GROUND-STATE ENERGY OF AN ELECTRON GAS IN A LATTICE OF POSITIVE POINT CHARGES

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The ground-state energy of an electron gas in a rigid lattice of positive point charges has been studied using the quantum statistical formalism of Bloch and de Dominicis.[1,2] The grand partition function of the system was expanded in powers of the coupling parameter between (i) the electrons and the lattice and (ii) pairs of electrons; this parameter is of course the square of the electronic charge. On account of the long-range forces, a certain number of divergences are met within this expansion; as usual one gets rid of them by (a) taking into account the electroneutrality of the whole system, and (b) summing infinite series of divergent terms.

Finally, taking the limit of zero temperature, one obtains the ground-state energy which can be conveniently expressed in terms of the parameter r_s, related to the density ρ of the electron gas by

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

Using as units the Bohr radius for r_s and the rydberg for the energy, we found the following expression of the ground-state energy for the case of a simple cubic lattice:

$$\epsilon(r_s) = \frac{3}{5}\left(\frac{9\pi}{4}\right)^{2/3}\frac{1}{r_s^2} - \frac{1}{3}\left(\frac{3\nu}{\pi}\right)^{2/3}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}\chi - \frac{3}{2\pi}\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s} + \{0.0622\ln r_s - 0.096\} - \frac{1}{6\pi^2}\sum_{\vec{u}\neq 0}\frac{1}{u^4}\left\{\frac{1-u^2}{2u}\ln\left|\frac{1+u}{1-u}\right| + 1\right\} + O(r_s \ln r_s). \tag{2}$$

ν is the ratio of the charge of a lattice point to the electron charge; the vector $\vec{u}$ is equal to $(\pi/3\nu)^{1/3}\vec{n}$, where (n_x, n_y, n_z) are integral numbers; χ is a constant defined as

$$\chi = -\sum_{\vec{\lambda}}\frac{1}{r_{\vec{\lambda}}} + \int\frac{1}{r}\,d\vec{r}, \tag{3}$$

where $\vec{\lambda}$ is a lattice vector.

The physical meaning of the various terms of (2) is the following: (a) The first term is the kinetic energy of a free electron gas; (b) the second term is the Madelung energy [see Eq. (3)] of a lattice of positive point charges in a uniform negative background; (c) the third term is the exchange energy of the electron gas, as calculated by Wigner[3]; (d) the fourth term is the correlation energy of the electron gas, as calculated by Gell-Mann and Brueckner[4]; and (e) the fifth term is the polarization energy of the free electron gas by the lattice, in the linear approximation.

The sum of terms (a), (c), and (d) in Eq. (2) is just the ground-state energy of an electron gas in a positive continuum; terms (b) and (e) arise from the lattice.

Expression (2) is plotted on Fig. 1 (curve I) for the special case $\nu = 1$; strictly speaking, this would correspond to "metallic hydrogen." The importance of the "structural" terms (b) and (e) in $\epsilon(r_s)$ is apparent when one compares curve I to curve II, the latter corresponding to an electron gas in a uniform positive background.[4] (For body-centered and face-centered cubic lattices, curves very similar to curve I are obtained.)

The ground-state energy of "metallic hydrogen" has been investigated before by Wigner and Huntington[5]; they first looked for approximate Bloch wave functions for independent electrons and next calculated exchange and correlation corrections. This method of approach is rather different from ours, which treats electron-lattice and electron-electron interactions in a symmetric way. It is then quite remarkable that the curve for $\epsilon(r_s)$ derived by Wigner and Huntington is very close to our curve I, as can be seen from Fig. 1. The abcissas and ordinates at the minimum are, respectively: $r_s = 1.64$, $\epsilon(r_s) = -1.05$ and $r_s = 1.59$, $\epsilon(r_s) = -0.99$. We may further expect that the exact minimum value of $\epsilon(r_s)$ for "metallic hydrogen" is near to (and probably somewhat below) -1 rydberg. This indicates that expansions for $\epsilon(r_s)$ like (2) converge satisfactorily in the region $r_s < 2$. This seems to be supported by the calculations of Dubois[6] for the term $O(r_s \ln r_s)$ of the correlation energy of an electron gas in a positive uniform background and also by our own rough estimations of the polarization energy $O(r_s)$ of the electrons by the lattice.

