COLLECTIVE OSCILLATIONS IN MANY ELECTRON ATOMS I. EIGENVALUES AND POLARIZATION

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Abstract

Following the work of Bloch, the Thomas-Fermi model is extended to collective oscillations. The eigenfunctions and frequencies for radial and nonradial l = 1 modes are found. The calculated static polarization is compared with experiment, both for ions and neutral atoms, and the classical oscillator strengths are computed.

I. INTRODUCTION

Once it is realized that the Thomas–Fermi model of many electron atoms is equivalent to the hydrostatic equilibrium of a degenerate electron gas in the Coulomb field, it is natural to generalize the model to include collective motion. This idea is the basis of Bloch's (1933) hydrodynamic model of the atom. Bloch applied his model, with remarkable success, to the problem of the slowing down of fast moving ions in a scattering medium. Because the determination of the eigenfrequencies of oscillation was then a difficult numerical problem, Bloch contented himself with estimating their contribution from the experimental results for a single element. Jensen (1937) used a crude model to estimate Bloch's parameter and found fortuitously good agreement with experiment. An analysis of the slowing down problem by Linhard (1954) confirms the usefulness of Bloch's model.

The motivation for the present paper is the need, in certain astrophysical problems (Michaud 1970), to determine the radiation pressure exerted on ions of high atomic number (typically >40) by the radiation field of a star. The oscillator strengths for the spectral lines are known only very approximately or not at all. In this context the Bloch model may be useful since, as in the case of the slowing down problem, a sum over a large number of frequencies is required and the model appears to estimate this sum quite accurately. The plan of the paper is to derive and solve the equation of hydrostatic equilibrium, to examine the radial and nonradial modes of oscillation, and to apply the results to the determination of the static polarization coefficient and the classical oscillator strengths.

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II. HYDROSTATIC EQUILIBRIUM

The electrons are assumed to form a completely degenerate electron gas with pressure P and density ρ . In the absence of external forces, the equation of hydrostatic equilibrium takes the form

$$\frac{1}{\rho}\frac{dP}{da} = -\frac{1}{\mu a^2} \left(Ze^2 - \frac{M(a)e^2}{\mu} \right),$$
(1)

where a is the radial coordinate, μ the electron mass, Ze the charge on the nucleus, and M(a) the mass within a sphere of radius a with the nucleus as centre. Since

$$M(a) = 4\pi \int_0^a \rho a^2 \, \mathrm{d}a \,, \tag{2}$$

we can eliminate M(a) from equation (1) to obtain

$$\frac{\mathrm{d}}{\mathrm{d}a} \left(\frac{a^2}{\rho} \frac{\mathrm{d}P}{\mathrm{d}a} \right) = \frac{4\pi \, a^2 e^2 \rho}{\mu^2}.\tag{3}$$

The above results apply to any barytropic fluid. For a strongly degenerate electron gas we have

$$P = (3/\pi\mu^4)^{2/3} h^2 \rho^{5/3}, \qquad (4)$$

so that, with new variables x and ϕ defined by

$$a = x\beta, \qquad \rho = (Z\mu/4\pi\beta^3)(\phi/x)^{3/2},$$
 (5)

where

$$\beta = 3^{2/3} h^2 / \pi^{4/3} \, \mu e^2 Z^{1/3} \, 2^{13/3} = (0 \cdot 468 \times 10^{-10} \, \mathrm{m}) / Z^{1/3} \,, \tag{6}$$

we find

$$d^2\phi/dx^2 = \phi^{3/2}/x^{1/2},$$
(7)

which is the Thomas–Fermi equation.

The direct use of the hydrostatic equation enables us to make an easy generalization of equation (7) to other problems. For example, if the atom is rotating, a centrifugal term must be added to equation (1) and then, recalling that thermodynamic equilibrium requires the rotation to be rigid, the equation of Sessler and Foley (1954) is easily deduced.

The boundary conditions on equation (7) are

$$\phi(0) = 1;$$
 $\phi(x_0) = 0, \quad x_0 \, d\phi/dx_0 = -(n+1)/Z;$ (8)

where x_0 is the radius of the atom, *n* is the number of times it has been ionized, and Amaldi's correction has been used.

