# Correction to Fuchs' calculation of the electrostatic energy of a Wigner solid

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In 1959 Plaskett found an error in Fuchs' calculation of the electrostatic energy of a Wigner solid and calculated the additive, lattice-dependent, correction term for the three cubic lattices. We extend his theory to treat any Bravais lattice in one, two, or three dimensions, showing that there is no correction term in one and two dimensions. For the simple hexagonal lattice, we calculate the correction term as a function of arbitrary $r = c/a$ ratio and find it has a minimum value at $r = r_m = (5/6)^{1/2}$. The magnitude of the correction $A$ to Fuchs' value $S$ can be 20% or more of $|S|$, and $|A_{\rm fcc} - A_{\rm bcc}|$ is much larger than $|S_{\rm fcc} - S_{\rm bcc}|$. If sph refers to a spherical approximation, we find $A_{\rm sph} < A_{\rm bcc} < A_{\rm fcc} < A_{\rm sh}(\rm min) < A_{\rm sc} < A_{\rm sh}$ (ideal), where *ideal* refers to $r_i = (8/3)^{1/2}$ and sh and sc mean simple hexagonal and simple cubic, respectively. The $A_{\rm bcc}$ reported by Callaway in another connection is incorrect.

## I. INTRODUCTION

The widely used method of Fuchs[1] for calculating the electrostatic energy of a Wigner[2] solid contains a serious error; this paper supplies the "correction terms" for three-dimensional Bravais lattices and shows there are no correction terms for one- and two-dimensional Bravais lattices. In three dimensions, the correction term may contribute a 20% or more change in the Fuchs value, but more important than its magnitude is its structure dependence, making it especially important in considering competing lattices. It is intimately related to an average potential, which arises elsewhere in solid-state theory and has been evaluated incorrectly by Callaway[3] in one case.

A Wigner solid is a theoretical model formed from one or more point charges per unit cell with a uniform neutralizing background of charge. Its early uses were directed toward electron (or hole) lattices and metallic hydrogen representations, with Fuchs'[1] work being 43 years ago. But interest has continued in it, especially in the last two decades, as representations of many phenomena including inversion layers near the surface of semiconductors, an electron crystal slightly above a free surface of liquid helium subjected to a perpendicular electric field, white dwarf stars, and crusts of pulsars. There is a great deal of literature on the subject; perhaps the papers listed in Ref. 4 suffice if one includes the references given by them. One might first refer to the work quoted there of Maradudin *et al.*,[4(a),4(b)] Carr *et al.*,[4(c)] Foldy,[4(d)] Care and March,[4(e)] Ashcroft *et al.*,[4(f),4(g)] de Wette,[4(h)] Herring and Hill,[4(i)] and Dyson.[4(j)] Unfortunately, our most important reference is to unpublished work, namely, that of Plaskett[5] who in 1959 uncovered the error and calculated the correction term for the three cubic lattices. We shall extend his work to treat the noncubic Bravais lattices in three dimensions and to treat the one- and two-dimensional Bravais lattices. With our Appendices, we independently check (and verify) Plaskett's evaluation of the cubic terms, which arise elsewhere in solid-state theory and for which Callaway's[3] result for the body-centered cubic is in error. We give the correction term for simple hexagonal with arbitrary $c/a$ ratio as a prototype of a noncubic Bravais lattice and as an example showing how the term varies as the lattice is deformed.

Consider a periodic charge distribution constructed as follows: Let point charges be placed on the lattice points of an $n$-dimensional ($n = 1, 2, 3$) Bravais lattice $\{\vec{\tau}\}$ embedded in a three-dimensional Euclidean space, and let there be a neutralizing uniform background of charge confined to the $n$-dimensional manifold. This we refer to as a Wigner[2] solid. The electrostatic energy of one point charge interacting with all other point charges and with the background is given by

$$K \equiv Q^2 \sum_{\tau}^{\infty\prime} \left( \frac{1}{\tau} - \frac{1}{\Omega} \int_{\tau} \frac{d^n r}{r} \right) - \frac{Q^2}{\Omega} \int_0 \frac{d^n r}{r} , \qquad (1.1)$$

where $\Omega$ is the "volume" per lattice point, $Q$ is the value of the point charge, and the cellular integrations are taken over proximity or primitive cells, with which not being specified yet. Also not yet specified are where the lattice point is located within a cell and the order in which the lattice points will be covered in the summation. For an arbitrary choice of these unspecified items, in general one does not have absolute convergence, and therefore $K$ is not uniquely defined. If one ignores this fact and without careful analysis applies the $\theta$-function method (TFM) of Ewald,[6] one will have followed the Fuchs procedure and will

 

conclude as he did that $K$ is equal to the well-defined quantity we denote with $S$,

$$S \equiv Q^2 \int_0^\infty \frac{1}{\sqrt{\pi x}} \left[ \sum_\tau{}' \exp(-x\tau^2) - \frac{1}{\Omega}\left(\frac{\pi}{x}\right)^{n/2} \right] dx$$

$$= Q^2 \int_0^\infty \frac{1}{\sqrt{\pi x}} \left[ \frac{1}{\Omega}\left(\frac{\pi}{x}\right)^{n/2} \sum_\gamma{}' \exp(-\gamma^2/4x) - 1 \right] dx$$

$$= \frac{4\pi Q^2}{\Omega} \int_0^\infty (4\pi y)^{(n-3)/2} \times \left( \sum_\gamma{}' \exp(-y\gamma^2) - \frac{\Omega}{(4\pi y)^{n/2}} \right) dy, \quad (1.2)$$

where $\{\vec{\gamma}\}$ is the reciprocal lattice normalized by $\exp(i\vec{\gamma}\cdot\vec{\tau}) = 1$. This may be evaluated by the TFM.[7,8] However, as Plaskett[5,9] showed, it is incorrect to equate $K$ and $S$, even for the cubic lattices where with centered proximity cells one has absolute convergence in Eq. (1.1). In particular, Plaskett showed for the three cubic lattices that

$$K = S + A, \quad (1.3)$$

where the "correction term" $A$ for these lattices is given by

$$A = \left(\frac{2\pi Q^2}{3\Omega}\right) W, \quad W = \frac{1}{\Omega}\int_0 r^2 d^3r, \quad (1.4)$$

where the integration is taken over a centered proximity cell of the $\tau$ lattice; hence $A$ is lattice dependent.

For absolute convergence in Eq. (1.1) we need the charge in one cell to satisfy three conditions for three-dimensional lattices: (i) be neutral (which is automatically satisfied in our model); (ii) have no dipole moment (which is satisfied for centered cells, either proximity or general primitive); and (iii) have no quadrupole moment. Centered proximity cells for the cubics have no quadrupole moment, but even for centered proximity cells the general three-dimensional Bravais lattice has nonzero quadrupole moments. These facts permit us to understand that correction terms should exist, and it is also possible to state without going into details how the $A$ term is lost in the Fuchs procedure.

Imagine that for a given lattice one has chosen two different cells (for the cellular integrations) leading to two different values of $K$ as defined by Eq. (1.1). Then clearly both of these cannot be equal to $S$, which is independent of the choice of cell. This tells us that some correction to $S$ is necessary, although it does not tell us that it may be expressed as an additive quantity. Thus we should expect some modification of Fuchs's result $K = S$ for the noncubic Bravais lattices with centered proximity cells, which would be lattice dependent. Whether or not the cubic lattices with centered proximity cells should also have a modification might not be clear at this stage.

