

Comments on the electrostatic energy of a Wigner solid

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A recent contention by Hall that Fuchs's calculation of the electrostatic energy of an infinite Wigner solid contains a fundamental error is not true. Fuchs calculated the average electrostatic energy per electron Φ_i , while Hall derived this quantity from the energy of the interaction of one electron with the rest of the lattice Φ_e by use of the relation $\Phi_i = (1/2)\Phi_e$; however, this relation is not valid in the case studied by Hall. Preliminary results for finite Wigner solids are discussed.

I. INTRODUCTION

In a recent paper,¹ Hall has claimed that Fuchs's calculation² of the electrostatic binding energy of an infinite Wigner solid contains a serious error; this is not so. Fuchs calculated the binding energy per electron Φ_i of a Wigner solid by using the Ewald method and he obtained the correct answers ($-1.79172r_s^{-1}$ Ry for fcc and $-1.79186r_s^{-1}$ Ry for bcc). The discrepancy arises because Hall derives Φ_i by first calculating the interaction energy of one electron with the rest of the lattice Φ_{e1} , and then using the relation

$$\Phi_i = \frac{1}{2}\Phi_{e1}. \tag{1}$$

However, Eq. (1) is valid only when the average potential in the lattice is zero,³ which is not the case in Hall's calculation.

In Sec. II we discuss Fuchs's and Hall's calculations in terms of the so-called spherical approximation,⁴ which is extremely simple but at the same time sufficiently accurate, to check the results of fancy summation methods without having to carry out a lattice summation. Examined in that way, the source of the discrepancy between Fuchs's and Hall's methods becomes immediately clear. In Sec. III we give a preliminary discussion of the situation for finite lattices.

II. SPHERICAL APPROXIMATION

The Wigner solid (electron lattice) consists of a regular lattice of electrons embedded in a uniform background of compensating positive charge. Here we are only interested in the static lattice. The potential energy of the system is

$$\Phi = \frac{e^2}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{R}_j - \vec{R}_i|} - e^2 \rho \sum_i \int_V \frac{d^3r}{|\vec{R}_i - \vec{r}|} + \frac{e^2 \rho^2}{2} \iint_V \frac{d^3r d^3r'}{|\vec{r} - \vec{r}'|}, \tag{2}$$

where e is the electronic charge, $e\rho$ the charge density of the neutralizing positive background, and \vec{R}_i the position of electron i . The three terms in the right-hand side are the electron-electron interaction, the electron-background interaction, and the self-energy of the background, respectively; V is the volume occupied by the lattice. If (with respect to the \vec{r}_i integration) we divide the total volume in Wigner-Seitz cells with total positive charge $+e$ and centered on the electrons we may write

$$\Phi = \sum_i \Phi_i = \sum_i \left(\frac{e^2}{2} \sum_{j \neq i} \frac{1}{|\vec{R}_j - \vec{R}_i|} - e^2 \rho \int_V \frac{d^3r}{|\vec{R}_i - \vec{r}|} + \frac{e^2 \rho^2}{2} \int_{\text{cell } i} \int_V \frac{d^3r_i d^3r'_i}{|\vec{r}_i - \vec{r}'_i|} \right). \tag{3}$$

For an infinite lattice all Φ_i [defined by Eq. (3)] are equal and represent the electrostatic energy of the system per electron; Φ_i is the quantity evaluated by Fuchs.

We write Φ_i as follows:

$$\Phi_i = \sum_{j \neq i} \left(\frac{e^2}{2} \frac{1}{|\vec{R}_i - \vec{R}_j|} - e^2 \rho \int_{\text{cell } j} \frac{d^3r_j}{|\vec{R}_i - \vec{r}_j|} + \frac{e^2 \rho^2}{2} \int_{\text{cell } i} \int_{\text{cell } j} \frac{d^3r_i d^3r'_j}{|\vec{r}_i - \vec{r}'_j|} \right) - e^2 \rho \int_{\text{cell } i} \frac{d^3r_i}{|\vec{R}_i - \vec{r}_i|} + \frac{e^2 \rho^2}{2} \iint_{\text{cell } i} \frac{d^3r_i d^3r'_i}{|\vec{r}_i - \vec{r}'_i|}. \tag{4}$$

The first term in Eq. (4) is small; in a cubic lattice it represents, as a result of the cubic symmetry of the lattice, in first approximation, the energy of interaction of a hexadecapole with a lattice of identical hexadecapoles (cf. Ref. 3, Appendix).

