

## Electron crystallization using localized representation

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**Abstract.** The character of the ground state of the electron crystal—an electron gas with periodic density and/or spin density is investigated. Calculations for non-magnetic, ferromagnetic and anti-ferromagnetic electron crystals based on the Koster-Kohn variational principle for direct calculation of Wannier functions are presented. The Wannier function is approximated by a symmetrically orthonormalized Gaussian. The orbital exponent of the Gaussian is used as a variational parameter. The effect of the positive background is suitably taken into account. The results of our calculation support Wigner's prediction of electron crystallization.

**Keywords.** Electron crystal; Wigner lattice; Wannier function; localized representation; Gaussians.

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### 1. Introduction

For a long time it has been believed that the ground state of the electron gas need not be of normal type. Wigner (1934, 1938) first suggested that the electron gas at the low density limit will favour a crystalline state and the electrons will occupy the sites of a body centred cubic lattice. In recent years there has been some experimental evidence for electron crystallization (Crandall and Williams 1972; Grimes and Adams 1979; Cole *et al* 1981; Mehrotra *et al* 1982; Gallet *et al* 1982; Koji Kajita 1985). It is reported (Care and March 1975) that it is possible to envisage electron crystallization in the following systems: (1) highly compensated semiconductors (2) inversion layers in silicon devices (3) outside suitable metal surfaces. We shall briefly summarize below the evidence for the electron crystallization in these areas: there are doubtless some others, perhaps more definitive, that are going to come to light as interest in this field grows.

In doped semiconductors one can control the free carrier density by compensating the material, and hence arrange, say, to have one electron per  $n$  donors, where  $n$  can easily be made 100. Thus, in this way one can readily simulate a really low electron density system. From various experiments it is known that, in such a system, the application of modest magnetic fields can alter crucially the Hall conducting properties. These results were interpreted by Durkan *et al* (1968), Durkan and March (1968) and Rosenbaum *et al* (1985) in terms of a Wigner transition. Subsequent experiments on electrical condition by Somerford (1971) are in general accord with such a description (Care and March 1971) and some high frequency experiments

purport to reveal a frequency to be associated with the Wigner lattice (Biskupski *et al* 1973).

On Si inversion layer, beautiful experiments have been carried out at Cambridge (Pepper *et al* 1974) in MOS and MNOS devices. Briefly, the MOS devices have led to a definite confirmation of the essential features of Anderson localization due to disorder. But in MNOS devices the disorder is minimized. There seems to be some evidence for a Wigner type transition, of a two dimensional kind, though as yet unexplained effects occur. This is also a promising area for further work regarding electron crystallization.

The region of conduction electron spill-out from metal surfaces is becoming quite clear in a number of applications. By now, in an electron gas frame work, density profiles exist which allow relatively successful calculation of a number of surface properties: work functions (Smith 1969) surface energies (Lang and Kohn 1970) and ion-ion interaction energies (Brown *et al* 1974). In this latter paper it had been pointed out that in the tail of this distribution where the electron density is really low, Coulomb repulsion effects might lead to a tendency to Wigner lattice formation. Recently Koji Kajita (1985) has observed Wigner crystallization of two dimensional electrons formed on the surface of solid neon. Another technique which is developing very fast in the study of surface properties is the low energy positron technique (Mills 1978). Here the formation of positronium on the surface of the metal mainly depends upon the low density electron spilled out from the surfaces. So the study about the positronium on the metal surface may throw light on the nature of electron density distribution. One can also estimate the positron life time in such a system and monitor the Wigner transition (Majumdar and Ramakrishnan 1973); Crandall and Williams (1972) and Crandall (1973) considered the possibility of a two dimensional Wigner crystallization in the electron trapped on the surface of liquid helium. This was experimentally first observed by Grimes and Adams (1979) and more recently by others (Mehrotra *et al* 1982; Gallet *et al* 1982).

On the theoretical side there have been efforts to understand, the character of the ground state of the electron crystal—an electron gas with periodic density. Care and March (1975) have reviewed the various theoretical work available at that time. After that there have been many theoretical discussions about electron crystallization. Shore *et al* (1978) have studied Wigner crystallization using density functional theory. Nagai and Fukuyama (1982, 1983) have investigated theoretically Wigner crystal in magnetic field. All the above calculations do not deal with the different magnetic states of the electron crystal. Only the calculations by Carr (1961) and Edwards and Hillel (1968) contain the discussion about the ferromagnetic and antiferromagnetic state of the electron crystal. Carr (1961) had shown that for  $r_s < 27$ , the system is antiferromagnetic and for  $r_s > 27$ , it is ferromagnetic. Edwards and Hillel's results show that for  $10 < r_s < 40$ , it is antiferromagnetic and for  $r_s > 40$ , it is ferromagnetic. We have reinvestigated this problem by representing, in a more suitable way, the localized electrons by Wannier function which has not been attempted earlier. Edwards and Hillel have used variational approach to the Hartree-Fock approximation and the corresponding orbitals are Bloch states. They have considered only a simple cubic lattice with cubic Fermi surface. We have considered b.c.c. lattice with spherical as well as cubic Fermi surfaces. Our calculation is in a localized representation of electrons by Wannier function which amounts to a certain infinite expansion of plane waves with fixed coefficients, but with one undetermined parameter for the whole

function. We present calculations for nonmagnetic, ferromagnetic and anti-ferromagnetic electron crystals.

In §2 we give our formalism of the theory. In §3 we give our treatment of the positive background. Section 4 will contain the special treatment of the antiferromagnetic crystal case. In §5 we present our numerical results and discussion.

