J. Phys. A: Math. Gen. **21** (1988) 1519-1531. Printed in the UK

Energy of static electron lattices

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Received 17 November 1986, in final form 24 November 1987

Abstract. A new approach to evaluating the static lattice energy of any given Wigner lattice is proposed. The method is much simpler than the traditional one and the results are much faster to evaluate. The new approach is applied to two-dimensional triangular lattices where it is shown that the triangular lattice is more stable than the square lattice. Three-dimensional hexagonal lattices are also investigated. In addition, we have placed many of our considerations on a rigorous mathematical footing.

1. Introduction

In 1934 Wigner introduced the concept of an electron gas bathed in a compensating background of positive charge as a model for a metal. He stated that in the static case the electrons would form a BCC lattice in the background of positive charge. In 1938 he presented a quantitative treatment of this problem, following a calculation by Fuchs (1935) who showed that for a given number density, the BCC lattice was the most stable of three common cubic structures, namely SC, BCC and FCC lattices. The evaluation of U(lattice)—the energy of an electron in a given lattice—involved finding by some means or other the difference of two divergent quantities. Of these, one term, U_1, measures the interaction of an electron with all the other electrons on their lattice sites. The second term, U_2, measures the interaction of an electron with the compensating positive background charge. Thus

$$U(\text{lattice}) = U_1 - U_2 \tag{1}$$

where

$$U_1 = \frac{e^2}{a_0} \sum{}' (l_1^2 + l_2^2 + l_3^2)^{-1/2} \tag{2}$$

and

$$U_2 = ne^2 \iiint_{(\Omega)} \frac{dx\, dy\, dz}{(x^2+y^2+z^2)^{1/2}}. \tag{3}$$

In (2) a_0 is some lattice parameter and the summation is over all integers (l_1, l_2, l_3) relevant to the given lattice. In (3), n is the number density and Ω is the normalisation

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0305-4470/88/071519+13$02.50

volume of the given lattice. For the three cubic lattices it is easily shown that in terms of e^2/a_0 we have (Zucker 1975)

$$U_1(\text{SC}) = \sum' \frac{1}{(m^2+n^2+p^2)^{1/2}} = a(1) \tag{4}$$

$$U_1(\text{FCC}) = \sum' \frac{1}{(m^2+n^2+p^2)^{1/2}} + \sum' \frac{(-1)^{m+n+p}}{(m^2+n^2+p^2)^{1/2}} = a(1)+d(1) \tag{5}$$

$$2U_1(\text{BCC}) = \sum' \frac{1}{(m^2+n^2+p^2)^{1/2}} + 3\sum' \frac{(-1)^{m+n}}{(m^2+n^2+p^2)^{1/2}} = a(1)+3c(1). \tag{6}$$

Each of (4), (5) and (6) contains the divergent 'sum' $a(1)$. Here and throughout Σ' indicates that the terms in which m, n and p are simultaneously zero are omitted. While U_2 is also divergent, if the 'correct' procedure is followed the divergencies can be made to cancel appropriately and finite results are obtained. A most detailed account of this procedure is made by Coldwell-Horsfall and Maradudin (1960) who give

$$\begin{aligned} &\text{(i)} \quad U(\text{SC}) = -2.837\,297(e^2/a_0) \\ &\text{(ii)} \quad U(\text{FCC}) = -4.584\,875(e^2/a_0) \\ &\text{(iii)} \quad U(\text{BCC}) = -3.639\,240(e^2/a_0). \end{aligned} \tag{7}$$

In the above, a_0 is the side of the cube. In terms of r_s, the radius of a sphere of volume equal to the volume per electron, we have

$$a_0^3 = \tfrac{4}{3}\pi r_s^3(\text{SC}) \qquad \tfrac{1}{4}a_0^3 = \tfrac{4}{3}\pi r_s^3(\text{FCC}) \qquad \tfrac{1}{2}a_0^3 = \tfrac{4}{3}\pi r_s^3(\text{BCC})$$

and thus

$$\begin{aligned} &\text{(i)} \quad U(\text{SC}) = -1.760\,119e/r_s \\ &\text{(ii)} \quad U(\text{FCC}) = -1.791\,753e/r_s \\ &\text{(iii)} \quad U(\text{BCC}) = -1.791\,860e/r_s \end{aligned} \tag{8}$$

in which the BCC lattice appears as the most stable.

With some considerable surprise, the present authors have noted that the numbers appearing in (7) are precisely the values of U_1 *alone* when evaluated by a method suggested by Zucker (1976). This was to consider $a(2s) := \Sigma'(m^2+n^2+p^2)^{-s}$, a three-dimensional analogue of the Riemann zeta function. Now $a(2s)$ is clearly analytic for $\text{Re}\, s > \frac{3}{2}$ and has a simple pole at $s = \frac{3}{2}$. Also $a(2s)$ possesses a simple functional equation, $a(2s) = K(s)a(3-2s)$ where $K(s) := \pi^{2s-3/2}\Gamma(\frac{3}{2}-s)/\Gamma(s)$, which allows for its analytic continuation to the region $\text{Re}\, s < \frac{3}{2}$.

