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MOTION EQUATIONS OF AN ELECTRON GAS

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The equation for the determination of the eigenfrequency spectrum for a spherically distributed and non-constant electron gas has been derived by means of Hamiltons variational principle. The Thomas–Fermi equation has been solved by means of the Ritz method for the evaluation of the electron density function in the Sn^{+4} ion.

1. Derivation of equations

Following Bloch [1] and Jensen [2] one can derive the flow equations of an electron gas from the variational principle. We define the action

$$\delta \int_{t_1}^{t_2} L dt = 0, \tag{1}$$

where the Lagrange function L is equal to

$$L = m_0 \int \varrho \frac{\partial \phi}{\partial t} d\tau - H. \tag{2}$$

Here m_0 and ϱ denote the electron mass and the electron density respectively.

The flow velocity $\vec{v}$ is connected with the flow potential ϕ through the well-known equation

$$\vec{v} = -\text{grad}\, \phi. \tag{3}$$

The last term H of equation (2) denotes the total energy of the flowing electron gas. Taking into account the exchange and the Weizsäckers corrections we get

$$H = (E_S + E_F + E_W + E_G) + (E_p^k + E_p^e) + E_A. \tag{4}$$

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The terms in the first and the second brackets represent the total kinetic and the total potential energy. The last term corresponds to the exchange energy. Now we introduce each of the energy terms [3, 4]

$$E_S = \frac{m_0}{2} \int \varrho (\mathrm{grad}\, \phi)^2 d\tau, \tag{5}$$

$$E_F = \kappa_F \int \varrho^{5/3} d\tau, \tag{6}$$

$$E_W = \kappa_W \int \frac{(\mathrm{grad}\, \varrho)^2}{\varrho} d\tau, \tag{7}$$

$$E_G = - \int g(\varrho) d\tau. \tag{8}$$

The function g is defined as follows:

$$g(\varrho) = \tfrac{1}{2} \kappa_F \varrho^{5/3} \quad \text{for} \quad r \leqslant \frac{\hbar}{2p_\mu},$$

$$g(\varrho) = \kappa_1 \varrho^{4/3} \frac{1}{r} - \kappa_2 \varrho \frac{1}{r^2} + \kappa_3 \frac{1}{r^5} \quad \text{for} \quad r \geqslant \frac{\hbar}{2p_\mu}. \tag{9}$$

Here $\hbar = \frac{h}{2\pi}$, and $p_\mu = (3\pi)^{1/3} \hbar \varrho^{1/3}$ is the magnitude of the maximum momentum

$$E_p^k = -Ze_0^2 \int \frac{\varrho}{r} d\tau, \tag{10}$$

$$E_p^e = \frac{e_0^2}{2} \iint \frac{\varrho(r)\varrho(r')}{r_{12}} d\tau d\tau', \tag{11}$$

$$E_A = -\kappa_A \int \varrho^{4/3} d\tau. \tag{12}$$

The normalization condition may be written

$$\int \varrho d\tau = N, \tag{13}$$

where N is the total number of electrons of the system being investigated. The constants have the following values [3, 4]

$$\begin{gathered} \kappa_F = \tfrac{3}{10} (3\pi^2)^{2/3} e_0^2 a_0, \quad \kappa_W = \tfrac{1}{8} e_0^2 a_0, \\ \kappa_1 = \tfrac{1}{8} (3\pi^2)^{1/3} e_0^2 a_0, \quad \kappa_2 = \tfrac{1}{24} e_0^2 a_0, \\ \kappa_3 = \frac{1}{5760\pi^2} e_0^2 a_0, \quad \kappa_4 = \tfrac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} e_0^2. \end{gathered} \tag{14}$$

The elementary positive charge, the Bohr radius of hydrogen and the atomic number are denoted by e_0, a_0 and Z respectively.

