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Surface Distortion and Electrostatic Balance of Metals*

Leonard Kleinman

Department of Physics, University of Texas, Austin, Texas 78712

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It is shown that the large internal electrostatic pressure found by Wannier for free-electron metals is a consequence of his having transformed some surface terms into internal terms while discarding other surface terms of the same magnitude. It is also shown that with small distortions of the surface electronic charge density and small displacements of the ions near the surface not only the pressure but also the force on every ion can be made to vanish.

The Hellmann¹-Feynman² theorem states that the total force on an atomic nucleus in a molecule is identically equal to the electrostatic force due to the other nuclei and the electronic charge distribution.³ Wannier *et al.*⁴ calculated the dilatational force for an infinite crystal of lithium and found an internal pressure of 4800 atm, which led them to speculate that simple free-electron-like metals do not exist. The present author⁵ pointed out that they had assumed periodic boundary conditions, that this periodicity is changed by a dilatation and that this change of boundary conditions voids the Hermiticity of the Hamiltonian which is needed for the derivation of the Hellmann-Feynman theorem. It was suggested that in a finite crystal the surface planes of ions would be slightly displaced so that the restoring force would cancel the internal pressure. Recently Wannier⁶ has stated that it is unusual to expect surface effects to cancel a quantity which is so large. It is the purpose of this paper to show that all contributions to the pressure arise at the surface, and that it is only because Wannier has transformed some of these terms into bulk terms, while discarding others, that he obtains his result.

In accordance with the Hellmann-Feynman theorem,

$$P = -\frac{\mathcal{N}}{3a^2N} \frac{\partial H}{\partial a}, \quad (1)$$

where $\mathcal{N} = 2$ for a bcc crystal is the number of atoms per cubic cell, N is the total number of atoms in the crystal, a is the lattice constant, and $\partial H/\partial a$ is the derivative of the electrostatic energy when the nuclei are moved while the electronic charge is held

fixed. We may write

$$\frac{\partial H}{\partial a} = \sum_i \frac{\partial H}{\partial \vec{R}_i} \cdot \frac{\partial \vec{R}_i}{\partial a} = 3 \sum_i \frac{\partial H}{\partial R_{iz}} n_{iz}, \quad (2)$$

where $\vec{R}_i = \vec{n}_i a$ and the components of \vec{n}_i take on half- and whole-integer values in the interior of the crystal. We have

$$\begin{aligned} \frac{\partial H}{\partial R_{iz}} = & Z^2 e^2 \sum_i' \frac{R_{iz} - R_{iz}}{|\vec{R}_i - \vec{R}_i|^3} \\ & - Ze^2 \left(\sum_{\text{cell}} \int \frac{(R_{iz}^0 - R_{iz} + z) \rho(\vec{r})}{|\vec{R}_i^0 - \vec{R}_i + \vec{r}|^3} d^3r \right. \\ & \left. - \int_{\text{all space}} \frac{(R_{iz} - z) \delta \rho(\vec{r})}{|\vec{R}_i - \vec{r}|^3} d^3r \right), \quad (3) \end{aligned}$$

where the prime on the first sum indicates $i \neq l$, R_{iz}^0 is the z component of a vector to the center of the i th unit cell, and we have replaced an integral of the charge density over all space by an integral of the periodic part of the charge density over the i th cell and a sum over all i plus a contribution due to the remaining charge density $\delta \rho(r)$. Note that $\vec{R}_i = \vec{R}_i^0$ except near the surface, where the ions may be displaced from their bulk positions along the surface normal direction,⁷ and that $\delta \rho(r) = 0$ except near the surface, where the charge density may vary from its periodic bulk value. Thus we have

$$P = -\frac{Ze^2 \mathcal{N}}{a^2 N} \sum_i \left(Z \sum_i' \frac{(R_{iz} - R_{iz})}{|\vec{R}_i - \vec{R}_i|^3} \right.$$

$$-\sum_i \int_{\text{cell}} \frac{(R_{iz}^0 - R_{iz} + z) \rho(\vec{r})}{|\vec{R}_i^0 - \vec{R}_i + \vec{r}|^3} d^3r + \int_{\text{all space}} \frac{(R_{iz} - z) \delta\rho(\vec{r})}{|\vec{R}_i - \vec{r}|^3} d^3r \Big) n_{iz} . \quad (4)$$

We note the seemingly trivial result that when the force on the l th ion (the quantity within the parentheses) vanishes for every l , the pressure vanishes. We also note that the force on the l th ion due to the ion and electronic charge density in the i th cell is of short range. This together with the crystal symmetry means that the l th ion contributes to P in Eq. (4) only if it is near the surface. We shall next derive Wannier's⁴ expression for the pressure in an infinite crystal, in which some of the contributions to (4) are transformed into bulk terms while the remaining surface terms (which we show are of the same magnitude) are discarded. This expression does not vanish when the force vanishes on every ion in the bulk.