This and other techniques allow a very rapid evaluation of all the sums in (4)-(6). The sums $c(1)$ and $d(1)$ are actually conditionally convergent when summed in the appropriate order (Borwein *et al* 1985).

Since it is much easier to evaluate the analytic continuations of the corresponding lattice sums without bothering to subtract divergent integrals 'the right way', the question arises as to whether using the former procedure is valid for all Coulomb lattices. In § 3 we shall attempt to justify doing just that. First, however, we shall detail the square lattice calculation, both by the traditional method and by our suggested method.

2. The square lattice

Throughout we shall work in units of e^2/a_0, where a_0 is the length of side of the unit square in the lattice. The energy per electron may be written as

$$U(\mathrm{sq}) = U_1(\mathrm{sq}) - U_2(\mathrm{sq})$$

where

$$U_1(\mathrm{sq}) = \sum{}' (m^2+n^2)^{-1/2} \qquad U_2(\mathrm{sq}) = \int\int (x^2+y^2)^{-1/2}\,\mathrm{d}x\,\mathrm{d}y.$$

Consider first U_1. Using the relation

$$\Gamma(n)z^{-n} = \int_0^\infty t^{n-1}\exp(-zt)\,\mathrm{d}t \tag{9}$$

we write U_1 as

$$U_1 = \pi^{-1/2}\sum{}' \int_0^\infty t^{-1/2}\exp[-(m^2+n^2)t]\,\mathrm{d}t \tag{10}$$

and split the range of integration into two parts, $(0, \pi)$ and (π, ∞). Thus $U_1 = U_{11} + U_{12}$ where

$$U_{11} = \pi^{-1/2}\sum{}' \int_\pi^\infty t^{-1/2}\exp[-(m^2+n^2)t]\,\mathrm{d}t \tag{11}$$

$$U_{12} = \pi^{-1/2}\sum{}' \int_0^\pi t^{-1/2}\exp[-(m^2+n^2)t]\,\mathrm{d}t. \tag{12}$$

In (11) we set $t = \pi x$ and hence

$$U_{11} = \sum{}' \int_1^\infty t^{-1/2}\exp[-(m^2+n^2)\pi t]\,\mathrm{d}t = \sum{}' \phi_{-1/2}[\pi(m^2+n^2)] \tag{13}$$

where

$$\phi_n(t) := \int_1^\infty x^n \exp(-xt)\,\mathrm{d}x$$

are integrals computed by Misra (1940) and Born and Misra (1940). In U_{12} we interchange sum and integral and remove the restriction on the sum by subtracting the $m = n = 0$ term. Thus

$$U_{12} = \pi^{-1/2}\sum \int_0^\pi t^{-1/2}\exp[-(m^2+n^2)t]\,\mathrm{d}t - \pi^{-1/2}\int_0^\pi t^{-1/2}\,\mathrm{d}t. \tag{14}$$

Now we use the Poisson transformation formula

$$\sum \exp[-(m^2+n^2)t] = (\pi/t)\sum \exp[-(m^2+n^2)\pi^2/t] \tag{15}$$

which we substitute into (14). We then perform the second integration in (14) and arrive at

$$U_{12} = \pi^{1/2}\sum \int_0^\pi t^{-3/2}\exp[-\pi^2(m^2+n^2)/t]\,\mathrm{d}t - 2. \tag{16}$$

We replace the restriction on the sum by adding back the $m=n=0$ term, and on substituting $t := \pi/x$ we have

$$U_{12} = \sum{}' \phi_{-1/2}[\pi(m^2+n^2)] - 2 + \pi^{1/2} \int_0^\pi t^{-3/2}\,dt.$$

On adding U_{11} and U_{12}

$$U_1 = 2\sum{}' \phi_{-1/2}[\pi(m^2+n^2)] - 2 + \pi^{1/2} \int_0^\pi t^{-3/2}\,dt. \tag{17}$$

Now we consider U_2. Using (9) we rewrite

$$U_2 = \int\int_{\mathbb{R}} \frac{dx\,dy}{(x^2+y^2)^{1/2}} = \pi^{-1/2} \int_0^\infty t^{-1/2} \int_0^\infty \int_0^\infty \exp[-(x^2+y^2)t]\,dx\,dy\,dt. \tag{18}$$