Fermi (1931) has integrated equation (7) with the boundary conditions (8) using a perturbation method. However, there is no difficulty, and a better agreement with experiment, if the direct equation is integrated. The radii for various values of (n+1)/Z are given in the second columns of Tables 1 and 2.

III. OSCILLATIONS

(a) Radial Modes

Although the radial modes are only of marginal interest in the problems to be considered, they are included here primarily because they can be used to estimate the error in the approximation adopted in subsection (b) for the nonradial modes. For the radial modes the Lagrangian description is the simplest to use. The equation of motion for the oscillating atom is

$$\ddot{r} = -\frac{1}{\rho} \frac{dP}{dr} - \frac{1}{\mu r^2} \left(Z e^2 - \frac{M(r) e^2}{\mu} \right),$$
(9)

where r denotes the radius of a spherical shell whose equilibrium radius is a. For small amplitude oscillations we set

$$r = a + \zeta, \qquad P = P_0 + \Delta P, \qquad \rho = \rho_0 + \Delta \rho, \tag{10}$$

where ζ , ΔP , and $\Delta \rho$ are small perturbations and the zero subscript denotes a quantity obtained from hydrostatic equilibrium. Since the matter lying in the shell between a and a+da lies in the shell between r and r+dr, we find

$$\rho_0 a^2 \mathrm{d}a = \rho r^2 \mathrm{d}r \,. \tag{11}$$

Further, for the fully degenerate gas we have

$$\Delta P/P = \frac{5}{3} \Delta \rho / \rho \,. \tag{12}$$

Manipulation of the foregoing results finally leads to the expression

$$\ddot{\zeta} = -\frac{4\zeta}{a\rho_0}\frac{\mathrm{d}P_0}{\mathrm{d}a} + \frac{5}{3\rho_0}\frac{\mathrm{d}}{\mathrm{d}a}\left(\frac{P_0}{a^2}\frac{\mathrm{d}(a^2\zeta)}{\mathrm{d}a}\right),\tag{13}$$

an equation that is well known in the literature of pulsating stars (see e.g. Rosseland 1949). Introducing the equation of state and the variables x and ϕ , together with an assumed time dependence exp(i ωt), we find

$$\frac{d^{2}\zeta}{dx^{2}} + \frac{d\zeta}{dx} \left(\frac{5\phi'}{2\phi} - \frac{1}{2x} \right) + \zeta \left(\frac{3xv^{2}}{5\phi} - \frac{1}{x^{2}} - \frac{\phi'}{x\phi} \right) = 0,$$
(14)

where the prime denotes differentiation with respect to x, and v is related to ω by

$$\omega = vZ\mu e^4 \pi^2 2^7/h^3 3\sqrt{5} = vZ \times 3 \cdot 139 \times 10^{16} \text{ s}^{-1}$$
(15)

or

$$\hbar\omega = \nu Z \times 1.518$$
 rydbergs.

The boundary condition on equation (14) is that ζ is finite everywhere. At the centre of the atom this implies $\zeta \propto x^2$, while at the surface

$$\zeta' + \zeta(3xv^2 - 5\phi')/12 \cdot 5\phi' = 0.$$
⁽¹⁶⁾

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Equation (14) with the boundary conditions defines a linear eigenvalue problem of the Sturm-Liouville type. The eigenvalues (v^2) are real and discrete. Denoting the eigenfunctions by ζ_k and the eigenvalues by v_k , the orthogonality condition

$$\int_{0}^{x_{0}} \phi^{3/2} x^{1/2} \zeta_{k} \zeta_{j} \, \mathrm{d}x = F_{k} \delta_{kj} \tag{17}$$

can be established for nondegenerate eigenfunctions.

The values of v_k for four values of (n+1)/Z are given in Table 1, while the first three eigenfunctions for (n+1)/Z = 0.20 are plotted in Figure 1. The eigenfunctions show that only the low density outer regions participate significantly in the classical oscillation. This feature severely limits the accuracy of the model, for not only must the number of electrons in the atomic volume be large but also the number near the surface must be large enough to define the modes.

