The Theoretical Constitution of Metallic Beryllium

CONYERS HERRING* AND A. G. HILL
George Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts

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Calculations of total energy as a function of lattice constant, and of some other properties, have been made for metallic beryllium, by a self-consistent field method. Since such calculations have not been made before for any but monovalent metals, the principal object was to find out how far the various assumptions which are usually made in them remain valid for higher valencies, and to test the practicability of certain methods of making the calculations. The theoretical values of binding energy, lattice constant, and compressibility agree reasonably well with experiment. The calculated work function, however, could be made to coincide with the experimental value only by assuming a surface double layer of over 5 volts, which seems impossibly large. This suggests a very large deviation of the exchange energy from the value for completely free electrons. An investigation of the behavior of the exchange energy yields an expression for the deviation from the free electron value which is valid for low electron densities, but not for those which occur in beryllium. The distribution of the electronic states in energy is found to be of the sort needed to account for the diamagnetism of beryllium. Concerning methods of calculation, it is shown that a rather complicated procedure is necessary to obtain quantitative results when a Hartree ion core field is used (as was done in the present case), and that construction of an empirical field is preferable. The assumption $E_k = E_0 + \alpha\hbar^2k^2/2m$, for the energy of an electron with wave vector k, cannot be used for calculations of lattice constant or compressibility for a divalent metal; it is therefore necessary to calculate directly the energies of states near the Fermi surface. This was done by the "orthogonalized plane wave" method, which is shown by tests to be capable of fairly high accuracy, though laborious. This method suggests a simple qualitative way of understanding a number of features of the electronic energy spectrum of a metal and its manner of variation with lattice constant. Incidental results include a proof that the interaction of the $1s$ shells is entirely negligible, and a calculation of the electrostatic interaction energy of the ions as a function of the c/a ratio.

1. INTRODUCTION

THE quantum theory of metals, in the form developed by Wigner and Seitz,[1] has proved rather successful in the explanation and quantitative calculation of a number of properties of alkali metals, such as binding energy, lattice constant, compressibility,[2] and work function.[3] So far no attempt has been made to calculate any of these properties for a divalent metal;[4] moreover, all the metals for which calculations of electronic energy bands[4] have been made have been cubic. The present work on beryllium was undertaken with several objects, of which the most important was that of finding out how far the various assumptions usually made in the application of the theory to monovalent metals remain valid for higher valencies. We also wanted to become familiar with the technique of calculating electronic energies in a crystal of this sort, and in particular to see what additional difficulties are introduced by the fact that the metal is divalent, and by the fact that it has a hexagonal lattice. Finally, we hoped to make a fairly detailed test of the practicability and accuracy of the "orthogonalized plane wave" method of calculating electronic energies and wave functions in crystals, recently described by one of us.[5]

Since the calculations which had to be made for beryllium were considerably more complicated than those which have been made for monovalent metals, and were in addition of an unfamiliar sort, it was not thought wise to try to carry them through with as high a precision as can be attained for alkalis. Nevertheless, sufficient accuracy had to be maintained so that a comparison of the results with experiment

* National Research Fellow, 1937–39. At Princeton University during completion of this work, 1939–40.

[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933) and **46**, 509 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935).

[2] J. Bardeen, J. Chem. Phys. **6**, 367, 372 (1938).

[3] E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935); J. Bardeen, Phys. Rev. **49**, 653 (1936).

[4] In addition to the calculations which have been referred to, there are in the literature calculations of the electron energy levels of a number of solids, made by the cellular method of Slater, Phys. Rev. **45**, 794 (1934). Two of these are for metals with more than one valence electron per atom: M. F. Manning and H. Krutter, Phys. Rev. **51**, 761 (1937), (Ca); M. F. Manning and M. I. Chodorow, Phys. Rev. **56**, 787 (1939) (W). However, in none of these cases has an attempt been made to calculate the total energy of the crystal.