We change to polar coordinates to evaluate the interior double integral. This leads easily to

$$U_2 = \pi^{1/2} \int_0^\infty t^{-3/2}\,dt = \pi^{1/2} \int_0^\pi t^{-3/2}\,dt + \pi^{1/2} \int_\pi^\infty t^{-3/2}\,dt$$

and so

$$U_2 = \pi^{1/2} \int_0^\pi t^{-3/2}\,dt + 2 \tag{19}$$

where the integral is again divergent. Subtract (19) from (17) and 'cancel' the identical divergent integrals to obtain

$$U(\mathrm{sq}) = 2\sum{}' \phi_{-1/2}[\pi(m^2+n^2)] - 4. \tag{20}$$

Thus

$$U(\mathrm{sq}) = -4 + 2[4\phi_{-1/2}(\pi) + 4\phi_{-1/2}(2\pi) + 4\phi_{-1/2}(4\pi) + 8\phi_{-1/2}(5\pi) + \ldots]$$

on summing over equal $k = m^2+n^2$. From the tables prepared by Born and Misra (1940) we find

$$\phi_{-1/2}(\pi) = 0.012\,189 \qquad \phi_{-1/2}(2\pi) = 2.77\times 10^{-4} \qquad \phi_{-1/2}(4\pi) = 2.7\times 10^{-7}$$

and subsequent terms are less than 10^{-8}. This gives

$$U(\mathrm{sq}) = -3.900\,265 \tag{21}$$

as calculated by the conventional method. However, for $\mathrm{Re}\,s > 1$ the sum $a_2(2s) = \Sigma'(n^2+m^2)^{-s}$ factors as $a_2(2s) = 4\zeta(s)\beta(s)$ where

$$\zeta(s) = 1 + 2^{-s} + 3^{-s} + 4^{-s} + \ldots \qquad (\mathrm{Re}\,s > 1)$$

$$\beta(s) = 1 - 3^{-s} + 5^{-s} - 7^{-s} + \ldots \qquad (\mathrm{Re}\,s > 0).$$

This result is often ascribed to Hardy (1919) but goes back at least to Lorenz (1871) and is derivable from Jacobi (1829). Thus we claim that

$$U(\mathrm{sq}) = U_1(\mathrm{sq}) = a_2(1) = 4\zeta(\tfrac{1}{2})\beta(\tfrac{1}{2}) = -3.900\,264\,924\ldots$$

in complete agreement with (21). Of course, $\zeta(\frac{1}{2})$ cannot be evaluated from the previous series but may be found from

$$(1-2^{1-s})\zeta(s) = 1 - 2^{-s} + 3^{-s} - 4^{-s} \ldots \qquad (\mathrm{Re}\,s > 0).$$

Clearly the second approach to evaluating $U(\mathrm{sq})$ is more satisfactory than the long drawn-out traditional method and we shall now attempt to justify its correctness for all electron lattices.

3. The general principle

We start by observing that the previous manipulations were not arbitrary, but rather were stable since any answer might be obtained by inappropriate processes. Some regular limiting procedure must be undertaken to guarantee a robust answer. We would like to propose the following principle: the rearrangements used should depend only on the geometry of the underlying lattice and not on the power s in the law of interaction.

The consequence of this principle is that we look for an appropriate analytic function for $U(\text{lattice}:s)$ and take as our answer the value of this function at $s=\frac{1}{2}$. We argue that this forces the answer to be $a_{\text{lat}}(1)$ where $a_{\text{lat}}(2s)$ is the d-dimensional sum over the lattice sites:

$$a_{\text{lat}}(2s)=\sum{}'(l_1^2+l_2^2+\ldots+l_d^2)^{-s}$$

in which the sum represents $a_{\text{lat}}(2s)$ for $\operatorname{Re} s>d/2$. This has an analytic continuation for $0<\operatorname{Re} s<d/2$, which, for the d-dimensional simple cubic lattice, is obtained via the functional relation

$$\pi^{-s}\Gamma(s)a_{\text{lat}}(2s)=\pi^{s-d/2}\Gamma(d/2-s)a_{\text{lat}}(d-2s).$$

Formally

$$U(\text{lattice}:s)=a_{\text{lat}}(2s)-U_2(s) \tag{22a}$$

where

$$U_2=c\int_{(\Omega)}\ldots\int\frac{\mathrm{d}x_1\ldots\mathrm{d}x_d}{(x_1^2+x_2^2+\ldots+x_d^2)^s}$$

while c is a constant appropriate to the lattice and Ω is some volume in d-dimensional space which gives electrical neutrality. Now split U_2 into the region inside the unit sphere and outside the unit sphere thus:

$$U_2(s)=U_2^{<}(s)+U_2^{>}(s)$$

and adding on the finite integral $U_2^{<}(s)$ when $0<\operatorname{Re} s<d/2$ to both sides of (22a) we have

