_{p+q}\, c_p \rangle / dt = \omega \langle c^{+}_{p+q}\, c_p \rangle \qquad (4.17)$$

$$i\, d(-e/m)(p+q/2)\, \langle c^{+}_{p+q}\, c_p \rangle / dt = \omega (-e/m)(p+q/2)\, \langle c^{+}_{p+q}\, c_p \rangle, \qquad (4.18)$$

where external potentials are assumed to be oscillating at a single frequency ω, we finally obtain the equations:

$$\begin{aligned} & \{\omega + \varepsilon_p - \varepsilon_{p+q} + \Sigma(p) - \Sigma(p+q)\} \langle c^{+}_{p+q} c_p \rangle \\ & \quad = [\, n(p) - n(p+q)\,]\, [v_q \langle \rho(q,t) \rangle \{1-G(q)\} - e\, \varphi(q,t) + (e/mc)\,(p+q/2)\cdot A(q,t)\,] \end{aligned} \qquad (4.19)$$

and

$$\{\omega + \varepsilon_{\mathbf{p}} - \varepsilon_{\mathbf{p+q}} + \Sigma(\mathbf{p}) - \Sigma(\mathbf{p+q})\}\ (-e/m)(\mathbf{p} + \mathbf{q}/2) < c^{+}_{\mathbf{p+q}}\, c_{\mathbf{p}} >$$

$$= [n(\mathbf{p}) - n(\mathbf{p+q})]\ [v_q(-e/m)(\mathbf{p} + \mathbf{q}/2) < \rho(\mathbf{q},t) > \{1 - G(q)\}$$

$$+ e(e/m)(\mathbf{p} + \mathbf{q}/2)\ \varphi(\mathbf{q},t) - 1/c\ (e/m)^2\ (\mathbf{p} + \mathbf{q}/2)(\mathbf{p} + \mathbf{q}/2) \cdot \mathbf{A}(\mathbf{q},t)]. \tag{4.20}$$

Eqs. (4.19) and (4.20) are consistent, since (4.20) can be obtained from (4.19) by multiplication by $(-e/m)(\mathbf{p} + \mathbf{q}/2)$. Eq. (4.19) differs from the result in Chapter 5 of Ref. 12 by the inclusion of the vector potential terms.

Now we can sum Eqs. (4.19) and (4.20) over $\mathbf{p}$ to obtain equations for the particle density and the current density. Since the external potentials are assumed to be oscillating with a single frequency component, as $\exp(-i\omega t)$, we substitute for the external potentials $\varphi(\mathbf{q},\omega) \exp(-i\omega t)$ and $\mathbf{A}(\mathbf{q},\omega) \exp(-i\omega t)$. Within linear response, a homogeneous electron gas responds at the same wave vector and frequency as the external perturbation, so we can replace $<\rho(\mathbf{q}t)>$ by $\rho(\mathbf{q},\omega) \exp(-i\omega t)$ and $<\mathbf{J}(\mathbf{q},t)>$ by $\mathbf{J}(\mathbf{q},\omega) \exp(-i\omega t)$ to obtain equations for the induced particle density and current density respectively:

$$\rho(\mathbf{q},\omega) = \underline{P}(\mathbf{q},\omega)\ v_q\{1 - G(q)\}\rho(\mathbf{q},\omega) - e\ \underline{P}(\mathbf{q},\omega)\ \varphi(\mathbf{q},\omega) + (e/mc)\ \underline{\mathbf{Q}}(\mathbf{q},\omega) \cdot \mathbf{A}(\mathbf{q},\omega) \tag{4.21}$$

and

$$\mathbf{J}(\mathbf{q},\omega) = (-e/m)\ \underline{\mathbf{Q}}(\mathbf{q},\omega)\ v_q\{1 - G(q)\}\rho(\mathbf{q},\omega) + (e/m)\ e\ \underline{\mathbf{Q}}(\mathbf{q},\omega)\ \varphi(\mathbf{q},\omega) - 1/c(e/m)^2\ \underline{\mathbf{R}}(\mathbf{q},\omega) \cdot \mathbf{A}(\mathbf{q},\omega) \tag{4.22}$$

where

$$\underline{P}(q,\omega) = \sum_{p} \left[\frac{n(p) - n(p+q)}{\omega + \varepsilon_p - \varepsilon_{p+q} + \Sigma(p) - \Sigma(p+q)} \right] \tag{4.23a}$$

$$\underline{Q}(q,\omega) = \sum_{p} \left[\frac{[n(p) - n(p+q)]\,(p + q/2)}{\omega + \varepsilon_p - \varepsilon_{p+q} + \Sigma(p) - \Sigma(p+q)} \right] \tag{4.23b}$$

and

$$\underline{R}(q,\omega) = \sum_{p} \left[\frac{[n(p) - n(p+q)]\,(p + q/2)\,(p + q/2)}{\omega + \varepsilon_p - \varepsilon_{p+q} + \Sigma(p) - \Sigma(p+q)} \right] \tag{4.23c}$$

By neglecting the exchange energies and G(q), replacing the polarization term $\underline{P}(q,\omega)$ by the less accurate RPA result $P^1(q,\omega)$, and similarly replacing $\underline{Q}(q,\omega)$ by $Q^1(q,\omega)$ and $\underline{R}(q,\omega)$ by $R^1(q,\omega)$, we obtain the induced density in the RPA:

$$\rho(q,\omega) = P^1(q,\omega)\, v_q\, \rho(q,\omega) - e\, P^1(q,\omega)\, \varphi(q,\omega) + (e/mc)\, Q^1(q,\omega) \cdot A(q,\omega) \tag{4.24}$$

and the current density in the RPA:

$$J(q,\omega) = (-e/m)\, Q^1(q,\omega)\, v_q\, \rho(q,\omega) + (e/m)\, e\, Q^1(q,\omega)\, \varphi(q,\omega) - 1/c\, (e/m)^2\, R^1(q,\omega) \cdot A(q,\omega)\ . \tag{4.25}$$

Here $P^1(q,\omega)$ is the RPA polarization diagram,

$$P^1(q,\omega) = \sum_{p} \left[\frac{n(p) - n(p+q)}{\omega + \varepsilon_p - \varepsilon_{p+q}} \right] \tag{4.26}$$

and similarly for $Q^1(q,\omega)$ and $R^1(q,\omega)$.

Now we can solve Eq. (4.24) to obtain the particle density self-consistently.

$$\rho(\mathbf{q},\omega) = \frac{-e\,P^1(\mathbf{q},\omega)\,\varphi(\mathbf{q},\omega) + (e/mc)\,\mathbf{Q}^1(\mathbf{q},\omega)\cdot\mathbf{A}(\mathbf{q},\omega)}{1-P^1(\mathbf{q},\omega)v_q} \qquad (4.27)$$

Now the RPA dielectric constant is defined as $\underline{\varepsilon}_{RPA}(q,\omega) = 1 - P^1(q,\omega)\,v_q$. This function was first evaluated by Lindhard [8], as a model for a dynamic dielectric function. It is rather easy to derive and has a simple basis. It also predicts correctly a number of properties of the electron gas such as the existence of plasmons [11, 16]. The real part of the dielectric function may be represented by a single formula (see, e.g., Ref. 12, Eq. 5.5.5). The imaginary part has a variety of functional forms for different values of (q,ω) (see Ref. 12, Eq. 5.5.6). In certain limits, the imaginary part of $\underline{\varepsilon}_{RPA}(q,\omega)$ is zero. In our subsequent work, its limiting behavior at zero frequency and in the small momentum transfer limit will be used extensively.

Eq. (4.25) cannot be solved self-consistently by itself, but it can be solved by substituting the result for ρ(q,ω). Below, we analyze separately the response to a transverse vector potential and to a longitudinal vector potential.

The transverse component of A(q,ω), denoted by $A_t(q,\omega)$, is unaffected by a change of gauge. Also $A_t(q,\omega)$ is independent of the longitudinal component $A_l(q,\omega)$ and the scalar potential φ(q,ω). We set $A_l(q,\omega) = \varphi(q,\omega) = 0$, and determine the response to a nonvanishing $A_t(q,\omega)$. For an electron gas that is homogeneous and isotropic prior to the perturbation, $\underline{Q}(q,\omega)$ and $Q^1(q,\omega)$ are both vector functions with direction **q**. Then

$$J_t(q,\omega) = -1/c\,(e/m)^2\,\mathbf{R}^1(q,\omega)\cdot A_t(q,\omega)\ , \qquad (4.28)$$

or equivalently,

$$J_t(q,\omega) = -1/c\,(e/m)^2 \sum_p \left[\frac{n(p) - n(p+q)}{\omega + \varepsilon_p - \varepsilon_{p+q}}\right] (p + q/2)(p + q/2) \cdot A_t(q,\omega) \qquad (4.29)$$

This result is consistent with the observation that particle-hole excitations of transverse character cannot decay via the longitudinal Coulomb interaction, as noted in Ref. 16; we note that v_q is not present in Eq. (4.29).

Changes of gauge interconvert the scalar potential and the longitudinal component of the vector potential. The change from A, φ to A′, φ′ given by

$$A' = A + \nabla\Lambda \qquad (4.30a)$$

$$\varphi' = \varphi - 1/c\ \partial\Lambda/\partial t \qquad (4.30b)$$

in q, ω space is

$$A' = A + i\,q\,\Lambda \qquad (4.31a)$$

$$\varphi' = \varphi + i\,\omega/c\,\Lambda \qquad (4.31b)$$

From Eqs. (4.21) and (4.27), we require

$$\omega\,\underline{P}(q,\omega) = \underline{Q}(q,\omega) \cdot q/m \qquad (4.32)$$

in general for gauge-invariance of the field-induced change in the particle density, and

$$\omega\,P^1(q,\omega) = Q^1(q,\omega) \cdot q/m \qquad (4.33)$$

for gauge invariance in the RPA.

If we consider the response to a perturbing scalar potential only, the longitudinal component of the induced current density in the RPA is

$$J_l(q,\omega) = e^2/m\ Q^1(q,\omega)\ \varphi(q,\omega)\ /\ [1-P^1(q,\omega)v_q]\ . \qquad (4.34)$$

The equation of continuity

$$\mathbf{q} \cdot \mathbf{J}_l(\mathbf{q},\omega) = -e\omega\, \rho(\mathbf{q},\omega) \tag{4.35}$$

connects $\rho(\mathbf{q},\omega)$ and $\mathbf{J}_l(\mathbf{q},\omega)$. This equation is satisfied when the gauge-invariance condition is met.

Alternately, we may consider the response to the longitudinal component of the vector potential only. In this case, we obtain

$$\begin{aligned}\mathbf{J}_l(\mathbf{q},\omega) = -1/c\, (e/m)^2 \{&\mathbf{Q}^1(\mathbf{q},\omega)\, v_q\, \mathbf{Q}^1(\mathbf{q},\omega) \cdot \mathbf{A}_l(\mathbf{q},\omega)\, [1-P^1(\mathbf{q},\omega)v_q]^{-1} \\ &+ \mathbf{R}^1(\mathbf{q},\omega) \cdot \mathbf{A}_l(\mathbf{q},\omega)\}\end{aligned} \tag{4.36}$$

We note that the diamagnetic current is omitted in Eq. (4.36), as before. For gauge invariance of $\mathbf{J}_l(\mathbf{q},\omega)$ it is required that

$$\omega\, \underline{\mathbf{Q}}(\mathbf{q},\omega) = \underline{\mathbf{R}}(\mathbf{q},\omega) \cdot \mathbf{q}/m \ , \tag{4.37}$$

and similarly for the corresponding functions in the RPA. From Eqs. (4.25), (4.33), and (4.37) in the RPA, we obtain

$$\mathbf{J}_l(\mathbf{q},\omega) = -1/c\, (e/m)^2\, \mathbf{R}^1(\mathbf{q},\omega) \cdot \mathbf{A}_l(\mathbf{q},\omega) \,/\, [1-P^1(\mathbf{q},\omega)v_q] \ . \tag{4.38}$$

Comparison of Eqs. (4.27), (4.28), and (4.38) shows that dielectric screening affects $\mathbf{J}_l(\mathbf{q},\omega)$ but not $\mathbf{J}_t(\mathbf{q},\omega)$ in the RPA.