## 2. Theoretical formalism

### a) Direct calculation of Wannier functions for an electron crystal

The calculation is based on the Koster–Kohn (1953, 1974) variational principle for direct calculation of Wannier functions. We start out from sets of OAO's (orthonormalized atomic orbitals) as basis functions and these are completely orthonormal. The unknown Wannier function is expanded in these basis functions as

$$W(\mathbf{m}, \mathbf{r}) = \sum_i \phi_i(\mathbf{m}, \mathbf{r}) C_i. \quad (1)$$

The Wannier functions thus obtained are automatically orthonormal. We then extremise the functional

$$\varepsilon = \int W^*(\mathbf{r}) H_{\text{eff}} W(\mathbf{r}) d\mathbf{r} \quad (2)$$

and in this we choose the effective Hartree-Fock operator.

The Hartree-Fock effective operator,  $H_{\text{eff}}$ , is characterized by the state under consideration which is a determinant filled with Bloch orbitals and spin functions in some way. To characterize the state we need the transformations

$$W = \psi U^+ \quad \psi = W U \quad (3)$$

with

$$U(\mathbf{m}, \mathbf{k}) = \frac{1}{\sqrt{N}} \exp(2\pi i \mathbf{k} \cdot \mathbf{m}). \quad (4)$$

We have considered the three cases NC (non-magnetic crystal), FC (ferromagnetic crystal) and AC (anti-ferromagnetic crystal). Like Edwards and Hillel (1968) we have

$$\rho_{NC}(X, X') = \rho_{NC}(\mathbf{r}, \mathbf{r}') [\alpha\alpha' + \beta\beta'] \quad (5a)$$

$$\rho_{FC}(X, X') = \rho_{FC}(\mathbf{r}, \mathbf{r}') \alpha\alpha' \quad (5b)$$

$$\rho_{AC}(X, X') = \rho_{AC}^+(\mathbf{r}, \mathbf{r}') \alpha\alpha' + \rho_{AC}^-(\mathbf{r}, \mathbf{r}') \beta\beta' \quad (5c)$$

and in terms of the Wannier function

$$\rho_{NC}(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{m}, \mathbf{m}'} W_{NC}(\mathbf{m}, \mathbf{r}) R_{NC}(\mathbf{m}, \mathbf{m}') W_{NC}^*(\mathbf{m}, \mathbf{r}') \quad (6)$$

$$\rho_{FC}(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{m}, \mathbf{m}'} W_{FC}(\mathbf{m}, \mathbf{r}) R_{FC}(\mathbf{m}, \mathbf{m}') W_{FC}^*(\mathbf{m}, \mathbf{r}') \quad (7)$$

$$\rho_{AC}^\pm(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{m}, \mathbf{m}'} W_{AC}(\mathbf{m}, \mathbf{r}) R_{AC}^\pm(\mathbf{m}, \mathbf{m}') W_{AC}^*(\mathbf{m}, \mathbf{r}') \quad (8)$$

We have

$$\begin{aligned}
 R_{NC}(\mathbf{m}, \mathbf{m}') &= \frac{1}{N} \sum_k^{k_{NC}} \exp(2\pi i \mathbf{k} \cdot (\mathbf{m} - \mathbf{m}')) \\
 &= V_{oa} \int_{FSNC} \exp(2\pi i \mathbf{k} \cdot (\mathbf{m} - \mathbf{m}')) dV_k
 \end{aligned} \tag{9}$$

and similar for the FC and special case is needed for AC.

b) *Densities in the Wannier representation*

To study the translational properties in the three cases we consider the densities ( $[\mathbf{r} = \mathbf{r}']; j = NC, FC, AC$ )

$$\begin{aligned}
 \rho_j(\mathbf{r}) &= \rho_j(\mathbf{r}, \mathbf{r}') \\
 \rho_j(\mathbf{r} - \mathbf{n}) &= \sum_{\mathbf{m}, \mathbf{m}'} W_j(\mathbf{m}, \mathbf{r} - \mathbf{n}) R_j(\mathbf{m}, \mathbf{m}') W_j^*(\mathbf{m}, \mathbf{r} - \mathbf{n})
 \end{aligned} \tag{10}$$

$$= \sum_{\mathbf{m}, \mathbf{m}'} W_j(\mathbf{m} + \mathbf{n}, \mathbf{r}) R_j(\mathbf{m}, \mathbf{m}') W_j^*(\mathbf{m}' + \mathbf{n}, \mathbf{r}). \tag{11}$$

From (9) we see that, at least for NC and FC we have

$$R_j(\mathbf{p} - \mathbf{n}, \mathbf{p}' - \mathbf{n}) = R_j(\mathbf{p}, \mathbf{p}') \text{ with } \mathbf{p} = \mathbf{m} + \mathbf{n} \tag{12}$$

and so

$$\rho_j(\mathbf{r} - \mathbf{n}) = \rho_j(\mathbf{r}). \tag{13}$$

We further notice that

$$\int \rho_{NC}(\mathbf{r}, \mathbf{r}) d\mathbf{r} = \frac{N}{2} \tag{14a}$$

$$\int \rho_{FC}(\mathbf{r}, \mathbf{r}) d\mathbf{r} = N \tag{14b}$$

$$\int \rho_{AC}(\mathbf{r}, \mathbf{r}) d\mathbf{r} = \frac{N}{2}. \tag{14c}$$

To calculate  $R_j$ , we must decide which shape of the Fermi surface (FS) we are going to use. For high densities a sphere seems to be natural, whereas for low densities a cube would seem to be more reasonable. Since we are going to present our calculations for both the above cases, here also we outline the calculation of  $R_j$  for both cases of FS. Now we will consider only NC and FC states.

From (14) we can write

$$\begin{aligned}
 \sum_{\mathbf{m}} R_{NC}(\mathbf{m}, \mathbf{m}) &= \frac{N}{2} \\
 \sum_{\mathbf{m}} R_{FC}(\mathbf{m}, \mathbf{m}) &= N.
 \end{aligned} \tag{15}$$

Combining (9) with the above equations and integrating over a cube gives

$$R_j^{(c)}(\mathbf{m}, \mathbf{m}') = V_{oa} \prod_{i=1}^3 \frac{\sin \pi b_i (m_i - m'_i)}{\pi (m_i - m'_i)} \tag{16}$$

and integrating over a sphere gives

$$R_j^{(S)}(\mathbf{m}, \mathbf{m}') = \frac{4\pi}{3} k_{Fj}^3 V_{oa} q(2\pi k_{Fj} |\mathbf{m} - \mathbf{m}'|) \quad (17)$$

where  $q(x) = 3(\sin x - x \cos x)/x^3$ ,  $k_{Fj}$  is the radius of the spherical FS and  $b_j$  is the cube edge of the cubic FS and  $V_{oa}$  is the volume per electron.