Summing all the terms in 4–12 we finally get the expression for the total energy

$$H = \frac{m_0}{2}\int \varrho(\text{grad }\phi)^2 d\tau + \kappa_F \int \varrho^{5/3} d\tau + \kappa_W \int \frac{(\text{grad }\varrho)^2}{\varrho} d\tau + \kappa_\Sigma \int \varrho^{5/3} d\tau$$

$$-Ze_0^2 \int \frac{\varrho}{r} d\tau + \frac{e_0^2}{2}\iint \frac{\varrho(r)\varrho(r')}{r_{12}} d\tau d\tau' - \kappa_A \int \varrho^{4/3} d\tau, \tag{15}$$

where $\kappa_\Sigma = \kappa_1+\kappa_2+\kappa_3$. For small fluctuations of the electron density we can write $\varrho = \varrho_0+\varrho_1$, where ϱ_1 denotes the perturbation which is small in comparison to the unperturbed electron density ϱ_0.

We now expand H into a series. The powers greater than the second for ϱ_1 are neglected. The derivatives are evaluated at $\varrho = \varrho_0$

$$H = H_0 + \frac{\partial H}{\partial \varrho}\varrho_1 + \tfrac{1}{2}\frac{\partial^2 H}{\partial \varrho^2}\varrho_1^2 + \ldots, \tag{16}$$

where H_0 is the energy of the unperturbed system

$$\frac{\partial H}{\partial \varrho}\varrho_1 = \frac{m_0}{2}\int \varrho_1(\text{grad }\phi)^2 d\tau + \tfrac{5}{3}\kappa_F \int \varrho_0^{2/3}\varrho_1 d\tau$$

$$+\kappa_W \int \frac{2\varrho_0 \text{ grad }\varrho_0(\text{grad}'\,\varrho) - (\text{grad }\varrho_0)^2\varrho_1}{\varrho_0^2} d\tau + \tfrac{5}{3}\kappa_F \int \varrho_0^{2/3}\varrho_1 d\tau - Ze_0^2 \int \frac{\varrho_1}{r} d\tau$$

$$+e_0^2 \iint \frac{\varrho_0(r)\varrho_1}{r_{12}} d\tau d\tau' - \tfrac{4}{3}\kappa_A \int \varrho_0^{1/3}\varrho_1 d\tau, \tag{17}$$

$$\tfrac{1}{2}\frac{\partial^2 H}{\partial \varrho^2}\varrho_1^2 = \tfrac{5}{9}\kappa_F \int \varrho_0^{-1/3}\varrho_1^2 d\tau + \kappa_W \int S(\varrho_0)\varrho_1^2 d\tau + \tfrac{5}{9}\kappa_\Sigma \int \varrho_0^{-1/3}\varrho_1^2 d\tau$$

$$+\frac{e_0^2}{2}\iint \frac{\varrho_1(r)\varrho_1(r')}{r_{12}} d\tau d\tau' - \tfrac{2}{9}\kappa_A \int \varrho_0^{-2/3}\varrho_1^2 d\tau, \tag{18}$$

$$S(\varrho_0) = \frac{(\text{grad}'\,\varrho)^2}{\varrho_0} + \frac{\text{grad}''\,\varrho}{\varrho_0} - \frac{2\text{ grad }\varrho_0(\text{grad}'\,\varrho)}{\varrho_0^2} + \frac{(\text{grad }\varrho_0)^2}{\varrho_0^3}. \tag{19}$$

Since the function H for $\phi = 0$ has the minimum, expression (16) reduces to

$$H = H_0 + \tfrac{1}{2}\frac{\partial^2 H}{\partial \varrho^2}\varrho_1^2 + \ldots. \tag{20}$$

According to (1) we get the following equations:

$$\delta \int_{t_1}^{t_2} L_1 dt = 0 \quad \text{with} \quad L_1 = m_0 \int \varrho_1 \frac{\partial \phi}{\partial t} d\tau - \left(H_0 + \tfrac{1}{2}\frac{\partial^2 H}{\partial \varrho^2}\varrho_1^2\right). \tag{21}$$

Since the variational function ϱ_1 is not present in H_0 we obtain

$$L_1 = m_0 \int \varrho_1 \frac{\partial \phi}{\partial t}\, d\tau - \tfrac{1}{2} \frac{\partial^2 H}{\partial \varrho^2} \varrho_1^2. \tag{22}$$