$$U(\text{lattice}:s)+U_2^{<}(s)=a_{\text{lat}}(2s)-U_2^{>}(s). \tag{22b}$$

Now $U_2^{<}(s)$ may be integrated to give for $\operatorname{Re} s<d/2$

$$U_2^{<}(s)=\frac{C}{d-2s}\qquad C=\Omega c2\pi^{d/2}/\Gamma(d/2)$$

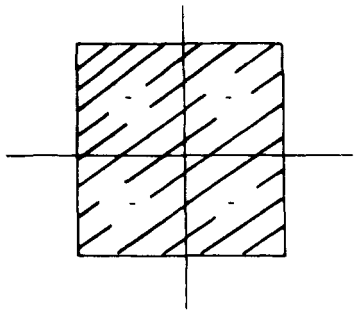
whereas, for $\operatorname{Re} s>d/2$ the other integral, $U_2^{>}$, is finite and by direct computation, or by appealing to the central symmetry of the integral, has the value $C/(2s-d)$. Now we argue as follows. The LHS of (22b), namely $U(\text{lattice}:s)+C/(d-2s)$ is an analytic

continuation of the RHS of (22*b*) for Re $s < d/2$. Thus, by comparing the two we have

$$U(\text{lattice}:s) = a_{\text{lat}}(2s)$$

for Re $s < d/2$ and hence for $s = \frac{1}{2}$ we have our result. By considering a precise limiting process we shall demonstrate why a unique 'answer' is to be obtained.

We shall consider the following model in d dimensions. In our model point charges will be located at lattice sites and these will be surrounded by an equal amount of opposite charge uniformly distributed over hypercubes centred at the lattice point and of side equal to one lattice spacing. This is illustrated below in two dimensions where the shaded portion represents positive charge of value equal to the point negative charge but uniformly distributed over a square.



We shall thus examine the precise limiting procedure:

$$\lim_{N\to\infty} \sigma_N(s) = \lim_{N\to\infty} \left(\sum_{-N}^{N} \cdots \sum_{-N}^{N}{}' (l_1^2 + l_2^2 + \ldots + l_d^2)^{-s} - \int_{-(N+1/2)}^{N+1/2} \cdots \int_{-(N+1/2)}^{N+1/2} (x_1^2 + x_2^2 + \ldots + x_d^2)^{-s} \, dx_1 \ldots dx_d \right)$$

$$= \lim_{N\to\infty} [\alpha_N(x) - \beta_N(s)] \tag{23}$$

although *a priori* this limit need not exist. This procedure maintains electrical neutrality throughout the limiting process. Further the model has zero-dipole moment, and in three dimensions zero quadrupole moment as well.

Consider first the multidimensional integral $\beta_N(s)$. Writing $x_j = (N + \frac{1}{2})X_j$ we have

$$\frac{\beta_N(s)}{(N+\frac{1}{2})^{d-2s}} = I(s) = \int_{-1}^{1} \cdots \int_{-1}^{1} (X_1^2 + \ldots + X_d^2) \, dX_1 \ldots dX_d. \tag{24}$$

Now $I(s)$ may be rewritten as

$$I(s) = 2d \int_{W_d} \cdots \int \frac{dX_1 \ldots dX_d}{(X_1^2 + \ldots + X_d^2)^s}$$

where W_d is the pyramidal region $|X_i| \leq X_d \leq 1$. Making the substitution $X_i = X_d x_i$ we have

$$I(s) = 2d \int_0^1 X_d^{d-1-2s} \, dX_d \int_{-1}^{1} \cdots \int_{-1}^{1} \frac{dx_1 \ldots dx_{d-1}}{(1 + x_1^2 + \ldots + x_{d-1}^2)^s}$$

$$= \frac{2d}{d-2s} C(s)$$

where

$$C(s)=\int_{-1}^{1}\cdots\int_{-1}^{1}\frac{dx_1\ldots dx_{d-1}}{(1+x_1^2+\ldots+x_{d-1}^2)^s}$$

and this integral clearly converges for Re $s>0$. Thus

$$\sigma_N(s)=\alpha_N(s)-(N+\tfrac{1}{2})^{d-2s}\frac{2d}{d-2s}C(s) \tag{25}$$

and the whole of the RHS of (25) is meromorphic for Re $s>0$ with a single simple pole at $s=d/2$. Note that

$$\beta_0(s)=2^{2s-d}2dC(s)/(d-2s) \tag{26}$$

gives an analytic continuation of the integral inside the unit hypercube. For Re $s>d/2$, $\sigma_N(s)$, as given by (23), is infinite since its defining integral is infinite. Then by (25) for Re $s>d/2$

$$\begin{aligned}\lim_{N\to\infty}\sigma_N(s)+\beta_0(s)&=\lim_{N\to\infty}\alpha_N(s)+\beta_0(s)\\&=a_{\text{lat}}(2s)+\beta_0(s)\end{aligned} \tag{27}$$

since $\beta_N(s)$ tends to zero. We use (26) to see that $a_{\text{lat}}(2s)+\beta_0(s)$ is analytic in Re $s>0$. The principle of analytic continuation allows us to conclude that (27) continues to hold in any half-plane in which the left-hand side exists and is known to be analytic. However, for $0<\text{Re } s<d/2$, $\beta_0(s)$ is a finite integral. Thus in the appropriate strip $\lim_{N\to\infty}\sigma_N(s)=a_{\text{lat}}(2s)$ for the particular limiting process we have undertaken—if it is, in fact, true that $\lim_{N\to\infty}\sigma_N(s)+\beta_0(s)$ exists and is analytic in the appropriate half-plane (or at least for $\frac{1}{2}<\text{Re } s<d/2$ with continuity at $\frac{1}{2}$).