### 3. Treatment of the positive background

The Hartree-Fock effective operator for a normal system with nuclei and electrons is

$$H_{\text{eff}}(1) = \frac{1}{2} \Delta_1 - \sum_g \frac{Z_g}{|\mathbf{r} - \mathbf{R}_g|} + \int \frac{dX_2 (1 - P_{12}) \rho(X_2, X_2)}{r_{12}} \quad (18)$$

For any extended system (solid or large molecule) great care is needed in evaluating matrix elements of the long range electro-static part

$$V_c(\mathbf{r}_1) = - \sum_g \frac{Z_g}{|\mathbf{r}_1 - \mathbf{R}_g|} + \int \frac{\rho(X_2, X_2)}{r_{12}} dX_2 \quad (19)$$

so that the large parts are cancelled out (Lowdin 1956; Delhalle 1978; Delhalle *et al* 1980; Monkhoest and Schwalm 1981). The two extreme cases of positive charge distributions are uniform distribution and point like nuclei. All the real situations lie between the above extreme cases. In the present problem we have taken the first extreme case and also a case where the positive charge distribution approximately represents the real situation.

#### a) Non-uniform positive background and charge neutrality problem

For the electron crystal it is desirable to have a distribution of positive charge which does not have to be uniform (Overhauser 1978; Hall 1981). We denote this distribution by  $P(\mathbf{r})$  and partition it like  $\rho(r)$

$$P(\mathbf{r}) = \sum_m^{B \cdot K} P_m(\mathbf{r}). \quad (20)$$

The total amount of positive charge must equal the number of electrons.

$$\int P(\mathbf{r}) dV = N. \quad (21)$$

We must also require, however that each unit cell is neutral, i.e.,

$$\int_{V_m} [P_m(\mathbf{r}) - \rho_m(\mathbf{r})] dV = 0 \quad (22)$$

i.e.

$$\int P_m(\mathbf{r}) dV = N_m. \quad (23)$$

In a crystal both  $\rho(\mathbf{r})$  and  $P(\mathbf{r})$  have the periodicity of the lattice. We can then expand

$$\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r}) - P(\mathbf{r}) \quad (24)$$

in a Fourier series labelled by the reciprocal lattice vectors  $\mathbf{K}$

$$\bar{\rho}(\mathbf{r}) = \sum_{\mathbf{K}} \bar{\rho}_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{r}). \quad (25)$$

In calculating the Fourier coefficients  $\bar{\rho}_{\mathbf{K}}$  it is sufficient, because of the periodicity of  $\bar{\rho}(\mathbf{r})$ , to integrate over one of the unit cells.

$$\begin{aligned} \bar{\rho}_{\mathbf{K}} &= \frac{1}{V} \int \bar{\rho}(\mathbf{r}) \exp(-i\mathbf{K} \cdot \mathbf{r}) dV \\ &= \frac{1}{V_{\text{oa}}} \int_{V_{\text{oa}}} \bar{\rho}(\mathbf{r}) \exp(-i\mathbf{K} \cdot \mathbf{r}) dV. \end{aligned} \quad (26)$$

The charge neutrality implies that

$$\begin{aligned} \int_V \bar{\rho}(\mathbf{r}) dV &= 0 = \sum_{\mathbf{K}} \bar{\rho}_{\mathbf{K}} \int \exp(i\mathbf{K} \cdot \mathbf{r}) dV \\ &= V \bar{\rho}_0 \end{aligned} \quad (27)$$

i.e.,

$$\bar{\rho}_0 = 0. \quad (28)$$

We therefore write

$$\bar{\rho}(\mathbf{r}) = \sum'_{\mathbf{K}} \bar{\rho}_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{r}). \quad (29)$$

In the electron gas  $\rho(\mathbf{r}) = n = \text{constant}$  and  $P(\mathbf{r})$  is chosen to be the same constant so that  $\bar{\rho}(\mathbf{r}) = 0$ ,  $V_c(\mathbf{r}_1) = 0$ ,  $E_c = 0$ . In the present case where  $\rho(\mathbf{r})$  varies periodically, we can reach the same goal by choosing  $P(\mathbf{r}) = \rho(\mathbf{r})$ . That also implies charge neutrality.

We can also imagine less drastic assumptions, in the sense that the condition

$$\int \bar{\rho}(\mathbf{r}) dV = 0 \quad (30)$$

can be satisfied without requiring

$$\bar{\rho}(\mathbf{r}) = 0 \text{ for all } \mathbf{r}. \quad (31)$$

We can choose  $P(\mathbf{r}) = \text{constant} (=n)$  eventhough  $\rho(\mathbf{r})$  varies. Then

$$\begin{aligned} \int_{V_m} P_m(\mathbf{r}) dV &= P V_{\text{oa}} = \int_{V_m} P_m(\mathbf{r}) dV = N_m = 1 \\ P &= \frac{1}{V_{\text{oa}}} = \frac{N}{N V_{\text{oa}}} = \frac{N}{V} = n. \end{aligned} \quad (32)$$

With this choice the constant  $n$  can be regarded as the zeroth Fourier component in

the expansion of the electron density

$$\begin{aligned}\rho(\mathbf{r}) &= \bar{\rho}(\mathbf{r}) + P(\mathbf{r}) = \bar{\rho}(\mathbf{r}) + n \\ &= n + \sum_{\mathbf{k}} K \exp(i\mathbf{K} \cdot \mathbf{r}) = \sum_{\mathbf{k}} \rho_{\mathbf{k}} \exp(i\mathbf{K} \cdot \mathbf{r}).\end{aligned}\quad (33)$$

The Fourier components of the density

$$\rho_{\mathbf{k}} = \frac{1}{V_{\text{oa}}} \int \rho(\mathbf{r}) \exp(-i\mathbf{K} \cdot \mathbf{r}) dV \quad (34)$$

can be calculated by means of Cartesian coordinates when  $\rho(\mathbf{r})$  is obtained from a superposition of Gaussians.

