Mc/sec is used in Eq. (11), it is found that

$$|H_J| = 1.03 \times 10^6 G,$$

with an uncertainty of about 1%. When the theoretical value $a_{calc}(3d^54s\ ^7S_3) = -144$ Mc/sec is used, the same equation gives $H_J = +1.8 \times 10^6$ G.

Freeman and Watson have followed a more detailed approach for the theoretical evaluation of the internal field.[9] They have made approximate spin-polarized Hartree-Fock calculations in which the core electrons are allowed a polarization due to the unpaired $4s$ electron as well as to the unpaired $3d$ electrons. Their result for the $3d^54s\ ^7S_3$ configuration gives -0.65×10^6 G from the core polarization and $+1.15 \times 10^6$ G from the $4s$ electron. The internal field is thus calculated to be $+0.50 \times 10^6$ G, a value somewhat closer to the measured value than the simpler estimate given above. Freeman and Watson emphasize that their result for the (pres-

ent) case of two unfilled shells is especially sensitive to several factors[10] which occur in the calculation.

Although the data suggest that b may be exactly 0, this value is entirely consistent with the data and with what would be expected for a (d^5s) state.

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[9] A. J. Freeman and R. E. Watson (private communication).

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Atomic Response Function*

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The response function of atoms is derived approximately within the framework of the time-dependent Hartree scheme for external fields of wavelength large compared to atomic dimensions. Solutions of the resulting dispersion equation correspond to new resonances of atoms. The theory is discussed in terms of the properties of the differential oscillator-strength distribution, or photoabsorption cross section, for the Hartree model and for the statistical model of the atom. An illustrative calculation in the statistical approximation exhibits qualitatively the conditions for the occurrence of these resonances.

INTRODUCTION

CONSIDER an atom in an external field of given frequency ω and of wavelength larger than atomic dimensions. The response of the atom to the field is discussed most conveniently in terms of the properties of its differential oscillator-strength distribution $g(\omega)$. This function is related directly to the photoabsorption cross section of the atom, i.e., the photoextinction coefficient per atom,

$$\sigma(\omega) = (2\pi^2 e^2/mc)g(\omega),$$

where

$$(2\pi^2 e^2/mc) = 8.067 \times 10^{-18}\ \text{Ry cm}^2,$$

with $\hbar$ Ry $= 13.6$ eV. Of recent, the need for comprehensive information about the properties of $g(\omega)$ in different frequency ranges for atoms throughout the periodic system has become acute in many fields, and has pointed to the limited description current atomic theory can afford of the response of an atom to an arbitrary external field.

The function $g(\omega)$ may be said to comprise all the fundamental information on the quantum dynamics of atoms. For a cursory survey of the dependence of $g(\omega)$ on frequency and atomic number Z, it is convenient to consider three frequency ranges. In the low-frequency range (1), where $0 \leq (\omega/\text{Ry}) \leq 1$, $g(\omega)$ essentially consists of the sharp lines familiar from optical spectroscopy, separated by frequency ranges of low absorption; in this range, $g(\omega)$ changes irregularly with Z and reflects in its details the atomic binding. In the high-frequency

range (3), where $(\omega/\mathrm{Ry}) \gtrsim Z^2$, $g(\omega)$ exhibits characteristic x-ray absorption edges; beyond the K-shell absorption edge, it tends monotonically to zero as $(\omega/\mathrm{Ry})^{-n}$, where $n \sim (2-4)$. In the intermediate frequency range (2), where $1 < (\omega/\mathrm{Ry}) < Z^2$, the contributions from the intermediate shells of the atom are expected to overlap strongly such that, on the whole, $g(\omega)$ should depend smoothly on ω. While $g(\omega)$ has been studied extensively in the frequency ranges (1) and (3), very little is known about the properties of $g(\omega)$ in range (2).

Our study is intended to contribute to the theory of $g(\omega)$ with particular emphasis on its properties in the intermediate frequency range $1 < (\omega/\mathrm{Ry}) < Z^2$. Section 1 summarizes the formalism of response functions and introduces an approximate integral equation for the propagator function of excitations in atoms. Contact is made with previous work in Sec. 2 by deriving from this integral equation the response function of atoms in the local electron-gas approximation. A Fredholm perturbation expansion yields new approximate solutions, in Sec. 3, by retaining coherence effects between all single-particle excitations of the atom. In the framework of the schematic Hartree model, these solutions give indications for atomic resonances which are basically collective in origin. In Sec. 4, the theory is restated in terms of the statistical model of the atom, with similar results. An illustrative example in the statistical approximation, given in Sec. 5, bears on the conditions for such collective resonances to occur and sketches some of their features.

1. FORMAL STATEMENT OF PROBLEM

We wish to calculate the rate of excitation of an atom from its ground state in an external field sufficiently weak for the Born approximation to be valid. The field is taken to be scalar, of a definite frequency and of a wavelength large compared to the dimensions of the atom. We describe its interaction with the atom by the density operator $\rho(\mathbf{x}) = \psi^\dagger(\mathbf{x})\psi(\mathbf{x})$ in the notation of second quantization. For a study of the absorption of light we should consider the interaction with a transverse field, of course, but in the long-wavelength limit, the responses of the atom to a transverse field and to a longitudinal field are connected in a simple way; the scalar field is chosen merely for mathematical convenience. Our presentation follows the lines of linear response theory as now widely used in many-particle physics, and we refer to the current literature for detailed expositions.[1]

Let the interaction be of the form

$$V = V_0 \int d^3x \exp[i(\mathbf{q}\cdot\mathbf{x} - \omega t)]\rho(\mathbf{x}) + \mathrm{c.c.}, \quad (1)$$

where $\mathbf{q}$ is the wave vector, and $\rho(\mathbf{x})$ the electron density of the atom at the point $\mathbf{x}$. All quantities are considered given in atomic units. In the following, we set $V_0 = 1$. The total transition rate of the atom from the ground state in Born approximation is given by

$$W = 2\pi \sum_n \delta(\omega - E_n) \left| \langle n | \int d^3x \rho(\mathbf{x}) \exp(i\mathbf{q}\cdot\mathbf{x}) | 0 \rangle \right|, \quad (2)$$

where $|0\rangle$ denotes the ground state of the system, and $|n\rangle$, E_n denote its excited states and the corresponding excitation energies.