[5] C. Herring, Phys. Rev. **57**, 1169 (1940).

would throw light on the validity of some of the more fundamental assumptions made in the course of the work. It was therefore thought at the beginning that the most convenient thing to do would be to make a Hartree self-consistent field solution for the electrons in the metal by using for the core wave functions the $1s$ wave functions given by Hartree and Hartree[6] for Be^{++}. This self-consistent field solution was obtained, and our final results are based on it; however, the calculation of the total energy from the Hartree wave functions turned out to be rather more laborious than we had anticipated, and in fact both theory and computation would have been much simplified by constructing at the outset an empirical field of the sort used by Seitz[1] for lithium. Section 2 consists in the derivation of the formula (28) for the total energy of a beryllium crystal, in the Hartree approximation; if an empirical field had been used these lengthy calculations would not have been necessary. Section 3 describes the approximately self-consistent potential field used for the calculations. The next four sections are devoted to the problem of finding the Hartree energy parameters E_k for the continuous distribution of valence electron states. The quantities directly calculated for this purpose are: (1) the energy E_0 of the lowest valence electron state, obtained by the method of Wigner and Seitz;[1] (2) $\alpha=(m/\hbar^2)[\partial^2E_k/\partial k^2]_{k=0}$, obtained by the method of Bardeen;[2] and (3) energies E_k of a number of states near the surface of the Fermi distribution, obtained by the orthogonalized plane wave method.[5] The distribution of the electronic states in energy can be estimated from these quantities by a graphical method. It is of less interest to know the number of states per unit range of E than the number per unit range of the quantity η defined by (29), since the latter is more closely connected with the ionization energies of the individual electronic states; consequently the distributions are calculated in Section 7 for η rather than for E. The difference between η_k and E_k consists of a number of terms, which can be calculated if the wave function φ_k is known. The graphical calculations of Section 7 are aided by the use of rough values of $\beta=(m/\hbar^2)(\partial^2E_k/\partial k^2)$, computed for the same wave vectors $\mathbf{k}$ for which the energies E_k mentioned above were calculated. In Section 8 a brief investigation is made of the validity of the assumption, usually made in calculations of this sort, that the exchange energy of the valence electrons in the metal is the same as that of a free electron gas of the same density. Section 9 contains all the results of the present work, and a discussion of their significance.

2. Total Energy in the Hartree Approximation

The notation employed in this and the following sections is for the most part the same as that of reference 5. Atomic units will be used, energies being measured in rydberg units and distances in units of the Bohr radius $\hbar^2/me^2$. For mathematical convenience periodic boundary conditions will be imposed:[7] it will be assumed that the crystal is of practically infinite extent, but that all the wave functions, potentials, etc. are trebly periodic in space, with periods $N_a\mathbf{t}_a$, $N_b\mathbf{t}_b$, $N_c\mathbf{t}_c$, where $\mathbf{t}_a$, $\mathbf{t}_b$, $\mathbf{t}_c$, are three fundamental translations of the crystal lattice, and N_a, N_b, N_c, are three very large integers. The parallelepiped defined by $N_a\mathbf{t}_a$, $N_b\mathbf{t}_b$, $N_c\mathbf{t}_c$, will be called the "fundamental volume" Ω; we assume it to consist of N unit cells each of volume Ω_0 and each containing n atoms ($n=2$ for beryllium). It will be assumed that each unit cell can be divided up into "atomic cells" each of volume Ω_0/n and all alike except for orientation. Mention will frequently be made of an "s sphere": this is a sphere with center at an atomic position and radius r_s so chosen that its volume equals the volume of an atomic cell. The symbol (ψ_1, ψ_2) will be used for the scalar product $\int_\Omega \psi_1^*\psi_2 d\tau$ of any pair of wave functions.

When periodic boundary conditions are employed one cannot speak of the electrostatic potential due to a charge distribution unless the integral of the charge density over Ω vanishes. So if we want to break up the electrostatic potential in the crystal, or the electrostatic self-energy, into contributions from different sources, we must use some artifice. For the potential due to any charge distribution satisfying our periodic

[6] D. R. Hartree and W. Hartree, Proc. Roy. Soc. London **A149**, 210 (1935); **A150**, 9 (1935).