In the next chapter, we show the form of the particle-density susceptibility, and then in subsequent chapters we analyze the current-density susceptibility.

5. CHARGE DENSITY SUSCEPTIBILITY

The linear response of the interacting electron gas to an added impurity charge was first evaluated by Langer and Vosko [13]. Screening of the scalar potential of an impurity charge gives rise to Friedel [14, 15] oscillations at large distances. The Friedel oscillations are real features of the charge distribution in metals containing impurities and have been detected via broadening of nuclear magnetic resonance lines in dilute Cu alloys by Rowland and Bloembergen [16a]. The experimental fact is that the presence of one foreign atom seems to eliminate about fifty Cu nuclei from the central resonance signal. If straightforward Fermi-Thomas screening [11, 12] applied, one would have an electrical disturbance limited to the near neighbor Cu nuclei alone.

Friedel oscillations are a consequence of the logarithmic singularity possessed by the RPA dielectric function. The origin of this singularity is the sharpness of the Fermi surface; one passes into a different physical regime when going from $k < 2k_F$ to $k > 2k_F$ because one is passing into a region in which the momentum transfer can no longer take an electron from one part of the Fermi surface to another [11]. This disturbance is therefore effective at rather large distances.

Since the polarization of the system satisfies the equation,

$$\mathbf{P}(\mathbf{k},\omega) = (1/4\pi)[\varepsilon(\mathbf{k},\omega) - 1] \cdot \mathbf{E}(\mathbf{k},\omega), \tag{5.1}$$

the charge density susceptibility is intimately related to the complex polarizability. In the subsequent sections of this chapter we evaluate the charge density susceptibility and the nonlocal polarizability density of the interacting electron gas as linear responses to an arbitrary perturbing scalar potential.

a. Relation between the nonlocal polarizability density and the dielectric constant [17]

The nonlocal polarizability density is a linear response tensor that gives the polarization $\mathbf{P}(\mathbf{r}, \omega)$ induced at a point $\mathbf{r}$ in a molecule by a perturbing electric field $\mathbf{E}(\mathbf{r}', \omega)$ that acts at the point $\mathbf{r}'$ [18-23]:

$$\mathbf{P}(\mathbf{r}, \omega) = \int d\mathbf{r}' \; \boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega) \cdot \mathbf{E}(\mathbf{r}', \omega) \quad . \tag{5.2}$$

Thus $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ represents the distribution of polarizability within a molecule or an extended quantum mechanical system. The purpose of this work is to gain information about the nature and functional form of the static polarizability density, by determining this property for a homogeneous electron gas at $T = 0$.

The induced polarization $\mathbf{P}(\mathbf{r}, \omega)$ in Eq. (5.7) is related to the change in charge density $\delta\rho(\mathbf{r}, \omega)$ due to $\mathbf{E}(\mathbf{r}', \omega)$ by [22]

$$\nabla \cdot \mathbf{P}(\mathbf{r}, \omega) = -\delta\rho(\mathbf{r}, \omega) \quad , \tag{5.3}$$

so $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ provides a complete description of the response to perturbing fields that are derivable from scalar potentials. The polarization can be interpreted as the density of the induced dipole moment, but it also includes quadrupolar and higher-order response [23].

The nonlocal polarizability density was introduced by Maaskant and Oosterhoff in a study of optical rotation in condensed media [18]. In their work, $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ is expressed as a difference of two components that are individually divergent as $\omega \rightarrow 0$, and each transition matrix element in the expression involves an operator specified only as an infinite series [18]. For response to fields that are derivable from a scalar potential, $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ can be recast in a computationally tractable form, via a connection [22] between its spatial Fourier transform and that of the charge-density susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ [24-29].

The function $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ determines the change in charge density at point $\mathbf{r}$ in response to a perturbing scalar potential acting at $\mathbf{r}'$, within linear response. This connection gives the *longitudinal* component of the polarizability density $\boldsymbol{\alpha}^{L}(\mathbf{r}, \mathbf{r}'; \omega)$ [22].

For small molecules, the spatial Fourier transforms of $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ (and therefore $\boldsymbol{\alpha}^{L}(\mathbf{k}, \mathbf{k}'; \omega)$) have been computed via pseudo-state methods [28], a stationary principle [25], and an Unsöld-type approximation [27; see also Refs. 26 and 29]. The point-atom-polarizability approximation (PAPA) [20, 30], truncated at the dipole terms, is equivalent to approximating $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ as a weighted sum of products of Dirac delta functions located at the nuclei. Modifications of the PAPA model to allow for distributed point multipoles [30, 31] can improve its approximation to the continuous polarizability distribution of the actual function $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega)$ and thus extend the range of validity of the PAPA model.

In this section (cf. [17]), we analyze the static, longitudinal polarizability density $\boldsymbol{\alpha}^{L}(\mathbf{r}, \mathbf{r}'; \omega = 0)$, for a homogeneous electron gas at zero temperature. Our intent is to gain a better understanding of $\boldsymbol{\alpha}(\mathbf{r}, \mathbf{r}'; \omega = 0)$, and to provide information for the development of approximations to molecular polarizability densities.

In this section, we derive an equation for the longitudinal component of the nonlocal polarizability density $\boldsymbol{\alpha}^{L}{}_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; 0)$ via its connection to the charge-density susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; 0)$. In wave-vector space [22],

$$\boldsymbol{\alpha}^{L}(\mathbf{k}, \mathbf{k}'; \omega) = \mathbf{k}\,\mathbf{k}'\,\alpha(\mathbf{k}, \mathbf{k}'; \omega) \,/\, (k\,k') \quad , \tag{5.4}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are unit vectors in the directions $\mathbf{k}$ and $\mathbf{k}'$, and

$$\alpha(\mathbf{k}, \mathbf{k}'; \omega) = \int d\mathbf{r} \int d\mathbf{r}' \;\; \alpha(\mathbf{r}, \mathbf{r}'; \omega)\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, e^{i\mathbf{k}'\cdot\mathbf{r}'} \quad . \tag{5.5}$$

In sum-over-states form, the charge-density susceptibility satisfies [24]

$$\alpha(\mathbf{k}, \mathbf{k}'; \omega) = 2/h \sum_{n}{}' \, \omega_{n0} \langle 0 \,|\, \rho(-\mathbf{k}) \,|\, n \rangle \langle n \,|\, \rho(\mathbf{k}') \,|\, 0 \rangle / (\omega_{n0}{}^{2} - \omega^{2}) \; . \qquad (5.6)$$

In Eq. (5.6), the sum runs over the excited states n, ω_{n0} denotes the transition frequency $(E_n - E_0)/h$, $\rho(\mathbf{k})$ is the Fourier transform of the electronic charge density operator,

$$\rho(\mathbf{k}) = -e \sum_{j} \exp(i\, \mathbf{k} \cdot \mathbf{r}_j) \; , \qquad (5.7)$$

and $\mathbf{r}_j$ is the coordinate for the jth electron.

Because of the translational invariance of the homogeneous electron gas, $\alpha(\mathbf{r}, \mathbf{r}'; \omega)$ depends only on $\mathbf{r} - \mathbf{r}'$, and therefore $\alpha(\mathbf{k}, \mathbf{k}'; \omega)$ takes the form

$$\alpha(\mathbf{k}, \mathbf{k}'; \omega) = (2\pi)^3 \alpha(\mathbf{k}, \omega)\, \delta(\mathbf{k}' - \mathbf{k}) \; . \qquad (5.8)$$

The susceptibility $\alpha(\mathbf{k}, \omega)$ gives the change in the $\mathbf{k}$, ω component of the charge density $\delta\langle\rho(\mathbf{k}, \omega)\rangle$ due to an external scalar potential $\delta\phi^{ex}(\mathbf{k}, \omega)$:

$$\delta\langle\rho(\mathbf{k}, \omega)\rangle = \alpha(\mathbf{k}, \omega)\, \delta\phi^{ex}(\mathbf{k}, \omega) \; . \qquad (5.9)$$

Linear response theory relates the susceptibility $\alpha(\mathbf{k}, \omega)$ to the retarded density-density correlation function $D^R(\mathbf{k}, \omega)$ [11]. In terms of the function $\Pi^R(\mathbf{k}, \omega)$ defined by $\Pi^R(\mathbf{k}, \omega) = h^{-1} D^R(\mathbf{k}, \omega)$:

$$\delta\langle\rho(\mathbf{k}, \omega)\rangle = e^2 \, \Pi^R(\mathbf{k}, \omega)\, \delta\phi^{ex}(\mathbf{k}, \omega) \; . \qquad (5.10)$$

In diagrammatic theory [11], $\Pi^R(\mathbf{k}, \omega)$ is the "retarded polarization part." From Eqs.(5.4), and (5.8)-(5.10),

$$\boldsymbol{a}^{L}(\mathbf{k}, \mathbf{k}'; \omega) = (2\pi)^3 e^2 \, k\, k' \, \Pi^R(\mathbf{k}, \omega)\, \delta(\mathbf{k}' - \mathbf{k}) / (k\, k') \; . \qquad (5.11)$$

Thus in coordinate space, the static longitudinal polarizability density is

$$\alpha^L_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; 0) = (2\pi)^{-3} e^2 \int d\mathbf{k}\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} k_\alpha k_\beta \Pi^R(\mathbf{k}, 0) k^{-2} . \tag{5.12}$$

We simplify Eq. (5.12) using [11]

$$\Pi^R(\mathbf{k}, 0) e^2 k^{-2} = (4\pi)^{-1} [\varepsilon(\mathbf{k}, 0)^{-1} - 1] , \tag{5.13}$$

and the Rayleigh expansion [32]

$$e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) j_\ell(kx) P_\ell(\cos\gamma) , \tag{5.14}$$

where $|\mathbf{r} - \mathbf{r}'| = x$, $j_\ell(kx)$ is the ℓth spherical Bessel function, and γ is the angle between $\mathbf{k}$ and $(\mathbf{r} - \mathbf{r}')$. In terms of the orientation angles θ_k, φ_k for the vector $\mathbf{k}$ and the angles θ, φ for $(\mathbf{r} - \mathbf{r}')$, the addition theorem for spherical harmonics gives [33]

$$P_\ell(\cos\gamma) = 4\pi (2\ell+1)^{-1} \sum_{m=-\ell}^{\ell} Y_\ell^m(\theta_k, \varphi_k) Y_\ell^{m*}(\theta, \varphi) . \tag{5.15}$$

For an isotropic, homogeneous electron gas, after specializing the result from Eqs. (5.12)-(15) to $\alpha^L_{zz}(\mathbf{r}, \mathbf{r}'; 0)$, we obtain

$$\alpha^L_{zz}(\mathbf{r}, \mathbf{r}'; 0) = 1/3\, (2\pi)^{-3} \int_0^\infty dk\, k^2 j_0(kx) [\varepsilon(k, 0)^{-1} - 1]$$

$$- 2/3\, (2\pi)^{-3} \int_0^\infty dk\, k^2 j_2(kx) [\varepsilon(k, 0)^{-1} - 1] P_2(\cos\theta) , \tag{5.16}$$

where $j_0(z) = z^{-1} \sin z$ and $j_2(z) = (3 z^{-3} - z^{-1}) \sin z - 3 z^{-2} \cos z$. The analytical results in Sec. c are based on Eq. (5.16) for $\alpha^L_{zz}(\mathbf{r}, \mathbf{r}'; 0)$. Other components of the polarizability tensor may be computed analogously.

b. Asymptotic results for the nonlocal polarizability density in the RPA [17]

In the random phase approximation (RPA) [5, 10], the dielectric function is [8, 11, 12, 16]

$$\varepsilon(k, 0) \;=\; 1 + 4\,\alpha\, r_s\, k_F^{\,2}\, (\pi k^2)^{-1}\, g(k/k_F)\ . \tag{5.17}$$