In view of (21) the two independent variations of ϱ_1 and ϕ for t_1 and t_2 yield the two following equations:

$$m_0 \frac{\partial \phi}{\partial t} = (P+Q)\varrho_1 - e_0 \varphi_1, \tag{23}$$

$$\frac{\partial \varrho_1}{\partial t} = \operatorname{div}(\varrho_0 \operatorname{grad} \phi) = 0, \tag{24}$$

where

$$P = \tfrac{10}{9}(\kappa_F + \kappa_\Sigma)\varrho_0^{-1/3} - \tfrac{4}{9}\kappa_A \varrho_0^{-2/3}, \tag{25}$$

$$Q = 2\kappa_W S(\varrho_0), \tag{26}$$

$$\varphi_1 = -e_0 \int \frac{\varrho_1(r')}{r_{12}}\, d\tau. \tag{27}$$

According to the well-known formula we get

$$\frac{\partial \varrho_1}{\partial t} = \operatorname{div}(\varrho_0 \operatorname{grad} \phi) = \varrho_0 \operatorname{div}(\operatorname{grad} \phi) + \operatorname{grad} \varrho_0 \operatorname{grad} \phi = \varrho_0 \nabla^2 \phi + \operatorname{grad} \varrho_0 \operatorname{grad} \phi. \tag{28}$$

If we differentiate equation (28) with respect to time we obtain

$$\frac{\partial^2 \varrho_1}{\partial t^2} = \varrho_0 \nabla^2 \frac{\partial \phi}{\partial t} + \operatorname{grad} \varrho_0 \operatorname{grad} \frac{\partial \phi}{\partial t}. \tag{29}$$

By operating on equation (23) with the Laplacian operator and taking into account

$$\nabla^2 \varphi = 4\pi e_0 \varrho \text{ and } \nabla^2 \varphi_1 = 4\pi e_0 \varrho_1, \tag{30}$$

we arrive at the equation

$$\nabla^2 \frac{\partial \phi}{\partial t} = \frac{1}{m_0}[\nabla^2(P+Q) - e_0 \nabla^2 \varphi_1]. \tag{31}$$

Substituting (23) and (31) into (29) we find that

$$\frac{\partial^2 \varrho_1}{\partial t^2} = \frac{\varrho_0}{m_0}[\nabla^2(P+Q) - e_0 \nabla^2 \varphi_1] + \frac{\operatorname{grad} \varrho_0}{m_0} \operatorname{grad}[(P+Q)\varrho_1 - e_0 \varphi_1]. \tag{32}$$

The last term $e_0 \varphi_1$ of this equation is small and can therefore be neglected.

Introducing

$$Z = P+Q, \tag{33}$$

and the function

$$\varrho_1 = \varrho_2(r)\sin\omega t \tag{34}$$

into (32) we get the equation for the determination of the eigenvalues

$$\frac{\varrho_0}{m_0}\left[\nabla^2(Z\varrho_2)-e_0\nabla^2\varphi_1\right]+\frac{\operatorname{grad}\varrho_0}{m_0}\operatorname{grad}(Z\varrho_2)+\omega^2\varrho_2 = 0. \tag{35}$$

2. The solution of the eigenvalue equation

To solve equation (35) in spherical coordinates, the well-known method of separation of variables in convenient [5], [6]. Introducing spherical coordinates we obtain (35) in the following form:

$$\frac{\varrho_0}{m_0}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial(Z\varrho_2)}{\partial r}\right]-4\pi e_0^2\varrho_2\right\}+\frac{\operatorname{grad}\varrho_0}{m_0}\frac{\partial(Z\varrho_2)}{\partial r}$$
$$+\frac{1}{r^2}\left[\frac{\partial^2(Z\varrho_2)}{\partial\vartheta^2}+\operatorname{ctg}\vartheta\frac{\partial(Z\varrho_2)}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2(Z\varrho_2)}{\partial\varphi^2}\right]+\omega^2\varrho_2 = 0. \tag{36}$$