Using the Fourier representation of  $r_{12}^{-1}$ , we get for  $V_c(\mathbf{r}_1)$

$$V_c(\mathbf{r}_1) = 4\pi \sum_{\mathbf{k}} \rho_{\mathbf{k}} \frac{\exp(i\mathbf{K} \cdot \mathbf{r})}{K^2}. \quad (35)$$

In the present calculation we need the matrix element of  $V_c(\mathbf{r}_1)$  with respect to the trial Wannier function.

What follows below is for the non-magnetic case. Similar results are obtained for the other cases with suitable modifications of relevant quantities. The orbital part of the Fock-Dirac density matrix is in terms of the Wannier functions,

$$\rho(\mathbf{r}, \mathbf{r}) = \sum_{\mathbf{m}, \mathbf{n}}^{B-k} W(\mathbf{m}, \mathbf{r}) R_w(\mathbf{m}, \mathbf{n}) W^*(\mathbf{n}, \mathbf{r}). \quad (36)$$

The actual calculation of the Fourier components (34) from (36) will proceed differently depending on the actual form of the Wannier functions.

We first study a general aspect which may be useful in actual situations. We introduce the notation

$$a(\mathbf{r}) = W(0, \mathbf{r}) \quad (37)$$

for the Wannier function centred at the origin. For calculation of  $\rho(\mathbf{r})$  we need the quantities

$$\begin{aligned}\Gamma_{\mathbf{k}}(\mathbf{m}, \mathbf{n}) &= \frac{1}{V_{\text{oa}}} \int_{V_{\text{oa}}} \exp(i\mathbf{K} \cdot \mathbf{r}) W(\mathbf{m}, \mathbf{r}) W^*(\mathbf{n}, \mathbf{r}) dV \\ &= \frac{1}{V_{\text{oa}}} \int \exp(i\mathbf{K} \cdot \mathbf{r}) a(\mathbf{r}) a^*(\mathbf{r} + \mathbf{m} - \mathbf{n}) dV.\end{aligned}\quad (38)$$

The Fourier transform of the function  $a(\mathbf{r})$  is essentially what Slater (1965) calls the momentum eigen-functions, i.e., the expansion coefficients in the expansion of the Bloch function in plane waves.

$$a^T(\mathbf{q}) = \int \exp(i\mathbf{q} \cdot \mathbf{r}) a(\mathbf{r}) dV \quad (39a)$$

$$a(\mathbf{r}) = \frac{1}{8\pi^3} \int \exp(-i\mathbf{q} \cdot \mathbf{r}) a^T(\mathbf{q}) d\mathbf{q} \quad (39b)$$

$$= \frac{\sqrt{V_{\text{oa}}}}{8\pi^3} \int \exp(i\mathbf{q} \cdot \mathbf{n}) A(\mathbf{q}) d\mathbf{q}, \quad \mathbf{q} = \mathbf{k} + \mathbf{k} \quad (39c)$$

Thus

$$a^T(\mathbf{r}) = \sqrt{V_{0a}} A(-\mathbf{q}) \quad (39d)$$

$$\rho_{\mathbf{k}} = \frac{1}{8\pi^3} \int d\mathbf{q} A(\mathbf{q}) A^*(\mathbf{K} + \mathbf{q}) f(\mathbf{q})$$

with

$$f(\mathbf{q}) = \sum_{\mathbf{m}'}^{Bk} R_w(\mathbf{m}') \exp(-i\mathbf{q} \cdot \mathbf{m}') \quad (40)$$

The Fourier transform of GTO is known analytically. In Shavift's notation (Shavift 1962)

$$G_i(r_A) = \exp(-\alpha_i |\mathbf{r} - \mathbf{A}|^2) \quad (41)$$

$$\begin{aligned} [G_i(r_A)]^T(\mathbf{q}) &= \int \exp(i\mathbf{q} \cdot \mathbf{r}) G_i(r_A) dV \\ &= \exp(i\mathbf{q} \cdot \mathbf{A}) \left(\frac{\pi}{\alpha_i}\right)^{3/2} \exp(-q^2/4\alpha_i). \end{aligned} \quad (42)$$

When the WF is a linear combination of GTO's the integration in (40) reduces to integration over a product of two functions of type (42) and  $\exp(-i\mathbf{q} \cdot \mathbf{m}')$ .

The numerical results using the above formalism is presented in §5. As pointed out earlier we have also done numerical calculation, as a special case, assuming uniform positive background where  $V_c(\mathbf{r}_1) = 0$ . These two results are compared in §5.

#### 4. Antiferromagnetic crystal

As we indicated in §2 the anti-ferromagnetic crystal case requires a special treatment. We can assume that the crystal structure is made up of two inter-penetrating sublattices. 1. Sub-lattice formed out of the corner atoms of the lattice. 2. Sub-lattice formed out of the body centred atom of the b.c.c lattice (figure 1).