How is the $A$ lost in the Fuchs method? In applying the TFM to Eq. (1.1), at a certain stage one would like to interchange the order of an integration and a summation, which, if done, leads to a loss of $A$. In Plaskett's work and in our extensions, the orders are still reversed so the TFM can be applied, but a correction term is found.

The correction term $A$ can be quite large, 20% or more of $S$, but of more significance in studies of competing structures is the fact that the differences between the $A$'s for two different structures can be many times larger than the differences between the $S$'s.

For one- and two-dimensional Bravais lattices, conditions (i) and (ii) above are satisfied by use of centered proximity cells, and that is all one needs to ensure absolute convergence. Conceivably there might still be a nonzero correction term, but we shall show there is not any. Thus, for example, the paper by Coldwell-Horsfall and Maradudin[4(a)] is in error, but that by Bonsall and Maradudin[4(b)] does not contain this error.

The TFM applied to the particular problem of evaluating $S$ is detailed in an appendix of the paper by Coldwell-Horsfall and Maradudin,[4(a)] where they evaluate $S$ for the three cubic lattices. More recently, Foldy[4(d)] has evaluated $S$ to ten significant figures for cubic lattices and for hexagonal close packed (non-Bravais) and slightly deformed body-centered cubic and hexagonal close packed. By the procedures of this paper, the $A$ for any Bravais lattice may be evaluated fairly easily to any desired accuracy, but we do not here report on an $A$ for a non-Bravais lattice.

In Appendix A we outline Plaskett's proof of Eqs. (1.3) and (1.4) for the cubic lattices. In Sec. II we extend Plaskett's work to secure the analogs of Eqs. (1.3) and (1.4) for noncubic Bravais lattices in three dimensions. In Sec. III we treat the one- and two-dimensional Bravais lattices. In Sec. IV we discuss our results with the aid of two tables, with the first table giving results of a study of the correction term for several lattices and the second table giving results for $A$, $S$, and $K$ for an electron lattice on the three cubic lattices.

## II. CORRECTION TERM FOR GENERAL THREE-DIMENSIONAL BRAVAIS LATTICES

We now extend the methods of Appendix A for the cubic lattices to treat a general Bravais lattice $\{\vec{\tau}\}$. Again we define $K$ by

$$K = Q^2 \sum_\tau{}' \left( \frac{1}{\tau} - \frac{1}{\Omega}\int_\tau \frac{d^3r}{r} \right) - \frac{Q^2}{\Omega}\int_0 \frac{d^3r}{r}. \quad (2.1)$$

As discussed in Sec. I, for absolute convergence in Eq. (2.1) on three-dimensional lattices we need the charge in one cell to satisfy three conditions: (i) be neutral; (ii) have no dipole moment; and (iii) possess no quadrupole moments, with all three being satisfied for cubic lattices with centered proximity cells. The problem with the noncubic Bravais lattices is that even a centered proximity cell in general gives nonvanishing quadrupole moments, yielding conditional convergence in Eq. (2.1) and nonuniqueness in the definition of $K$. (Nevertheless, it will be noted that however the limit in the summation is taken, at each stage the total charge associated with the finite sum is neutral.)

For the general Bravais lattice we fix the definition of $K$ in two steps. First, we use centered proximity cells, and, second, we specify that the $\tau$ lattice be covered by summing first over points within a finite radius and thereafter letting the radius of the sphere go to infinity. This definition provides a consistent basis for comparing any set of "competing" Bravais lattices for two reasons: (a) It is consistent with the unique definition we already have for the cubic lattices; and (b) if a noncubic Bravais lattice is gradually deformed until it becomes a cubic lattice, its $K$ value smoothly changes to that of the appropriate cubic value. This leaves open the question of how to define $K$ consistently for a set of lattices in which some of the lattices are not Bravais, say the set containing the face-centered cubic and the hexagonal-close-packed lattices.

We now have a task in analysis slightly more difficult than that of Appendix A. This arises from the fact that the second equation in Eq. (A11) does not hold for noncubic Bravais lattices, and $b_\tau(t)$ is defined differently, namely, by

$$b_\tau(t) \equiv \exp(-t\tau^2)\frac{1}{\Omega}\int_0 x^2[t - 2(\hat{x}\cdot\vec{\tau})^2t^2]\,d^3x. \tag{2.2}$$

With this new definition we still have an equation like Eq. (A14) holding, namely,

$$K = Q^2 \sum_\tau{}' \,\text{-}\!\!\int_0^\infty \frac{1}{\sqrt{\pi t}}\, a_\tau(t)\,dt$$

$$= Q^2 \sum_\tau{}' \,\text{-}\!\!\int_0^\infty \frac{1}{\sqrt{\pi t}}(a_\tau - b_\tau)\,dt + Q^2 \sum_\tau{}' C_\tau, \tag{2.3}$$

$$C_\tau \equiv \,\text{-}\!\!\int_0^\infty \frac{1}{\sqrt{\pi t}} b_\tau(t)dt\,, \tag{2.4}$$

but, unlike Eq. (A14), here the last term in Eq. (2.3) is not zero in general. Nevertheless, analogs of Eqs. (A16)–(A21) hold, giving finally

$$K = S + L, \tag{2.5}$$

$$L \equiv -Q^2 \,\text{-}\!\!\int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' b_\tau(t) + Q^2 \sum_\tau{}' C_\tau, \tag{2.6}$$

with $S$ still given by Eq. (A23) or Eq. (1.2).

To simplify $L$ further, we use the identity

$$t - 2(\hat{x}\cdot\vec{\tau})^2t^2 = t - \tfrac{2}{3}\tau^2t^2 + \tfrac{2}{3}t^2[\tau^2 - 3(\hat{x}\cdot\vec{\tau})^2], \tag{2.7}$$

yielding

$$L = -Q^2\int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2)\left(\frac{1}{\Omega}\int_0 x^2\,d^3x\right)(t - \tfrac{2}{3}\tau^2t^2)\,dt$$

$$- \tfrac{2}{3}Q^2\int_0^\infty \frac{t^2}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2)\frac{1}{\Omega}\int_0 x^2[\tau^2 - 3(\hat{x}\cdot\vec{\tau})^2]\,d^3x\,dt + Q^2\sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}\left(\frac{1}{\Omega}\int_0 x^2\,d^3x\right)\exp(-t\,\tau^2)(t - \tfrac{2}{3}\tau^2t^2)\,dt$$

$$+ \tfrac{2}{3}Q^2\sum_\tau{}'\int_0^\infty \frac{t^2}{\sqrt{\pi t}}\exp(-t\tau^2)\frac{1}{\Omega}\int_0 x^2[\tau^2 - 3(\hat{x}\cdot\vec{\tau})^2]\,d^3x\,dt. \tag{2.8}$$

By the arguments of Appendix A, the first term in Eq. (2.8) becomes

$$A = \frac{2\pi Q^2}{3\Omega}W, \quad W \equiv \frac{1}{\Omega}\int_0 r^2\,d^3r, \tag{2.9}$$

and the third term vanishes. Denote the sum of the second and fourth terms by $\frac{2}{3}Q^2\Delta$, giving

$$L = A + \tfrac{2}{3}Q^2\Delta. \tag{2.10}$$

We shall next show that $\Delta$ vanishes, which will give the final result

$$K = S + A, \tag{2.11}$$

which is identical to our result for the cubic lattices.