We shall seek the solution in the form:

$$\varrho_2 = R(r)Y(\vartheta,\varphi). \tag{37}$$

Substituting (37) into (36), multiplying through by $\dfrac{r^2}{Z\varrho_2}$ and re-arranging, we obtain

$$\frac{\varrho_0}{m_0}\left\{\frac{1}{RZ}\left[2rR\frac{\partial Z}{\partial r}+2r^2\frac{\partial R}{\partial r}\frac{\partial Z}{\partial r}+r^2R\frac{\partial^2 Z}{\partial r^2}+2rZ\frac{\partial R}{\partial r}+r^2Z\frac{\partial^2 R}{\partial r^2}\right]-4\pi e_0^2r^2\right\}$$
$$+\frac{\operatorname{grad}\varrho_0}{m_0}\frac{r^2}{ZR}\left[Z\frac{\partial R}{\partial r}+R\frac{\partial Z}{\partial r}\right]+\frac{\omega^2r^2}{Z} = -\frac{1}{Y}\left[\frac{\partial^2 Y}{\partial\vartheta^2}+\operatorname{ctg}\vartheta\frac{\partial Y}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right]. \tag{38}$$

The left-hand side of this equation is a function of r only, while the right-hand side is a function of ϑ and φ. Hence, both sides must be equated to the same constant, which we denote by $\lambda = n(n+1)$.

After a slight re-arrangement, the separated equations become

$$\frac{\varrho_0}{m_0}\left\{\frac{1}{RZ}\left[2rR\frac{\partial Z}{\partial r}+2r^2\frac{\partial R}{\partial r}\frac{\partial Z}{\partial r}+r^2R\frac{\partial^2 Z}{\partial r^2}+2rZ\frac{\partial R}{\partial r}+r^2Z\frac{\partial^2 R}{\partial r^2}\right]\right.$$
$$\left.-\frac{4\pi e_0^2r^2}{Z}\right\}+\frac{\operatorname{grad}\varrho_0 r^2}{m_0ZR}\left(Z\frac{\partial R}{\partial r}+R\frac{\partial Z}{\partial r}\right)+\frac{\omega^2r^2}{Z}-n(n+1) = 0 \tag{39}$$

$$\frac{\partial^2 Y}{\partial\vartheta^2}+\operatorname{ctg}\vartheta\frac{\partial Y}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial^2\varphi^2}+n(n+1)Y = 0. \tag{40}$$

Multiplying equation (39) by $\frac{RZ}{r}$ we obtain

$$Z \frac{\varrho_0}{m_0} \frac{\partial^2 R}{\partial r^2} + \left(\frac{2\varrho_0}{m_0} \frac{\partial Z}{\partial r} + \frac{2\varrho_0}{m_0} \frac{Z}{r} + \frac{\operatorname{grad} \varrho_0}{m_0} Z \right) \frac{\partial R}{\partial r}$$

$$+ \left(\frac{2\varrho_0}{m_0 r} \frac{\partial Z}{\partial r} + \frac{\varrho_0}{m_0} \frac{\partial^2 Z}{\partial r^2} - 4\pi \frac{\varrho_0 e_0^2}{m_0} + \frac{\operatorname{grad} \varrho_0 \partial Z}{m_0 \partial r} + \omega^2 - \frac{n(n+1)}{r^2} Z \right) R = 0. \tag{41}$$

In order to solve this equation we will have to know the function ϱ_0. The solution of (41) shall satisfy the following conditions:

$$R(0) = \text{finite}, \quad R(\infty) = 0. \tag{42}$$

As an example we consider the Sn^{+4} ion.

3. *The unperturbed electron density* ϱ_0

In order to determine the electron density, the total energy for $\phi = 0$ must be minimized by a suitable choice of ϱ_0. In this case we use the Ritz variational method. Calculations of this type begin with the choice of a certain trial function, which is given in analytical form and depends on the number of parameters. The variation is carried out with respect to these parameters. We take into account only three contributions to the total energy of the Sn^{+4} ion: the kinetic energy of electrons (6), the potential energy of their interaction with the nucleus (10), and the potential energy of their mutual interaction (11).