If there are  $N$  electrons in the b.c.c lattice then each sublattice will have  $N/2$  electrons. The sub-lattice Bloch-type orbitals are defined as (Larson and Thorson 1966)

$$\begin{aligned} \chi(\mathbf{k}) &= \frac{1}{\sqrt{2}} [\psi(\mathbf{k}) + \psi(\bar{\mathbf{k}})] \\ \bar{\chi}(\mathbf{k}) &= \frac{1}{\sqrt{2}} [\psi(\mathbf{k}) - \psi(\bar{\mathbf{k}})] \end{aligned} \quad (43)$$

where  $\bar{\mathbf{k}} = \mathbf{k} + \mathbf{K}$  and

$$\begin{aligned} \rho_{\lambda c}^+(\mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{k}}^{k_{\lambda c}^+} \chi(\mathbf{k}, \mathbf{r}) \chi^*(\mathbf{k}, \mathbf{r}') \\ \rho_{\lambda c}^-(\mathbf{r}, \mathbf{r}') &= \sum_{\mathbf{k}}^{k_{\lambda c}^-} \bar{\chi}(\mathbf{k}, \mathbf{r}) \bar{\chi}^*(\mathbf{k}, \mathbf{r}'). \end{aligned} \quad (44)$$

It is interesting to point out that the above particular kind of Fock-Dirac matrix (44)



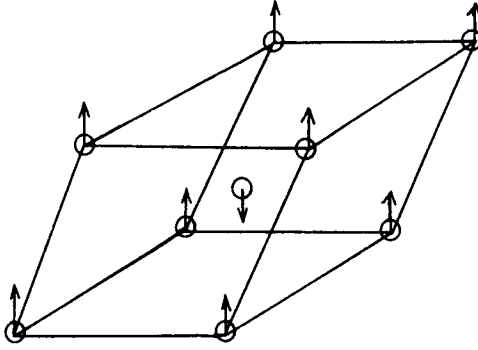


Figure 1. Wigner crystal AC case.

that we use here corresponds to a special case of the AMO method, namely the 'Most alternating' one, with  $\theta = 0$ , ie.,  $\theta = \pi/4$  (Calais and Sperber 1973). We have

$$\rho_{AC} = \rho_{AC}^+ + \rho_{AC}^-.$$

In terms of Wannier functions

$$\rho_{AC} = \frac{1}{2} \sum_{\mathbf{m}, \mathbf{m}'} W_{AC}(\mathbf{m}, \mathbf{r}) [R_{AC}^+ + R_{AC}^-] W_{AC}^*(\mathbf{m}, \mathbf{r}') \quad (45)$$

with

$$R_{AC}^+(\mathbf{m}, \mathbf{m}') = \frac{2}{N} \left[ \sum_k^{k_{AC}^+} \exp(2\pi i k(m-m')) (1 - \exp(-2\pi i K m) + \exp(2\pi i K m') + \exp(2\pi i K(m-m'))) \right] \quad (46)$$

$$R_{AC}^-(\mathbf{m}, \mathbf{m}') = \frac{2}{N} \left[ \sum_k^{k_{AC}^-} \exp(2\pi i k(m-m')) (1 - \exp(-2\pi i K m) - \exp(2\pi i K m') + \exp(2\pi i K(m-m'))) \right]. \quad (47)$$

The final expressions for  $R_{AC}^+(\mathbf{m}, \mathbf{m}')$  for both spherical and cubic Fermi surfaces are found to be:

Cubic F.S. case

$$R_{AC}^+(\mathbf{m}, \mathbf{m}') = V_{oa} + \prod_{j=1}^3 \frac{\sin b_{FAC}^+(m_j - m_j')}{\pi(m_j - m_j')} \times (2 + \exp(2\pi i K m') + \exp(-2\pi i K m')). \quad (48)$$

Spherical F.S. case

$$R_{AC}^+(\mathbf{m}, \mathbf{m}') = V_{oa}^+ 4\pi k_{FAC}^+{}^3 q(2\pi i K m) \times (2 + \exp(2\pi i K m') + \exp(-2\pi i K m')). \quad (49)$$

We get similar expressions for  $R_{AC}^-(\mathbf{m}, \mathbf{m}')$ . The numerical results are presented in §5 along with the other cases.

## 5. Results and discussion

We have chosen single Gaussians of the form

$$\phi(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2)$$

as our orbitals. The Wannier function is approximated by a symmetrically orthonormalized Gaussian

$$W(\mathbf{r}) = \sum_{\mathbf{m}} \phi(\mathbf{m}, r) \Delta^{-1/2}(\mathbf{m}, 0) \quad (50)$$

where  $\Delta$  is the overlap matrix (Lowdin 1956)  $\Delta^{-1/2}$  is calculated by means of a method given by one of the authors (Calais and Appel 1964). We then extremize the functional given by (2), with the appropriate  $H_{\text{eff}}$ . The orbital exponent of the Gaussian is used as a variational parameter. As discussed in §3, first a calculation is performed for the case where a complete cancellation between the Coulomb term and the uniform positive background is assumed. Energies were calculated as a function of  $r_s$ , the electron density parameter. For all the three cases (NC, FC and AC) calculations were done for both cubic and spherical Fermi surfaces. The results are presented in tables 1 to 6. The results of the calculations for the 2nd case where we have taken the contribution from the positive background are also presented graphically in figure 2. In the figure for FC case the difference in the energies between spherical FS and cubic FS is small so we have given only one graph. In the figures and in the tables  $E_A$  is the Hartree-Fock ground state energy for the non-magnetic electron gas given by

$$E_G = \frac{0.458}{r_s} \left( \frac{2.413}{r_s} - 1 \right) \text{Rydberg}$$

**Table 1.** Energies corresponding to NC case.

$r_s$	$\alpha$	$E_G (R_{yd})$	$E (R_{yd})$	$(E - E_G)/ E_G $
<i>Spherical FS</i>				
9.0	0.042	-0.03725	-0.05148	-0.38231
10.0	0.039	-0.03475	-0.05239	-0.50765
11.0	0.037	-0.03250	-0.05281	-0.62490
12.0	0.036	-0.03049	-0.05298	-0.73748
15.0	0.035	-0.02562	-0.05304	-1.07042
20.0	0.035	-0.02013	-0.05350	-1.63439
<i>Cubic FS</i>				
8.0	0.0450	-0.03998	-0.04945	-0.23689
9.0	0.0425	-0.03724	-0.05131	-0.37767
10.0	0.0400	-0.03475	-0.05232	-0.50569
11.0	0.0375	-0.03250	-0.05279	-0.62419
12.0	0.0350	-0.03049	-0.05295	-0.73676
15.0	0.0350	-0.02562	-0.05304	-1.07042
20.0	0.0350	-0.02013	-0.05305	-1.63439