The summand-integrands of the two terms making up $\Delta$ are identical, but the orders of the $t$ integration and the $\tau$ summation are reversed in the two. In both terms we split the domain of $t$ into $0 \leq t \leq 1/4c$ and $1/4c \leq t \leq \infty$, schematically denoting it by writing

$$\Delta=\left(-\int_0^{1/4c}\sum_\tau'-\int_{1/4c}^{\infty}\sum_\tau'\right)+\left(\sum_\tau'\int_0^{1/4c}+\sum_\tau'\int_{1/4c}^{\infty}\right). \tag{2.12}$$

Then we note that the second and fourth terms of Eq. (2.12) cancel, because it follows from the Weierstrass test for uniform convergence that

$$\int_{1/4c}^{\infty}\frac{t^2}{\sqrt{\pi t}}\sum_\tau'\tau^2\exp(-t\tau^2)\frac{1}{\Omega}\int_0 x^2[1-3(\hat{x}\cdot\hat{\tau})^2]\,d^3x\,dt$$
$$=\sum_\tau'\int_{1/4c}^{\infty}\frac{t^2\tau^2}{\sqrt{\pi t}}\exp(-t\tau^2)\frac{1}{\Omega}\times\int_0 x^2[1-3(\hat{x}\cdot\hat{\tau})^2]\,d^3x\,dt, \tag{2.13}$$

yielding

$$\Delta=-\int_0^{1/4c}\frac{t^2}{\sqrt{\pi t}}\sum_\tau'\tau^2\exp(-t\tau^2)\frac{1}{\Omega}\times\int_0 x^2[1-3(\hat{x}\cdot\hat{\tau})^2]\,d^3x\,dt$$
$$+\sum_\tau'\int_0^{1/4c}\frac{t^2}{\sqrt{\pi t}}\tau^2\exp(-t\tau^2)\frac{1}{\Omega}\times\int_0 x^2[1-3(\hat{x}\cdot\hat{\tau})^2]\,d^3x\,dt. \tag{2.14}$$

For use in the second term of Eq. (2.14) note that

$$\lim_{c\to\infty}\int_0^{1/4c}t^{3/2}\exp(-t\tau^2)\,dt=0. \tag{2.15}$$

The first term of Eq. (2.14) can be rewritten with the aid of the Poisson summation formula[8]

$$\sum_\tau'\tau^2[1-3(\hat{x}\cdot\hat{\tau})^2]\exp(-t\tau^2)=\frac{1}{4t^2}\frac{1}{\Omega}\left(\frac{\pi}{t}\right)^{3/2}\sum_\gamma'\gamma^2[3(\hat{x}\cdot\hat{\gamma})^2-1]\exp(-\gamma^2/4t) \tag{2.16}$$

to give

$$-\frac{\pi}{4\Omega}\int_0^{1/4c}\frac{1}{t^2}\frac{1}{\Omega}\int_0 x^2\sum_\gamma'\gamma^2[3(\hat{x}\cdot\hat{\gamma})^2-1]\exp(-\gamma^2/4t)\,d^3x\,dt$$
$$=-\frac{\pi}{\Omega}\int_c^{\infty}\frac{1}{\Omega}\int_0 x^2\sum_\gamma'\gamma^2[3(\hat{x}\cdot\hat{\gamma})^2-1)\exp(-s\gamma^2)\,d^3x\,ds$$
$$=-\frac{\pi}{\Omega^2}\int_0 x^2\sum_\gamma'\gamma^2[3(\hat{x}\cdot\hat{\gamma})^2-1]\int_c^{\infty}\exp(-s\gamma^2)\,ds\,d^3x$$
$$=-\frac{\pi}{\Omega^2}\int_0 x^2\sum_\gamma'[3(\hat{x}\cdot\hat{\gamma})^2-1]\exp(-c\gamma^2)\,d^3x, \tag{2.17}$$

which vanishes as $c$ approaches infinity. Thus $\Delta$ equals zero as required to complete the proof of Eqs. (2.11) and (2.9), which are identical to Eqs. (A22) and (A30), respectively, found by Plaskett for the cubic lattices.

## III. CORRECTION TERM FOR ONE- AND TWO-DIMENSIONAL LATTICES

First consider a two-dimensional Bravais lattice $\{\vec{\tau}\}$, embedded in a three-dimensional space, with an area $\Omega$ per lattice point and with a reciprocal lattice $\{\vec{\gamma}\}$ normalized by $\exp(i\vec{\gamma}\cdot\vec{\tau})=1$. Again, let point charges $Q$ be placed on all lattice points and let there be a uniform neutralizing background of charge. Continuing the analogy, write

$$K\equiv Q^2\sum_\tau'\left(\frac{1}{\tau}-\frac{1}{\Omega}\int_\tau\frac{d^2r}{r}\right)-\frac{Q^2}{\Omega}\int_0\frac{d^2r}{r}, \tag{3.1}$$

with the integrations taken over cells in the plane of the lattice. For absolute convergence here we need

$$\frac{1}{\Omega}\int_\tau\frac{d^2r}{r}=\frac{1}{\tau}+O\left(\frac{1}{\tau^3}\right), \tag{3.2}$$

for which it suffices for the domain of integration to be a centered cell, proximity or primitive. Accordingly, with it understood in the rest of this section that all cellular integrations are taken over centered cells, we turn to the task of modifying the analysis of Appendix A and Sec. II to treat our two-dimensional case.

The proof of the lemma

$$\frac{1}{\Omega}\int_\tau\frac{d^2r}{r}=\int_0^{\infty}\frac{1}{\sqrt{\pi t}}\int_\tau\exp(-tr^2)\,d^2r\,dt \tag{3.3}$$

is identical to that for the lemma of Eq. (A3). Fol-

lowing Eq. (A7), we write

$$K=\overline{K}-\frac{1}{\Omega}\int_0\frac{d^3r}{r},\quad \overline{K}=\sum_\tau{}'\int_0^\infty\frac{1}{\sqrt{\pi t}}a_\tau(t)dt, \tag{3.4}$$

$$a_\tau(t)\equiv\exp(-t\tau^2)-\frac{1}{\Omega}\int_\tau\exp(-tr^2)\,d^2r, \tag{3.5}$$

where we would like to invert the order of summation and integration in Eq. (3.4). Equation (A10) also gives for two dimensions

$$a_\tau(t)=-\exp(-t\tau^2)\times\sum_{n=1}^{\infty}\sum_{m=0}^{n}\frac{(-1)^n}{m!\,(n-m)!}\frac{1}{\Omega}\times\int_0(2\vec{x}\cdot\vec{\tau}t)^m(x^2t)^{n-m}\,d^2x. \tag{3.6}$$

From here the two-dimensional lattices gives rise to a few differences.