The transition rate can be related to the autocorrelation function of the density fluctuations in the usual manner,

$$R(\mathbf{q},\omega) = -\int_{-\infty}^{+\infty} dt\, e^{i\omega t} \int d^3x\, d^3x'$$

$$\times \exp(-i\mathbf{q}\cdot\mathbf{x}) | \langle 0 | T[\rho(\mathbf{x},t)\rho(\mathbf{x}',0)] | 0 \rangle | \exp(i\mathbf{q}\cdot\mathbf{x}'), \quad (3)$$

where

$$\rho(\mathbf{x},t) = e^{iHt}\rho(\mathbf{x})e^{-iHt},$$

H being the Hamiltonian of the system in the absence of an external field. T denotes the Wick time-ordering symbol. On introducing the eigenstates of H, Eq. (3) can be written for $\omega \neq 0$ as

$$R(\mathbf{q},\omega) = \lim_{\epsilon \to 0} \sum_n \left\{ \frac{\left| \langle n | \int d^3x \rho(\mathbf{x}) \exp(i\mathbf{q}\cdot\mathbf{x}) | 0 \rangle \right|^2}{\omega - E_n + i\epsilon} \right.$$

$$\left. - \frac{\left| \langle n | \int d^3x \exp(-i\mathbf{q}\cdot\mathbf{x})\rho(\mathbf{x}) | 0 \rangle \right|^2}{\omega + E_n - i\epsilon} \right\}. \quad (4)$$

The poles of $R(\mathbf{q},\omega)$ give the excitation energies of the system, while the transition rate can be expressed as

$$W = -2\,\mathrm{Im}R(\mathbf{q},\omega). \quad (5)$$

Because of the sum rule

$$-2\int_0^\infty \mathrm{Im}R(\mathbf{q},\omega)\omega d\omega = \pi q^2 N, \quad (6)$$

where N is the number of electrons in the atom, we can introduce a differential oscillator-strength distribution $g(\omega)$, defined as

$$g(\omega) = -(2\omega/\pi q^2)\,\mathrm{Im}R(\mathbf{q},\omega), \quad (7)$$

and, by Eq. (6), normalized such that

$$\int_0^\infty g(\omega)d\omega = N. \quad (8)$$

[1] Cf., e.g., D. Pines, *The Many-Body Problem* (W. A. Benjamin, New York, 1961); A. J. Glick, Ann. Phys. (N. Y.) **17**, 61 (1962).

The study of the function $g(\omega)$ under various assumptions about the dynamic response of the atom is the primary concern of this paper.

The formulation of our problem, Eq. (7), in terms of the complex response function, Eq. (4) suggests a study of the propagator function

$$Q(\mathbf{x},\mathbf{x}',\omega) = -i \int_{-\infty}^{+\infty} dt\, e^{i\omega t} \langle 0 | T(\rho(\mathbf{x},t)\rho(\mathbf{x}',0)) | 0 \rangle \quad (9)$$

from which the function $R(\mathbf{q},\omega)$ is to be calculated according to

$$R(\mathbf{q},\omega) = \int d^3x\, d^3x'\, \exp[-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')] Q(\mathbf{x},\mathbf{x}',\omega). \quad (10)$$

The further formal development along these lines would entail a study of the equation satisfied by the two-particle Green's function, as discussed frequently in current literature. Since we aim at a discussion of the properties of the differential oscillator-strength distribution $g(\omega)$ under simplifying assumptions, we shall not pursue here these general questions, but rather turn to a description of the approximations to be considered as starting points for our further considerations. We base our development on an approximate description of the atom corresponding closely, in physical terms, to the linearized time-dependent Hartree equations, in which the shifts of the energy levels due to many-particle effects are accounted for by a time-dependent Hartree field. Instead of working directly with the time-dependent Hartree equations, however, we start out from an equivalent integral equation for the propagator function $Q(\mathbf{x},\mathbf{x}',\omega)$.

As our zeroth-order approximation, we employ the conventional Hartree-Fock description and assume the single-particle energies and the one-electron wave functions $u_i(\mathbf{x})$ to be known both for the occupied and the virtual unoccupied states. In the ground state, the N lowest levels are taken to be occupied, and for simplicity we assume that the ground state is nondegenerate. Elementary excitations in the system imply the raising of an electron from an occupied to an unoccupied level, i.e., particle-hole excitations. Such excitations couple to each other through the Coulomb interaction. It is our task, then, to find at least approximately the resulting new states of the atom, which manifest themselves as resonances of $Q(\mathbf{x},\mathbf{x}',\omega)$.

First, we introduce the propagator function $Q_0(\mathbf{x},\mathbf{x}',\omega)$ corresponding to the elementary excitations without interaction. We obtain Q_0 with the use of Eqs. (4) and (9) by replacing $|0\rangle$ and $|n\rangle$ by the corresponding Hartree-Fock states, and E_n by the energies of the corresponding particle-hole excitation energies, to be denoted by ω_n,

$$Q_0(\mathbf{x},\mathbf{x}',\omega) = \lim_{\epsilon \to 0} \sum_n \left\{ \frac{\Phi_n(\mathbf{x})\Phi_n^*(\mathbf{x}')}{\omega - \omega_n + i\epsilon} - \frac{\Phi_n^*(\mathbf{x})\Phi_n(\mathbf{x}')}{\omega + \omega_n - i\epsilon} \right\}. \quad (11)$$

$\Phi_n(\mathbf{x})$ denotes the "wave function" of the particle-hole pair, i.e., the product $u_i^*(\mathbf{x})u_j(\mathbf{x})$ of the corresponding one-electron wave functions associated with the Hartree-Fock states i and j.