**Table 2.** Energies for FC case

$r_s$	$\alpha$	$E_G(R_{yd})$	$E(R_{yd})$	$(E - E_G)/ E_G $
<i>Spherical FS</i>				
5.0	0.1395	-0.04740	-0.21199	-3.47229
6.0	0.1420	-0.04563	-0.21216	-3.64862
7.0	0.1415	-0.04287	-0.21220	-3.94907
8.0	0.1415	-0.03998	-0.21221	-4.30724
9.0	0.1415	-0.03725	-0.21221	-4.69730
10.0	0.1415	-0.03475	-0.21221	-5.10668
11.0	0.1415	-0.03250	-0.21221	-5.52862
12.0	0.1415	-0.03049	-0.21221	-5.95919
15.0	0.1415	-0.02562	-0.21221	-7.28214
<i>Cubic FS</i>				
5.0	0.1485	-0.04740	-0.21088	-3.44903
6.0	0.1425	-0.04563	-0.21207	-3.64683
7.0	0.1415	-0.04287	-0.21220	-3.94898
8.0	0.1415	-0.03998	-0.21220	-4.30722
9.0	0.1415	-0.03725	-0.21221	-4.69730
10.0	0.1415	-0.03475	-0.21221	-5.10668
11.0	0.1415	-0.03250	-0.21221	-5.52861
12.0	0.1415	-0.03049	-0.21221	-5.95919
15.0	0.1415	-0.02562	-0.21221	-7.28215

**Table 3.** Energies for AC case.

$r_s$	$\alpha$	$E_G(R_{yd})$	$E(R_{yd})$	$(E - E_G)/ E_G $
<i>Cubic FS</i>				
6.0	0.0360	-0.04564	-0.05713	-0.25184
7.0	0.0268	-0.04288	-0.05671	-0.32256
8.0	0.0175	-0.03998	-0.06565	-0.64189
9.0	0.0129	-0.03725	-0.07365	-0.97743
10.0	0.0105	-0.03475	-0.06576	-0.89226
11.0	0.0355	-0.03250	-0.05304	-0.63207
12.0	0.0355	-0.03049	-0.05305	-0.73979
15.0	0.0355	-0.02562	-0.05305	-1.07050
20.0	0.0355	-0.02014	-0.05305	-1.63444
<i>Spherical FS</i>				
5.0	0.116	-0.04740	0.00043	1.00908
6.0	0.088	-0.04564	-0.02492	0.45384
7.0	0.070	-0.04288	-0.03821	0.10887
8.0	0.059	-0.03998	-0.04539	-0.13543
9.0	0.049	-0.03725	-0.04930	-0.32366
10.0	0.044	-0.03475	-0.05136	-0.47809
11.0	0.040	-0.03250	-0.05238	-0.61153
12.0	0.037	-0.03049	-0.05283	-0.73242
13.0	0.036	-0.02869	-0.05299	-0.84683
14.0	0.036	-0.02707	-0.05304	-0.95879
15.0	0.036	-0.02562	-0.05305	-1.07042
20.0	0.036	-0.02014	-0.05305	-1.63446

**Table 4.** Energy values for NC Case (with non-uniform positive background).

$r_s$	$\alpha$	$E_G (R_{yd})$	$E (R_{yd})$	$(E - E_G)/ E_G $
<i>Spherical FS</i>				
9.0	0.0390	-0.03725	-0.05088	-0.36610
10.0	0.0360	-0.03475	-0.05141	-0.47951
11.0	0.0330	-0.03250	-0.05142	-0.58189
12.0	0.0305	-0.03049	-0.05108	-0.67514
13.0	0.0285	-0.02869	-0.05054	-0.76131
14.0	0.0270	-0.02707	-0.04987	-0.84215
15.0	0.0255	-0.02562	-0.04917	-0.91896
16.0	0.0245	-0.02430	-0.04844	-0.99254
18.0	0.0230	-0.02203	-0.04699	-1.13298
20.0	0.0220	-0.02014	-0.04566	-1.26756
<i>Cubic FS</i>				
9.0	0.0405	-0.03725	-0.05067	-0.36038
10.0	0.0365	-0.03475	-0.05136	-0.47789
11.0	0.0335	-0.03250	-0.05144	-0.58254
12.0	0.0310	-0.03049	-0.05115	-0.67739
13.0	0.0285	-0.02869	-0.05064	-0.76500
14.0	0.0270	-0.02707	-0.05002	-0.84728
15.0	0.0260	-0.02562	-0.04934	-0.92559
16.0	0.0250	-0.02430	-0.04864	-1.00082
18.0	0.0235	-0.02203	-0.04726	-1.14496
20.0	0.0225	-0.02014	-0.04599	-1.28385