A detailed account of the results reported above

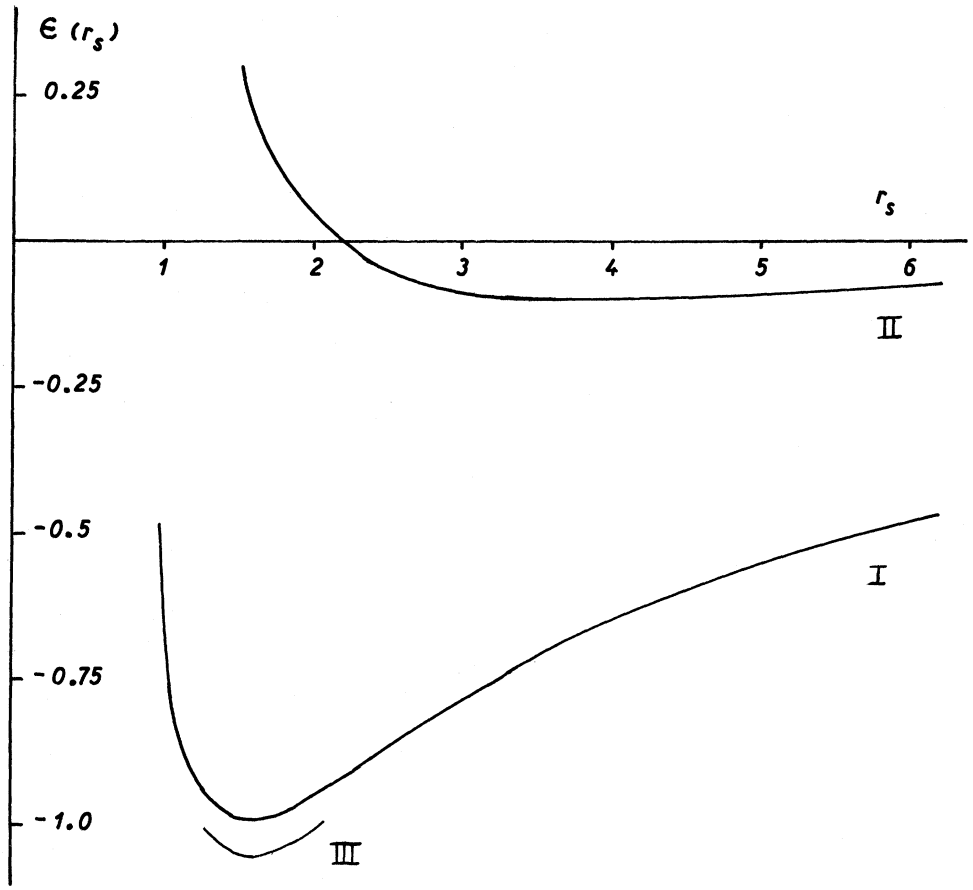

FIG. 1. Graph of $\epsilon(r_s)$ (in rydbergs). (I) Equation (3) for $\nu=1$; (II) electron gas in uniform positive background[4]; (III) curve of Wigner and Huntington.[5]

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[1]C. Bloch and C. de Dominicis, Nuclear Phys. 7, 459 (1958).

[2]C. Bloch and C. de Dominicis, Nuclear Phys. 10, 181 (1959).

[3]E. P. Wigner, Phys. Rev. 46, 1002 (1934).

[4]M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

[5]E. P. Wigner and H. B. Huntington, J. Chem. Phys. 3, 764 (1935).

[6]D. F. Dubois, Ann. Phys. 7, 174 (1959).