For the infinite crystal, since every ion is an interior ion, we have $\vec{R}_i^0 = \vec{R}_i$; also, $\delta\rho(\vec{r})$ is at worst a double layer, which gives no force in the interior, plus quadrupole and higher multipoles, which are of short range and also give no force in the interior. Therefore, neglecting $\delta\rho(\vec{r})$ and replacing \vec{R}_i^0 by \vec{R}_i , we may write Wannier's⁴ result

$$P_{\text{internal}} = \frac{\pi Z e^2}{a^2} \sum_j' \left(\frac{Z R_{jz}}{\vec{R}_j^3} - \int_{\text{cell}} \frac{(R_{jz} + z) \rho(\vec{r})}{|\vec{R}_j + \vec{r}|^3} d^3r \right) n_{jz} , \quad (5)$$

where we have taken the average of Eq. (4) with what is obtained from (4) by interchanging i and l and used translational invariance to substitute $-N n_{jz} R_{jz} / R_j^3$ for terms of the form

$$(n_{iz} - n_{il})(R_{iz} - R_{il}) / |R_i - R_l|^3 .$$

Note that even though the force on each ion (the quantity in large parentheses summed over j) vanishes, the quantity in the brackets times n_{jz} does not vanish when summed over j . One might naively suppose that the neglected surface contributions are smaller than the bulk contributions by a factor of $N^{-1/3}$. That this is not the case is due to the factor n_{iz} in Eq. (4) which has the value $\frac{1}{2}N^{1/3}$ on the surface, whereas the factor n_{jz} in (5) is always of order unity because the factor in large parentheses multiplying it rapidly approaches zero as R_j becomes large. The reader should not be misled into thinking that the pressure in the interior of a metal depends on the state of the surface. In principle one could determine the interior pressure by measur-

ing the momentum transfer across an imaginary plane due to electrons crossing it (kinetic pressure) and add to this the effect of forces transmitted across the plane due to the interaction of charges on opposite sides of it. In metals these forces are short range and so the pressure is independent of the state of the surface. This does not justify neglecting surface terms in a Hellmann-Feynman calculation, because the kinetic pressure is not derivable from the local charge distribution.

We have calculated P_{internal} for Li taking $\rho(\vec{r})$ to be a constant. The two terms in Eq. (5) are the z components of the force on an ion at the origin due to another ion located at \vec{R}_j and due to a unit cell of electrons centered at \vec{R}_j . We chose the unit cell to be a rectangular parallelepiped of dimension $a \times a \times \frac{1}{2}a$ so that the z surfaces of the crystal are smooth⁸ (see Fig. 1). We first summed over infinite planes of ions and slabs of electronic charge with fixed n_{jz} . The infinite slabs of charge yield a force identical to an infinite plane of charge of density $1/a^2$ lying in the plane of the ions. This force is just $2\pi/a^2$; however, because the infinite sum over the ions in the plane must be cut off at some finite value, we took the planes of charge to be finite as well so that

$$F_{jz}^{\text{el}} = \left\{ 8 \tan^{-1} \left[1 + 2 \left(\frac{N_{\pm} + \frac{1}{2}}{n_{jz}} \right)^2 \right]^{1/2} - 2\pi \right\} e^2 / a^2 , \quad (6)$$

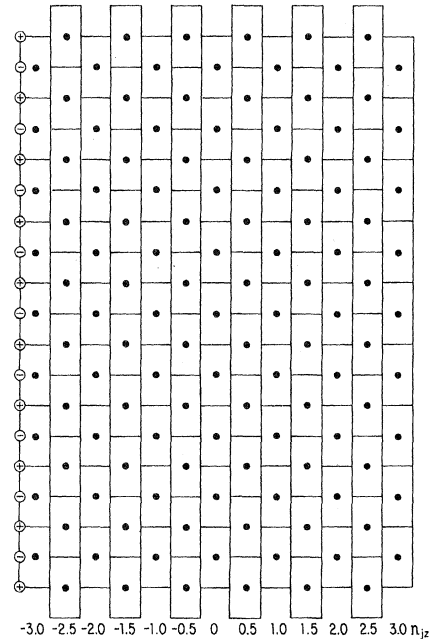


FIG. 1. Rectangular parallelepiped unit cells of a bcc lattice. The positive and negative spheres represent a distortion of the electronic charge on the left-hand surface.

TABLE I. Forces on an ion l due to successive planes of ions plus electrons in bcc structure (in units of e^2/a^2).