For centered cells, we have

$$\int_0\vec{x}\cdot\vec{\tau}\,d^2x=0. \tag{3.7}$$

Thus, if $d$ is the maximum value of $|\vec{x}|$ within the centered cell containing the origin,

$$|a_\tau(t)|\le\exp(-t\tau^2)[\exp(2d\tau+d^2t)-1-2d\tau t], \tag{3.8}$$

which is information we now use to show that the orders of summation and integration in Eq. (3.4) can be inverted. To prove it, we write

$$\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_\tau{}'a_\tau dt=\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau\le T}{}'a_\tau dt+\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau>T}a_\tau dt, \tag{3.9}$$

and we shall show that the last term vanishes as $T$ approaches infinity, which yields

$$\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_\tau{}'a_\tau dt=\lim_{T\to\infty}\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau\le T}{}'a_\tau dt=\sum_\tau{}'\int_0^\infty\frac{1}{\sqrt{\pi t}}a_\tau dt \tag{3.10}$$

as required. The vanishing of the last term in Eq. (3.9) follows from

$$\left|\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau>T}a_\tau dt\right|\le\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau>T}|a_\tau(t)|\,dt=\sum_{\tau>T}\int_0^\infty\frac{1}{\sqrt{\pi t}}|a_\tau(t)|\,dt, \tag{3.11}$$

with the last step following from the monotone convergence theorem of Lebesgue integration. Evaluating the integral, we have

$$\left|\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_{\tau>T}a_\tau dt\right|\le\sum_{\tau>T}\left((\tau^2-2d\tau-d^2)^{-1/2}-\frac{1}{\tau}-\frac{d}{\tau^2}\right)=\sum_{\tau>T}O\left(\frac{1}{\tau^3}\right), \tag{3.12}$$

which is as small as we want, as required, giving

$$\overline{K}=\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_\tau{}'a_\tau(t)\,dt=\int_0^\infty\frac{1}{\sqrt{\pi t}}\sum_\tau{}'\left[\exp(-t\tau^2)-\frac{1}{\Omega}\int_\tau\exp(-tr^2)\right]dt, \tag{3.13}$$

$$K=\int_0^\infty\frac{1}{\sqrt{\pi t}}\left[\sum_\tau{}'\exp(-t\tau^2)-\frac{1}{\Omega}\left(\frac{\pi}{t}\right)\right]dt=\int_0^\infty\frac{1}{\sqrt{\pi t}}\left[\frac{1}{\Omega}\left(\frac{\pi}{t}\right)\sum_\gamma{}'\exp(-\gamma^2/4t)-1\right]dt=\frac{4\pi}{\Omega}\int_0^\infty\frac{1}{\sqrt{4\pi s}}\left(\sum_\gamma{}'\exp(-s\gamma^2)-\frac{\Omega}{4\pi s}\right)ds. \tag{3.14}$$

Thus, for all two-dimensional Bravais lattices $K$ equals $S$ and there is no correction term.

By comparing our discussions of the convergence problems for the two- and three-dimensional lattices and how these lead to a correction term for three-dimensional lattices but not for the two-dimensional ones, it is clear that there are no correction terms for the one-dimensional Bravais lattice.

## IV. DISCUSSION OF RESULTS

In Table I we have collected some of the results detailed in Appendix B on the calculation of the "correction integral" $W$ defined by Eq. (1.4) for the cubic and the simple hexagonal lattices. For comparison among the cubic lattices, we have included Callaway's[3] value of $W$, which appears in the literature in another connection, and the "spherical" approximation" in which the proximity cell is replaced by a sphere of equal volume. It should be noted that Callaway's value for the bcc lattice falls roughly midway between the correct values for bcc and fcc, so the error is not small in comparison with the difference between $W_{\rm fcc}$ and $W_{\rm bcc}$. Also, the difference between $W_{\rm bcc}$ (or Callaway's[3] value for $W_{\rm bcc}$) and $W_{\rm sph}$ is quite large compared to the difference between $W_{\rm fcc}$ and $W_{\rm bcc}$.

In Appendix B we have shown that $W$ for the simple hexagonal (sh) lattice with an arbitrary ratio $r=c/a$ is given by

$$W_{\rm sh}(r)=\left(\frac{4}{3}\right)^{1/3}\frac{(5+3r^2)}{36r^{2/3}}\Omega^{2/3}, \tag{4.1}$$

TABLE I. Correction integral $W$, related to the correction term $A$ by $A=(2\pi Q^2/3\Omega)W$, with $W=\Omega^{-1}\int_0 r^2 d^3r$, and with the integration taken over a centered proximity cell. For cubic lattices, $a$ is the edge length of the fundamental cube.

| Lattice | | |
|---|---|---|
| sc | $\frac{1}{4}a^2=\frac{1}{4}\Omega^{2/3}$ | $\simeq 0.250\,000\,0\Omega^{2/3}$ |
| fcc | $\frac{3}{32}a^2=\frac{3}{32}4^{2/3}\Omega^{2/3}$ | $\simeq 0.236\,235\,1\Omega^{2/3}$ |
| bcc | $\frac{19}{128}a^2=\frac{19}{128}2^{2/3}\Omega^{2/3}$ | $\simeq 0.235\,629\,8\Omega^{2/3}$ |
| bcc (Callaway)[a] | $\frac{\sqrt{221}}{100}a^2=\frac{\sqrt{221}}{100}2^{2/3}\Omega^{2/3}$ | $\simeq 0.235\,984\,1\Omega^{2/3}$ |
| sph approx.[b] | $\frac{3}{5}\left(\frac{9}{16\pi^2}\right)^{1/3}\Omega^{2/3}$ | $\simeq 0.230\,900\,8\Omega^{2/3}$ |
| sh (ideal)[c] | $\frac{13}{36}2^{-1/3}\,\Omega^{2/3}$ | $\simeq 0.286\,614\,1\Omega^{2/3}$ |
| sh (min.)[c] | $\frac{5}{24}(\frac{8}{5})^{1/3}\,\Omega^{2/3}$ | $\simeq 0.243\,668\,1\Omega^{2/3}$ |

[a] J. Callaway, Ref. 3.
[b] See Appendix B. In the spherical approximation to $W$ the centered proximity cell is replaced by a sphere of equal volume.
[c] See Appendix B. The "ideal" value of the ratio $r=c/a$ for simple hexagonal is $(\frac{8}{3})^{1/2}$, and the value for minimum $W$ is $(\frac{5}{6})^{1/2}$.

which has a minimum value at $r=r_m=(\frac{5}{6})^{1/2}$. The corresponding $W_{sh}(\min)$ is seen from Table I to fall roughly midway between $W_{sc}$ and $W_{fcc}$. The order relation

$$W_{sph}<W_{bcc}<W_{fcc}<W_{sh}(\min)<W_{sc}<W_{sh}(\text{ideal}) \tag{4.2}$$

displays some of these results and also shows where $W_{sh}$(ideal) falls, where the "ideal" value of $r$ is $r_i=(\frac{8}{3})^{1/2}$.

The methods we used in Appendix B to evaluate the $W$'s are very straightforward. Clearly, for any Bravais lattice $W$ can be calculated to any desired accuracy, although it may get a little tedious for a proximity cell with many different surface facets (low symmetry of the lattice). Moreover, exact analytical expressions can be found for $W$ as a function of various deformation parameters describing some family of lattices resulting from deformation of a given lattice. As we have illustrated in one simple case, the simple hexagonal lattice with arbitrary $c/a$ ratio, this permits finding extrema of $W$ and hence $A$.