Next, we introduce the approximate integral equation which forms the basis for our discussion

$$Q(\mathbf{x},\mathbf{x}',\omega) = Q_0(\mathbf{x},\mathbf{x}',\omega) + \int Q_0(\mathbf{x},\mathbf{x}'',\omega) \frac{1}{|\mathbf{x}''-\mathbf{x}'''|}$$

$$\times Q(\mathbf{x}''',\mathbf{x}',\omega) d^3x'' d^3x'''. \quad (12)$$

In the language of many-particle perturbation theory, the approximation inherent in our basic Eq. (12) corresponds to neglecting all but the so-called "bubble" diagrams describing elementary particle-hole excitations, with the obvious difference that, in the present context, the elementary excitations refer to the Hartree-Fock states of the atom rather than to the plane-wave states of extended systems.

It is evident from the structure of Eq. (12) that excitations of different symmetry will not mix; one has to couple the particle-hole excitations in $Q_0(\mathbf{x},\mathbf{x}',\omega)$ to the appropriate quantum numbers before attempting to solve the equation. For our discussion, only the case of dipolar excitations is of interest.

Before proceeding further, we digress briefly to establish contact with the theory of the extended uniform electron gas in the high-density limit, and quote its results for reference in our subsequent discussions. Inserting the free-electron energies and wave functions in Eq. (11), we obtain

$$Q_0(\mathbf{x},\mathbf{x}',\omega) = \frac{1}{(2\pi)^3} \int d^3q\, \exp[i\mathbf{q}(\mathbf{x}-\mathbf{x}')] Q_0(q,\omega), \quad (13)$$

where

$$Q_0(q,\omega) = \frac{2}{(2\pi)^3} \int d^3p\, \theta_-(|p|-p_F)\theta_+(|\mathbf{p}+\mathbf{q}|-p_F)$$

$$\times \{ [\omega - (\tfrac{1}{2}q^2 + \mathbf{p}\cdot\mathbf{q}) + i\epsilon]^{-1}$$

$$- [\omega + (\tfrac{1}{2}q^2 + \mathbf{p}\cdot\mathbf{q}) - i\epsilon]^{-1} \}. \quad (13a)$$

In Eqs. (13), (13a), $\mathbf{q}$ denotes the momentum difference of the particle-hole excitation, $\mathbf{p}$ the momentum of the hole state, p_F the Fermi momentum, and

$$\theta_\pm = \tfrac{1}{2}(1 \pm x/|x|).$$

On writing in analogy to Eq. (13)

$$Q(\mathbf{x},\mathbf{x}',\omega) = \frac{1}{(2\pi)^3} \int d^3q\, \exp[i\mathbf{q}(\mathbf{x}-\mathbf{x}')] Q(q,\omega) \quad (14)$$

and inserting Eqs. (13) and (14), Eq. (12) has the well-known solution

$$Q(q,\omega) = \frac{Q_0(q,\omega)}{1 - (4\pi/q^2)Q_0(q,\omega)}. \quad (15)$$

For later reference, we quote the solution in the limit $q \to 0$,

$$\lim_{q \to 0} Q(q,\omega) = \frac{q^2 \rho}{\omega^2 - \omega_0^2}, \qquad (16)$$

where ρ is the density of the gas, and $\omega_0 = (4\pi\rho)^{1/2}$ the classical plasma frequency.

From Eq. (15) follow all the dielectric properties of the electron gas, as first derived by Lindhard.[2]

2. ATOMIC RESPONSE FUNCTION IN THE ELECTRON-GAS APPROXIMATION

In this section we give a brief discussion of a simple approximation to the function $g(\omega)$, which, although neither new or revealing with regard to collective behavior, nevertheless is pertinent to our later discussions. One of the simplest assumptions one can make about the excitation spectrum in the framework of noninteracting particles is to associate with each point in the atom a single frequency, which is a function only of the local density. Such a model and its application to physical phenomena has been employed in particular by Lindhard and Scharff,[3] and we refer to their paper for a detailed discussion. In the simplest version, one chooses the frequency to be equal to just the classical plasma frequency $\omega_0(\mathbf{x}) = [4\pi\rho(\mathbf{x})]^{1/2}$. This choice of resonance frequency is equivalent, of course, to assuming that the local response to the field is the same as that of a uniform electron gas of a density equal to the local density.

It is a straightforward matter to rederive the expression for $g(\omega)$ in the form given by Lindhard and Scharff by introducing the corresponding approximations in solving the integral equation. The local density fluctuations at a wave vector $\mathbf{q}$ and frequency ω are given by Eq. (10), for which we find the expression

$$R(\mathbf{q},\omega) = \int d^3x \frac{Q_0(q,\omega)}{1 - (4\pi/q^2)Q_0(q,\omega)}, \qquad (17)$$

where $Q_0(q,\omega)$, given by Eq. (13a), depends on the local density through

$$p_F(\mathbf{x}) = [3\pi^2\rho(\mathbf{x})]^{1/3}.$$

Thus, the atom responds locally at the wave number only of the external field. In the long-wavelength limit, the response function reduces to

$$\lim_{q \to 0} R(\mathbf{q},\omega) = q^2 \int d^3x \frac{\rho(\mathbf{x})}{\omega^2 - \omega_0^2(\mathbf{x})}. \qquad (18)$$

We insert in Eq. (7) and obtain the expression of

Lindhard and Scharff,

$$g(\omega) = \int d^3x \rho(\mathbf{x})\delta(\omega - \omega_0(\mathbf{x})), \qquad (19)$$

i.e., $g(\omega)$ is equal to the number of electrons with frequencies in the range $[\omega, \omega + d\omega]$.

In this model, therefore, the function $g(\omega)$ maps the charge distribution of the atom and, consequently, is essentially a smooth function of frequency in the relevant frequency range. It exhibits no collective resonances reminiscent, say, of the giant resonances in nuclei, because the model assumes *ab initio* that each spherical shell of the atomic cloud responds separately.