$(R_{lx} - R_{lx})/a$	Ions	Electrons	Total
± 0.5	$\pm 5.494\,723\,90$	$\mp 6.279\,654\,19$	$\mp 0.784\,930\,28$
± 1.0	$\pm 6.326\,657\,77$	$\mp 6.276\,186\,61$	$\pm 0.050\,539\,11$
± 1.5	$\pm 6.270\,604\,78$	$\mp 6.272\,591\,96$	$\mp 0.001\,987\,18$
± 2.0	$\pm 6.269\,140\,17$	$\mp 6.269\,052\,04$	$\pm 0.000\,088\,12$
± 2.5	$\pm 6.265\,525\,99$	$\mp 6.265\,529\,78$	$\mp 0.000\,003\,78$
± 3.0	$\pm 6.247\,852\,63$	$\mp 6.261\,985\,48$	$\pm 0.000\,000\,16$

and the ionic force is obtained by summing n_{jx} and n_{jy} between $\pm N_1$. In Table I we list the force due to the ions and the planes of electronic charge. We took $N_1 = 800$ for integer values of n_{jx} and $N_1 = 800.5$ for half-integer values of n_{jx} . Although for these N_1 neither the ionic nor electronic contributions has converged, their sum has converged to the number of significant figures listed. Multiplying the last column in Table I by $e^2 n_{jx}/a^4$ and summing over n_{jx} we obtain

$$P_{\text{internal}} = -110\,000 \text{ atm.} \quad (7)$$

This is to be compared with Wannier's⁴ value of +4800 atm. The difference is a consequence of Wannier having chosen the standard truncated octahedron unit cell, so that the surface of his crystal is waffled. To eliminate this waffling, equal amounts of positive and negative charge must be added at the surface. The $\delta\rho(\vec{r})$ term in Eq. (4) which was neglected by Wannier will then give a contribution of -114 800 atm to the pressure, bringing the two calculations into agreement.⁹

In the real crystal the charge density at the surface will of course be neither waffled nor the step function we have used. We can easily make the pressure vanish by rearranging the surface charge with the addition of small positive and negative spheres of charge¹⁰ as shown in Fig. 1. In Table II we list the force on an ion in the surface plane and in the first two interior planes due to its neighboring planes (calculated directly from Table I) and due to the added surface charges, each chosen to be of magnitude $0.049e$. Because the force on ions further in the interior is negligible and because to order $N^{-1/3}$, $n_{lx} = \frac{1}{2}N^{1/3}$ for these three planes, we see from Eq. (4) that¹¹ $P = -e^2 \mathcal{N}/a^2$ times the sum

TABLE II. Force on ions in the surface and first two interior planes due to all other planes of ions plus electrons and due to surface charge distribution $\delta\rho(r)$.

	Other planes	Surface	Total
Surface	-0.736 29	+0.710 85	-0.025 44
First interior	+0.048 65	-0.022 27	+0.026 38
Second interior	-0.001 90	+0.000 96	-0.000 94

of these forces which vanishes.

Although the total pressure just calculated vanishes, the crystal is not in equilibrium because the force on individual ions does not vanish. It can be made to vanish by allowing the planes of ions to move while keeping the electronic charge fixed, i.e., by allowing n_{lx} to take other than integer and half-integer values. This is a straightforward but tedious calculation for the bcc lattice. On the other hand for a simple cubic crystal the calculation is quite simple. Our simple step-function charge distribution is a much more reasonable model than it was in the bcc case, and so we take $\delta\rho(\vec{r}) = 0$. The force on the surface ions is $+0.05063e^2/a^2$ and on the first interior planes of ions is $+0.00009e^2/a^2$ [obtained by summing the integer $(R_{lx} - R_{lx})/a$ terms in Table I]. As the l th plane of ions moves outward a distance $\Delta_{lx} = (R_{lx} - R_{lx}^0)/a$ in response to this force, a restoring force $-4\pi\Delta_{lx}e^2/a^2$ is set up by the l th slab of electronic charge. Assuming that all except the surface and first interior planes of ions are fixed and interpolating from Table III, we easily find that the surface plane moves outward $0.00395a$ and the first interior plane only $0.00009a$. The second interior plane will move less the 1% of the distance the first interior plane moved and so on for each succeeding plane to make the force vanish on every ion in the crystal.

In conclusion, although the internal pressure in a metal crystal is independent of the state of the surface, the Hellmann-Feynman formula is not. We have shown that Wannier's separation of the Hellmann-Feynman formula into bulk and surface terms is artificial and leads to a conditionally convergent result. We have further shown that for the equilibrium lattice constant of a free-electron metal, not only the pressure but also the force on every ion vanishes according to the Hellmann-Feynman theorem, provided only that there is a slight distortion of the surface charge (relative to the bulk charge) and a very small displacement of the surface ions.