For the cubic electron lattices ($Q=e$), we have used our values of $W$ to calculate in atomic units the associated values of the correction term $A$, which are presented in Table II. We also show Foldy's calculated values of $S$, rounded off to seven significant figures, which suffices for our present purposes.

It is seen immediately that the relative positions of $K=S+A$ for the three lattices remains unchanged in the sense that the bcc lattice is the most stable and the sc the least. However, the addition of the correction term is still important, especially if one wishes to compare these lattices with others or if one contemplates calculations with more sophisticated models including zero-point

TABLE II. In atomic units for an electron lattice ($Q=e$), the electrostatic energy of one electron interacting with all other electrons and the uniform background of charge is given by $K=S+A$, where $A$ is the correction term to the previously reported $S$ value found by the Fuchs' procedure. The energy is in Rydbergs, $r_s$ is in Bohr radii, and the volume per electron is $\frac{4}{3}\pi r_s^3$.

| Lattice | $S\times(2\text{ Ry}/r_s)$ Foldy[a] | $A\times(2\text{ Ry}/r_s)$ This work | $(S+A)\times(2\text{ Ry}/r_s)$ |
|---|---|---|---|
| sc | −1.760 119 | 0.324 815 | −1.435 304 |
| fcc | −1.791 747 | 0.306 931 | −1.484 816 |
| bcc | −1.791 859 | 0.306 144 | −1.485 715 |

[a] L. L. Foldy, Ref. 4(d).

vibrations and various quantum effects. Additionally, it is also clear from the work of Foldy[4(d)] and that of Straus and Ashcroft[4(f)] relating to familiar lattices slightly deformed that the lattice-dependent $A$ should be taken into account in studying competing lattices and stability questions.

Table II shows that $A$ can be an appreciable fraction of $S$, but, more important is the illustration of Table II that the differences between two $A$'s can be greater than the differences between the two associated $S$'s.

There are several calculations not included here that would be of considerable interest; we call attention to two. It would be of interest to have the values of $S$ for the sh lattice calculated for a domain of $c/a$ values containing the value $r_m=(\frac{5}{6})^{1/2}$ for which $W$, and hence, $A$ has a minimum. Whether or not $S$ for the sh lattice has an extremum in the vicinity of $r_m$ is not yet known. A second matter of considerable interest would be the determination of the correction terms for non-Bravais lattices [such as the hexagonal closed packed (hcp) lattice] so that one could consistently compare, say, $K$ for the fcc and the hcp lattices.

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## APPENDIX A

Consider a direct cubic lattice $\{\vec{\tau}\}$ with a volume $\Omega$ per lattice point and the reciprocal lattice $\{\vec{\gamma}\}$ normalized by $\exp(i\vec{\gamma}\cdot\vec{\tau})=1$. Let a point charge $Q$ be placed on all lattice points, and let a uniform neutralizing charge of opposite sign be placed throughout the volume. If the point charges are electrons, this Wigner solid is an electron crystal; if the point charges are protons, this model might be used as a starting point for a representation of metallic hydrogen. The electrostatic energy of interaction of one point charge with all other point charges and the uniform background is given by the quantity

$$K=Q^2\left[\sum_\tau{}'\left(\frac{1}{\tau}-\frac{1}{\Omega}\int_\tau\frac{d^3r}{r}\right)-\frac{1}{\Omega}\int_0\frac{d^3r}{r}\right]. \tag{A1}$$

Since all of the volume is eventually covered by the cellular integrations plus summation, it might appear that either the proximity cell or any valid primitive cell, centered or not, could be used in the integration over a cell, but this is not so. For absolute convergence, hence uniqueness of $K$, we need to use a centered proximity cell, since this is the only choice for which the charge within a cell satisfies all three of the conditions: (i) neutrality of charge; (ii) no dipole moment; and (iii) no quadrupole moment. Then for the cubics we have

$$\frac{1}{\Omega}\int_\tau\frac{d^3r}{r}=\frac{1}{\tau}+O\left(\frac{1}{\tau^4}\right). \tag{A2}$$

Accordingly, in the remainder of this Appendix the use of a centered proximity cell will be understood as being used for the domain of integration in all cellular integrations.

Next we prove the lemma

$$\int_\tau\frac{d^3r}{r}=\int_0^\infty\frac{1}{\sqrt{\pi t}}\left(\int_\tau\exp(-tr^2)\,d^3r\right)dt. \tag{A3}$$

For any finite region $R$, we have

$$\int_R\frac{d^3r}{r}=\int_R\int_0^\infty\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,dt\,d^3r$$

$$=\int_R\int_\epsilon^T\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,dt\,d^3r$$

$$+\int_R\left(\int_0^\epsilon+\int_T^\infty\right)\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,dt\,d^3r, \tag{A4}$$

and

$$\int_R\int_0^\epsilon\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,dt\,d^3r<\int_R\int_0^\epsilon\frac{1}{\sqrt{\pi t}}\,dt\,d^3r$$

$$=2\left(\frac{\epsilon}{\pi}\right)^{1/2}\int_R d^3r,$$

$$\int_R\int_T^\infty\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,dt\,d^3r$$

$$<\int_R\int_T^\infty\frac{1}{\sqrt{\pi T}}\exp(-tr^2)\,dt\,d^3r$$

$$=\frac{1}{\sqrt{\pi T}}\int_R\frac{\exp(-Tr^2)}{r^2}d^3r. \tag{A5}$$

Taking the limits $\epsilon\to 0$ and $T\to\infty$ gives

$$\int_R\frac{d^3r}{r}=\int_0^\infty\int_R\frac{1}{\sqrt{\pi t}}\exp(-tr^2)\,d^3r\,dt, \tag{A6}$$

which completes the proof if $R$ is taken to be the proximity cell centered about the $\tau$ point.

Writing for the moment

$$K=\bar{K}-\frac{Q^2}{\Omega}\int_0\frac{d^3r}{r}, \tag{A7}$$

we have from our lemma

$$\bar{K}=Q^2\sum_\tau{}'\left(\frac{1}{\tau}-\frac{1}{\Omega}\int_\tau\frac{d^3r}{r}\right)$$

$$=Q^2\sum_\tau{}'\int_0^\infty\frac{1}{\sqrt{\pi t}}a_\tau(t)\,dt, \tag{A8}$$

$$a_\tau(t) \equiv \exp(-t\tau^2) - \frac{1}{\Omega}\int_\tau \exp(-tr^2)\,d^3r, \tag{A9}$$

where we now want to investigate the possibility of inverting the order of summation and integration in Eq. (A8).