One might suppose that these shortcomings can be remedied to some extent by taking into account the effects of the density gradient in a way similar to the Weizsäcker correction in the statistical Thomas-Fermi model, while maintaining the idea of a local electron-gas approximation. This amounts to replacing the step functions in Eq. (13) by the quantum-mechanical expressions

$$\langle \theta_\pm [p^2 - p_F^2(\mathbf{x})] \rangle_\mathbf{R} = \int d^3r$$

$$\times \exp(-i\mathbf{p}\cdot\mathbf{r})\langle \mathbf{x}| \theta_\pm [p_{\mathrm{op}}^2 - p_F^2(\mathbf{x})]|\mathbf{x}\rangle, \qquad (20)$$

where $\mathbf{r} = \mathbf{x} - \mathbf{x}'$, and $\mathbf{R} = (\mathbf{x} + \mathbf{x}')/2$. This integral can be solved by a formula due to Glauber[4] in an approximation which depends on the commutator of $\mathbf{p}_{\mathrm{op}}$ and $p_F(\mathbf{x})$ and all its powers; the final result can be expressed in terms of Airy integrals. For evaluating $Q_0(q,\omega)$, it turned out to be most convenient to work with the integral representation

$$\langle \theta_\pm(z) \rangle = \pm \frac{1}{2\pi i} \lim_{\epsilon \to 0} \int_{-\infty}^{+\infty} \frac{\exp[i(zt - t^3)]}{t \mp i\epsilon} dt, \qquad (21)$$

with $z = (p^2 - p_F^2)/(p_F|\nabla p_F|)^{2/3}$.

However, the result in the long-wavelength limit reduces exactly to the result for a gas with no density gradient. That is, corrections to Eq. (19) due to the density gradient will appear only if one takes into account effects deriving from the actual wavelength of the external field. We shall not discuss such effects in this work.

The conclusion of this brief discussion is that the local approximation of the type incorporated in Eq. (19) cannot exhibit possible collective resonances in the response of atoms. We are led to expect that in order to find such resonances, approximations to the solution of the integral equation must be found which preserve the phase relation between the response of different parts of the atom.

[2] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. 28, No. 8 (1954).

[3] J. Lindhard and M. Scharff, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. 27, No. 15 (1953).

[4] R. J. Glauber, Phys. Rev. 84, 395 (1951)

3. APPROXIMATE SOLUTION OF INTEGRAL EQUATION

An exact solution of the integral equation is possible only under very special assumptions about the matrix elements of the interaction. In general, one has to resort to approximation methods, chosen in such a manner, however, that they in contrast to approximations as the one discussed in Sec. 2, retain the salient features of atomic dynamics which can cause new resonances in the complex response function $R(\mathbf{q},\omega)$. For example, the ordinary perturbation expansion of Eq. (12) repeats to all orders just the resonances in $Q_0(\mathbf{x},\mathbf{x}',\omega)$; therefore, it is ruled out as an acceptable approximation method since new possible resonances are coherence effects arising from the interaction to all others.

We employ the Fredholm expansion, which constructs the solution to the integral equation as the ratio of two entire functions in the coupling constant. For the present, let us consider the expansion of the solution of Eq. (12) only to the lowest order terms in the interaction in both numerator and denominator,

$$Q(\mathbf{x},\mathbf{x}',\omega) = Q_0(\mathbf{x},\mathbf{x}',\omega)$$

$$+ \frac{\displaystyle\int d^3y\, d^3z\, Q_0(\mathbf{x},\mathbf{y},\omega)\frac{1}{|\mathbf{y}-\mathbf{z}|}Q_0(\mathbf{z},\mathbf{x}',\omega)}{1-\displaystyle\int d^3y\, d^3z\, Q_0(\mathbf{y},\mathbf{z},\omega)\frac{1}{|\mathbf{y}-\mathbf{z}|}}. \quad (22)$$

Because of the reasons given in Sec. 1, it is understood that Eq. (22) considers only the subset of $Q_0(\mathbf{x},\mathbf{x}',\omega)$ corresponding to the symmetry type of the excitation.

The new resonances, shifted relative to those of Q_0 by the Coulomb interaction, are the solutions of the dispersion relation

$$1 = \int d^3y\, d^3z\, Q_0(\mathbf{y},\mathbf{z},\omega)\frac{1}{|\mathbf{y}-\mathbf{z}|}. \quad (23)$$

The general nature of these results is best elucidated in terms of the dipolar excitations of a model similar to the so-called schematic model[5] in discussing the qualitative features of giant resonances in nuclei. We choose the quantization axis along the direction of the wave vector of the external field and consider the excitations corresponding to the quantum numbers $L=1$, $M=1$, $S=0$. We approximate the matrix elements of the Coulomb interaction by the expression

$$V_{n,m} = \lambda_n \lambda_m D_n D_m, \quad (24)$$

where D_n and D_m are the dipole matrix elements for the particle-hole excitations n and m; λ_n and λ_m are coupling parameters of dimension frequency which depend mainly on the corresponding hole state, so that for given hole

states, the variation between matrix elements with different particle states is governed predominantly by the dipole matrix elements. For Eq. (24), the integral equation (12) can be solved directly. We find in the limit $|\mathbf{q}| \to 0$ the expression

$$R(q,\omega) = q^2 \left\{ \sum_n \frac{f_n}{\omega^2 - \omega_n^2} \right.$$

$$\left. + \left\{ \sum_n \lambda_n \frac{f_n}{\omega^2 - \omega_n^2} \right\}^2 \middle/ \left(1 - \sum_n \lambda_n^2 \frac{f_n}{\omega^2 - \omega_n^2} \right) \right\}, \quad (25)$$

where $f_n = 2\omega_n D_n^2$ is the oscillator strength of the particle-hole excitation n in atomic units. The summation includes, of course, an integration over the continuous part of the spectrum.

Equation (25) coincides with the result obtained from the first-order Fredholm formula Eq. (22), which proves it to be the exact solution of the integral equation for the schematic model. As the higher order corrections to Eq. (22) obviously also vanish for oscillations of the uniform electron gas at a given wave number $\mathbf{q}$, we expect Eq. (22) to be useful for gaining some insight into the collective behavior of atoms.