**Table 5.** Energies corresponding to FC case (with non-uniform positive background).

$r_s$	$\alpha$	$E_G (R_{yd})$	$E (R_{yd})$	$(E - E_G)/ E_G $
<i>Spherical FS</i>				
6.0	0.1215	-0.04564	-0.20656	-3.52599
7.0	0.1125	-0.04288	-0.20208	-3.71300
8.0	0.1055	-0.03998	-0.19724	-3.93285
9.0	0.1015	-0.03725	-0.19257	-4.17012
10.0	0.0990	-0.03475	-0.18835	-4.42012
11.0	0.0980	-0.03250	-0.18468	-4.68174
12.0	0.0980	-0.03049	-0.18158	-4.95470
14.0	0.1005	-0.02708	-0.17693	-5.53440
16.0	0.1040	-0.02431	-0.17403	-6.15920
18.0	0.1095	-0.02203	-0.17251	-6.82919
20.0	0.1140	-0.02014	-0.17203	-7.54252
<i>Cubic FS</i>				
5.0	0.1380	-0.04740	-0.20855	-3.39975
6.0	0.1240	-0.04564	-0.20656	-3.52599
7.0	0.1135	-0.04288	-0.20248	-3.72228
8.0	0.1070	-0.03998	-0.19788	-3.94881
9.0	0.1030	-0.03725	-0.19343	-4.19318
10.0	0.1010	-0.03475	-0.18942	-4.45102
11.0	0.1000	-0.03250	-0.18596	-4.72096
12.0	0.1005	-0.03049	-0.18304	-5.00251
14.0	0.1025	-0.02708	-0.17868	-5.59918
16.0	0.1060	-0.02431	-0.17599	-6.23982
18.0	0.1105	-0.02203	-0.17459	-6.92363
20.0	0.1150	-0.02014	-0.17416	-7.64747

**Table 6.** Energies corresponding to AC case (with non-uniform positive background).

$r_s$	$\alpha$	$E_G (R_{yd})$	$E (R_{yd})$	$(E - E_G)/ E_G $
<i>Cubic FS</i>				
6.0	0.0360	-0.04564	-0.05713	-0.25182
7.0	0.0270	-0.04288	-0.05670	-0.32243
8.0	0.0175	-0.03998	-0.06565	-0.64188
9.0	0.0130	-0.03725	-0.07356	-0.97481
10.0	0.0105	-0.03475	-0.06576	-0.89224
11.0	0.0315	-0.03250	-0.05216	-0.60457
12.0	0.0305	-0.03049	-0.05171	-0.69582
13.0	0.0295	-0.02869	-0.05118	-0.78389
14.0	0.0280	-0.02708	-0.05055	-0.86702
16.0	0.0260	-0.02431	-0.04917	-1.02259
18.0	0.0255	-0.02203	-0.04809	-1.18243
20.0	0.0250	-0.02014	-0.04724	-1.34591
<i>Spherical FS</i>				
5.0	0.1150	-0.04740	0.00131	1.02754
6.0	0.0865	-0.04564	-0.02379	0.47875
7.0	0.0680	-0.04288	-0.03681	0.14148
8.0	0.0555	-0.03998	-0.04373	-0.09367
9.0	0.0465	-0.03725	-0.04734	-0.27095
10.0	0.0400	-0.03475	-0.04706	-0.41199
11.0	0.0350	-0.03250	-0.04969	-0.52870
12.0	0.0310	-0.03049	-0.04965	-0.62829
13.0	0.0280	-0.02869	-0.04922	-0.71537
14.0	0.0255	-0.02708	-0.04855	-0.79309
16.0	0.0220	-0.02431	-0.04688	-0.92860
18.0	0.0190	-0.02203	-0.04508	-1.04625
20.0	0.0180	-0.02013	-0.04334	-1.15232

In table 7 we have given  $R$  matrices values for the three cases.

All our calculations predict energies which are well below the usual groundstate energy  $E_G$ . From the tables the following points may be observed.

The values of  $\alpha$ , for all the cases quickly converge to certain values when  $r_s$  increases. Also the change in the ground state energy is small as  $r_s$  increases. For the uniform positive background case for NC and FC the energies for spherical FS are slightly lower than the energies corresponding to cubic FS. A similar feature has been observed in the ferromagnetic state of an electron gas by Calais and Sykja (1982). In AC the situation is entirely different. For this the cubic Fermisurface case has lower energy and also the curve has a minimum corresponding to  $r_s = 9$ . Among all the three crystals' cases the FC case has the lowest energy.

It is of importance to note the special character of the AC curves. As pointed out here the cubic fermisurface has less energy than the spherical Fermisurface. This is not something out of the way. A similar result was reported by Calais and Sperber (1973) in their calculation for Lithium crystal. The minimum in the curve for AC alone is to be noted. This situation strongly predict a crystallization in antiferromagnetic phase. This is also called the Wigner crystal. When the positive background is assumed to be non uniform, it contributes to the ground state energy. From tables