Now, for all lattices in two dimensions, $\sigma_N(s)+\beta_0(s)$ can be shown to tend to an analytic limit in the right half-plane. In the appendix we prove this for the square lattice. While it might seem reasonable to presume that this holds generally, it is in fact false. Considerations similar to those given in the appendix show that, for the simple cubic lattice in three dimensions, the limit is analytic for $\frac{1}{2}<\text{Re } s<\frac{3}{2}$ but is discontinuous at $\frac{1}{2}$. Indeed $\lim_{s\to 1/2+}\lim_{N\to\infty}\sigma_N(s)=a_{\text{lat}}(1)$ (the 'correct' answer) but differs by $\pi/6$ from $\lim_{N\to\infty}\sigma_N(\frac{1}{2})$ (the rectangular limit).

In addition, in two dimensions one can also show that the limit over expanding circles, namely the limit as $N\to\infty$ of

$$\tau_N(s)=\sum_{1\leqslant(n^2+m^2)\leqslant N}(n^2+m^2)^{-s}-\iint_{1\leqslant(x^2+y^2)\leqslant N}(x^2+y^2)^{-s}\,dx\,dy$$

is analytic for Re $s>\frac{1}{3}$. As a consequence, when the integral inside the unit circle is reintroduced, the corresponding limiting value at $s=\frac{1}{2}$ is also $4\zeta(\frac{1}{2})\beta(\frac{1}{2})$.

4. Additional examples

Granted the general applicability of the previous meta-principle—which we have illustrated already for SC, FCC, BCC and square lamina lattices—we can easily determine

U(lattice) for many other lattices. Thus for the two-dimensional (equilateral) triangular lattice, tri, we know that

$$a_{\text{tri}}(2s) = \sum'_{n+m \text{ even}} \frac{2^{2s}}{(n^2+3m^2)^s} = \sum' \frac{1}{(m^2+mn+n^2)^s}$$

and the standard factorisation given in Zucker and Robertson (1976) and Borwein and Borwein (1987), yields from (26)

$$U(\text{tri}) = a_{\text{tri}}(1) = 6\zeta(\tfrac{1}{2})L_{-3}(\tfrac{1}{2}) = -4.213\,422\,7006\ldots$$

where

$$L_{-3} = 1 - 2^{-s} + 4^{-s} - 5^{-s} + \ldots$$

in terms of the lattice parameter a_0. In terms of r_s, the radius as before of a circle equal in area to the area per electron, we have

$$a_0^2 = \pi r_s^2(\text{sq}) \qquad (\sqrt{3}/2)a_0^2 = \pi r_s^2(\text{tri})$$

so that

$$U(\text{sq}) = -2.200\,488\,843 e^2/r_s \qquad U(\text{tri}) = -2.212\,205\,221 e^2/r_s$$

and the static triangular lattice is energetically the more stable.

We have also investigated other three-dimensional lattices, in particular various hexagonal lattices. A simple hexagonal lattice is a structure formed by stacking planes of two-dimensional triangular lattices directly above each other. The direction of stacking is known as the c axis and the separation of planes in terms of the nearest-neighbour distance, R, in the triangular lattice is called the axial ratio, c. If particles on such a lattice interact with an r^{-s} potential, it is simple to show that the appropriate lattice sums are given by

$$H(2s:c) = \sum' (m^2+3n^2+c^2p^2)^{-s} + \sum [(m-\tfrac{1}{2})^2 + 3(n-\tfrac{1}{2})^2 + c^2p^2]^{-s}.$$