FREQUENCIES FOR RADIAL MODES r. β is the radius of the atom and v, is the frequency of the kth mode in unit.					
$x_0 \beta$ is the radius of the atom and y_0 is the frequency of the kth mode in units		FREQUENCIES	FOR RADIAL MOI	DES	
$x_0 p$ is the radius of the atom and x_k is the frequency of the k fit mode in this	$x_0 \beta$ is the radius	s of the atom and v_i	is the frequency	of the <i>k</i> th mode i	n units
of $3 \cdot 139 \times 10^{16} Z s^{-1}$ (see equation (15))		of $3 \cdot 139 \times 10^{16} Z$	s ⁻¹ (see equatio	on (15))	

TABLE 1

(n+1)/Z	<i>x</i> ₀	ν_1	ν_2	v_3
0.20	6.986	0·108	0·178	0.245
0.15	8.528	0.0709	0.116	0.159
0.10	10.97	0.0404	0.0657	0.0903
0.05	16.11	0.0166	0.0268	0.0367

A quantum formulation of the nonradial modes is easily made since the equation of motion (9) can be obtained using Hamilton's equations of motion with the Hamiltonian (see e.g. Rosseland 1949)

$$H = \int_0^M \left\{ \frac{1}{2} \dot{r}^2 + U(\rho) - \frac{1}{r\mu} \left(Z e^2 - \frac{M(r) e^2}{\mu} \right) \right\} \mathrm{d}m, \qquad (18)$$

where dm is an element of mass and $U(\rho)$ is the internal energy.

(b) Nonradial Modes

In the absence of viscosity and external forces, the Eulerian equation of motion is

$$\rho \,\partial \boldsymbol{v}/\partial t + \rho(\boldsymbol{v} \cdot \nabla)\boldsymbol{v} = -\nabla P + \rho \boldsymbol{f},\tag{19}$$

with the equation of continuity

$$\partial \rho / \partial t + \nabla \cdot (\rho v) = 0.$$
⁽²⁰⁾

In these equations v is the velocity and ρf is the force per unit volume due to the Coulomb interaction. We assume that the motions are small and denote the Eulerian

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(22)

perturbations by δP , $\delta \rho$, and δf . The equations for the small perturbations become

$$\rho_0 \,\partial \boldsymbol{v}/\partial t = -\nabla \,\delta P + \delta \rho \boldsymbol{f} + \rho_0 \,\delta \boldsymbol{f} \tag{21}$$



Fig. 1.—Eigenfunctions ζ_k for the first three radial modes k = 1, 2, and 3 with (n+1)/Z = 0.20. The results show that only the low density outer regions participate significantly in the classical oscillation.

For the fully degenerate gas

and

$$\delta P/P_0 = \frac{5}{3} \delta \rho / \rho_0, \qquad (23)$$

and, using equations (21) and (23) and the equation of hydrostatic equilibrium, it is readily shown that

$$\nabla \mathbf{x} \mathbf{v} = \mathbf{0},$$

if it was zero initially. We can therefore write

$$\boldsymbol{v} = \nabla \boldsymbol{\Phi} \,. \tag{24}$$

Since the eigenfunctions show that it is mainly the outer low-density regions which participate in the motion, it is reasonable to suppose that the δf term in equation (21) may be neglected. This approximation is equivalent to that of Cowling (1942) in the theory of oscillating stars. In the present context it evidently should improve as (n+1)/Z increases since the Coulomb forces near the surface are then dominated by the contribution from the interior. An estimate of the error can be conveniently made by applying the approximation to the radial modes.