In Eq. (5.17), $\alpha = (4/9\pi)^{1/3}$. The density of the electron gas is characterized by the dimensionless ratio $r_s = r_0\,/a_0$, where a_0 is the Bohr radius and the volume per particle V/N satisfies $V/N = 4\pi\,/3\; r_0^{\,3}$. The wavenumber k_F of the highest occupied state in the electron gas at $T = 0$ is given by $k_F = 1/(\alpha r_0)$; k_F is designated the Fermi wavenumber [11]. The function g(z) is [8, 11, 12, 16]

$$g(z) \;=\; 1/2 - (2z)^{-1}\, (1 - z^2/4)\, \ln\, \left|\, (1 - z/2)\, /\, (1 + z/2)\, \right|\ . \tag{5.18}$$

We find the form of $\mathscr{a}^L_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ for large $|\,\mathbf{r} - \mathbf{r}'\,|$ following the method of Ref. 11. Since g(z) is an even function of z,

$$\begin{aligned}
\mathscr{a}^L_{zz}(\mathbf{r}, \mathbf{r}'; 0) \;=\; & (2\pi)^{-3}\, (6ix)^{-1} \int_{-\infty}^{\infty} dk\, k\, e^{ikx}\, [\varepsilon(k, 0)^{-1} - 1] \\
& - 2/3\, (2\pi)^{-3}\, \wp \int_{-\infty}^{\infty} dk\, k^2\, \{ (2i)^{-1}\, [3\, (kx)^{-3} - (kx)^{-1}] - 3/2\, (kx)^{-2} \} \\
& \qquad e^{ikx}\, [\varepsilon(k, 0)^{-1} - 1]\, P_2(\cos\theta)\ ,
\end{aligned} \tag{5.19}$$

where $\wp$ denotes the principal value of the integral (see the Appendix). After rewriting $g(k/k_F)$ in the form [11]

$$\begin{aligned}
g(k/k_F) = {} & 1/2 - (2\, k\, k_F)^{-1}\, (k_F^{\,2} - k^2/4) \\
& \times \lim_{\eta \to 0^+} 1/2\, \ln\, \{\, [(k - 2\, k_F)^2 + \eta^2\,]\, /\, [(k + 2\, k_F)^2 + \eta^2]\, \}\ ,
\end{aligned} \tag{5.20}$$

we evaluate the integrals in Eq. (5.19) by complex contour integration around the contour shown in Appendix A. In the upper half plane (in k), the integrands have simple poles near ik_{TF} where k_{TF} is the Thomas-Fermi wavenumber given by $k_{TF} = (4\alpha r_s/\pi)^{1/2}\, k_F$. In the second integral in Eq. (5.24), the function $3\, k^2\, (kx)^{-3}\, e^{ikx}\, [\varepsilon(k, 0)^{-1} - 1]$ has an additional pole at $k = 0$. Both integrands have branch points (in the function g) at $\pm\, 2k_F \pm i\eta$, with branch cuts originating at these points, as shown in Figure A.1 in Appendix A, which also gives the details of the calculation. Results for integrals around the branch cuts C(1) and C(2) in the upper half plane (of k) are:

$$\int_{C(1)} dk\, k^n\, e^{ikx}\, [\varepsilon(k, 0)^{-1} - 1]$$

$$= 2^{n+1}\, \pi\, \xi\, k_F{}^{n-1}\, x^{-2} \exp(2ik_F x)\, (4 + \xi)^{-2}$$

$$\times \left\{ -i + 2\, [\xi\, (C - 3/2 + \ln 4\, k_F x) - 8 + (2n + 3)(1 + \xi/4)] \,/\, [k_F x (4 + \xi)] + \dots \right\} \tag{5.21}$$

and

$$\int_{C(2)} dk\, k^n\, e^{ikx}\, [\varepsilon(k, 0)^{-1} - 1]$$

$$= (-1)^{n+1}\, 2^{n+1}\, \pi\, \xi\, k_F{}^{n-1}\, x^{-2} \exp(-2ik_F x)\, (4 + \xi)^{-2}$$

$$\times \left\{ -i - 2\, [\xi\, (C - 3/2 + \ln 4\, k_F x) - 8 + (2n + 3)(1 + \xi/4)] \,/\, [k_F x (4 + \xi)] + \dots \right\} \tag{5.22}$$

where $n \geq -1$, ξ is defined by $\xi \equiv k_{TF}{}^2/(2k_F{}^2) \equiv 2\, \alpha\, r_s\, \pi^{-1}$, and C is Euler's constant ($C \approx 0.577216$). The result obtained for $\sigma^L{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ is

$$\begin{aligned}\mathscr{a}^{L}_{zz}(\mathbf{r},\mathbf{r}';0) = {} & (2\pi)^{-3}\,4\pi/3\,x^{-3}\,\xi\,(4+\xi)^{-2}\,\big\{\cos(2k_Fx)+2\,(k_Fx)^{-1}\,(4+\xi)^{-1} \\ & \times\sin(2k_Fx)\,[3-\xi(C-1/4)-\xi\ln(4k_Fx)]\,\big\} \\ & +(2\pi)^{-3}\,8\pi/3\,x^{-3}\,\xi\,(4+\xi)^{-2}\,P_2(\cos\theta)\,\big\{\cos(2k_Fx)-2\,(k_Fx)^{-1}\,\xi \\ & \times(4+\xi)^{-1}\sin(2k_Fx)\,[C+1/2+\ln(4k_Fx)]\,\big\} \\ & +\ (2\pi)^{-3}\,\pi\,x^{-3}\,P_2(\cos\theta)\ ,\end{aligned} \tag{5.23}$$

where $x = |\mathbf{r}-\mathbf{r}'|$. Fig. 1 [17] shows the asymptotic form of $\mathscr{a}^{L}_{zz}(\mathbf{r},\mathbf{r}';0)$ from Eq. (5.23), with $r_s = 4$. The error due to terms omitted from Eq. (5.23) is of the order $(a\,x^{-5} + b\,x^{-5}\ln k_Fx)$.

In Eqs. (5.19) and (5.23), $\mathscr{a}^{L}_{zz}(\mathbf{r},\mathbf{r}';0)$ has two components which transform differently under rotations, one as P_0 and the other as P_2. We have not found the integrals needed for the P_2 component in any earlier work. However, the integrals needed for the P_0 component have previously been used to find the change in the charge density $\delta\langle\rho(x)\rangle$ induced in an electron gas when a point charge Ze is inserted at an origin a distance x away [11, 12, 13]:

$$\begin{aligned}\delta\langle\rho(x)\rangle = {} & (2\pi)^{-3}\,Ze\int d^3\mathbf{k}\ \exp(i\mathbf{k}\cdot\mathbf{x})\,[\varepsilon(\mathbf{k},0)^{-1}-1] \\ = {} & Ze/(4\pi^2\,ix)\int_{-\infty}^{\infty} k\,e^{ikx}\,[\varepsilon(k,0)^{-1}-1]\,dk\ .\end{aligned} \tag{5.24}$$

Thus, comparison of asymptotic results for $\delta\langle\rho(x)\rangle$ serves as a check on the P_0 component of Eq. (5.23). Specializing Eqs. (5.21) and (5.22) to n = 1, we obtain

$$\begin{aligned}\delta\langle\rho(x)\rangle = {} & Ze\,\pi^{-1}\,2\xi\,(4+\xi)^{-2}\,x^{-3}\,\big\{\cos(2k_Fx)-2\,(4+\xi)^{-1}\,(k_Fx)^{-1} \\ & \times\sin(2k_Fx)\,[\,\xi\,(C-1/4)-3+\xi\ln 4k_Fx]+\ldots\,\big\}\ ,\end{aligned} \tag{5.25}$$

in agreement with the result of Fetter and Walecka [11] for large x.

We note that Eqs. (5.21) and (5.22) can also be used to obtain the asymptotic form of the charge-density susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; 0)$ in the RPA:

$$\alpha(\mathbf{r}, \mathbf{r}'; 0) = (2\pi)^{-3} (2ix)^{-1} \int_{-\infty}^{\infty} k^3 e^{ikx} [\varepsilon(k, 0)^{-1} - 1]\, dk$$

$$= (2\pi)^{-3}\, 16\pi\, k_F{}^2\, x^{-3}\, \xi\, (4 + \xi)^{-2} \left\{ \cos(2k_F x) - 2\,(4 + \xi)^{-1} (k_F x)^{-1} \right.$$

$$\left. \times \sin(2k_F x)\, [\, \xi\,(C + 3/4) + 1 + \xi \ln 4k_F x] + \ldots \right\}, \qquad (5.26)$$

with x defined as above. The susceptibility $\alpha(\mathbf{r}, \mathbf{r}'; 0)$ gives the change in charge density induced by a scalar potential of *arbitrary spatial variation*. This contrasts with the function $\delta\langle\rho(x)\rangle$ previously computed in Refs. 11 and 13, since $\delta\langle\rho(x)\rangle$ is the response specific to a single added point-charge impurity.

The asymptotic form of $\boldsymbol{\alpha}^{L}{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ contains oscillatory terms and a non-oscillatory term (the last). Mathematically, the oscillatory, long-range terms in $\boldsymbol{\alpha}^{L}{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$, $\delta\langle\rho(x)\rangle$, and $\alpha(\mathbf{r}, \mathbf{r}'; 0)$ are produced by integrations along the branch cuts in $\varepsilon(\mathbf{k}, 0)$, within the RPA. The oscillations in $\boldsymbol{\alpha}^{L}{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ are evident in Figure 1 [17].

The non-oscillatory, long-range (x^{-3}) term in $\boldsymbol{\alpha}^{L}{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ has a different mathematical and physical origin. It stems from the singularity of the integrand in the P_2-component at k = 0, and an identical term is present even at Thomas-Fermi level. In the Thomas-Fermi approximation, the dielectric function is [12]

$$\varepsilon_{TF}(k, 0) = 1 + k_{TF}{}^2/k^2 . \qquad (5.27)$$

When Eq. (5.27) is substituted into Eq. (5.16) for $\boldsymbol{\alpha}^{L}{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$, the resulting integrands have simple poles at $k = 0$ and $k = \pm\, i\, k_{TF}$. Hence by complex contour integration, we

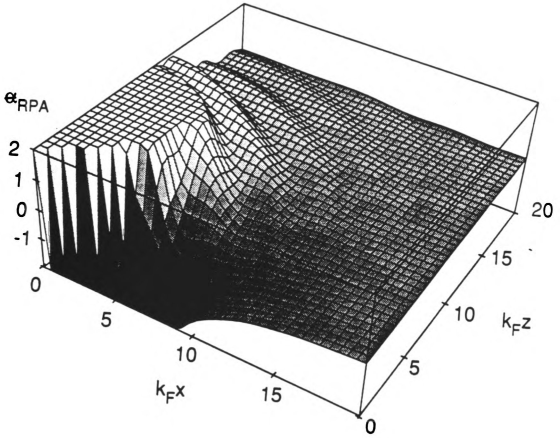

Figure 1. Asymptotic form of the nonlocal polarizability density in the random phase approximation, from Eq. (23). The figure shows $\alpha_{RPA} \equiv (2\pi)^3\, 3/\pi\, k_F^{-3}\, 10^3\, \alpha^L{}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ as a function of $k_F x \equiv k_F\, (\mathbf{r} - \mathbf{r}')_x$ and $k_F z \equiv k_F\, (\mathbf{r} - \mathbf{r}')_z$, with $r_s = 4$. The range of plotted α_{RPA} values is [-2.0, 2.0]. Friedel oscillations are evident in the plot.

obtain

$$\alpha^{L}{}_{TF,zz}(\mathbf{r},\mathbf{r}';0) = (2\pi)^{-3}\,\pi/3\;\;P_2(\cos\theta)\,k_{TF}{}^{3}$$

$$\times\,\{\;3\,(k_{TF}x)^{-3} - \exp(-k_{TF}x)\,[\;3\,(k_{TF}x)^{-3} + 3\,(k_{TF}x)^{-2} + (k_{TF}x)^{-1}]\,\}$$

$$-\,(2\pi)^{-3}\,\pi/6\;k_{TF}{}^{3}\exp(-k_{TF}x)\,(k_{TF}x)^{-1}\;. \qquad (5.28)$$

The long-range (x^{-3}), non-oscillatory component of the polarizability density in Eqs. (5.23) and (5.28) reflects charge screening. For example, when a perturbing point charge + Ze is added to the electron gas, the change in net charge inside a large sphere centered on the perturber approaches – Ze, as the radius R_i of the sphere increases [11, 12]. Equation (5.2) relates the induced polarization $\mathbf{P}(\mathbf{r})$ to the induced change in charge density; therefore as R_i increases,

$$\int \mathbf{P}(\mathbf{r})\cdot d\mathbf{S}_i \;=\; -\int \delta\rho(\mathbf{r})\,dV_i \;\rightarrow\; Ze\;, \qquad (5.29)$$

where the integrals run over the surface $d\mathbf{S}_i$ and the volume dV_i of the sphere of radius R_i. Thus, for sufficiently large R_i, the polarization on the surface of the sphere must vary as $R_i{}^{-2}$. The non-oscillatory, x^{-3} terms in the Thomas-Fermi and RPA expressions for $\alpha^{L}{}_{zz}(\mathbf{r},\mathbf{r}';0)$ give rise to the required $R_i{}^{-2}$ component of the polarization.