Using our principle the energy of such a lattice of electrons is given, in terms of e^2/R, by

$$U(\text{hex}) = H(1:c).$$

By the techniques described in Zucker (1976), after some detailed algebra, $H(1:c)$ can be converted to rapidly converging sums and double sums of cosech functions:

$$\begin{aligned} H(1:c) = {} & \frac{-16\log 2}{3c} - \frac{\sqrt{3}\pi c}{18} + \frac{\sqrt{3}c}{3}\left[2\sum_1^\infty \frac{\operatorname{cosech}(c\pi m)}{cm}\right. \\ & \left. + 2\sum_1^\infty \frac{\operatorname{cosech}(c\pi m/\sqrt{3})}{c/\sqrt{3}} + 4\sum_1^\infty\sum_1^\infty \frac{\operatorname{cosech}(m^2+n^2/3)^{1/2}c\pi}{c(m^2+n^2/3)^{1/2}}\right] \\ & + \frac{4\sqrt{3}}{3c}\left(2\sum_1^\infty \frac{\operatorname{cosech}(2\pi m/c)}{2m/c} + 4\sum_1^\infty\sum_1^\infty \frac{\operatorname{cosech}(4m^2/3+4n^2/c^2)^{1/2}\pi}{(4m^2/3+4n^2/c^2)^{1/2}}\right) \\ & + \frac{4\sqrt{3}}{c}\left(2\sum_1^\infty \frac{\operatorname{cosech}(\sqrt{12}\pi m/c)}{\sqrt{12}m/c} + 4\sum_1^\infty\sum_1^\infty \frac{\operatorname{cosech}(12m^2+12n^2/c^2)^{1/2}\pi}{(12m^2+12n^2/c^2)^{1/2}}\right) \\ & - \frac{\sqrt{3}}{c}\left(2\sum_1^\infty (-1)^m \frac{\operatorname{cosech}(\sqrt{3}\pi m/c)}{\sqrt{3}m/c}\right. \\ & \left. + 4\sum_1^\infty\sum_1^\infty (-1)^{m+n} \frac{\operatorname{cosech}(3m^2+3n^2/c^2)^{1/2}\pi}{(3m^2+3n^2/c^2)^{1/2}}\right). \end{aligned}$$

We have evaluated these for several values of c (table 1, column 2). The only corresponding results we know in the literature are those given by Hund (1925, 1935) for $c=2$ and $c=\sqrt{(\frac{8}{3})}$. The latter value for c is the so-called ideal ratio. Hund's values were calculated by the traditional Ewald method and the numerical accuracy was low. He gives

$$H(1:\sqrt{(\tfrac{8}{3})})=-2.238 \qquad H(1:2)=-1.796.$$

As in the case of the three cubic lattices we convert the values in terms of e^2/R into terms of e^2/r_s. For the simple hexagonal lattice the volume of a unit cell is $3\sqrt{3}cR^3/2$ and with three electrons per cell the volume per electron is $\sqrt{3}cR^3/2$. Hence

$$\sqrt{3}cR^3/2=4\pi r_s^3/3 \qquad r_s/R=(3\sqrt{3}c/8\pi)^{1/3}.$$

Multiplying $H(1:c)$ by $(3\sqrt{3}c/8\pi)^{1/3}$ yields $U(\text{hex})$ in terms of e^2/r_s (table 1, column 3). It is seen there that $U(\text{hex})$ has a minimum for c near 1. The speed with which $H(1:c)$ may be computed using (27) prompted us to locate the minimum more precisely and it occurs near $c=0.93$ (table 2).

We have also evaluated U for the hexagonal close-packed (HCP) structure, which may be regarded as two equal interpenetrating hexagonal crystals with ideal axial ratios, one lattice based at the origin (0, 0, 0) and the other at $(\frac{1}{2},\frac{1}{3},\frac{1}{2})$. The lattice sums for such a structure in terms of R may be written

$$\begin{aligned}\text{HCP}(2s) &= H(2s:\sqrt{(\tfrac{8}{3})})+\sum[(m-\tfrac{1}{2})^2+3(n-\tfrac{1}{6})^2+\tfrac{8}{3}(p-\tfrac{1}{2})^2]^{-s}\\ &\quad+\sum[m^2+3(n-\tfrac{1}{3})^2+\tfrac{8}{3}(p-\tfrac{1}{2})^2]^{-s}\\ &= H(2s:\sqrt{(\tfrac{8}{3})})+H^*(2s). \qquad (28)\end{aligned}$$

Table 1.

c^2	$U(\text{hex})/(e^2/R)$	$U(\text{hex})/(e^2/r_s)$
$\frac{1}{4}$	−3.263 230 504	−1.531 505 030
$\frac{9}{16}$	−3.253 618 321	−1.747 971 578
$\frac{3}{4}$	−3.143 633 242	−1.771 826 683
1	−2.995 711 953	−1.771 389 474
$\frac{3}{2}$	−2.730 799 747	−1.727 636 634
2	−2.502 936 140	−1.661 251 716
$\frac{8}{3}$	−2.238 722 127	−1.558 866 728
4	−1.795 017 494	−1.337 291 317

Table 2.

c^2	$U(\text{hex})/(e^2/r_s)$
0.91	−1.774 209 795
0.92	−1.774 594 877
0.928	−1.774 642 569
0.93	−1.774 640 829