Toward that end, write

$$\begin{aligned} a_\tau(t) &= \exp(-t\tau^2)\left(1 - \frac{1}{\Omega}\int_0 \exp(-2\vec{x}\cdot\vec{\tau}t - x^2t)\,d^3x\right) \\ &= \exp(-t\tau^2)\left(1 - \frac{1}{\Omega}\int_0 \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}(2\vec{x}\cdot\vec{\tau}t + x^2t)^n\,d^3x\right) \\ &= -\exp(-t\tau^2)\frac{1}{\Omega}\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\int_0 (2\vec{x}\cdot\vec{\tau}t + x^2t)^n\,d^3x \\ &= -\exp(-t\tau^2)\sum_{n=1}^{\infty}\sum_{m=1}^{n}\frac{(-1)^n}{m!(n-m)!}\frac{1}{\Omega}\int_0 (2\vec{x}\cdot\vec{\tau}t)^m \\ &\qquad \times (x^2t)^{n-m}\,d^3x. \end{aligned} \tag{A10}$$

The last expression is further simplified by noting that for centered cubic proximity cells, we have

$$\int_0 \vec{x}\cdot\vec{\tau}\,d^3x = 0, \quad \int_0 (\vec{x}\cdot\vec{\tau})^2\,d^3x = \tfrac{1}{3}\tau^2\int_0 x^2\,d^3x. \tag{A11}$$

Hence,

$$\begin{aligned} a_\tau(t) &= -\exp(-t\tau^2)\sum_n{}^{*}\sum_m{}^{*}\frac{(-1)^n}{m!(n-m)!}\frac{1}{\Omega} \\ &\qquad \times \int_0 (2\vec{x}\cdot\vec{\tau}t)^m(x^2t)^{n-m}\,d^3x + b_\tau(t), \end{aligned} \tag{A12}$$

$$b_\tau(t) \equiv \exp(-t\tau^2)\frac{1}{\Omega}\int_0 x^2(t - \tfrac{2}{3}\tau^2t^2)\,d^3x, \tag{A13}$$

where the asterisk on the summation means that the terms $n=0$; $n=1$, $m=0,1$; $n=2$, $m=2$ have been omitted. Then

$$\begin{aligned} \bar{K} &= Q^2\sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}a_\tau(t)\,dt \\ &= Q^2\sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}(a_\tau - b_\tau)\,dt \\ &\quad + Q^2\sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}b_\tau(t)\,dt. \end{aligned} \tag{A14}$$

The last term in Eq. (A14) is zero, because

$$\tfrac{2}{3}\tau^2\int_0^\infty \exp(-t\tau^2)t^{3/2}\,dt = \int_0^\infty \exp(-t\tau^2)t^{1/2}\,dt, \tag{A15}$$

and we shall prove one can interchange the order of summation and integration on the first term, which will yield

$$\begin{aligned} \bar{K} &= Q^2\sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}a_\tau\,dt \\ &= Q^2\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_\tau{}'[a_\tau(t) - b_\tau(t)]\,dt \\ &= Q^2\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_\tau{}'a_\tau(t)\,dt \\ &\quad - Q^2\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_\tau{}'b_\tau(t). \end{aligned} \tag{A16}$$

To prove the interchangability for the $(a_\tau - b_\tau)$ term, write

$$\begin{aligned} &\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_\tau{}'(a_\tau - b_\tau)\,dt \\ &\qquad = \int_0^\infty \frac{1}{\sqrt{\pi\tau}}\sum_{\tau\le T}{}'(a_\tau - b_\tau)\,dt \\ &\qquad + \int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_{\tau>T}(a_\tau - b_\tau)\,dt, \end{aligned} \tag{A17}$$

the second term of which we shall show goes to zero as $T\to\infty$, which will prove

$$\begin{aligned} &\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_\tau{}'(a_\tau - b_\tau)\,dt \\ &\qquad = \lim_{T\to\infty}\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_{\tau\le T}{}'(a_\tau - b_\tau)\,dt \\ &\qquad = \sum_\tau{}'\int_0^\infty \frac{1}{\sqrt{\pi t}}(a_\tau - b_\tau)\,dt, \end{aligned} \tag{A18}$$

as required.

To show the second term of (A17) vanishes as $T\to\infty$, let $d$ be the maximum value of $|\vec{x}|$ in the proximity cell at the origin. Then we have

$$\begin{aligned} |a_\tau - b_\tau| &\le \exp(-t\tau^2)\sum_n\sum_m{}^{*}\frac{1}{m!(n-m)!} \\ &\qquad \times (2d\tau t)^m(d^2t)^{n-m} \\ &= \exp(-t\tau^2)[\exp(2d\tau t + d^2t) - 1 - 2d\tau t \\ &\qquad - d^2t - 2d^2\tau^2t^2]. \end{aligned} \tag{A19}$$

and

$$\begin{aligned} \left|\int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_{\tau>T}(a_\tau - b_\tau)\,dt\right| &\le \int_0^\infty \frac{1}{\sqrt{\pi t}}\sum_{\tau>T}|a_\tau - b_\tau|\,dt \\ &= \sum_{\tau>T}\int_0^\infty \frac{1}{\sqrt{\pi t}}|a_\tau - b_\tau|\,dt, \end{aligned} \tag{A20}$$

where the last step is by the monotone convergence theorem of Lebesque integration. The last integral is easily evaluated, and we get

$$\left| \int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_{\tau>T} (a_\tau - b_\tau)\, dt \right|$$

$$\leq \sum_{\tau>T} \left( (\tau^2 - 2d\tau - d^2)^{-1/2} - \frac{1}{\tau} - \frac{d}{\tau^2} - \frac{2d^2}{\tau^3} \right)$$

$$= \sum_{\tau>T} O\left(\frac{1}{\tau^4}\right), \tag{A21}$$

which is as small as we want, as required.

Thus with Eqs. (A7), (A8), and (A16), we have secured

$$K = S + A, \tag{A22}$$

$$S \equiv Q^2 \int_0^\infty \frac{1}{\sqrt{\pi t}} \left[ \sum_\tau{}' \exp(-t\tau^2) - \frac{1}{\Omega}\left(\frac{\pi}{t}\right)^{3/2} \right] dt, \tag{A23}$$

$$A \equiv -Q^2 \int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' b_\tau(t), \tag{A24}$$

with other forms of $S$ given in Eq. (1.2). In the published literature $K$ has been set equal to $S$, which leads us to call $A$ a "correction term" in this paper. We now simplify greatly the expression for $A$ in Eq. (A24) (which cannot be integrated term by term).

Equations (A13) and (A24) give

$$A = -Q^2 \int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2) \frac{1}{\Omega} \int_0 x^2 (t - \tfrac{2}{3}\tau^2 t^2)\, d^3x\, dt$$

$$= -\frac{Q^2}{\Omega} \int_0 x^2 d^3x \int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2)(t - \tfrac{2}{3}\tau^2 t^2)\, dt. \tag{A25}$$

The Poisson summation formula[8] gives

$$\sum_\tau{}' \exp(-t\tau^2)(t - \tfrac{2}{3}\tau^2 t^2)$$

$$= \frac{1}{6\Omega}\left(\frac{\pi}{t}\right)^{3/2} \sum_\gamma{}' \gamma^2 \exp(-\gamma^2/4t) - t. \tag{A26}$$

We substitute (A26) into (A25) and set $t = 1/4s$ to give

$$J \equiv \int_0^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2)(t - \tfrac{2}{3}\tau^2 t^2)\, dt$$

$$= \frac{1}{6\Omega} \int_0^\infty \frac{1}{\sqrt{\pi t}} \left[ \left(\frac{\pi}{t}\right)^{3/2} \sum_\gamma{}' \gamma^2 \exp(-\gamma^2/4t) - 6\Omega t \right] dt$$

$$= \frac{4\pi}{6\Omega} \int_0^\infty \left( \sum_\gamma{}' \gamma^2 \exp(-s\gamma^2) - \frac{3\Omega}{16\pi^{3/2} s^{5/2}} \right) ds. \tag{A27}$$