The equations of motion now become

$$\partial \Phi / \partial t + W \delta \rho = 0, \qquad (25)$$

$$\partial(\delta\rho)/\partial t + \nabla \cdot (\rho_0 \,\nabla \Phi) = 0, \qquad (26)$$

where

$$W = 5P/3\rho^2$$
. (27)

A typical oscillatory solution will take the form

$$\Phi = \Phi_k \sin \omega_k t, \qquad \delta \rho = -\eta_k \cos \omega_k t, \qquad (28a, b)$$

in which case we have

$$\Phi_k \omega_k - W \eta_k = 0, \qquad \eta_k \omega_k + \nabla \cdot (\rho_0 \nabla \Phi_k) = 0, \qquad (29a, b)$$

so that

$$\omega_k^2 \Phi_k + W \nabla \cdot (\rho_0 \nabla \Phi_k) = 0.$$
(30)

If we replace Φ_k by $\Phi_k Y_{lm}$, where Y_{lm} is a spherical harmonic and Φ_k is now a function of radius alone, equation (30) then becomes

$$\frac{d^2 \Phi_k}{dx^2} + \frac{d\Phi_k}{dx} \left(\frac{3\phi'}{2\phi} + \frac{1}{2x} \right) + \Phi_k \left(\frac{3xv_k^2}{5\phi} - \frac{l(l+1)}{x^2} \right) = 0,$$
(31)

where v_k is defined as in equation (15). Differentiating equation (31) with respect to x and taking l = 0 (radial modes), we find

$$\frac{d^2\zeta}{dx^2} + \frac{d\zeta}{dx} \left(\frac{5\phi'}{2\phi} - \frac{1}{2x} \right) + \zeta \left(\frac{3xv^2}{5\phi} - \frac{\phi'}{\phi x} - \frac{1}{x^2} + \frac{3\phi''}{2\phi} \right) = 0,$$
(32)

where $\zeta = d\Phi_k/dx$. From a comparison of equations (32) and (14) we see that the Cowling approximation has introduced the term $3\phi''/2\phi$ in the coefficient of ζ . The numerical integration of (32) shows that the approximation results in values of v_k which, for the fundamental, are too low by about 15%. The error decreases as the mode number increases.

Jensen (1937) has given the surface boundary condition on the equations of motion as the vanishing of the radial component of the velocity. The correct boundary condition is that the density variation following the motion (the Lagrangian variation) shall vanish at the surface. This condition is satisfied by requiring Φ to be finite at the surface. At the centre Φ must also remain finite. For the nonradial modes this implies that Φ vanishes at the centre.

Sturm-Liouville theory shows that equation (31) possesses an infinite number of discrete real eigenvalues (v_k^2) . The orthogonality condition is easly shown to be

$$\int (\Phi_j \Phi_k / W) \, \mathrm{d}v = I_k \,\delta_{kj}. \tag{33}$$

Other orthogonality relations involving η_k can be found using equation (29a). Finally we note that certain sum rules can be established using equation (31). These are derived in the Appendix.

The eigenvalues for the dipole (l = 1) modes are given in Table 2. It can be seen that the quantity v_k varies with the mode number k approximately as k, and

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this enables the higher eigenvalues to be estimated quite accurately. By using an approximate analytical solution of equation (31) it can be shown that

$$x_0^3 v_k^2 \sim 0.8 \pi^2 \{ (n+1)/Z \} k^2$$
,

TABLE 2

which is confirmed by the numerical results.

16.1

22.7

FREQUENCIES AND OSCILLATOR STRENGTHS FOR NONRADIAL $l = 1$ MODES The radius x_0 and frequency v_k are as defined in Table 1 while $q_k = f_k/Z$ where f_k is the oscillator strength									
(n+1)/Z	x_0	v_1	v_2	v ₃	q_1	q_2	q_3		
0.200	6.99	0.0705	0.140	0.208	0.210	0.092	0.060		
0.175	7.76	0.0567	0.112	0 ·166	0.203	0·092	0.061		
0.150	8.53	0.0458	0.0908	0.134	0 ·1 8 6	0.087	0.028		
0.125	9· 5 9	0.0353	0.0699	0.103	0.171	0.082	0.057		
0.100	11.0	0.0260	0.0513	0.0758	0.151	0·076	0.054		
0.075	13.0	0.0177	0.0350	0.0516	0.127	0.0 67	0.048		