We note that charge is conserved overall for the electron gas, so Eq. (5.11) holds. A surface charge of Ze develops at the outer boundary of the electron-gas system, on a sphere of radius R_s. In the calculations, the limit $R_s \rightarrow \infty$ is taken before the limit $R_i \rightarrow \infty$.

For numerical results based on the RPA and a more accurate dielectric function derived by Vashishta and Singwi [34, 35], see Ref. 17.

c. Fourier Transform of dynamic Charge Density Susceptibility

The dynamic charge-density susceptibility can be evaluated by extension of the approach used in the previous sections. The susceptibility is determined by the following integral over wave vector k and frequency ω:

$$\alpha(x, t) = (2\pi)^{-4} (2ix)^{-1} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega\, k^3 \exp(ikx) \exp(-i\omega t) [\varepsilon(k, \omega)^{-1} - 1], \tag{5.30}$$

where $x = |\mathbf{r} - \mathbf{r}'|$, t is the time elapsed between perturbation and response points, and $\varepsilon(k, \omega)$ is the frequency-dependent dielectric function. Within the RPA, the dielectric function is connected to the lowest-order polarization insertion $\Pi^0(k, \omega)$ via

$$\varepsilon(k, \omega) = 1 - U_0(k)\, \Pi^0(k, \omega), \tag{5.31}$$

with $U_0(k) = 4\pi e^2/k^2$. Below, we use scaled variables q and ν, defined by $q = k/k_F$ and $\nu = m\omega/(\hbar k_F^2)$. Then for positive ν,

$$\begin{aligned} \mathrm{Re}\, \Pi^0(q, \nu) = {} & 2mk_F/(4\pi^2 \hbar^2) \{-1 + 1/(2q) [1 - (\nu/q - q/2)^2] \\ & \times \ln |[1 + (\nu/q - q/2)] [1 - (\nu/q - 2/q)]| \\ & - 1/(2q) [1 - (\nu/q + q/2)^2] \ln |[1 + (\nu/q + q/2)]/[1 - (\nu/q + q/2)]|\}. \end{aligned} \tag{5.32}$$

The imaginary part takes on different functional forms, depending upon the value of q and the relation between q and ν:

i) If $q > 2$, $q^2/2 + q \geq \nu \geq q^2/2 - q$, or if $q < 2$ and $q + q^2/2 \geq \nu \geq q - q^2/2$, then

$$\mathrm{Im}\, \Pi^0(q, \nu) = -mk_F/(4\pi q \hbar^2) [1 - (\nu/q - q/2)^2]. \tag{5.33}$$

ii) If $q < 2$, and $0 \leq \nu \leq q - q^2/2$, then

$$\text{Im}\,\Pi^0(q, \nu) = -mk_F\nu/(\hbar^2\, 2\pi\, q). \tag{5.34}$$

$\Pi^0(q, \nu)$ is even in q, Re $\Pi^0(q, \nu)$ is even in ν, and Im $\Pi^0(q, \nu)$ is odd in ν. The integral over k can be found by complex contour integration in the q plane, with the contour closed in the upper half-plane. Poles in the upper half-plane of q (with a finite displacement from the real axis) do not contribute to the asymptotic value of the susceptibility density, because the terms due to such poles decay exponentially with increasing x. There are nonvanishing, asymptotic contributions from poles on the real axis, and from integrations around the branch cuts of the log functions in Re $\Pi^0(q,\nu)$. To locate the branch cuts, we rewrite

$$\ln \left| [1 + (\nu/q - q/2)]/[1 - (\nu/q - q/2)] \right|$$

$$= \lim_{\eta \to 0} 1/2 \ln \{ [(1 + \nu/q - q/2)^2 + \eta^2] / [(1 - \nu/q + q/2)^2 + \eta^2] \} \tag{5.35}$$

and similarly for the second logarithmic term. There are four equations defining the origins of the branch cuts:

a) $1 + \nu/q - q/2 = \pm\, i\eta$ (5.36)

b) $1 - (\nu/q - q/2) = \pm\, i\eta$ (5.37)

c) $1 + (\nu/q + q/2) = \pm\, i\eta$ (5.38)

d) $1 - (\nu/q + q/2) = \pm\, i\eta$. (5.39)

When $\nu < 1/2$, the origins of the branch cuts lie just above and below the real axis, at points with real components given by $q^{(a)}_\pm = 1 \pm (1 + 2\nu)^{1/2}$, $q^{(b)}_\pm = -1 \pm (1 + 2\nu)^{1/2}$, $q^{(c)}_\pm = -1 \pm (1 - 2\nu)^{1/2}$, $q^{(d)}_\pm = 1 \pm (1 - 2\nu)^{1/2}$. Thus for small but non-zero ν, there are eight branch points in the upper half plane. The branch cuts are all taken parallel to the Im q axis, with those originating in the upper half plane running out to Im q = $+\infty$; cuts originating in the lower half plane run to Im q = $-\infty$. As ν approaches 1/2, two branch cuts in the upper half plane coalesce, with real components of the origins at Re q = 1; and a second pair in the upper half-plane coalesces at Re q = -1. (Similarly, there are two pairwise coalescences in the lower half-plane). For $\nu > 1/2$, there are four branch-cut origins just above the real axis, four just below the real axis, and two (with vanishing separation as $\eta \to 0$) in each quadrant of the complex q plane. We run branch cuts between the two branch points in each quadrant that are well off the real axis, and choose the remaining branch cuts as before. Then the integral to be evaluated takes the form

$$\int_{-\infty}^{\infty} f(q)\,dq = -\int_{C^1} f(q)\,dq - \int_{C^2} f(q)\,dq - \int_{C^3} f(q)\,dq - \int_{C^4} f(q)\,dq \ + i\,\pi\,\Sigma_n K_n$$

$$\left[-\int_{C^5} f(q)\,dq - \int_{C^6} f(q)\,dq - \int_{C^7} f(q)\,dq - \int_{C^8} f(q)\,dq \right], \qquad (5.40)$$

asymptotically. K_n denotes the residue at the nth pole on the real axis, and we have neglected contributions from residues at poles with a finite displacement into the upper half-plane, as explained above). The contours C^1-C^8 run around the branch cuts (down on the right, up on the left); integrals along the contours C^1-C^4 always contribute in the expression above, while integrals along C^5-C^8 contribute only when $\nu < 1/2$.

First, we focus on the integral along C^1, with origin $q^{(a)}_+ = 1 + (1 + 2\nu)^{1/2}$:

$$-\int_{C^1} f(q)\,dq \ = (2\pi)^{-4}\,(2\,i\,x)^{-1}\ i\int_{-\infty}^{\infty} d\omega \quad \int_0^{\infty} du \ \ (q^{(a)}_+ + iu)^3 \exp[i\,(q^{(a)}_+ + iu)\,x]$$

$$\times \exp(-i\omega t)\,[\varepsilon_R(q^{(a)}_+ + iu,\,\omega)^{-1} - \varepsilon_L(q^{(a)}_+ + iu,\,\omega)^{-1}], \qquad (5.41)$$

where $\varepsilon_R(q^{(a)}_+ + iu,\,\omega)$ denotes the value of the dielectric function to the right of the branch cut, and $\varepsilon_L(q^{(a)}_+ + iu,\,\omega)$, the value to the left. These differ because of the difference in the phase of the logarithm across the cut. The equation above simplifies further to

$$-\int_{C^1} f(q)\,dq = (2\pi)^{-4}\,(2\,i\,x)^{-1}\; i\int_{-\infty}^{\infty} d\omega \quad \int_0^{\infty} du\,(q^{(a)}_{+} + iu)^3 \exp[i\,(q^{(a)}_{+} + iu)\,x]$$

$$\times \exp(-i\omega t)\; U_0(q^{(a)}_{+} + iu)\;[\Pi^0{}_R(q^{(a)}_{+} + iu, \nu) - \Pi^0{}_L(q^{(a)}_{+} + iu, \nu)]$$

$$\div \{[1 - U_0(q^{(a)}_{+} + iu)\,\Pi^0{}_L(q^{(a)}_{+} + iu, \nu)\,]\,[\,1 - U_0(q^{(a)}_{+} + iu)\,\Pi^0{}_R(q^{(a)}_{+} + iu, \nu)\,]\}.$$

(5.42)

Next, we observe that the difference $\Pi^0{}_R(q^{(a)}_{+} + iu, \nu) - \Pi^0{}_L(q^{(a)}_{+} + iu, \nu)$ is linear in u, to lowest order. We obtain the leading asymptotic term by retaining the u dependence here and in $\exp[i\,(q^{(a)}_{+} + iu)\,x]$, but in the remaining factors, we replace $q^{(a)}_{+} + iu$ simply by the value at the origin of the branch cut $q^{(a)}_{+}$. This gives a contribution from the C^1 integral equal to

$$-\int_{C^1} f(q)\,dq \;=\; (2\pi)\text{-}4\;(2\,i\,x)\text{-}1\; i\,(q^{(a)}_{+})^3 \exp[i\,q^{(a)}_{+}x\,]\; U_0(q^{(a)}_{+})$$

$$\int_{-\infty}^{\infty} d\omega \exp(-i\omega t)\;\{[1 - U_0(q^{(a)}_{+})\,\Pi^0(q^{(a)}_{+}, \nu)\,]\int_0^{\infty} du\,\mathcal{L}(q^{(a)}_{+}, u)\exp(-ux),$$

(5.43)

where $\mathcal{L}(q^{(a)}_{+}, u)$ denotes the linear term in $\Pi^0{}_R(q^{(a)}_{+} + iu, \nu) - \Pi^0{}_L(q^{(a)}_{+} + iu, \nu)$. The u integral in this expression can be evaluated analytically. Then summing the contributions from C^1-C^8 (with $n < 1/2$) or C^1-C^4 (with $n > 1/2$) gives the branch-cut contributions to $\alpha(x, \omega)$.

Contributions to $\alpha(x, \omega)$ of a second type come from the poles of the integrand on the real-q axis, where $\varepsilon(q, \omega) = 0$. These poles are also the poles of $\Pi(q, \omega)$, so they occur at the excitation energies of electron-gas states that are connected to the ground state via the density operator [11]. The poles occur on the real q axis when

$$1 = U_0(q)\,\mathrm{Re}\,\Pi^0(q, \Omega_q)\ , \tag{5.44}$$

and

$$\mathrm{Im}\,\Pi^0(q, \Omega_q) = 0\ . \tag{5.45}$$

The dispersion relation (5.44) has the approximate solution (see Ref. 11, Sec. 15):

$$\Omega_q\ =\ \pm\,\Omega_{pl}\,[1 + 9/10\,(q/q_{TF})^2 + \ldots\,] \tag{5.46}$$

where Ω_{pl} is the plasma frequency:

$$\Omega_{pl}\ =\ (4\,\pi\,ne^2/m)^{1/2} \tag{5.47}$$

and q_{TF} is the Thomas-Fermi wavenumber,

$$q_{TF}\ =\ (6\,\pi\,ne^2/\varepsilon_F{}^0)^{1/2}\ . \tag{5.48}$$

For a specified real frequency ω, we substitute ω for Ω_q in Eq. (5.46), then solve for q. We designate the positive solution q*. If Ω_q and q* satisfy the condition $|\Omega_q| > \hbar q^* k_F/m + \hbar q^{*2}/2m$, then $\mathrm{Im}\,\Pi^0(q^*, \Omega_q)$ vanishes, and there are poles on the real q axis at ±q*, for that value of ω. The residues at these poles contribute to the asymptotic value of the integral in Eq. (5.40). The poles correspond to ***undamped plasma oscillations***, which occur within the RPA. (We note that for numerical purposes, it may also be necessary to include contributions from poles that are slightly displaced from the real axis, although the formal asymptotic contribution of these poles vanishes.)