We calculate the differential oscillator-strength distribution for the schematic model. On inserting Eq. (25) in Eq. (7), one finds

$$g(\omega) = \sum_i \left\{ \sum_n \lambda_n f_n P[\Omega_i^2 - \omega_n^2]^{-1} \right\}^2 \middle/$$

$$\left\{ \sum_n \lambda_n^2 f_n P[\Omega_i^2 - \omega_n^2]^{-2} \right\} \delta(\omega - \Omega_i). \quad (26)$$

P denotes that the principal value shall be taken in the continuous part of the spectrum. Equation (26) shows absorption at frequencies Ω_i, which are solutions of the dispersion equation

$$1 = \sum_n \lambda_n^2 \frac{f_n}{\omega^2 - \omega_n^2}. \quad (27)$$

Equation (26) reduces to the function

$$g(\omega) = \sum_n f_n \delta(\omega - \omega_n)$$

of the single-particle excitations if and only if all $\Omega_n \equiv \omega_n$, which obtains for all $\lambda_n \to 0$.

Knowing the quantities ω_n, f_n and λ_n one can solve for the resonance frequencies by numerical or graphical methods. Here, we follow an earlier discussion[6] and indicate only in a qualitative way the nature of the solutions of Eq. (27) and the corresponding properties of $g(\omega)$ in three different situations.

(a) In a frequency range where the separation between adjacent levels is small, the right-hand side of Eq. (27) oscillates rapidly between minus and plus infinity whenever the frequency passes through the range between neighboring levels, $(\omega_m; \omega_{m+1})$, i.e., a root $\Omega_m \simeq \omega_m$ exists

[5] G. E. Brown, *Lectures on Many-Body Problems* (NORDITA, Copenhagen, 1961).

[6] W. Brandt, Phys. Rev. **111**, 1042 (1958).

between any two such adjacent levels. These states are best characterized as slightly modified particle-hole excitations with no bearing on collective phenomena, because at such frequencies Eq. (26) reduces essentially to a partial sum of the form

$$\sim \sum_{m}^{(a)} \Delta_m \delta(\omega - \Omega_m). \tag{28}$$

The effective oscillator strengths associated with these states, Δ_m, are in general very small.

(b) In a frequency range where the excitation energies of the noninteracting particle-hole states are so widely spaced that $\lambda_l^2 f_l \ll |\omega_{l+1}^2 - \omega_l^2|$, one root appears in the range between ω_l and ω_{l+1} which is given approximately by

$$\Omega_l^2 \simeq \omega_l^2 + \lambda_l^2 f_l \left[1 - \sum_{k \neq l} \frac{\lambda_k^2 f_k}{\omega_l^2 - \omega_k^2} \right]^{-1}. \tag{29}$$

That is, the square of the resonance frequency appearing between ω_l^2 and ω_{l+1}^2 ($\omega_{l+1} > \omega_l$) consists of a single-particle component and a collective component. The state may be considered more or less collective in nature, depending on which component dominates. For a uniform electron gas in the long-wavelength limit, $\omega_l = 0$ and $\lambda_l^2 f_l = \omega_0^2$, i.e., the excitation in that case is entirely collective. States of the kind described by Eq. (29) contribute to $g(\omega)$ the partial sum

$$\sim \sum_{l}^{(b)} f_l \left[1 + \lambda_l \left(\sum_{k \neq l} \frac{\lambda_k f_k}{\omega_l^2 - \omega_k^2} \right) \middle/ \left(1 - \sum_{k \neq l} \frac{\lambda_k^2 f_k}{\omega_l^2 - \omega_k^2} \right) \right]^2$$
$$\times \delta(\omega - \Omega_l). \tag{30}$$

If the second term in the brackets is small compared to 1, the states again may be considered to be slightly modified single-particle states, as in range (a). Whenever this term becomes $\gtrsim 1$, the interaction causes a redistribution of the single-particle spectrum proportional to $\lambda_l^2 f_l$. However, there still exists a one-to-one relation between Ω_l and ω_l, i.e., in range (b) as in (a), $g(\omega)$ retains the characteristics of single-particle spectra.

The particle-hole spectrum in atoms suggests that the conditions for these types of solutions with modified single-particle spectra in situations (a) and (b) may be fulfilled best by the valence shells, where the levels below the ionization edge are closely spaced, and by the innermost shells, where the high-excitation energies to unoccupied states make the single-particle contribution to the dominating component. The modification of the single-particle spectrum by the interaction in the sense of Eq. (30) should be most pronounced for excitations of the electrons just below the valence shells, where the level spacing is sufficiently large for the conditions of range (b) to apply, but where the single-particle and collective contributions are comparable. One may reasonably suppose, therefore, that in general $g(\omega)$ will have the properties of a modified single-particle spec-

trum at frequencies corresponding approximately to the frequency ranges (1) and (3) referred to in the Introduction.

(c) Consider now a situation where a gap exists between groups of discrete levels in the particle-hole excitation spectrum, which is either empty, or contains parts of the continuous spectrum of small total oscillator strength. If, then, at frequencies slightly larger than all the levels below the gap

$$\sum_{\omega_n < \omega} \frac{\lambda_n^2 f_n}{\omega^2 - \omega_n^2} > 1,$$

one root can exist in the spectral range of the gap. For a root sufficiently far from the gap edges, the resonance frequency is given by

$$\Omega_i^2 = \langle \omega_i^2 \rangle_{av} + \langle \lambda_i^2 f_i \rangle_{av}, \tag{31}$$

where to leading terms in the shift,

$$\langle \omega_i^2 \rangle_{av} \simeq \left(\sum_{\omega_n < \Omega_i} \lambda_n^2 f_n \omega_n^2 \right) \middle/ \left(\sum_{\omega_n < \Omega_i} \lambda_n^2 f_n \right);$$

$$\langle \lambda_i^2 f_i \rangle_{av} \simeq \left(\sum_{\omega_n < \Omega_i} \lambda_n^2 f_n \right) \middle/ \left(1 + \sum_{\omega_n > \Omega_i} \frac{\lambda_n^2 f_n}{\omega_n^2} \right).$$

We introduce the following averages over the distribution of particle-hole excitations

$$\langle \lambda_i^\nu f_i \rangle_{av} = \sum_{\omega_n < \Omega_i} \lambda_n^\nu f_n + (-1)^\nu \sum_{\omega_n > \Omega_i} (\lambda_n')^\nu f_n, \tag{32}$$

where for large shifts $\lambda_n' \simeq \Omega_i^2 \lambda_n / \omega_n^2$. By Eq. (26), states of the type described by Eq. (31) contribute to $g(\omega)$ the term

$$g_{coll} \simeq \sum_{i}^{(c)} \frac{\langle \lambda_i f_i \rangle_{av}^2}{\langle \lambda_i^2 f_i \rangle_{av}} \delta(\omega - \Omega_i). \tag{33}$$

Equation (33) couples all single-particle states into new resonances of the atom as a whole.