The total energy, i.e. the sum of (6), (10) and (11), must be minimized by a suitable choice of ϱ_0 with the constraint (13) giving

$$E = \int \left[\kappa_F \varrho_0^{5/3} - \frac{Ze_0^2}{r} \varrho_0 + \tfrac{1}{2} e_0^2 \varrho_0 \int \frac{\varrho(r')}{|\vec{r} - \vec{r}'|} d\tau' \right] d\tau. \tag{43}$$

The trial function is chosen to be of an analytical form which is likely to be close to the solution of the Thomas–Fermi equation and tends to infinity as $r^{-3/2}$ at $r = 0$. At the same time this function must fall off exponentially, just as the electron density calculated on the basis of wave mechanics falls off. The function with these properties is [7]:

$$\varrho_0 = \frac{N}{A} \frac{e^{-x}}{x^3} \left(\sum_{i=0}^{n} c_i x^i \right)^3, \tag{44}$$

where A denotes the normalization constant and $n = 0, 1, 2, \ldots$ determines the first, second and further approximations. The parameter $x = \sqrt{\frac{r}{\lambda}}$ which appears in the theory of the Thomas–Fermi atom was used as the independent variable in place of r which is the true radial distance. With x and r both expressed in Bohr units, the relation between them is as follows:

$$r = \mu x, \tag{45}$$

where

$$\mu = 0.88534Z^{-1/3}.$$

In our calculation we take a simpler trial function

$$\varrho_0 = \frac{N}{A} \frac{e^{-x}}{x^3} (1+c_1 x)^3, \tag{46}$$

where c_1 and λ are undetermined coefficients. The solution of the two equations

$$\frac{\partial E}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial E}{\partial \lambda} = 0 \tag{47}$$

yields the numerical values of these parameters

$$c_1 = 0.30337, \quad 1/\lambda = 50.58397. \tag{48}$$

Inserting $x = \sqrt{\frac{r}{\lambda}}$ and the normalization constant into (46) we get

$$\varrho_0 = \frac{N}{4\pi\lambda^3 W_4} \frac{e^{-\sqrt{\frac{r}{\lambda}}}}{\left(\frac{r}{\lambda}\right)^{3/2}} \left(1+c_1\sqrt{\frac{r}{\lambda}}\right)^3, \tag{49}$$

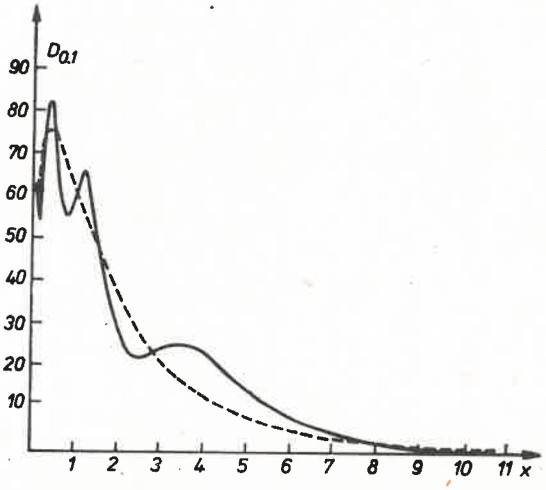

Fig. 1. Radial electron density of the Sn^{+4} ion. x in a_0 units, the radial density D_0 and D_1 in $1/a_0$ units

where $W_4 = 4+36c_1+144c_1^2+240c_1^3$. Having determined the function ϱ_0 we can evaluate the radial charge density defined as

$$D = 4\pi r^2 \varrho_0, \tag{50}$$

and compare it with the radial charge density determined by means of the more accurate core radial wave functions given by Herman and Skillman [8].

The spherically averaged radial charge density is given by

$$D_1 = 4\pi \sum (n, l)(2l+1)P_{nl}^2, \tag{51}$$

where n, l are quantum numbers, and P_{nl} are normalized wave functions.

Figure 1 shows the electron radial density in the Sn^{+4} ion. The solid line gives the density calculated by the Hartree–Fock–Slater method [8], and the dashed line by the Thomas–Fermi method. The statistical density distribution, as can be seen in Fig. 1, approximates well the density obtained with the H–F–S method. Putting equations (25)–(27), (33) and (49) into equation (41), which is subject to boundary conditions (42) we solve our eigenvalue problem. Consequently equation (41) must be solved by numerical methods.

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