The spherical approximation assumes that the Wigner-Seitz cells are spheres for which the over-

lap is neglected; then the first term in (4) vanishes and we have

$$\begin{aligned} \Phi_i^{\text{sph}} = & -e^2 \rho \int_{\text{sph cell } i} \frac{d^3 r_i}{|\vec{r}_i - \vec{R}_i|} \\ & + \frac{e^2 \rho^2}{2} \iint_{\text{sph cell } i} \frac{d^3 r_i d^3 r'_i}{|\vec{r}_i - \vec{r}'_i|}. \end{aligned} \quad (5)$$

Using $\vec{R}_i = 0$ (centered cells) these integrals are easily evaluated, giving

$$\Phi_i^{\text{sph}} = -\frac{3e^2}{2\mathcal{R}} + \frac{3e^2}{5\mathcal{R}} = -0.9 \frac{e^2}{\mathcal{R}}, \quad (6)$$

where \mathcal{R} is the radius of the spherical cell. Expressing \mathcal{R} in Bohr radii a_0 ($=\hbar^2/m e^2$), i.e., $\mathcal{R} = r_s a_0$, and the energy in Ry ($=e^2/2a_0$) we find

$$\Phi_i^{\text{sph}} = -\frac{1.8}{r_s} \text{Ry}. \quad (7)$$

Because of the accuracy of the spherical approximation, the real value of Φ_i should be quite close to $-1.8r_s^{-1}$ Ry, and this is indeed so: $\Phi_i^{\text{bcc}} = -1.791860r_s^{-1}$ Ry (Ref. 5). This shows that Fuchs has applied the Ewald method correctly.

To analyze Hall's method in the same way, we now consider the energy of one electron with the rest of the lattice, Φ_{e1} . We have

$$\Phi_{e1} = e^2 \sum_{j \neq i} \frac{1}{|\vec{R}_j - \vec{R}_i|} - e^2 \rho \int_V \frac{d^3 r}{|\vec{r} - \vec{R}_i|}. \quad (8)$$

This can be written as

$$\begin{aligned} \Phi_{e1} = & \sum_{j \neq i} \left(\frac{e^2}{|\vec{R}_j - \vec{R}_i|} - e^2 \rho \int_{\text{cell } j} \frac{d^3 r_j}{|\vec{r}_j - \vec{R}_i|} \right) \\ & - e^2 \rho \int_{\text{cell } i} \frac{d^3 r_i}{|\vec{r}_i - \vec{R}_i|}. \end{aligned} \quad (9)$$

In the spherical approximation the first term vanishes and we have

$$\Phi_{e1}^{\text{sph}} = -e^2 \rho \int_{\text{sph cell } i} \frac{d^3 r_i}{|\vec{r}_i - \vec{R}_i|} = -\frac{3.0}{r_s} \text{Ry}. \quad (10)$$

To obtain the value of Φ_i Hall then implicitly uses Eq. (1), which gives in this approximation

$$\Phi_i^{\text{sph}}(\text{Hall}) = -\frac{1.5}{r_s} \text{Ry}. \quad (11)$$

Thus the spherical-approximation equivalent of Hall's "correction" term A becomes

$$A^{\text{sph}} = \Phi_i^{\text{sph}}(\text{Hall}) - \Phi_i^{\text{sph}} = \frac{0.3}{r_s} \text{Ry}. \quad (12)$$

The error in Hall's method, and consequently the appearance of the correction term A , results from the use of Eq. (1), which is not justified in this case; Eq. (1) is valid only when the average potential in the crystal is zero. This can be seen

by evaluating the expression for the total electrostatic energy of the crystal,

$$\Phi = \frac{1}{2} \int e \rho_{\text{tot}} V d^3 r, \quad (13)$$

where $e \rho_{\text{tot}} = -e\delta(\vec{R}_i) + e/v_{\text{cell}}$ is the total charge density and V the potential in the crystal; the integration is over the entire volume of the crystal. In an infinite crystal all Wigner-Seitz cells contribute equally to Φ so that

$$\Phi_i = \frac{1}{2} \int_{\text{cell}} e \rho_{\text{tot}} V d^3 r. \quad (14)$$

Using the expression for the average potential $V_{\text{av}} = (1/v_{\text{cell}}) \int_{\text{cell}} V d^3 r$, evaluation of Eq. (14) gives

$$\Phi_i = \frac{1}{2} [-eV(0) + eV_{\text{av}}] = \frac{1}{2} (\Phi_{e1} + \Phi_b), \quad (15)$$

where Φ_b is the energy of the positive background in the average potential of the lattice. From Eq. (15) it is clear that Eq. (1) is valid when $V_{\text{av}} = 0$.