This situation is likely to correspond somewhat to the giant resonances known to exist in nuclei. In atoms, such contributions may come from groups of closely spaced particle-hole excitations to particle states above the ionization edge, acting coherently to give rise to collective resonances. Resonance phenomena of this sort lie in frequency range (2).

The effects of the resonance conditions on the damping of the resonance will not be discussed in the present context.

The preceding remarks were intended only as a qualitative orientation regarding the possible nature of coherent modes in atoms. Work is in progress to explore the relevance of this simple model for real atoms, which will be reported separately. The results to be expected from such an investigation will depend on details of the properties of a specific atom in question. It is of some interest, therefore, to undertake a simplified treatment

based on the statistical model of the atom which expresses collective phenomena in atoms as smooth functions of the atomic number Z.

4. ATOMIC RESPONSE FUNCTION IN THE STATISTICAL APPROXIMATION

In rederiving the results of Sec. 3 for the statistical model of the atom, we assume, as in Sec. 2, that the energy spectrum of particle-hole excitations and the unperturbed propagator is locally the same as that of an infinite electron gas of density equal to the local density $\rho(\mathbf{x})$. However, we do not insist on local momentum conservation, as in Sec. 2, which led to the result that each spherical atomic shell responds only to the wave number of the external field. We employ the Fredholm expansion instead, whereby we retain in an approximate manner the coherence between the response of different parts of the atom, analogous to the response of the atom as a whole as sketched in the preceding section for the Hartree model.

The statistical model of the atom is justified, at least formally, only for large Z. Our treatment makes use of

this by only retaining terms to leading order of Z in each term of the expansion. Consistency with the choice of the propagator of the infinite electron gas for the unperturbed $Q_0(\mathbf{x},\mathbf{x}',\omega)$ requires that also the kernel and the iterated kernels of the integral equation (12) be those of the infinite electron gas; i.e.,

$$K_n(\mathbf{x},\mathbf{x}',\omega) = (2\pi)^{-3} \int d^3q$$

$$\times \exp[i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')][4\pi Q_0(q,\omega)/q^2]^n,$$

$$n=1, 2, 3, \cdots. \quad (34)$$

With Eq. (34), an approximate solution of Eq. (12) obtains from the Fredholm expansion by summing both numerator and denominator and retaining the leading terms in Z in each order of the interaction. To each order in the interaction, the terms containing only $K_n(\mathbf{x},\mathbf{x}',\omega)$ are of higher order in Z than any of the products of traces and kernels of lower order, and the latter are neglected. One obtains

$$Q(\mathbf{x},\mathbf{x}',\omega) \simeq Q_0(\mathbf{x},\mathbf{x}',\omega) + \left[\int d^3y \{\sum_n K_n(\mathbf{x},\mathbf{y},\omega)\} Q_0(\mathbf{y},\mathbf{x}',\omega) \right] \bigg/ \left[1 - \int d^3x \{\sum_n K_n(\mathbf{x},\mathbf{x},\omega)/n\} \right]$$

$$= Q_0(\mathbf{x},\mathbf{x}',\omega) + [1+F(\omega)]^{-1}(2\pi)^{-3} \int d^3q \, \exp[i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')] \frac{Q_0(q,\omega)4\pi Q_0(q,\omega)/q^2}{1-4\pi Q_0(q,\omega)/q^2}, \quad (35)$$

where

$$F(\omega) = (2\pi)^{-3} \int d^3x d^3q \, \ln\{1-4\pi Q_0(q,\omega)/q^2\}, \quad (36)$$

with the notation $2 \ln\{G\} = \ln|GG^*| + \ln(G/G^*)$; in the imaginary part, only the principal values between $-i\pi$ and $+i\pi$ are retained. Inserting Eq. (35) in Eq. (10) yields the response function

$$R(\mathbf{q},\omega) = \int d^3x \frac{Q_0(q,\omega)}{1-4\pi Q_0(q,\omega)/q^2} - \frac{F(\omega)}{1+F(\omega)}$$

$$\times \int d^3x \frac{Q_0(q,\omega)4\pi Q_0(q,\omega)/q^2}{1-4\pi Q_0(q,\omega)/q^2}. \quad (37)$$

In the long-wavelength limit, $|\mathbf{q}| \to 0$, Eq. (37) reduces to

$$R(q,\omega) = q^2 \left\{ \int d^3x \frac{\rho(\mathbf{x})}{\omega^2-\omega_0^2(\mathbf{x})} - \frac{F(\omega)}{1+F(\omega)} \right.$$

$$\left. \times \int d^3x \frac{\omega_0^2(\mathbf{x})}{\omega^2} \frac{\rho(\mathbf{x})}{\omega^2-\omega_0^2(\mathbf{x})} \right\}. \quad (38)$$

As in Eq. (25), the first term in Eq. (38) is just the response of the individual spherical atomic shells in the

electron-gas approximation as given in Eq. (18). The second term arises from the modification due to the response of the atom as a whole.