In this section, we have shown how to reduce the evaluation of $\alpha(x, t)$, asymptotic in x, to a single remaining quadrature over ω. Numerical (or analytical) investigation of the ω-integral is reserved to future work.

6. CURRENT DENSITY SUSCEPTIBILITY

There has been considerable interest in quantum derivations of the conductivity using the density matrix formalism. Kubo [2] has given a formal solution and Kohn and Luttinger [36] have shown how the Boltzmann equation appears in a certain approximation. Among the earlier work, we mention papers by Dresselhaus and Mattis [37] and Mattis and Bardeen [38], related to an anomalous skin effect in normal metals. For a free electron gas in the absence of a magnetic field, expressions for conductivities are given in Mattis and Dresselhaus's paper mentioned above. In the Coulomb gauge an expression for the current density is obtained by taking into account particle-like excitations, as in Mattis and Bardeen's paper.

The response of an insulator to a weak external electromagnetic field of long wave-length was studied by Ambegaokar and Kohn [39] from a many-particle point of view. They treated the Coulomb interaction between electrons to all orders of perturbation theory and analyzed the structure of the corresponding Feynman graphs. In their analysis they defined proper and improper polarization graphs. The proper polarization graphs occur for both transverse and longitudinal fields. Improper polarization graphs occur only in the response to a longitudinal field. We remark that there has to be a close connection of their graphical analysis to our equation of motion.

Here we study the paramagnetic current density susceptibility in a gauge wherein the scalar potential ϕ is zero, and the vector potential alone represents the applied electromagnetic field. Then the longitudinal electric field can be expressed in terms of the longitudinal vector potential. The gauge invariance condition gurrentees that the a longitudinal electric field gives rise to the same current, whether it is described by a vector potential or by a scalar potential.

a. Transverse Current Density Susceptibility

Eq. (4.26) serves as the starting point of our evaluation of the transverse current density susceptibility. The momentum transfer **q** is fixed along the **z** direction, and by considering the x component of the induced current density and replacing the summation by integration over p, we obtain the transverse susceptibility density $\chi_{xx}(q\hat{z},\omega)$ as

$$\chi_{xx}(q\hat{z},\omega) = (e/m)^2\int d^3p \left[\frac{n(\mathbf{p})}{\omega+\varepsilon_p-\varepsilon_{p+q}} - \frac{n(\mathbf{p})}{\omega+\varepsilon_{p-q}-\varepsilon_p}\right](p\,\mathrm{Sin}\,\theta\ \ \mathrm{Cos}\,\phi)^2 \tag{6.1}$$

The transverse susceptibility simplifies to

$$\frac{-(e/m)^2}{(2\pi)^2}\int_0^{p_F} p^4\,dp\int_0^{\pi}\mathrm{Sin}^3\,\theta\,d\theta\left[\frac{1}{\omega+\varepsilon_q-(pq/m)\mathrm{Cos}\ \theta+i\eta} - \frac{1}{\omega-\varepsilon_q-(pq/m)\mathrm{Cos}\ \theta+i\eta}\right] \tag{6.2}$$

where $\varepsilon_q = q^2/2m$, η is a small positive quantity, and an extra factor of 2 is introduced to account for the spin summation. By evaluating the angular integral followed by the momentum integral (Appendix B), we obtain the following results for the transverse susceptibility.

$$
\begin{aligned}
\chi_{xx}(q,\omega) = -(e/m)^2/(2\pi)^2 \Bigg\{ & 2mp^3_F/3 \\
& - (m/q)^3 \Bigg[(\omega+\varepsilon_q + i\eta)^2 \Big\{ 1/2[p^2_F - (m/q)^2(\varepsilon_q+\omega + i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi+\omega+i\eta}{\varepsilon q-\xi+\omega+i\eta}\right] \\
& \qquad + (\varepsilon_q+\omega + i\eta)(p_F m/q) \Big\} \\
& \qquad + (\omega-\varepsilon_q + i\eta)^2 \Big\{ 1/2[p^2_F - (m/q)^2(\varepsilon_q-\omega - i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi-\omega-i\eta}{\varepsilon q-\xi-\omega-i\eta}\right] \\
& \qquad + (\varepsilon_q-\omega - i\eta)(p_F m/q) \Big\} \Bigg] \\
& + (m/q) \Bigg[1/4[p^4_F - (m/q)^4(\varepsilon_q+\omega + i\eta)^4] \quad \ln\left[\frac{\varepsilon q+\xi+\omega+i\eta}{\varepsilon q-\xi+\omega+i\eta}\right] \\
& \qquad + 1/4(m/q)^4(\varepsilon_q+\omega + i\eta)^4 \Big\{ 2\xi/(\varepsilon_q+\omega + i\eta) + 2/3[\xi/(\varepsilon_q+\omega + i\eta)]^3 \Big\} \\
& \qquad + 1/4[p^4_F - (m/q)^4(\varepsilon_q-\omega - i\eta)^4] \quad \ln\left[\frac{\varepsilon q+\xi-\omega-i\eta}{\varepsilon q-\xi-\omega-i\eta}\right] \\
& \qquad + 1/4\,(m/q)^4(\varepsilon_q-\omega - i\eta)^4 \Big\{ 2\xi/(\varepsilon_q-\omega - i\eta) + 2/3[\xi/(\varepsilon_q-\omega - i\eta)]^3 \Big\} \Bigg] \Bigg\}
\end{aligned}
\tag{6.3}
$$

where $\xi = qp_F/m$. By taking into account the identity (B.3) the above equation can be further simplified in the limit $\eta \to 0^+$.

b. Longitudinal Current Density Susceptibility

Eq. (4.30) serves as the starting point of our evaluation of the longitudinal current density susceptibility. By considering the z component of the induced current density and replacing the summation by integration over p we obtain the longitudinal current susceptibility density $\chi_{zz}(q\hat{z},\omega)$ as

$$\chi_{zz}(q\hat{z},\omega) = \frac{(e/m)^2\int d^3p \left[\frac{n(p)}{\omega+\varepsilon_p-\varepsilon_{p+q}} - \frac{n(p)}{\omega+\varepsilon_{p-q}-\varepsilon_p}\right] [\,p^2\,\mathrm{Cos}^2\theta\, + q^2/4]}{\varepsilon_{RPA}(q,\omega)}$$

$$+ \frac{(e/m)^2\int d^3p \left[\frac{n(p)}{\omega+\varepsilon_p-\varepsilon_{p+q}} + \frac{n(p)}{\omega+\varepsilon_{p-q}-\varepsilon_p}\right] pq\,\mathrm{Cos}\,\theta}{\varepsilon_{RPA}(q,\omega)} \qquad (6.4)$$

The numerator of the longitudinal susceptibility simplifies to

$$\mathrm{NLS}(q\hat{z},\omega) = \frac{-2}{(2\pi)^2}\int_0^{p_F} p^4\,dp \int_{-1}^{+1} x^2dx \left[\frac{1}{\omega+\varepsilon_q-(pqx/m)+i\eta} - \frac{1}{\omega-\varepsilon_q-(pqx/m)+i\eta}\right]$$

$$\frac{+2\,q}{(2\pi)^2}\int_0^{p_F} p^3dp \int_{-1}^{+1} x\,dx \left[\frac{1}{\omega+\varepsilon_q-(pqx/m)+i\eta} + \frac{1}{\omega-\varepsilon_q-(pqx/m)+i\eta}\right]$$

$$+\, q^2\, P^1(qz,\omega)\,/4 \qquad (6.5)$$

where $P^1(q,\omega)$ is the RPA polarization diagram and $x = \mathrm{Cos}\,\theta$. By evaluating the angular integral followed by the momentum integral (Appendix B), we obtain the following result for the numerator of the longitudinal susceptibility denoted by NLS(qz,ω):

$$
\begin{aligned}
\mathrm{NLS}(qz,\omega) = -2/(2\pi)^2 \Bigg\{ & 2mp^3{}_F/3 \\
& +(m/q)^3(\omega+\varepsilon_q + i\eta)^2 \Big\{ 1/2[p^2{}_F - (m/q)^2(\varepsilon_q+\omega + i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi+\omega+i\eta}{\varepsilon q-\xi+\omega+i\eta}\right] \\
& \qquad + (\varepsilon_q+\omega + i\eta)(p_F m/q) \Big\} \\
& +(m/q)^3(\omega-\varepsilon_q + i\eta)^2 \Big\{ 1/2[p^2{}_F - (m/q)^2(\varepsilon_q-\omega - i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi-\omega-i\eta}{\varepsilon q-\xi-\omega-i\eta}\right] \\
& \qquad + (\varepsilon_q-\omega - i\eta)(p_F m/q) \Big\} \\
& -(m^2/q)(\omega+\varepsilon_q + i\eta) \Big\{ 1/2[p^2{}_F - (m/q)^2(\varepsilon_q+\omega + i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi+\omega+i\eta}{\varepsilon q-\xi+\omega+i\eta}\right] \\
& \qquad + (\varepsilon_q+\omega + i\eta)(p_F m/q) \Big\} \\
& +(m^2/q)(\omega-\varepsilon_q + i\eta) \Big\{ 1/2[p^2{}_F - (m/q)^2(\varepsilon_q-\omega - i\eta)^2] \quad \ln\left[\frac{\varepsilon q+\xi-\omega-i\eta}{\varepsilon q-\xi-\omega-i\eta}\right] \\
& \qquad + (\varepsilon_q-\omega - i\eta)(p_F m/q) \Big\} \\
& + q^2\, P^1(q,\omega)/4 \Bigg\} .
\end{aligned}
\tag{6.6}
$$

Here again we can make use of the identity (B.3) and take the limit $\eta \to 0^+$ for further simplification.

7. CHANGES IN ELECTRONIC POLARIZABILITY DENSITIES DUE TO SHIFTS IN NUCLEAR POSITION

The nonlocal polarizability density $\boldsymbol{\alpha}(\mathbf{r}; \mathbf{r}', \omega)$ gives the ω-frequency component of the polarization induced at point **r** in a molecule by an external electric field $\mathbf{F}(\mathbf{r}', \omega)$ acting the point **r**′, within linear response [18-23]. This property reflects the *distribution* of polarizable matter within the molecule; it represents the full response to external fields derived from scalar potentials of arbitrary spatial variation. Thus $\boldsymbol{\alpha}(\mathbf{r}; \mathbf{r}', \omega)$ is a fundamental molecular property. It has applications in theories of local fields and light scattering in condensed media [20], and in approximations for dispersion energies [22], and collision-induced polarizabilities [23, 41] of molecules interacting at intermediate range.

The hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ gives the polarization induced at **r** by the lowest-order nonlinear response to a field of frequency ω′ acting at **r**′ and a field of frequency ω′′ acting at **r**′′.