IV. POLARIZATION

0.0208

0.00894

We assume that the system is perturbed by a uniform oscillating electrical field

0.0307

0.0132

$$\boldsymbol{E} = \boldsymbol{E}_0 \exp(\mathrm{i}\omega t) \,. \tag{34}$$

0.0976

0.0588

0.054

0.035

The equations of motion (25) and (26) are now replaced by

0.0106

0.00455

$$\partial \Phi / \partial t + W \delta \rho + (E \cdot r) e / \mu = 0, \qquad (35)$$

$$\partial(\delta\rho)/\partial t + \nabla \cdot (\rho_0 \,\nabla\Phi) = 0. \tag{36}$$

Since we can write

0.050

0.025

$$\Phi = \sum_{k} B_{k} \Phi_{k}, \qquad \delta \rho = \sum_{k} A_{k} \eta_{k}, \qquad (37a, b)$$

where B_k and A_k are functions of t, we find, on substituting these expansions into equations (35) and (36) and using the orthogonality conditions,

$$\dot{B}_{k} + \omega_{k} A_{k} + \left(\frac{e}{I_{k} \omega_{k} \mu}\right) E \cdot \int r \eta_{k} \, \mathrm{d}v = 0, \qquad (38)$$

$$\dot{A}_k - \omega_k B_k = 0. \tag{39}$$

On eliminating B_k and solving the resulting equation, we then obtain

$$A_{k} = -\frac{e}{\mu I_{k}} \frac{1}{\omega_{k}^{2} - \omega^{2}} \left(\int z \eta_{k} \, \mathrm{d}v \right) E_{0} \exp(\mathrm{i}\omega t), \qquad (40)$$

0.041

0.028

where the direction of E has been taken as the z axis. The dipole moment p is given by

$$p = -(e/\mu) \int z \,\delta\rho \,\,\mathrm{d}v\,,\tag{41}$$

which from equation (37b) becomes

$$p = -(e/\mu) \sum_{k} A_{k}(t) \int z \eta_{k} \, \mathrm{d}v \, .$$

Substituting for A_k from equation (40) we find

$$p = \frac{e^2}{\mu^2} \sum_{k} \frac{1}{I_k(\omega_k^2 - \omega^2)} \left(\int \eta_k z \, \mathrm{d}v \right)^2 E.$$
 (42)

The polarization factor α is then

$$\alpha = \frac{e^2}{\mu^2} \sum_{k} \frac{1}{I_k(\omega_k^2 - \omega^2)} \left(\int \eta_k z \, \mathrm{d}v \right)^2,$$
(43)

and for a static or slowly varying field

$$\alpha = \frac{e^2}{\mu^2} \sum_k \left(\int \frac{\Phi_k z \, \mathrm{d}v}{W} \right)^2 / \int \frac{\Phi_k^2 \, \mathrm{d}v}{W}. \tag{44}$$

In terms of the variables x and ϕ

$$\alpha = a_0^3 \left(\frac{27\pi}{2^{10}Z}\right) x_0^5 \sum_k \left(\int_0^1 \Phi_k u^{5/2} \phi^{1/2} du\right)^2 / \int \Phi_k^2 \phi^{1/2} u^{3/2} du, \qquad (45)$$

where a_0 is the radius of the first Bohr orbit $(0.529 \times 10^{-8} \text{ cm})$ and $u = x/x_0$. From the sum rule (A8) in the Appendix

$$\alpha = a_0^3 \left(\frac{27\pi}{2^{10}Z}\right) x_0^{9/2} \int_0^1 u^{7/2} \phi^{1/2} \, \mathrm{d}u \,,$$

$$\alpha = \left(\frac{0 \cdot 0123 \times 10^{-24}}{Z}\right) x_0^{9/2} \int_0^1 u^{7/2} \phi^{1/2} \, \mathrm{d}u \quad \mathrm{cm}^3 \,.$$
(46)

or

Values of $Z\alpha$ for selected values of (n+1)/Z are:

The theoretical values are compared in Figure 2 with experimental results for ions (Gombás 1956) and neutral atoms (Teachout and Pack 1971). It is evident that the results for ions are considerably better than those for the neutral atoms.