We recall that the derivation of Eq. (38) is based explicitly on the assumption that we are dealing with a bounded system of a given number of electrons. It does not seem obvious from Eq. (36) that $F(\omega)$ should vanish in the limit of an infinite system of constant number density. However, one can demonstrate the proper limiting behavior of $F(\omega)$ along the following lines. The integrand in Eq. (36) depends on the electron density through $Q_0(q,\omega)$ and thus on r. For a spherically symmetric density distribution, we can integrate by parts over the radial coordinate while keeping $\mathbf{q}$ fixed. This leads to a new integrand containing the gradient of the electron density as a factor. The integrated part vanishes for a bounded system such as an atom, where the density is finite at the origin and vanishes sufficiently rapidly at infinity. This result shows that $F(\omega)$ and, hence, the atomic response as compared to that of the uniform electron gas depends in an essential way on the gradient of the electron density. If we let the density gradient go to zero, $F(\omega) \to 0$, and we retrieve the response function Eq. (17) in the uniform gas approximation.

The differential oscillation-strength distribution can

now be derived according to Eq. (7).

$$g(\omega) = g_1(\omega) + g_2(\omega), \qquad (39)$$

where

$$g_1(\omega) = \int d^3x \rho(\mathbf{x}) \, \mathrm{Re}[1 + F(\omega(\mathbf{x}))]^{-1} \delta[\omega - \omega_0(\mathbf{x})] \quad (39a)$$

is the continuous distribution of the atom of Eq. (19), modified by the interaction, while the second term

$$g_2 = \frac{2\omega}{\pi} \mathrm{Im}\left[\frac{F(\omega)}{1 + F(\omega)}\right] \int d^3x \frac{\omega_0^2(\mathbf{x})}{\omega^2} P\left[\frac{\rho(\mathbf{x})}{\omega^2 - \omega_0^2(\mathbf{x})}\right] \quad (39b)$$

accounts for the atomic resonances. The appearance of the denominator in Eq. (39a) suggests the possibility for new resonances in the electron cloud of the atom. For, if real roots exist of the eigenvalue equation

$$[1 + F(\omega)] = 0, \qquad (40)$$

$g(\omega)$ shows at these resonance frequencies sharp absorption lines for $\mathrm{Im}F(\omega) \to 0$, or correspondingly broader peaks if $\mathrm{Im}F(\omega)$ is finite.

Equations (39a) and (39b), as derived for the statistical model, appear to correspond loosely to the cases (a,b) and to (c), respectively, in the schematic Hartree model.

Work is in progress to calculate $g(\omega)$ for the statistical Thomas-Fermi model of the atom under realistic assumptions about the damping terms in $F(\omega)$. In the next section we discuss qualitatively the content of Eq. (39) for a model sufficiently simplified to give explicit results.

5. AN ILLUSTRATIVE EXAMPLE

For a first estimate of $F(\omega)$, Eq. (36), we note that the real part of $4\pi Q_0(q,\omega)/q^2$ varies with the electron density as $\rho(\mathbf{x})$ or as $\rho^{1/3}(\mathbf{x})$, depending on whether $|\mathbf{q}|$ is small or large compared to ω/p_F. However, the contributions from small $|\mathbf{q}|$ should dominate over most of the frequency range of interest. This agrees also with the philosophy adopted in our Fredholm expansion, since after forming the traces of the iterated kernels, the contributions from small $|\mathbf{q}|$ are of higher order in Z than those from large $|\mathbf{q}|$. We neglect the finite imaginary part of Q_0 which appears only for higher values of $|\mathbf{q}|$. For our calculation then, we use the approximation

$$\frac{4\pi Q_0(q,\omega)}{q^2} \sim \lim_{|\mathbf{q}| \to 0} \frac{4\pi}{q^2} Q_0(q,\omega) = \frac{\omega_0^2(\mathbf{x})}{\omega^2}, \quad (41)$$

subject to the cutoff condition in momentum space

$$q_{\max}(\mathbf{x}) = \alpha^{1/3} r_s^{1/2}(\mathbf{x}) p_F(\mathbf{x}), \qquad (42)$$

where $\alpha^{1/3}$ is a constant of order 1, and

$$r_s(\mathbf{x}) = (4\pi\rho(\mathbf{x})/3)^{-1/3}.$$

For momenta larger than $q_{\max}$, the collective states will decay rapidly into electron-hole pairs, and hence cease

to be well-defined states of excitation. In this approximation, the first part of Eq. (39) becomes

$$g_1(\omega) = \int d^3x \rho(\mathbf{x}) P[1 + F(\omega(\mathbf{x}))]^{-1} \delta(\omega - \omega_0(\mathbf{x})). \quad (43)$$

To calculate g_2, we expand $1 + F(\omega)$ about the roots Ω_i of Eq. (40), and take the imaginary parts,

$$g_2(\omega) = \sum_i \Omega_i^{-2} \left(\frac{dF(\omega)}{d\omega^2}\right)_{\Omega_i}^{-1} \int d^3x P \frac{\rho(\mathbf{x})\omega_0^2(\mathbf{x})}{\Omega_i^2 - \omega_0^2(\mathbf{x})}$$

$$\times \delta(\omega - \Omega_i). \quad (44)$$

If roots of Eq. (40) exist, the neglect of a finite imaginary part of $F(\omega)$ in favor of the simple approximations Eqs. (41) and (42) gives unphysically sharp resonance lines in g_2, of course, and leads to spurious negative contributions to g_1 near such resonances. Nevertheless, a study of Eqs. (43) and (44) suggests the type of interaction effects one may expect to find by an exhaustive analysis of Eq. (39) under physically more realistic assumptions.