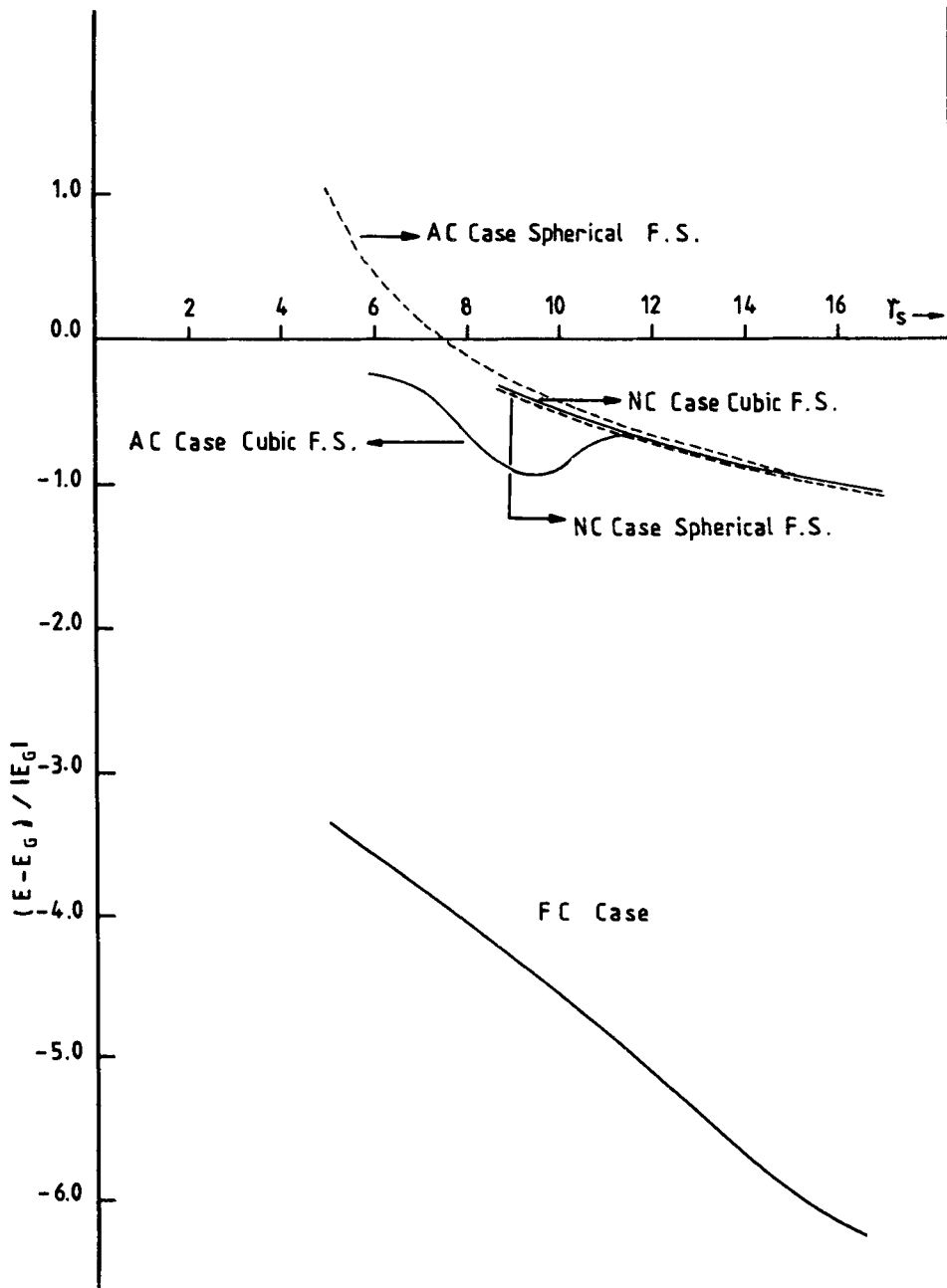


Figure 2.  $(E - E_G) / |E_G|$  vs  $r_s$  for different crystals (Present work).

4 to 6 we see that the contribution from positive background has slightly lifted up the  $E$  values. Also for all the three cases the energies corresponding to cubic FS are lower than the spherical FS energies. This situation is similar to what has been observed by Carr (1961) and Edwards and Hillel (1968).

For comparison, we have plotted the results of Edwards and Hillel (1968) in figure 3. Our results agree with their results that at low densities the ground state is

Table 7

*R*-Matrices

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NC-Cubic F.S		
0.500000	0.000000	0.129006
0.000000	0.500000	0.129006
0.129006	0.129006	0.500000
NC Spherical F.S		
0.500000	0.054443	0.119014
0.054443	0.500000	0.119014
0.119014	0.119014	0.500000
FC Cubic F.S		
1.000000	-0.184126	0.099738
-0.184126	1.000000	0.099738
0.099738	0.099738	1.000000
FC Spherical F.S		
1.000000	0.049364	0.038594
-0.049364	1.000000	0.038594
0.038594	0.038594	1.000000
AC Cubic F.S		
1.000000	0.000000	0.000516
0.000000	1.000000	0.000000
0.000516	0.000000	1.000000
AC Spherical F.S		
1.000000	0.000000	0.615025
0.000000	1.000000	0.000000
0.615025	0.000000	1.000000

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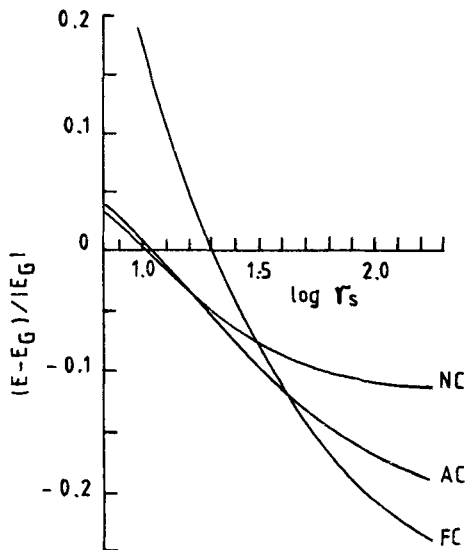


Figure 3.  $(E - E_G) / |E_G|$  vs  $r_s$  for different crystals (Edwards and Hillel's work).

**Table 8.** Comparison of  $\alpha$  values for AC with  $\alpha$  value from Wigner's Theory

$r_s$	$\alpha = \frac{1}{2r_s^{3/2}}$	$\alpha$ (calculated)
6.0	0.0340	0.0360
7.0	0.0270	0.0268
8.0	0.0221	0.0175
9.0	0.0185	0.0129
10.0	0.0158	0.0105

ferromagnetic crystal. They have predicted crystalline antiferromagnetic state over a large intermediate density range. But in our case corresponding to AC case for cubic FS we get a minimum (figure 2) which in an indirect way may indicate a crystalline antiferromagnetic state at that density. It occurs around  $r_s = 10$ , which is the lower limit for the density range for antiferromagnetic crystalline state in their calculation.

Wigner in his paper has pointed out that for sufficiently large  $r_s$  the wave function of the crystallized electron should be a Gaussian. He gets this result since he is considering zero-point vibration. Wigner claims that the orbital exponent of the Gaussian  $\alpha$  ( $=$  his  $(\alpha/2)$ ) should go like

$$\frac{1}{2r_s^{3/2}}$$

We find in AC case for cubic fermisurface the values of  $\alpha$  are found to behave as indicated above. The numbers are given in table 8. It is worth to mention again that only for this case we got a minimum in the  $(E - E_G)/|E_G|$  vs  $r_s$  curve and also it corresponds to the interesting case of Wigner crystallization.

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