The electronic polarization $\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega)$ induced in a molecule by an external field $\mathbf{F}(\mathbf{r}, \omega)$ depends on the polarizability density $\boldsymbol{\alpha}(\mathbf{r}; \mathbf{r}', \omega)$, the hyperpolarizability density $\beta(\mathbf{r}; \mathbf{r}', \omega', \mathbf{r}'', \omega'')$ and higher-order nonlinear response tensors:

$$\mathbf{P}^{\mathrm{ind}}(\mathbf{r}, \omega) = \int d\mathbf{r}'\, \boldsymbol{\alpha}(\mathbf{r}; \mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) + 1/2 \int d\omega' \int d\mathbf{r}'\, d\mathbf{r}''\, \beta(\mathbf{r}; \mathbf{r}', \omega - \omega', \mathbf{r}'', \omega') : \mathbf{F}(\mathbf{r}', \omega - \omega')\, \mathbf{F}(\mathbf{r}'', \omega') + \ldots \tag{7.1}$$

This work focuses on the changes in the frequency-dependent molecular polarizability density when a nucleus shifts infinitesimally. In Ref. 42 it is shown that the derivative of the static polarizability $\partial\alpha_{\alpha\beta}(0)/\partial R^{I}_{\gamma}$ is related to the nonlinear response tensor $\beta(\mathbf{r};\mathbf{r}',0,\mathbf{r}'',0)$. This accounts for the connection between the polarizability derivative and the quadratic electric field shielding tensor at nucleus I, noted by Buckingham and Fowler [43].

The purpose of this work is to prove that the relation between $\partial\alpha_{\alpha\beta}(\mathbf{r};\mathbf{r}',0)/\partial R^{I}_{\gamma}$ and the nonlinear response tensors generalizes to the frequency-dependent case.

From Eq. (7.1), if a molecule is placed in a static external field $\mathbf{F}^{s}(\mathbf{r})$, its reaction to an additional external field $\mathbf{F}^{e}(\mathbf{r},\omega)$ [44] can be characterized by the effective polarizability density $\alpha^{e}(\mathbf{r};\mathbf{r}',\omega;\mathbf{F}^{s})$, given by

$$\alpha^{e}(\mathbf{r};\mathbf{r}',\omega;\mathbf{F}^{s}) = \alpha(\mathbf{r};\mathbf{r}',\omega;\mathbf{F}^{s}=0) + \int d\mathbf{r}''\;\beta(\mathbf{r};\mathbf{r}',\omega,\mathbf{r}'',0)\cdot\mathbf{F}^{s}(\mathbf{r}'') + \ldots \tag{7.2}$$

The permutation symmetry of the β hyperpolarizability density has been employed to obtain this result.

A shift $\delta\mathbf{R}^{I}$ in the position of nucleus I in a molecule changes the nuclear Coulomb field acting on the electrons. In this section, we prove directly that the resulting change in polarizability density is determined by the same hyperpolarizability density $\beta_{\alpha\beta\gamma}(\mathbf{r};\mathbf{r}',\omega',\mathbf{r}'',\omega'')$ that fixes the response to external fields. Specifically, we show

$$\partial\alpha_{\beta\gamma}(\mathbf{r};\mathbf{r}',\omega)/\partial R^{I}_{\alpha} = \int d\mathbf{r}''\;\beta_{\beta\gamma\delta}(\mathbf{r};\mathbf{r}',\omega,\mathbf{r}'',0)\;Z^{I}\,T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{I}), \tag{7.3}$$

where Z^{I} is the charge on nucleus I and $T_{\delta\alpha}(\mathbf{r}'',\mathbf{R}^{I})$ is the dipole propagator,

$$T_{\alpha\beta}(\mathbf{R}^{I},\mathbf{r}) = \nabla_{\alpha}\nabla_{\beta}\left(|\mathbf{R}^{I}-\mathbf{r}|^{-1}\right). \tag{7.4}$$

The proof is via time dependent perturbation theory. We first calculate the nonlinear polarization of an isolated atom in an electromagnetic field. The atom may be characterized by a complete set of unperturbed eigenstates $|n\rangle$ satisfying a Schrödinger wave equation with energy eigenvalues E_n. In the presence of the perturbing Hamiltonian H', the new ground state is denoted by $|\psi\rangle$. $|\psi\rangle$ is expressed as an expansion in $|n\rangle$ with coefficients $a_n^{(s)}$, where s refers to the order of of perturbation:

$$|\psi\rangle = \Sigma_{n,s}\, a_n^{(s)}\, |n\rangle\,. \tag{7.5}$$

The $a_n^{(s)}$ are determined by the Schrödinger equation to satisfy

$$\partial a_n^{(s+1)}(t)/\partial t = (i\hbar)^{-1}\, \Sigma_{n'} \langle n\, |H'|\, n'\rangle\, a_{n'}^{(s)} + \;(i\hbar)^{-1} \langle n\, |H^0|\, n\rangle\, a_n^{(s+1)} \tag{7.6}$$

subject to the initial condition

$$a_n^{(0)}\,(t{=}0) = \;\delta_{ng}\,,\;\; a_n^{(s)}\,(t{=}0) = 0\;\; \text{for } s \neq 0 \tag{7.7}$$

where the subscript g refers to the unperturbed ground state. The polarization **P** is the expectation value of the polarization operator in the perturbed ground state.

$$\mathbf{P} = \langle\psi|\mathbf{P}|\psi\rangle\,/\,\langle\psi|\psi\rangle \tag{7.8}$$

The perturbing Hamiltonian has the form,

$$H' = -\int d^3\mathbf{r}\; \mathbf{E}^{\omega}(\mathbf{r})\cdot \mathbf{P}(\mathbf{r})\, \mathrm{Cos}\; \omega t. \tag{7.9}$$

To include all terms proportional to $(\mathbf{E}^{\omega})^2$, the perturbation expansion must be pursued to second order, so that the first three terms of Eq. (7.5) need to be considered:

$$|\psi\rangle = \Sigma_n (\delta_{ng} + a_n^{(1)} + a_n^{(2)}\,|n\rangle \tag{7.10}$$

The coefficients are found from Eqs. (7.6), (7.7) and (7.9) and are

$$a_n^{(1)}(t) = (-1/\hbar)\,\langle H^{-\omega}\rangle_{ng} \left[\frac{\exp i(\omega_{ng}+\omega)t}{(\omega_{ng}+\omega)} + \frac{\exp i(\omega_{ng}-\omega)t}{(\omega_{ng}-\omega)} \right] \tag{7.11}$$

$$\begin{aligned} a_n^{(2)}(t) = (1/\hbar^2)\ \Sigma_m \langle H^{-\omega 1}\rangle_{nm}\langle H^{-\omega 2}\rangle_{mg} \Bigg[& \frac{\exp i(\omega_{ng}+\omega_1+\omega_2)t}{(\omega_{mg}+\omega_1)(\omega_{ng}+\omega_1+\omega_2)} \\ & + \frac{\exp i(\omega_{ng}-\omega_1+\omega_2)t}{(\omega_{mg}-\omega_1)(\omega_{ng}-\omega_1+\omega_2)} + \frac{\exp i(\omega_{ng}+\omega_1-\omega_2)t}{(\omega_{mg}+\omega_1)(\omega_{ng}+\omega_1-\omega_2)} \\ & + \frac{\exp i(\omega_{ng}-\omega_1-\omega_2)t}{(\omega_{mg}-\omega_1)(\omega_{ng}-\omega_1-\omega_2)} \Bigg] \end{aligned} \tag{7.12}$$

Evaluation of the expectation value in Eq. (7.8) gives the polarizability $\alpha(\mathbf{r};\mathbf{r}',\omega)$ and hyperpolarizability $\beta(\mathbf{r};\mathbf{r}',\omega_1,\mathbf{r}'',\omega_2)$ respectively as [45]

$$\alpha(\mathbf{r};\mathbf{r}',\omega) = (-\hbar)^{-1}\ \Sigma'_n \left[\frac{\langle P\rangle_{gn}\langle H^{-\omega}\rangle_{ng}}{(\omega_{ng}-\omega)} + \frac{\langle H^{-\omega}\rangle_{gn}\langle P\rangle_{ng}}{(\omega_{ng}+\omega)} \right] \tag{7.13}$$

$$\begin{aligned} \beta(\mathbf{r};\mathbf{r}',\omega_1,\mathbf{r}'',\omega_2) = K(-\omega_\sigma;\ \omega_1,\omega_2)(-\hbar)^{-2}\, I_{1,2}\ \Sigma'_n\Sigma'_m \Bigg[& \frac{\langle P\rangle_{gm}\langle \overline{H^{-\omega 2}}\rangle_{mn}\langle H^{-\omega 1}\rangle_{ng}}{(\omega_{mg}-\omega_\sigma)(\omega_{ng}-\omega_1)} \\ & + \frac{\langle H^{-\omega 2}\rangle_{gm}\langle \overline{H^{-\omega 1}}\rangle_{mn}\langle P\rangle_{ng}}{(\omega_{mg}+\omega_2)(\omega_{ng}+\omega_\sigma)} + \frac{\langle H^{-\omega 2}\rangle_{gm}\langle \overline{P}\rangle_{mn}\langle H^{-\omega 1}\rangle_{ng}}{(\omega_{mg}+\omega_2)(\omega_{ng}-\omega_1)} \Bigg] \end{aligned} \tag{7.14}$$

where $\omega_\sigma = \omega_1 + \omega_2$.

The symbol I denotes a permutation operator: for example, $I_{1,2}$ denotes the average of all terms generated by simultaneously permuting the frequencies ω_1 and

ω_2, and the corresponding operators. The notation $\sum'$ denotes a summation from which the ground state is excluded. The barred notation $\overline{\langle H'^{\omega}\rangle}_{mn}$ is shorthand for the expression $\langle H'^{\omega}\rangle_{mn} - \langle H'^{\omega}\rangle_{gg}$. The numerical coefficients K depend on the nonlinear optical process of interest. Their evaluation has been discussed in Ref. 48.

A shift $\delta \mathbf{R}^I$ in the position of nucleus I in a molecule changes the nuclear Coulomb field acting on the electrons. This shift can be considered as a static perturbation, and any perturbed state can be written as

$$|n^p\rangle = |n\rangle + \sum_m \frac{|m\rangle\langle m|H'|n\rangle}{(E_n - E_m)} \; . \tag{7.15}$$

Now we expand all states and energy denominators in the polarizability expression, Eq. (7.13), to first order in the nuclear shift perturbation, and neglect the higher order terms. In addition we replace the difference between the first order correction to the energy $(\Delta E_n - \Delta E_g)$ by $(\langle H'(\mathbf{r}'')\rangle_{nn} - \langle H'(\mathbf{r}'')\rangle_{gg})$. The resulting effective polarizability density can be written as,

$$\alpha^e(\mathbf{r};\mathbf{r}',\omega) = \alpha^0(\mathbf{r};\mathbf{r}',\omega) + \alpha^p(\mathbf{r};\mathbf{r}',\omega) + \ldots \tag{7.16}$$

$$\alpha^p(\mathbf{r};\mathbf{r}',\omega) = (-\hbar)^{-2} \int d\mathbf{r}''\, \mathbf{E}(\mathbf{r}'') \cdot \sum_n{}' \left[\frac{\langle P(\mathbf{r})\rangle_{gn} \langle H'^{\omega}(\mathbf{r}')\rangle_{ng} \langle H'(\mathbf{r}'')\rangle_{nn}}{(\omega_{ng} - \omega)^2} \right.$$

$$\left. - \frac{\langle P(\mathbf{r})\rangle_{gn} \langle H'^{\omega}(\mathbf{r}')\rangle_{ng} \langle H'(\mathbf{r}'')\rangle_{gg}}{(\omega_{ng} - \omega)^2} \right.$$

$$+\sum_n{}' \sum_m{}' \frac{\langle P(\mathbf{r})\rangle_{gn}\langle H^{-\omega}(\mathbf{r}')\rangle_{nm}\langle H'(\mathbf{r}'')\rangle_{mg}}{\omega_{mg}\,(\omega_{ng}-\omega)} + \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle H'(\mathbf{r}'')\rangle_{gm}\langle P(\mathbf{r})\rangle_{mn}}{\omega_{mg}\,(\omega_{ng}-\omega)}$$

$$+\sum_n{}' \sum_{m\neq n} \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle P(\mathbf{r})\rangle_{gm}\langle H'(\mathbf{r}'')\rangle_{mn}}{\omega_{mn}\,(\omega_{ng}-\omega)} + \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{mg}\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{nm}}{\omega_{mn}(\omega_{ng}-\omega)}$$

$$+ \left[(\omega_{ng}-\omega) \text{ replaced by } (\omega_{ng}+\omega)\right]\left[\text{complex conjugate of the rest}\right]\Bigg] \quad . \qquad (7.17)$$