The classical oscillator strengths are

$$f_k = \frac{1}{5} v_k^2 Z x_0^{9/2} \left(\int \Phi_k \phi^{1/2} u^{5/2} \, \mathrm{d}u \right)^2 / \int \Phi_k^2 \phi^{1/2} u^{3/2} \, \mathrm{d}u = Z q_k.$$
(47)

Using equation (A6) of the Appendix we find for the dipole moment

$$\sum_{k} f_{k} = Z - (n+1).$$
(48)

Values of q_k for the first three modes are given in Table 2 for each value of (n+1)/Z considered. The complete calculations have been extended to k = 10, and these are available from the author on request.



Fig. 2.—Comparison of theoretical values of $Z\alpha$ as a function of (n+1)/Z with experimental results for ions from Gombás (1956) and for neutral atoms from Teachout and Pack (1971).

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Appendix

Consider the Sturm-Liouville eigenvalue equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(H\frac{\mathrm{d}y_n}{\mathrm{d}x}\right) + y_n(p+g\lambda_n) = 0, \qquad (A1)$$

where H, p, and g are known functions of x. The orthogonality condition is

$$\int y_n y_{n'} g \, \mathrm{d}x = I_n \delta_{nn'}. \tag{A2}$$

If we multiply equation (A1) by x, integrate over the domain of x, and assume that $xH dy_n/dx$ and Hy_n vanish at both limits, we find

$$\int (px + dH/dx)y_n \, dx + \lambda_n \int xy_n g \, dx = 0.$$
 (A3)

Multiplying equation (A3) by $\int xy_n g \, dx$ and summing over all modes,

$$\sum_{n} \left(\int (px + dH/dx) y_n \, dx \right) \int x y_n g \, dx + \sum_{n} \lambda_n \left(\int x y_n g \, dx \right)^2 = 0.$$
 (A4)

But

 $\int Fx \, \mathrm{d}x = \sum_{n} \left(\int Fy_n \, \mathrm{d}x \, \int xy_n \, \mathrm{d}x \right),$

where we assume that the eigenfunctions are normalized so that I_n in equation (A2) is unity. Equation (A4) then becomes

$$\sum_{n} \lambda_n \left(\int x y_n g \, \mathrm{d}x \right)^2 = -\int (px + \mathrm{d}H/\mathrm{d}x) x \, \mathrm{d}x = \int (H - px^2) \, \mathrm{d}x \,, \qquad (A5)$$

provided xH vanishes at both limits. Since for equation (31)

$$H = \phi^{3/2} x^{1/2}, \qquad p = \phi^{3/2} x^{1/2} \{ -l(l+1)/x^2 \}, \qquad g = \frac{3}{5} \phi^{1/2} x^{3/2},$$

the conditions for equation (A5) to hold are satisfied, and therefore

$$\sum_{k} v_{k}^{2} \left(\int \Phi_{k} \phi^{1/2} u^{5/2} \, \mathrm{d}u \right)^{2} / \int \Phi_{k}^{2} \phi^{1/2} u^{3/2} \, \mathrm{d}u = \frac{5}{3x_{0}^{9/2}} \left(1 - \frac{n+1}{Z} \right) \left(1 + l(l+1) \right).$$
(A6)

Moreover

$$\int F^2 g \, \mathrm{d}x = \sum_k \left(\int F g \, y_k \, \mathrm{d}x \, \int F y_k g \, \mathrm{d}x \right) = \sum_k \left(\int F g \, y_k \, \mathrm{d}x \right)^2. \tag{A7}$$

In terms of the eigenfunctions of equation (31), and with F = x, we find

$$\int_{0}^{1} \phi^{1/2} x^{7/2} dx = \sum_{k} \left(\int \Phi_{k} \phi^{1/2} x^{5/2} dx \right)^{2} / \int \Phi_{k}^{2} \phi^{1/2} x^{3/2} dx.$$
(A8)

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