[7] M. Born, Ency. Math. Wiss. 5, iii, p. 587; M. Born and J. H. C. Thompson, Proc. Roy. Soc. **A147**, 594 (1934).

boundary conditions we shall accordingly use what may be called the "neutralized potential" of the distribution.[8] If ρ is such a charge distribution and $\bar{\rho}$ is its average value over Ω, the neutralized potential Φ due to ρ is defined as that solution of

$$\nabla^2\Phi = -4\pi(\rho-\bar{\rho}),$$

which satisfies the periodicity conditions and has average value 0. In other words, Φ is the potential due to the combination of ρ with a homogeneous charge distribution of such sign and density as to neutralize ρ over Ω. It is not hard to see that the final electrostatic energy per atom of a neutral crystal will be independent of whether neutralized or ordinary potentials are used in calculating it. To make the analogy with the usual electrostatic potential as close as possible, we shall write $2Z/D(\mathbf{r})$ for the neutralized potential, in rydbergs per electron, due to a charge Z times the electronic charge located at the origin: thus $D(\mathbf{r})$ is practically the same as r whenever r is small compared with the dimensions of the fundamental volume.

If V_j is the neutralized potential due to the charge distributions of all the Hartree eigenfunctions except φ_j, the Hartree functions φ_j will satisfy

$$(H_0+V_j)\varphi_j = E_j\varphi_j, \tag{1}$$

where

$$H_0 = -\nabla^2 - \sum_\nu 2Z/D(\mathbf{r}-\mathbf{R}_\nu) + c; \tag{2}$$

here Z is the nuclear charge (4 for beryllium), $\mathbf{R}_\nu$ runs over the position vectors of all nuclei in the fundamental volume, and c is a constant fixing the zero for E_j, which we are free to choose as we please. It will be a sufficiently good approximation to assume that when j is a core state φ_j is the same as the Hartree $1s$ function for a free Be^{++} ion (hence that φ_j is localized about a particular atom); when j is a valence electron state φ_j will be taken to be a Bloch wave[9] of the form $\exp(i\mathbf{k}_j\cdot\mathbf{r})u_{k_j}(\mathbf{r})$, where u_{k_j} has the translational periodicity of the lattice. In both cases φ_j is assumed normalized to 1 over Ω, which for the core state is practically infinite. With wave functions of this form V_j is practically the same for all valence electron states, but is different for the core states. Wigner and Seitz have pointed out that the potential for a valence electron inside any s sphere is approximately

$$v(r)+(3X/r_s - Xr^2/r_s^3), \tag{3}$$

where $v(r)$ is the potential due to the ion at the center, and where the second term is the potential due to a charge of X electrons uniformly distributed over the volume of the s sphere ($X=2$ for beryllium). When j is a valence electron state we may write

$$(H_0+V_j) = -\nabla^2 + U_0. \tag{4}$$

The average value of U_0 is equal to c, and it will be convenient to choose c equal to the average of (3) over an s sphere: this may be written

$$c = \frac{3}{4\pi r_s^3}\int_\infty [v(r)+2X/r]d\tau - 3X/5r_s, \tag{5}$$

provided we assume $v(r) = -2X/r$ for $r \gtrsim r_s$.

Since the φ_j for valence electron states are eigenfunctions of a single Hamiltonian, they are all orthogonal to one another. But since the Hamiltonian for the core states is different, the φ_j for valence electron states will not be orthogonal to those for the core states. The customary procedure[10] in determining the total energy by the Hartree method commences by replacing the Hartree eigenfunctions by a set of orthogonal linear combinations of them. Accordingly we shall define the functions

$$\psi_j = \varphi_j + \Delta\varphi_j \tag{6}$$

to be such an orthogonal and normal set. We may specify $\Delta\varphi_j = 0$ when j is a core state (this implies neglect of the small overlap of core functions of different atoms[11]); and when j is a

[8] This conception is similar to that used when electrostatic potentials are calculated by the method of Ewald. See for example the article of M. Born and M. Göppert-Mayer in the *Handbuch der Physik* (Berlin, 2nd ed., 1933), Vol. 24/2, p. 711. We use periodic boundary conditions and neutralized potentials, rather than working with a finite crystal, because it is desirable to be able to break up the electrostatic energy into parts without the danger that some of the parts may depend on the size and shape of the crystal.

[9] F. Bloch, Zeits. f. Physik **52**, 555 (1929).

[10] D. R. Hartree and M. M. Black, Proc. Roy. Soc. London **A139**, 311 (1933).