The last two terms in $\alpha^P(\mathbf{r};\mathbf{r}',\omega)$ can be rewritten by splitting the sum into two parts, the first part with $m \neq g$ and the second part with $m = g$.

$$\text{Fifth term} = \sum_n{}'\sum_{m\neq n}{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle P(\mathbf{r})\rangle_{gm}\langle H'(\mathbf{r}'')\rangle_{mn}}{\omega_{mn}\,(\omega_{ng}-\omega)} - \sum_n{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle P(\mathbf{r})\rangle_{gg}\langle H'(\mathbf{r}'')\rangle_{gn}}{\omega_{ng}\,(\omega_{ng}-\omega)} \qquad (7.18)$$

$$\text{Sixth term} = \sum_n{}'\sum_{m\neq n}{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{mg}\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{nm}}{\omega_{mn}\,(\omega_{ng}-\omega)} - \sum_n{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{gg}\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{ng}}{\omega_{ng}\,(\omega_{ng}-\omega)} \qquad (7.19)$$

We can rewrite Eq. (7.18) by permuting m and n as,

$$\text{Fifth term} = \sum_n{}'\sum_{m\neq n}{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{mg}\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{nm}}{\omega_{nm}\,(\omega_{mg}-\omega)} - \sum_n{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle P(\mathbf{r})\rangle_{gg}\langle H'(\mathbf{r}'')\rangle_{gn}}{\omega_{ng}\,(\omega_{ng}-\omega)} \qquad (7.20)$$

By adding the first two terms in Eq. (7.19) and Eq. (7.20) we obtain the single term

$$\sum_n{}'\sum_{m\neq n}{}' \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{mg}\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{nm}}{(\omega_{mg}-\omega)(\omega_{ng}-\omega)}$$

By adding the above expression and the first term of $\alpha^P(\mathbf{r};\mathbf{r}',\omega)$, we can rewrite $\alpha^P(\mathbf{r};\mathbf{r}',\omega)$ as

$$\alpha^{P}(\mathbf{r};\mathbf{r}',\omega) = (-\hbar)^{-2}\int d\mathbf{r}''\,\mathbf{E}(\mathbf{r}'')\cdot\Bigg[\sum_n{}'\sum_m{}' \frac{\langle P(\mathbf{r})\rangle_{gn}\langle H'(\mathbf{r}'')\rangle_{nm}\langle H^{-\omega}(\mathbf{r}')\rangle_{mg}}{(\omega_{mg}-\omega)(\omega_{ng}-\omega)}$$

$$+\frac{\langle P(\mathbf{r})\rangle_{gn}\langle H^{-\omega}(\mathbf{r}')\rangle_{nm}\langle H'(\mathbf{r}'')\rangle_{mg}}{\omega_{mg}\,(\omega_{ng}-\omega)} + \frac{\langle H^{-\omega}(\mathbf{r}')\rangle_{ng}\langle H'(\mathbf{r}'')\rangle_{gm}\langle P(\mathbf{r})\rangle_{mn}}{\omega_{mg}(\omega_{ng}-\omega)}$$

$$+\,[(\omega_{ng}-\omega)\text{ replaced by }(\omega_{ng}+\omega)\,][\text{complex conjugate of the rest}\,]\Bigg]. \qquad (7.21)$$

The expression in brackets is identically equal to $\beta(\mathbf{r};\mathbf{r}',\omega,\mathbf{r}'',0)$ (with all permutations counted). This proves directly that the resulting change in polarizability is determined by the same hyperpolarizability density $\beta(\mathbf{r};\mathbf{r}',\omega_1,\mathbf{r}'',\omega_2)$ that fixes the response to external fields. Thus we prove the validity of Eq. (7.2) and Eq. (7.3).

8. SUMMARY AND CONCLUSIONS

We have unified the asymptotic expansions of linear response functions of an interacting Fermi gas in its ground state with a uniform positive charge background, so that the whole system is neutral. The results obtained are valid within the random phase approximation.

In chapter 4 we demonstrated the possibility of studying the induced current density by use of the equation-of-motion method, as a linear response to a vector potential. We separated the transverse and longitudinal current-density susceptibilities, and in accord with physical expectations, there is no screening in the transverse current density susceptibility.

In chapter 5 we have given a generalization of the Langer and Vosko result by evaluating the charge density susceptibility and the nonlocal polarizability density for a scalar potential of arbitrary spatial variation. The static longitudinal component of the nonlocal polarizability density is related to the dielectric function of the electron gas. The asymptotic analysis shows that $\alpha^{L}_{zz}(\mathbf{r}, \mathbf{r}'; 0)$ has two long-range components within the random phase approximation. One is associated with Friedel oscillations in the charge density, and it reflects the impossibility of constructing a smooth function with the restricted set of wavevectors for the states in the electron gas that are unoccupied at $T = 0$ $(k > k_F)$ [11, 12, 16]. The second long-range component is an $|\mathbf{r} - \mathbf{r}'|^{-3}$ non-oscillatory term due to charge screening. Because of its physical origin, the presence of this term has significant implications for calculations of $\alpha^{L}(\mathbf{r}, \mathbf{r}'; 0)$ for individual molecules: it raises the possibility of long-range, intramolecular polarization effects. As an extension of the above work, we have reduced the calculation of the asymptotic, dynamic charge density susceptibility (within the RPA) to a single quadrature over frequency.

In chapter 6 we have obtained explicit expressions for current density susceptibilities within the RPA in a gauge where in the scalar potential is zero.

In chapter 7 we obtained a connection between linear and nonlinear response tensors, via a direct perturbation theory of general validity. We proved directly that the electronic charge distribution responds to the change in Coulomb field due to a shift in the position of the nucleus via the same hyperpolarizability density that describes its response to external fields.

APPENDIX A

This appendix provides mathematical details on the derivation of the asymptotic form of the nonlocal polarizability density $\alpha^L_{zz}(r, r'; 0)$ in the RPA, as given in Eq. (5.23). It also provides auxiliary results for the derivation of Eqs. (5.25), (5.26), and (5.28), and brief comment on the numerical evaluation of the RPA and VS polarizability densities. In deriving Eq. (5.23), we start with Eq. (5.16), which we first express in terms of integrals over the full real axis from $-\infty$ to ∞, and then evaluate by complex contour integration. To convert Eq. (5.16) to Eq. (5.19), we have used the fact that g(z) is an even function of its argument. In Eq. (5.16), the integrand containing $j_2(kx)$ is well-behaved as $k \rightarrow 0$, since $\lim_{k \rightarrow 0} (kx)^{-1} \sin kx = 1$. In contrast $(kx)^{-1} \exp(ikx)$ diverges as $k \rightarrow 0$. The convergent integral in Eq. (5.16) can be expressed in terms of the Cauchy principal value of the integral containing $(kx)^{-1} \exp(ikx)$, however, as in Eq. (5.19). The Cauchy principal value of the integral is designated by $\wp$; it is defined as a symmetric limit:

$$\wp \int_{-\infty}^{\infty} dk\, k^2\, j_2(kx)\, e^{ikx}\, F(k)$$

$$\lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{-\varepsilon} dk\, k^2\, j_2(kx)\, e^{ikx}\, F(k) \quad + \int_{\varepsilon}^{\infty} dk\, k^2\, j_2(kx)\, e^{ikx}\, F(k)\ . \tag{A.1}$$

The function g defined in Eq. (5.20) has branch points at $\pm 2k_F \pm i\eta$. By choosing the branch cuts shown in Figure 1, we ensure that g is real on the real axis, as required [11]. Also with this choice, g is real on the imaginary axis, in the limit $\eta \rightarrow 0$.

The integrals in Eq. (5.19) are evaluated by complex contour integration, with the contour shown in Fig. A.1. The only singularity enclosed by the contour is a simple pole,

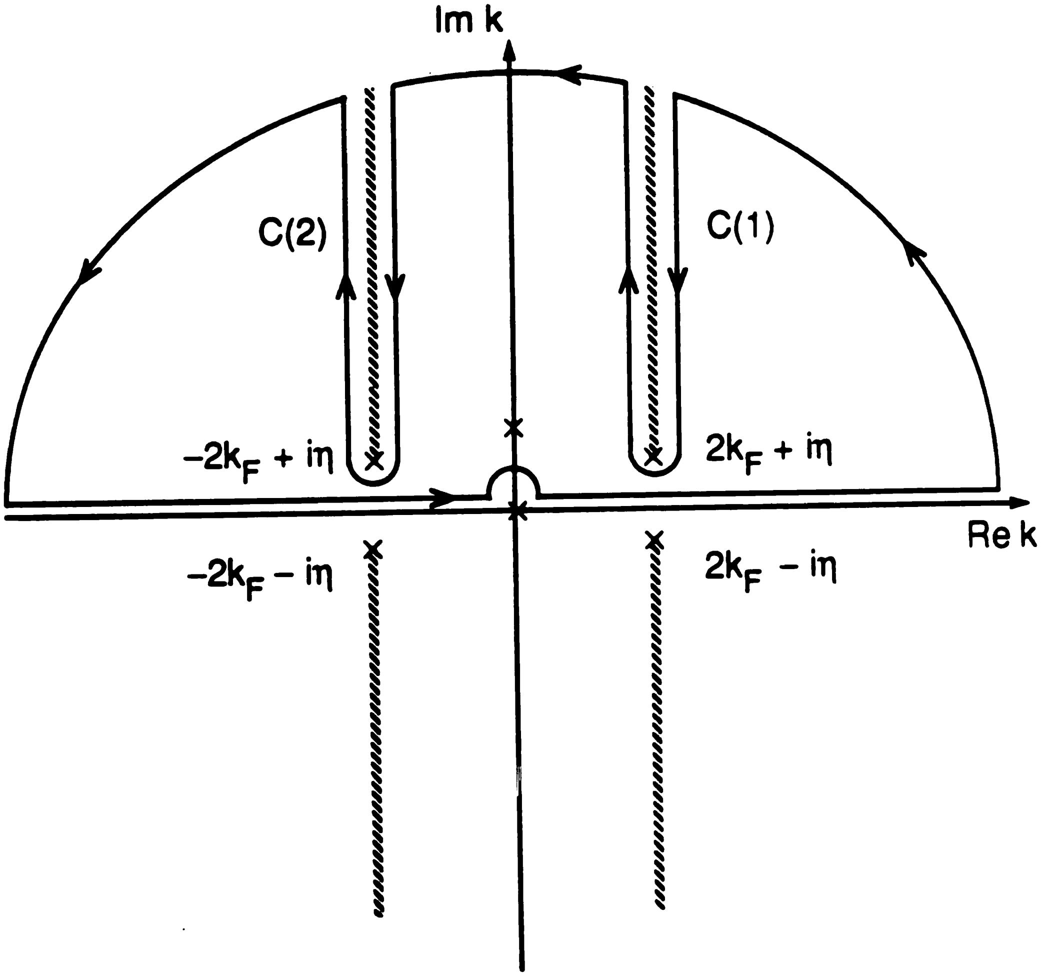

Figure A.1. Contour in the complex k plane, used for evaluation of the nonlocal polarizability density in the RPA. Branch cuts are shown as striped lines; the symbol × marks the branch cut origins at the points $\pm 2k_F \pm i\eta$, a pole at $k = 0$, and a pole near $i\,k_{TF}$.