We rewrite $J$ as

$$J = \lim_{c\to 0} \left[ \int_{1/4c}^\infty \frac{1}{\sqrt{\pi t}} \sum_\tau{}' \exp(-t\tau^2)(t - \tfrac{2}{3}\tau^2 t^2)\, dt \right.$$

$$\left. + \frac{4\pi}{6\Omega} \int_c^\infty \left( \sum_\gamma{}' \gamma^2 \exp(-s\gamma^2) - \frac{3\Omega}{16\pi^{3/2} s^{5/2}} \right) ds \right]. \tag{A28}$$

It is easily seen that the first term in (A28) vanishes and that we have

$$J = \lim_{c\to 0} \frac{4\pi}{6\Omega} \left( \sum_\gamma{}' \exp(-c\gamma^2) - \frac{\Omega}{(4\pi c)^{3/2}} \right)$$

$$= \lim_{c\to 0} \frac{4\pi}{6\Omega} \left[ \left( \frac{\Omega}{(4\pi c)^{3/2}} \sum_\tau{}' \exp(-\tau^2/4c) - 1 \right.\right.$$

$$\left.\left. + \frac{\Omega}{(4\pi c)^{3/2}} \right) - \frac{\Omega}{(4\pi c)^{3/2}} \right]$$

$$= -\frac{2\pi}{3\Omega}, \tag{A29}$$

giving

$$A = \left(\frac{2\pi}{3\Omega} Q^2\right) W, \quad W = \frac{1}{\Omega} \int_0 r^2\, d^3r \tag{A30}$$

for cubic lattices, where the integration is taken over a centered proximity cell.

## APPENDIX B

In this Appendix we evaluate the quantity

$$W = \frac{1}{\Omega} \int_0 r^2\, d^3r \tag{B1}$$

for the simple cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), and simple hexagonal (sh) lattices, where the integration is in every case taken over a centered proximity cell. For comparison, we also give the approximation to $W$ found by replacing the proximity cell with a sphere of equal volume.

### Simple cubic

The proximity cell is a cube; let $a$ denote its edge length, which gives $\Omega = a^3$. Then

$$W = \frac{1}{a^3} \int_{-a/2}^{a/2} \int_{-a/2}^{a/2} \int_{-a/2}^{a/2} (x^2 + y^2 + z^2)\, dx\, dy\, dz$$

$$= \frac{3}{a^3} \int_{-a/2}^{a/2} \int_{-a/2}^{a/2} \int_{-a/2}^{a/2} x^2\, dx\, dy\, dz = \frac{a^2}{4} = \frac{\Omega^{2/3}}{4}. \tag{B2}$$

### Face-centered cubic

The proximity cell is a polyhedron with 12 equivalent faces, each formed from a parallelogram with sides of equal length. Let $a$ denote the edge length of the fundamental cube containing four lat-

tice points, then $\Omega = 4a^3$. To cover the entire proximity cell, we need consider only one pyramid with one of the parallelograms as base and with a height of $a/2\sqrt{2}$. We take, for the purpose of integration, the base to lie in the $\hat{x},\hat{y}$ plane and the axis of the pyramid to lie along $\hat{z}$. Then we can span the pyramid with the vectors

$$\vec{v}_1 = \frac{a}{8}\hat{x} - \frac{a}{4\sqrt{2}}\hat{y}$$

$$\vec{v}_2 = \frac{a}{8}\hat{x} + \frac{a}{4\sqrt{2}}\hat{y} \tag{B3}$$

$$\vec{v}_3 = \frac{a\sqrt{2}}{4}\hat{z},$$

$$\vec{r} = r_1\vec{v}_1 + r_2\vec{v}_2 + r_3\vec{v}_3,$$

$$-r_3 \le r_1, r_2 \le r_3, \quad 0 \le r_3 \le 1. \tag{B4}$$

The Jacobian for a transformation from Cartesian coordinates to the coordinates $r_1, r_2, r_3$ is given by

$$J = \vec{v}_3 \cdot (\vec{v}_1 \times \vec{v}_2) = \frac{\Omega}{16} = \frac{a^3}{4}. \tag{B5}$$

We also write

$$r^2 = \sum_i \sum_j g_{ij} r_i r_j, \quad g_{ij} = \vec{v}_i \cdot \vec{v}_j \tag{B6}$$

and readily find

$$(g_{ij}) = \left(\frac{a}{8}\right)^2 \begin{pmatrix} 3 & -1 & 0 \\ -1 & 3 & 0 \\ 0 & 0 & 8 \end{pmatrix}. \tag{B7}$$

With these relations we write $W$ as

$$W = \frac{12J}{\Omega} \sum_i \sum_j g_{ij} I_{ij} = \frac{3}{4} \sum_i \sum_j g_{ij} I_{ij}, \tag{B8}$$

$$I_{ij} \equiv \int_0^1 dr_3 \int_{-r_3}^{r_3} dr_2 \int_{-r_3}^{r_3} r_i r_j \, dr_1. \tag{B9}$$

Evaluating the $I_{ij}$ yields

$$I_{11} = I_{22} = \tfrac{4}{15}, \quad I_{33} = \tfrac{4}{5}, \quad I_{12} = 0 = I_{21}, \tag{B10}$$

and

$$W = \tfrac{3}{4}[2g_{11}(\tfrac{4}{15}) + g_{33}(\tfrac{4}{15})] = \tfrac{3}{32}a^2$$

$$= (\tfrac{3}{32})16^{1/3}\Omega^{2/3} \simeq 0.236\,235\,1\,\Omega^{2/3}. \tag{B11}$$

### Body-centered cubic

Let $a$ denote the edge length of the fundamental cube containing two lattice points, so $\Omega = 2a^3$. Then the proximity cell can be constructed from two types of pyramids. One type has a height equal to $\frac{1}{2}a$ and a square base with edge length $a/2\sqrt{2}$; there are six of these with the axes of the pyramids lying along the cubic axes of the fundamental cube. The other has a height of $(a\sqrt{3})/4$ and a hexagonal base with an edge length of $(a\sqrt{2})/4$; there are eight of these with the axes of the pyramids lying along the principal axes of the fundamental cube.

Accordingly let

$$W = W_1 + W_2, \tag{B12}$$

where $W_{1,2}$ denotes the contributions to $W$ from the two respective types of pyramidal volumes. We next evaluate first $W_1$ and then $W_2$.