For a statistical model of the atom, we turn to an approximate description of the atomic structure due to Bohr.[7] We assign to the nth electron in an atom the orbital radius a_n and the orbital velocity v_n given by

$$a_n = \nu^2/n,$$

$$v_n = n/\nu, \quad n = 1, 2, \cdots Z. \qquad (45)$$

The effective quantum number ν increases from a value close to 1 for the inner electrons to a broad maximum very nearly equal to $Z^{1/3}$ for the intermediate atomic shells, again to drop to values close to 1 for the outer electrons. These three ranges of ν correspond to the three frequency ranges referred to in the Introduction, since the frequencies $\omega(a_n)$ are proportional to v_n/a_n.
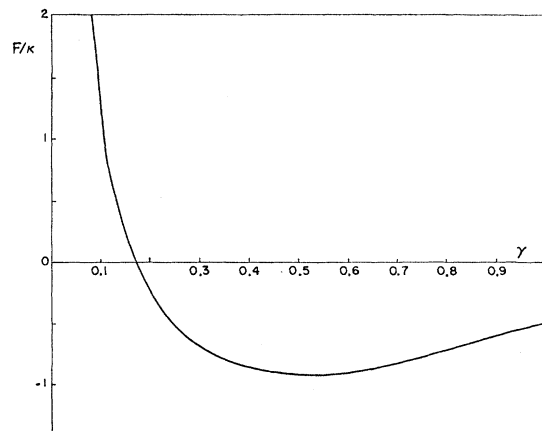

FIG. 1. $F(\omega)/\kappa$ versus (ω/ω_c), Eq. (47), for the illustrative statistical example.

[7] N. Bohr, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. 18, No. 8, 99 (1948); N. Bohr and J. Lindhard, ibid. 28, No. 7, 9 (1954).

For sufficiently large Z, the frequency range (2) dominates, and to a good approximation one can set $\nu \simeq Z^{1/3}$ throughout the atom. Equation (45) describes an atom where $\omega_0{}^2(x) = \omega_c{}^2 x^{-4}$, for $x \geq 1$, where $\omega_c = K_c Z$; ω_c and K_c are cutoff constants corresponding to a cutoff radius $r_c \sim Z^{-1/3}$, and $x = (r/r_c)$. It is convenient to introduce the abreviations $\gamma = (\omega/\omega_c)$, $\Gamma_i = (\Omega_i/\omega_c)$ and

$$\hat{g}(\gamma) = Z^{-1}\omega_c g(\omega).$$

For this model, we obtain from Eq. (36)

$$F(\gamma) = \kappa Y(\gamma), \tag{47}$$

where $\kappa \equiv (3/4)^{1/2}(\alpha/K_c)$ is a cutoff parameter of the model of order unity. The function $Y(\gamma)$ is shown in Fig. 1. Equation (40) has no root for $\kappa < 1.11$, and two roots for $\kappa > 1.11$.

Equation (43) yields

$$\hat{g}_1(\gamma) = (2\gamma^{1/2})^{-1}\{1 + \kappa Y(\gamma)\}^{-1}. \tag{48}$$

For $\kappa = 0$, we retrieve the unmodified continuous differential oscillator-strength distribution of Eq. (19). The interaction modifies this by the expression in the brackets. As shown in Fig. 2, the curves of $\hat{g}_1$ shift to higher frequencies with increasing κ, and develop a peak. When $\kappa > 1.11$, the curves have discontinuities near the resonances, as indicated schematically for
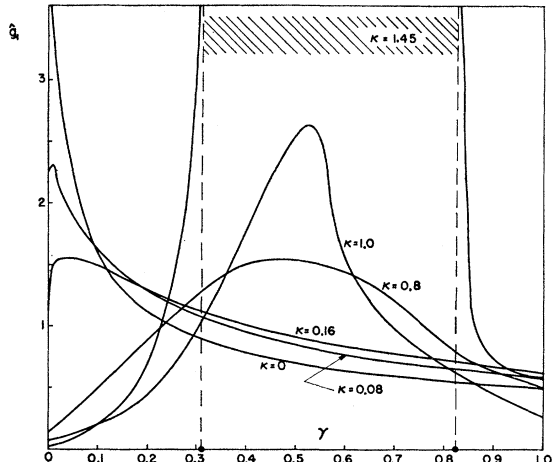

FIG. 2. The oscillator-strength distribution $\hat{g}_1$, Eq. (48), of the illustrative statistical example. For $\kappa < 1.11$, no collective atomic modes exist. The areas under the curves $\hat{g}_1$ are normalized to unity. For $\kappa > 1.11$, $\hat{g}_1$ breaks up over the frequency range of the atomic modes, as indicated schematically for $\kappa = 1.45$ by the crosshatched strip. The two points ($\bullet$) mark the resonance frequencies for $\kappa = 1.45$.
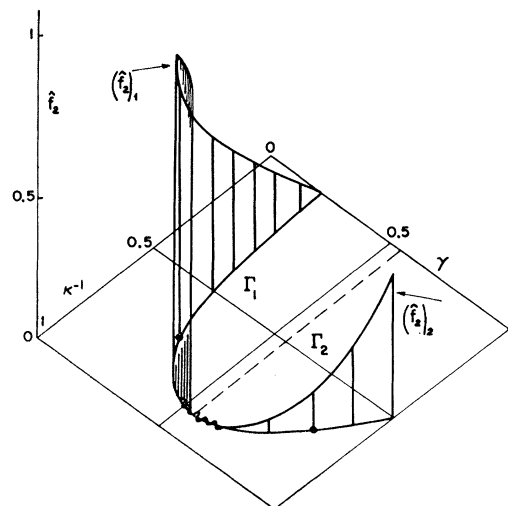

FIG. 3. The atomic resonances and the partitioning of their collective oscillator strengths, Eq. (49), of the illustrative statistical example, for different values of κ. The diagram shows only an average behavior of the oscillator strength near $\kappa \sim 1.11$ and $\gamma \sim 0.54$, where the two roots merge (wavy line). The two points ($\bullet$) correspond to the case $\kappa = 1.45$ of Fig. 2.

$\kappa = 1.45$. Concurrently, a contribution appears from Eq. (44),

$$\hat{g}_2(\gamma) = \sum_{1,2} (\hat{f}_2)_i \delta(\gamma - \Gamma_i). \tag{49}$$

The base plane in Fig. 3 contains the solution curve for Eq. (40). The two roots move apart with increasing κ, and change their share in the nearly κ-independent total atomic oscillator strength. The atomic modes appear in this model calculation as unphysically sharp absorption lines because finite damping terms have been neglected. Still, this example suggests that collective atomic modes, where they exist, may well accrue a significant fraction of the total oscillator strength of the atom.

ACKNOWLEDGMENTS