located near ik_{TF} (see below). The integral over the large semicircular portion of the contour vanishes in the limit as $R \rightarrow \infty$, where R is the radius of the semicircle. The integral of $k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1]$ along the smaller semicircle around $k = 0$ (with radius κ, $\kappa \rightarrow 0$) has the value $i\pi$ when $n = -1$; for larger n, the integral along the smaller semicircle vanishes. Hence, by the residue theorem,

$$\wp \int_{-\infty} dk\, k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1] + i\pi \delta_{n,-1} + \int_{C(1)} dk\, k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1]$$

$$+ \int_{C(2)} dk\, k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1] = 2\pi i K_1 , \tag{A.2}$$

where K_1 is the residue at the enclosed pole. The contours C(1) and C(2) run around the branch cuts, in the sense shown in Fig. 1. Since

$$[\varepsilon(k, 0)^{-1} - 1] = -k_{TF}^2 g(k/k_F) / [k^2 + k_{TF}^2 g(k/k_F)] , \tag{A.3}$$

the integral around C(1) is

$$\int_{C(1)} dk\, k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1]$$

$$= i k_{TF}^2 \int_{\eta}^{\infty} dv \{ (2k_F + iv)^{n+2} \exp[i (2k_F + iv) x] (g_R - g_L)$$

$$\times [(2k_F + iv)^2 + k_{TF}^2 g_L]^{-1} [(2k_F + iv)^2 + k_{TF}^2 g_R]^{-1} \} \tag{A.4}$$

and similarly for C(2)

$$\int_{C(2)} dk\, k^n e^{ikx} [\varepsilon(k, 0)^{-1} - 1]$$

$$= i k_{TF}^2 \int_{\eta}^{\infty} du \{ (-2k_F + iu)^{n+2} \exp[i (-2k_F + iu) x] (g_R - g_L)$$

$$\times [(-2k_F + iu)^2 + k_{TF}^2 g_L]^{-1} [(-2k_F + iu)^2 + k_{TF}^2 g_R]^{-1} \} . \tag{A.5}$$

In Eqs. (A.4) and (A.5), g_R and g_L denote the values of g at points immediately to the right or left of the branch cuts. For the integral along C(1),

$$g_R - g_L = -(4k_F v + iv^2)\,\pi / [8\,(2k_F + iv)\,k_F] \tag{A.6}$$

and for the integral along C(2)

$$g_R - g_L = (-4k_F u + iu^2)\,\pi / [8\,(-2k_F + iu)\,k_F] \ . \tag{A.7}$$

Because of the factors of exp(−vx) and exp(−ux) appearing in Eqs. (A.4) and (A.5) respectively,the dominant contribution to the integrals comes from small v or u, when x is large (i.e., from points near the branch origins). Laplace's method is not directly applicable to the integrals, though, due to the logarithmic singularities remaining in g_R and g_L [46]. Therefore, we expand the integrands for small v or u, retain the terms of the two leading orders, and then use the analytical theory given by Olver to obtain asymptotic expansions (in x) for the integrals with logarithmic singularities [46]. We also use [47, a]

$$\int_0^\infty v^2 \ln v\, e^{-vx}\, dv = 2\,x^{-3}\,(3/2 - C - \ln x) \ , \tag{A.8}$$

where C is Euler's constant. Algebraic simplification yields Eqs. (5.21) and (5.22). Errors in these equations due to the first omitted term in the asymptotic expansion are of the order

$(a\,x^{-4} + b\,x^{-4} \ln k_F x)$.

To complete the calculation, we must determine the residue K_1 of the integrand at the pole in the upper half plane. This pole occurs at k_p, the root of

$$k_p = i\,k_{TF}\,g^{1/2}(k_p/k_F) \ , \tag{A.9}$$

and the residue at the pole is

$$K_1 = -1/2\, k_p^{n-1}\, k_{TF}^2\, g(k_p/k_F)\exp(ik_px)\ . \tag{A.10}$$

We recast Eq. (B.9) in terms of the new, real variable c_p defined by $k_p = i\, c_p\, k_{TF}$. We also define $\zeta = (4\alpha r_s/\pi)^{1/2}$. Then c_p satisfies

$$c_p^2 = g(ic_p\zeta)\ . \tag{A.11}$$

In the limit $\eta \to 0$, evaluation of g at points on the imaginary axis yields

$$g(ic_p\zeta) = 1/2 + (c_p\zeta)^{-1}\,[1 + (c_p\zeta)^2/4]\arctan[c_p\zeta/2]\ . \tag{A.12}$$

Hence the location of the pole depends on r_s. When $r_s = 2.0$, $c_p = 1.056$; when $r_s = 4.0$, $c_p = 1.114$; and when $r_s = 6.0$, $c_p = 1.172$. The residue K_1 is

$$K_1 = -1/2\,(ic_p)^{n-1}\, k_{TF}^{n+1}\, g(ic_p\zeta)\exp(-c_pk_{TF}x)\ . \tag{A.13}$$

Therefore, the contribution to the integral from the pole in the upper half-plane decays exponentially with x, and for large x it is negligible relative to the error in the asymptotic expansions of the integrals along C(1) and C(2).

Use of Eqs. (5.21), (5.22), and (A.2) yields Eqs. (5.23), (5.25), and (5.26) in the main text. We obtain Eq. (5.28) with the use of auxiliary integrals

$$\int_0^\infty k\,(k^2 + k_{TF}^2)^{-1}\sin kx\ dk = \pi/2\exp(-k_{TF}x) \tag{A.14}$$

$$\int_0^\infty (k^2 + k_{TF}^2)^{-1}\cos kx\ dk = \pi/(2k_{TF})\exp(-k_{TF}x) \tag{A.15}$$

and

$$\int_0^\infty k^{-1}\,(k^2 + k_{TF}^2)^{-1}\sin kx\ dk = \pi/(2k_{TF}^2)\,[1 - \exp(-k_{TF}x)]\ . \tag{A.16}$$

APPENDIX B

The integral needed to evaluate the transverse susceptibility is [47, b]

$$\int_0^{\pi} \frac{\mathrm{Sin}^3\,\theta\, d\theta}{a+b\,\mathrm{Cos}\,\theta} = (2a/b^2) + (1/b)[1 - (a/b)^2] \quad \ln\left[\frac{a+b}{a-b}\right] \tag{B.1}$$

The equality needed to evaluate all resulting momentum integrals is [47, c]

$$\int dx\, x^m \ln(ax+b) = [1/(m+1)][x^{m+1} - (-b/a)^{m+1}] \ln(ax+b) - [1/(m+1)](-b/a)^{m+1} \sum_{r=1}^{m+1} (1/r)(-ax/b)^r \tag{B.2}$$

We have used the following identity in order to simplify the current susceptibility densities:

$$\ln(a+i\eta)=\ln|a|+i\tan^1(\eta/a) \tag{B.3}$$

REFERENCES

1. H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

1a. H. J. Kreuzer, *Nonequilibrium Thermodynamics and its Statistical Foundation* (Oxford, Clarenden Press, 1981) Ch. 9.

2. R. Kubo, J. Phys. Soc. Japan **12**, 570 (1951).

3. L. Onsager, Phys. Rev. **37**, 405 (1931).

4. D. N. Zubarev, Sov. Phys. Usp. **3**, 320 (1960).

5. D. Pines and D. Bohm. Phys. Rev. **85**, 338 (1952).

6. J. Bardeen, Phys. Rev. **52**, 688 (1937).

7. R. A. Ferrel, Phys. Rev. **107**, 450 (1957).

8. J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Phys. Medd **28**, No. 8 (1954).

9. P. Nozières and D. Pines, Phys. Rev. **109**, 741, 762, 1062 (1958).

10. H. Ehrenreich and M. H. Cohen. Phys. Rev. **115**, 786 (1959).

11. A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971), Ch. 5.

12. G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1990), Ch. 5.

13. J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1960).

14. J. Friedel, Advan. Phys. **3**, 446 (1954).

15. J. Friedel, Nuovo Cimento, Suppl. **2**, 287 (1958).

16. P. Nozières and D. Pines, *The Theory of Quantum Liquids*, Vol. 1 (Benjamin, New York, 1966), Ch. 5.

16a. T. J. Rowland and N. Bloembergen, Phys. Rev. **119**, 912 (1960).

17. R. Nimalakirthi and K. L. C. Hunt, J. Chem. Phys. **98**, 3066 (1993).

18. W. J. A. Maaskant and L. J. Oosterhoff, Mol. Phys. **8**, 319 (1964).

19. L. M. Hafkensheid and J. Vlieger, Physica **75**, 57 (1974).

20. T. Keyes and B. M. Ladanyi, Mol. Phys. **33**, 1271 (1977).

21. J. E. Sipe and J. Van Kranendonk, Mol. Phys. **35**, 1579 (1978).

22. K. L. C. Hunt, J. Chem. Phys. **78**, 6149 (1983).

23. K. L. C. Hunt, J. Chem. Phys. **80**, 393 (1984).

24. B. Linder, Adv. Chem. Phys. **12**, 225 (1967); B. Linder and D. A. Rabenold, Adv. Quantum Chem. **6**, 203 (1972); T. B. MacRury and B. Linder, J. Chem. Phys. **58**, 5388, 398 (1973).

25. A. Koide, J. Phys. **B 9**, 3173 (1976).

26. M. Krauss and D. B. Neumann, J. Chem. Phys. **71**, 107 (1979); M. Krauss, D. B. Neumann, and W. J. Stevens, Chem. Phys. Lett. **66**, 29 (1979); M. Krauss, W. J. Stevens, and D. B. Neumann, ibid. **71**, 500 (1980); M. Krauss and W. J. Stevens, ibid. **85**, 423 (1982).

27. B. Linder, K. F. Lee, P. Malinowski, and A. C. Tanner, Chem Phys. **52**, 353 (1980); P. Malinowski, A. C. Tanner, K. F. Lee, and B. Linder, ibid. **62**, 423 (1981);S.Wozniak, K. F.Raof, and B. Linder, J. Chem. Phys. **79**, 220 (1983).

28. A. Koide, W. J. Meath, and A. R. Allnatt, Chem. Phys. **58**, 105 (1981).

29. M. E. Rosenkrantz and M. Krauss, Phys. Rev. **A 32**, 1402 (1985).

30. J. Applequist, J. R. Carl, and K.-K. Fung, J. Am. Chem. Soc. **94**, 2952 (1972); J. Applequist, Acc. Chem. Res. **10**, 79 (1977); J. Chem. Phys. **83**, 809 (1985).

31. A. J. Stone, Chem. Phys. Lett. **155**, 102, 11 (1989); A. J. Stone and C. S.Tong, Chem. Phys. **137**, 121 (1989).

32. G. Arfken, *Mathematical Methods for Physicists*, 2nd ed. (Academic, New York, 1970), p. 557.

33. C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Quantum Mechanics*, Vol. 1 (Wiley, New York, 1977), p. 688.

33a. P. Vashishta and K. S. Singwi, Phys. Rev. **B 6**, 875 (1972).

34. P. Vashishta and K. S. Singwi, Phys. Rev. **B 6**, 875 (1972).

35. K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1968); K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H. Land, Phys. Rev. **B 1**, 1044 (1970); K. S. Singwi and M. P. Tosi, Solid State Phys. **36**, 177 (1981).

36. W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

37. G. Dresselhaus and D. C. Mattis, Phys. Rev. **111**, 403 (1958).

38. D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

39. V. Ambegaokar and W. Kohn, Phys. Rev. **117**, 423 (1960).

40. K. L. C. Hunt, Y. Q. Liang, R. Nimalakirthi, and R. A. Harris, J. Chem. Phys. **91**, 5251 (1989).

41. K. L. C. Hunt and J. E. Bohr, J. Chem. Phys. **84**, 6141 (1986).

42. K. L. C. Hunt, J. Chem. Phys. **90**, 4909 (1989).

43. P. W. Fowler and A. D. Buckingham, Chem. Phys. **98**,167 (1985)

44. A. D. Buckingham, Proc. R. Soc. London, Ser. **A 267**, 271 (1962); and D. M. Bishoop, Mol. Phys. **42**, 1219 (1981); J. Chem. Phys. **86**, 5613 (1987).

45. B. J. Orr and J. F. Ward, Mol. Phys. **20**, 513 (1971).

46. F. W. J. Olver, *Asymptotics and Special Functions* (Academic, New York, 1974), Ch. 3, Ch. 9.

47. I. S. Gradshteyn and I. W. Ryzhik, *Tables of Integrals, Series, and Products* (Academic, New York, 1965), 4th Ed., (a) 4.352.2. (b) 3.644.5 (c) 2.729.1