Again our principle gives $U(\text{HCP})=\text{HCP}(1)$ in terms of R for an electron lattice. $H(1:\sqrt{(\frac{8}{3})})$ is given by (27) and in table 1. In terms of cosech sums we have the rapidly convergent identity:

$$H^*(1)=-2\sqrt{2}\pi/9-\sum_1^\infty \frac{\operatorname{cosech}(\sqrt{32}\pi m/3)}{m}$$

$$+\frac{2\sqrt{3}}{3}\sum_1^\infty \frac{\operatorname{cosech}(\sqrt{\tfrac{32}{3}}\pi m}{m}-\frac{1}{3}\sum_1^\infty \frac{\operatorname{cosech}(\sqrt{32}\pi m)}{m}$$

$$+4\sqrt{2}\sum_1^\infty\sum_1^\infty [1+(-1)^{m+n}]\frac{\operatorname{cosech}((8m^2/3+8n^2)^{1/2}\pi)}{(8m^2/3+8n^2)^{1/2}}$$

$$-\frac{4\sqrt{2}}{3}\sum_1^\infty\sum_1^\infty [1+(-1)^{m+n}]\frac{\operatorname{cosech}((8m^2/3+8n^2/9)^{1/2}\pi)}{(8m^2/3+8n^2/9)^{1/2}}.$$

For the HCP structure the volume of a hexagonal cell is $3\sqrt{2}R^3$ but there are six electrons per cell. Hence we have

$$\sqrt{2}R^3/2=4\pi r_s^3/3 \qquad r_s/R=(3\sqrt{2}/8\pi)^{1/3}$$

and we obtain

$$U(\text{HCP})=-3.241\,858\,662e^2/R=-1.791\,676\,267e^2/r_s.$$

Foldly (1978), by the traditional method, found that $U(\text{HCP})=-1.791\,676\,24e^2/r_s$ and noted that it the axial ratio is 1.0016 times the ideal value then the last two figures read 90 instead of 24, and he claims this is the real minimum.

We present one final example of the diamond lattice. This may be considered as two equal interpenetrating FCC lattices, one based on $(0,0,0)$ the other on $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. In terms of the cube side of an FCC lattice the diamond lattice sums are easily shown to be

$$\text{di}(2s)=\text{FCC}(2s)+2^{2s-1}[\text{BCC}(2s)-\text{SC}(2s)]$$

and again our principle gives $U(\text{di})=\text{di}(1)$ in terms of e^2/a_0. Using (4)-(7)

$$\text{di}(1)=\frac{a(1)+3c(1)+d(1)}{2}=-5.386\,789\,045.$$

For the diamond lattice the volume of a cubic cell is a_0^3 and this has eight electrons per cell. Hence

$$a_0^3/2=4\pi r_s^3 \qquad r_s/a_0=(3/32\pi)^{1/3}$$

and we obtain

$$U(\text{di})=-1.670\,851\,406e/r_s$$

in complete agreement with Foldy's (1978) value obtained conventionally. For all the three-dimensional structures considered the BCC remains energetically the most stable.

Appendix

Let

$$\sigma_N(s) = \sum_{-N}^{N}\sum_{-N}^{N}(m^2+n^2)^{-s} - \iint_{-(N+1/2)}^{N+1/2} \frac{dx\,dy}{(x^2+y^2)^s}. \tag{A1}$$

We now show that $\lim_{N\to\infty}\sigma_N(s)$ exists, is analytic for $0<\operatorname{Re} s<1$, and equals $a_2(2s)$, the analytic continuation of the infinite series. We consider a bounded region $\Omega := \{s|\operatorname{Re} s > c > 0, |s| < R\}$. All order terms will be uniform with respect to s in Ω. We require a lemma.

Lemma. If f is any twice continuously differentiable function

$$\left| N^{-1}\sum_{n=1}^{N} f\left(\frac{n}{N}\right) - \int_0^1 f(t)\,dt - \frac{1}{2N}[f(1)-f(0)]\right| \leq \frac{M}{N^2}$$

where

$$M = \tfrac{1}{12}\sup_{0\leq t\leq 1}|f''(t)|.$$

This follows from the trapezoidal rule or the Euler-MacLaurin summation formula.

Now recall from (24) and (25) that the integral on the right-hand side of (A1) is equal to

$$4\frac{(N+\frac{1}{2})^{2-2s}}{1-s}\int_0^1 (1+t^2)^{-s}\,dt$$

which also supplies an analytic continuation of the original integral in the right half-plane. Thus