TABLE III. Force on an ion l (in units of e^2/a^2) due to first two neighboring planes of ions plus electrons in simple cubic structure as a function of their separation.

$(R_{lx} - R_{lx})/a^2$	Force
1.000	0.050 539 11
1.001	0.050 212 72
1.002	0.049 888 46
1.003	0.049 566 32
1.004	0.049 246 29
1.005	0.048 928 36
1.006	0.048 612 50
2.000	0.000 088 12
2.002	0.000 087 02
2.004	0.000 085 93
2.006	0.000 084 86

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¹H. Hellmann, *Einführung in die Quantenchemie* (Franz Deuticke, Leipzig, 1937), p. 285.

²R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

³If the core electrons are tightly bound, the theorem can be stated in terms of the ion cores and valence electron charge distribution.

⁴G. H. Wannier, C. Misner, and G. Schay, Jr., *Phys. Rev.* **185**, 983 (1969).

⁵L. Kleinman, *Phys. Rev. B* **1**, 4189 (1970).

⁶G. H. Wannier and G. Meissner, *Phys. Rev. B* **3**, 1240 (1971).

⁷We neglect edges where surface planes intersect.

⁸The fact that the x and y surfaces are corrugated does not effect the z component of force except near the x and y surfaces, but since the sign of this component of force changes as n_{jz} changes by increments of 0.5, it yields a negligible contribution to the pressure, down by a factor

of $N^{-1/3}$ from the terms we are considering.

⁹Equation (5) is conditionally convergent, and one may obtain any value one wishes for P_{internal} by varying either the shape or the location of the center of the unit cells. However, for a finite crystal the pressure given by Eq. (4) is unique, and any change in the definition of the unit cell gives a corresponding change in the definition of the surface charge, so that P remains unchanged.

¹⁰Note that $\delta\rho$ represents the surface charge-density anomaly due to nuclei and electrons of the metal in their free response to whatever external forces act on them; if $\delta\rho$ included the charges producing these external forces Eq. (4) would yield zero pressure for any state of compression (because the total force on every ion always vanishes). Because we use the equilibrium lattice constant, we expect the charge distribution of the metal to be such that Eq. (4) yields zero pressure.

¹¹A factor of 2 due to the two z surfaces cancels the factor of $\frac{1}{2}$.

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Study of the Line Shapes for the Radio-Frequency Size Effect in Cadmium[†]

D. A. Boudreau*[‡] and R. G. Goodrich

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

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The behavior of the line shapes of the radio-frequency size effect has been observed in cadmium both below and in the vicinity of the surface-impedance singularities as a function of surface condition and temperature. It is shown that recent theoretical line-shape calculations based on phenomenological parameters give quantitative and qualitative agreement with experiment, and on the basis of this, inferences on the role of surface scattering in measurements of the radio-frequency surface impedance are outlined. Comments concerning the implications of the present results on past measurements are given.

I. INTRODUCTION

In the past several years, the radio-frequency size effect (RFSE)^{1,2} has become an important and widely used method for investigating the Fermi surfaces (FS) of high-purity metals. This technique involves the measurement of the radio-frequency (rf) surface impedance of a thin slab of a high-purity metal as a function of the dc magnetic field applied in the plane of the slab. At magnetic field strengths such that a large number of electronic orbits just span the sample thickness, a discontinuity in the surface impedance is observed. Through the use of the Lorentz equation, one can then relate real space-orbit dimensions to corresponding FS dimensions in k space in order to extract an extremal caliper of the FS. The necessity of interpreting the various line shapes which occur has been inherent in these studies. In particular, which point of the observed singularity corresponds to the actual FS caliper has been a central problem. In this pursuit, theoretical solutions of the boundary

value problem have been attempted under various assumptions to try to bring into focus the mechanisms involved in selecting the particular electron orbits which give rise to the observed signals. In lieu of a definitive theoretical treatment, some investigators have exploited an observed frequency dependence of the line shapes by using extrapolation methods to obtain caliper values, while others have relied upon the implications of the existing theory, supported by some qualitative agreement found in its general ability to produce a reasonable facsimile of the observed RFSE singularities. Notwithstanding the difficulty in ascribing relative accuracy³⁻⁵ to these two techniques, there is yet another problem involved in that the line shape for a given caliper may vary drastically under seemingly identical experimental conditions.^{6,7} Furthermore, although not central to the issue of caliper point assignment, there remains an associated question concerning the magnetic field dependence of the surface impedance at fields well below that at which the RFSE singularity occurs. The present investigation was made