Consider a pair of pyramids of the first type with tips of the pyramids at the origin of coordinates and with the axes of the pyramids lying along the positive and negative $z$ axes, respectively. Then

$$W_1 = \frac{3}{\Omega}\int_{-a/2}^{a/2} dz \int_{-z/2\sqrt{2}}^{z/2\sqrt{2}} dy \int_{-z/2\sqrt{2}}^{z/2\sqrt{2}} (x^2 + y^2 + z^2)\, dz$$

$$= \frac{3}{\Omega}\int_{-a/2}^{a/2} \left[ z^2 \left( \int_{-z/2\sqrt{2}}^{z/2\sqrt{2}} dx \right)^2 + 2\int_{-z/2\sqrt{2}}^{z/2\sqrt{2}} y^2 dy \int_{-z/2\sqrt{2}}^{z/2\sqrt{2}} dx \right] dz$$

$$= \frac{13a^2}{(5)(64)}. \tag{B13}$$

For the second type, consider a pair of pyramids placed tip to tip at the origin with the pyramidal axes lying along a straight line; for the purpose of integration, choose this line to lie along the $z$-axis so the two parallel bases lie in $x,y$ planes. To span the volume of the pyramids, we choose the vectors

$$\vec{u}_1 = \tfrac{1}{8}a\sqrt{2}(\hat{x} - \sqrt{3}\,\hat{y}),$$

$$\vec{u}_2 = \tfrac{1}{8}a\sqrt{2}(x + \sqrt{3}\,\hat{y}), \tag{B14}$$

$$\vec{u}_3 = \tfrac{1}{4}a\sqrt{3}\,\hat{z}.$$

Then the position vector is conveniently written

$$\vec{r} = R_1\vec{u}_1 + R_2\vec{u}_2 + R_3\vec{u}_3. \tag{B15}$$

The Jacobian for a transformation from Cartesian coordinates to the $R_i$ coordinates is given by

$$J = \vec{u}_3 \cdot (\vec{u}_1 \times \vec{u}_2) = \tfrac{3}{32}\Omega. \tag{B16}$$

In terms of the new coordinates we have

$$r^2 = \sum_i \sum_j G_{ij} R_i R_j, \quad G_{ij} = \vec{u}_i \cdot \vec{u}_j, \tag{B17}$$

and readily find that

$$(G_{ij})=\left(\frac{a^2}{16}\right)\begin{pmatrix}2&-1&0\\-1&2&0\\0&0&3\end{pmatrix}. \tag{B18}$$

We collect these relations and also note that the hexagonal faces (bases of the pyramids) can be viewed as being composed of three parallelograms yielding equal contributions to the integral, giving

$$W_2=\frac{12J}{\Omega}\sum_i\sum_j G_{ij}L_{ij} \tag{B19}$$

$$L_{ij}=\int_{-1}^{1}dR_3\int_0^{R_3}dR_2\int_0^{R_3}R_iR_j\,dR_3. \tag{B20}$$

Evaluating the $L_{ij}$ yields

$$L_{11}=L_{22}=\tfrac{2}{15},\quad L_{33}=\tfrac{2}{5},\quad L_{12}=L_{21}=\tfrac{1}{10}, \tag{B21}$$

$$\begin{aligned}W_2&=\left(\frac{12}{\Omega}\right)\left(\frac{3\Omega}{32}\right)[2G_{11}(\tfrac{2}{15})+G_{33}(\tfrac{2}{5})+2G_{12}(\tfrac{1}{10})]\\&=\tfrac{9}{20}(\tfrac{2}{3}G_{11}+G_{33}+\tfrac{1}{2}G_{12})\\&=\tfrac{9}{20}[\tfrac{2}{3}(\tfrac{1}{8}a^2)+\tfrac{3}{16}a^2-\tfrac{1}{2}(\tfrac{1}{16}a^2)]=\tfrac{69}{640}a^2.\end{aligned} \tag{B22}$$

Finally, we have

$$W=\tfrac{19}{128}a^2=\tfrac{19}{128}4^{1/3}\Omega^{2/3}\cong 0.235\,629\,8\Omega^{2/3}. \tag{B23}$$

### Spherical approximation

If the proximity cell is replaced by a sphere of equal volume and the integration in Eq. (B1) is taken over this sphere, one easily finds that this approximate value of $W$, which we denote with $W_{\rm sph}$, is given by

$$W=\left(\frac{3}{5}\right)\left(\frac{9}{16\pi^2}\right)^{1/3}\Omega^{2/3}\simeq 0.230\,900\,8\Omega^{2/3}. \tag{B24}$$

### Simple hexagonal

The simple hexagonal (sh) lattice provides a case of special interest for two reasons: First, it is a noncubic Bravais lattice, and, second, with variation of its $c/a$ ratio it supplies a one-parameter class of lattices for which we can calculate $W$ as a function of the parameter $r=c/a$. Here we are using the usual notation wherein $a$ is the distance between first neighbors within a close-packed plane, and $c$ is the distance between these planes.

The proximity cell is a right cylinder of height $c$ and with a hexagonal base with edge length $a/\sqrt{3}$, and the volume per lattice point is given by $\Omega=(ca^2\sqrt{3})/2=(r\sqrt{3}\,a^3)/2$. To span its volume, we introduce the vectors

$$\vec{w}_1=\frac{a}{2\sqrt{3}}\hat{x}-\frac{a}{2}\hat{y},\quad \vec{w}_2=\frac{a}{2\sqrt{3}}\hat{x}+\frac{a}{2}\hat{y},\quad \vec{w}_3=c\hat{z}, \tag{B25}$$

$$J=\vec{w}_1\cdot(\vec{w}_2\times\vec{w}_3)=ca^2/2\sqrt{3}=\Omega/3, \tag{B26}$$

$$\vec{r}=s_1\vec{w}_1+s_2\vec{w}_2+s_3\vec{w}_3, \tag{B27}$$

$$r^2=\sum_i\sum_j T_{ij}s_is_j, \tag{B28}$$

$$(T_{ij})\equiv(\vec{w}_i\cdot\vec{w}_j)=\begin{pmatrix}\frac{1}{3}a^2&-\frac{1}{6}a^2&0\\-\frac{1}{6}a^2&\frac{1}{3}a^2&0\\0&0&c^2\end{pmatrix}. \tag{B29}$$

These relations permit us to evaluate $W$ as follows:

$$W=\frac{3}{\Omega}J\sum_i\sum_j T_{ij}J_{ij}, \tag{B30}$$

$$J_{ij}\int_{-1/2}^{1/2}ds_3\int_0^1 ds_2\int_0^1 s_is_j\,ds_1. \tag{B31}$$

The $J_{ij}$ are readily evaluated permitting us to write

$$\begin{aligned}W&=[2T_{11}(\tfrac{1}{3})+T_{33}(\tfrac{1}{12})+2T_{12}(\tfrac{1}{4})]\\&=(\tfrac{1}{36})(5a^2+3c^2)=(\tfrac{1}{36}a^2)(5+3r^2)\\&=(\tfrac{1}{36})(\tfrac{4}{3})^{1/3}\cdot\frac{(5+3r^2)}{r^{2/3}}\Omega^{2/3},\end{aligned} \tag{B32}$$

which is a relatively simple expression for $W$ as a function of $r$.

From Eq. (B32), it is seen that $W$ has a minimum value at $r$ equal to $r_m=(5/6)^{1/2}\simeq 0.913$, where

$$W_m\equiv W(r-r_m)=12(25)^{1/3}\Omega^{2/3}\simeq 0.243\,668\,1\Omega^{2/3}. \tag{B33}$$

It is of interest to compare this value with $W_i=W(r=r_i)$, where $r_i=(\frac{8}{3})^{1/2}$ is the "ideal" ratio. It follows immediately that

$$W_i=\tfrac{13}{36}2^{-1/3}\Omega^{2/3}\simeq 0.286\,614\,1\Omega^{2/3}. \tag{B34}$$

Finally, we collect a portion of the results from this appendix and summarize them in the order relation

$$W_{\rm sph}<W_{\rm bcc}<W_{\rm fcc}<W_{\rm sh}({\rm min})<W_{\rm sc}<W_{\rm sh}({\rm ideal}). \tag{B35}$$

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