$$\begin{aligned}
\sigma_N(s) &= \sigma_{N-1}(s)\\
&= 8\sum_{n=1}^{N}(N^2+n^2)^{-s} + 4N^{-2s}(1-2^{-s})\\
&\quad -\frac{4}{1-s}[(N+\tfrac{1}{2})^{2-2s}-(N-\tfrac{1}{2})^{2-2s}]\int_0^1 (1+t^2)^{-s}\,dt\\
&= \frac{8}{N^{2s-1}}\left\{\frac{1}{N}\sum_{n=1}^{N}\left[1+\left(\frac{n}{N}\right)^2\right]^{-s} - \int_0^1 (1+t^2)^{-s}\,dt - \frac{2^{-s}-1}{2N}\right\}\\
&\quad +\frac{4}{N^{2s-2}}\int_0^1 (1+t^2)^{-s}\,dt\left\{\frac{2}{N}-\frac{1}{s-1}\left[\left(1+\frac{1}{2N}\right)^{2-2s}-\left(1-\frac{1}{2N}\right)^{2-2s}\right]\right\}\\
&= \frac{8}{N^{2s-1}}\left[O\left(\frac{1}{N^2}\right)\right] \qquad \text{(by the lemma)}\\
&\quad +\frac{4}{N^{2s-2}}\int_0^1 (1+t^2)^{-s}\,dt\left[O\left(\frac{1}{N^3}\right)\right].
\end{aligned}$$

Hence $\delta_N(s) := \sigma_N(s) - \sigma_{N-1}(s)$ is analytic in Ω and $|\delta_N(s)| \leq MN^{-2c-1}$ where M is independent of s in Ω. It follows that

$$\sigma(s) = \lim_{N\to\infty} \sigma_N(s) = \sum_{n=1}^{\infty} [\sigma_n(s) - \sigma_{n-1}(s)] + \sigma_0(s) = \delta(s) + \sigma_0(s)$$

where, by the Weierstrass M test, $\delta(s) := \lim_{N\to\infty} \sigma_N(s) - \sigma_0(s)$ is analytic in Ω and so for $\operatorname{Re} s > 0$. However

$$\sigma_0(s) = -\int_{-1/2}^{-1/2}\int \frac{dx\,dy}{(x^2+y^2)^s}$$

is analytic only for $0 < \operatorname{Re} s < 1$. Now for $\operatorname{Re} s > 1$, $\delta(s)$ can be explicitly evaluated from (25) to give

$$\delta(s) = a_2(2s) - \lim_{N\to\infty} 4C(s)\frac{(N+\frac{1}{2})^{2-2s} - (\frac{1}{2})^{2-2s}}{2-2s}$$

so that

$$\delta(s) = a_2(2s) + 4\frac{C(s)2^{2s-2}}{2-2s} \tag{A2}$$

where

$$C(s) = \int_{-1}^{1} \frac{dx}{(1+x^2)^2}.$$

By analytic continuation (A2) holds for $\operatorname{Re} s > 0$ since all three functions in (A2) are meromorphic for $\operatorname{Re} s > 0$. Now for $0 < \operatorname{Re} s < 1$ one may explicitly integrate σ_0 to obtain $\sigma_0(s) = -4.2^{2s-2}C(s)/(2-2s)$. Hence for $0 < \operatorname{Re} s < 1$

$$\lim_{N\to\infty} \sigma_N(s) = \delta(s) + \sigma_0(s) = a_2(2s)$$

which gives the desired result. (Note that, for $\operatorname{Re} s > 1$, $\sigma_N(s) = \infty$ for each N.)

Note added in proof. Our attention has been drawn to a paper by Bonsall and Maradudin (1977). They have calculated the lattice energy of two-dimensional crystals by the traditional method. Their results and ours agree precisely.

References

Bonsall L and Maradudin A A 1977 *Phys. Rev.* B **15** 1959-73
Born M and Misra R D 1940 *Proc. Camb. Phil. Soc.* **36** 466-78
Borwein D, Borwein J M and Taylor K F 1985 *J. Math. Phys.* **26** 2999-3009
Borwein J M and Borwein P B 1987 *Pi and the AGM* (New York: Wiley)
Coldwell-Horsfall R A and Maradudin A A 1960 *J. Math. Phys.* **1** 395-404
Foldy L L 1978 *Phys. Rev.* B **17** 4889-94
Fuchs K 1935 *Proc. R. Soc.* **151** 585-602
Hardy G H 1919 *Mess. Math.* **49** 85-91
Hund F 1925 *Z. Phys.* **34** 833-57
—— 1935 *Z. Phys.* **94** 11-21
Jacobi G G I 1829 *Fundamenta Nova Theoriae Functionum Ellipticarum* (Konigsberg)

Lorentz L 1871 *Tidsskrift Math.* **1** 97-114
Misra R D 1940 *Proc. Camb. Phil. Soc.* **36** 173-82
Wigner E P 1934 *Phys. Rev.* **46** 1002-11
Zucker I J 1975 *J. Phys. A: Math. Gen.* **8** 1734-45
—— 1976 *J. Phys. A: Math. Gen.* **9** 499-505
Zucker I J and Robertson M M 1976 *J. Phys. A: Math. Gen.* **9** 1215-25