[11] The effect of such overlapping on the total energy gives just the Heitler-London value for the potential energy of the repulsive force between the ions. It is shown in Appendix I that this repulsive force must be negligible, although no attempt has been made to calculate it for the Hartree wave functions.

valence electron state

$$\psi_j(\mathbf{r}) = \frac{\varphi_j(\mathbf{r}) - \sum_\nu a_j(\nu)\varphi_{1s}(\mathbf{r}-\mathbf{R}_\nu)}{1-\sum_\nu |a_j(\nu)|^2}, \qquad (7)$$

where $a_j(\nu) = (\varphi_{1s\nu}, \varphi_j)$ is the scalar product of the $1s$ function on the νth nucleus with φ_j. In the Hartree approximation the total energy W_H relative to widely separated Be^{++} ions and electrons consists of three parts: the kinetic energy of the valence electrons, the electrostatic energy of the crystal relative to the decomposed state, and the exchange energy minus the exchange energy in the decomposed state. Each of these three must be calculated with the ψ_j.

In calculating the sum of these three terms we need not for the present restrict ourselves to the case of beryllium, and accordingly Eq. (13) below will hold for any values of Z, X, and n. The electrostatic term may be broken up into the neutralized interaction energy of the ions, that of the valence electrons, and that of the ions with the valence electrons. In calculating the neutralized interaction energy of two different ions μ and ν, it is convenient to picture each ion as composed of a positive point charge equal to the charge X carried by an ion, and a neutral distribution consisting of the core electrons and a positive point charge $(Z-X)$. The interaction energy of the neutral distributions of μ and ν is zero, if we neglect overlapping. The energy of the neutral distribution of μ in the neutralized potential due to the point charge X at $\mathbf{R}_\nu$ is

$$\int_\infty \frac{X}{\Omega}[v(|\mathbf{r}-\mathbf{R}_\mu|)+2X/|\mathbf{r}-\mathbf{R}_\mu|]d\tau,$$

where $-X/\Omega$ is the constant charge density used in forming the neutralized potential of the point charge X, and the quantity in brackets is the negative of the (ordinary, not neutralized) potential due to the neutral distribution on μ. Adding twice this to the interaction energy $2X^2/D(\mathbf{R}_\mu-\mathbf{R}_\nu)$ of the point charges gives the neutralized interaction energy of the two ions. We can now write

$$\begin{aligned}\text{Electrostatic part of } W_H = {} & \tfrac{1}{2}\sum_{\mu\neq\nu}\left\{2X^2/D(\mathbf{R}_\mu-\mathbf{R}_\nu)+2X/\Omega\int[v(r)+2X/r]d\tau\right\} \\ & +\tfrac{1}{2}\sum_{i,j\ \text{valence}}\int_\Omega\int_\Omega \frac{\psi_j^*(\mathbf{r})\psi_i^*(\mathbf{r}')2\psi_j(\mathbf{r})\psi_i(\mathbf{r}')d\tau d\tau'}{D(\mathbf{r}-\mathbf{r}')} \\ & +\sum_{j\ \text{valence}}\int_\Omega|\psi_j(\mathbf{r})|^2\sum_\nu\left[\frac{-2Z}{D(\mathbf{r}-\mathbf{R}_\nu)}+\sum_{i\ \text{core on}\ \nu}\int_\Omega\frac{2|\psi_i(\mathbf{r}')|^2}{D(\mathbf{r}-\mathbf{r}')}d\tau'\right]d\tau. \qquad (8)\end{aligned}$$

In the summations in (8) and henceforth, unless otherwise stated, states i or j with the same orbital wave function but different spins are to be counted separately.