Returning to the spherical-approximation equivalent of Hall's calculation we now have to evaluate Φ_b^{sph} . This is very simple, because Φ_b^{sph} is simply the energy of the background in the average potential in an isolated Wigner sphere; it is found to be $\Phi_b^{\text{sph}} = -0.6r_s^{-1}$ Ry. Using Eq. (15) we thus find the familiar value $\Phi_i^{\text{sph}} = -1.8r_s^{-1}$ Ry.

Two comments are in order.

(1) The reason for the frequently made tacit assumption of the validity of Eq. (1) (cf. Refs. 1 and 6) is the apparent ease with which Eq. (1) can be derived. The usual argument (cf. Ref. 3, Appendix) is, that for an infinite crystal, the third term in the right-hand side of Eq. (2) cancels half of the second term; comparison of this modification of Eq. (2) with Eq. (8) then leads to Eq. (1). It is now clear that taking a simple difference of these two infinite terms is not justified.

(2) Birman⁴ has shown that in the Ewald method the average potential is implicitly chosen to be zero. This explains why the evaluation of Φ_{e1} with this method,^{5,6} together with the use of Eq. (1), leads to the correct results for Φ_i .

III. FINITE WIGNER LATTICES

When rapidly converging summation methods are employed to evaluate Coulomb sums, such as for the electron lattice,^{1,2,5,6} these are necessarily always carried out over infinite lattices and the question of the boundaries of the crystal does not arise. The spherical approximation applies to both finite and infinite crystals, since only effects due to the central Wigner-Seitz cell enter into the result; but the method assumes that all electrons are surrounded by identical Wigner-Seitz cells. If we consider a finite Wigner lattice, it is some-

TABLE I. Values (in r_s^{-1} Ry) of the potential energy of the central electron Φ_{e1}^c in cubical and spherical samples of sc-, fcc-, and bcc-structured electron lattices.

Structure	No. of electrons summed over	Cube	Sphere
sc	132 650	-2(1.435 32)	
	1 030 300	-2(1.435 33)	
	523 304		-2(1.757 79)
	1 767 062		-2(1.759 70)
fcc	515 150	-2(1.588 82)	
	261 562		-2(1.791 87)
bcc	257 650	-2(1.862 15)	
	131 018		-2(1.801 54)

what problematical as to how the background should be terminated at the surface, but in applying the spherical approximation it is implicitly assumed that the background terminates abruptly at the boundaries of the Wigner-Seitz cells at the surface. For finite fcc- and bcc-structured electron lattices this procedure will lead to waffled surfaces, which would not correspond to "real," smooth surfaces. In contrast, for a rectangularly shaped electron lattice with simple cubic (sc) structure, the surfaces that obtain for the background are pairs of (100)-, (010)-, and (001)-oriented planes, because the Wigner-Seitz cells are cubes.

In order to get an idea of how the choice of surface and the boundaries of the background effect the results for the potential energy of the central electron Φ_{e1}^c , we have carried out computer summations for cubical and spherical samples of sc-, fcc-, and bcc-structured electron lattices. In each case the size of the cubical or spherical background followed from the condition of charge neutrality. The results are summarized in Table I. We notice that the results fall into two groups: those close to $\Phi_{e1}^{sph} = -2(1.5)r_s^{-1}$ Ry and those close to $-2(1.8)r_s^{-1}$ Ry. It is noteworthy that the results for sc (cube) are virtually identical to Hall's re-

sult $-2(1.435 04)$. This is not surprising because this is the only case in which the Wigner-Seitz cells give rise to the proper flat background boundary at the surfaces of the crystal. What is surprising, however, is that the other cases, with the exception of fcc (cube), are all close to $-2(1.8)$, i.e., close to the results of infinite summations in which the average potential is chosen to be zero. Apparently, the surface smoothing and redistribution of surface charge in the finite summation is equivalent with the choice of zero average potential in the finite summation. For a full understanding of this problem, the question of the redistribution of both positive and negative charge at the surface needs to be studied in detail. This problem has been discussed by Kleinman⁷ in a different context. Similar problems for ionic crystals have been considered by von Laue⁸ and Ewald and Juretschke.⁹

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