Let us introduce the abbreviations $C_{ij}(\psi)$ for the double integral in the second term of (8), and $A_{ij}(\psi)$ for the corresponding exchange integral. Then remembering (1), (2), and (5), the total energy is

$$\begin{aligned}W_H = {} & \sum_{j\ \text{valence}}(\psi_j, H_0\psi_j)+\Big[\tfrac{1}{2}\sum_{i,j\ \text{valence}}+\sum_{\substack{i\ \text{core}\\ j\ \text{valence}}}\Big]C_{ij}(\psi) \\ & -\Big[\tfrac{1}{2}\sum_{\substack{i,j\ \text{valence}\\ \text{spins}\ \|}}+\sum_{\substack{i\ \text{core}\\ j\ \text{valence}\\ \text{spins}\ \|}}\Big]A_{ij}(\psi)+\tfrac{1}{2}\sum_{\mu\neq\nu}2X^2/D(\mathbf{R}_\mu-\mathbf{R}_\nu)+3nNX^2/5r_s. \qquad (9)\end{aligned}$$

We shall now investigate the consequences of inserting (6) in (9). In the first term of (9) we have, using (1)

$$\begin{aligned}(\psi_j, H_0\psi_j) &= (\psi_j, \{H_0+V_j-V_j\}\psi_j) \\ &= -(\varphi_j, V_j\varphi_j)-2\Re(\Delta\varphi_j, V_j\varphi_j)-(\Delta\varphi_j, V_j\Delta\varphi_j) \\ &\quad +E_j[1+2\Re(\varphi_j, \Delta\varphi_j)]+(\Delta\varphi_j, \{H_0+V_j\}\Delta\varphi_j), \qquad (10)\end{aligned}$$

where the symbol $\Re$ means "real part of." Since ψ_j and φ_j are both normalized

$$2\Re(\varphi_j, \Delta\varphi_j) = -(\Delta\varphi_j, \Delta\varphi_j). \tag{11}$$

The second term of (9) is, with neglect of terms containing three or more $\Delta\varphi$'s,

$$\Big[\tfrac{1}{2}\sum_{i,j\text{ valence}} + \sum_{\substack{i\text{ core}\\ j\text{ valence}}}\Big]C_{ij}(\psi) = \Big[\tfrac{1}{2}\sum_{i,j\text{ valence}} + \sum_{\substack{i\text{ core}\\ j\text{ valence}}}\Big]C_{ij}(\varphi)$$
$$+2\Re\sum_{j\text{ valence}}(\Delta\varphi_j, V_j\varphi_j) + \sum_{j\text{ valence}}(\Delta\varphi_j, V_j\Delta\varphi_j)$$
$$+\tfrac{1}{2}\sum_{i,j\text{ valence}}\int_\Omega\int_\Omega \frac{2[2\Re\Delta\varphi_i(\mathbf{r}')\varphi_i^*(\mathbf{r}')][2\Re\Delta\varphi_j(\mathbf{r})\varphi_j^*(\mathbf{r})]}{D(\mathbf{r}-\mathbf{r}')}d\tau d\tau', \tag{12}$$

where $C_{ij}(\varphi)$ is a double integral like the one in (8), but with the ψ's replaced by φ's. Thus the first term of (12) is just

$$\sum_{j\text{ valence}}(\varphi_j, V_j\varphi_j).$$

The combination of (9), (10), (11), and (12) gives, to the order of accuracy of (12)

$$W_H = \sum_{j\text{ valence}} E_j - \tfrac{1}{2}\sum_{i,j\text{ valence}} C_{ij}(\varphi) - \tfrac{1}{2}\sum_{\substack{i,j\text{ valence}\\ \text{spins }||}} A_{ij}(\psi)$$
$$-\sum_{\substack{i\text{ core}\\ j\text{ valence}\\ \text{spins }||}} A_{ij}(\psi) + \sum_{j\text{ valence}}(\Delta\varphi_j, \{H_0+V_j-E_j\}\Delta\varphi_j)$$
$$+Q+\tfrac{1}{2}\sum_{\mu\neq\nu} 2X^2/D(\mathbf{R}_\mu-\mathbf{R}_\nu)+3nNX^2/5r_s, \tag{13}$$

where Q stands for the last term of (12). In (13), which applies to any metal with sufficiently compact core wave functions, the first three terms are the only ones which would be present if the Hartree field were used in the same way as the empirical fields used by Wigner and Seitz[1] for sodium, and by Seitz[1] for lithium. The fourth term is the exchange between valence electrons and cores. The fifth term, whose physical meaning is less directly obvious, will be shown below to give important contributions to the binding energy of beryllium. Moreover, since it contains two $\Delta\varphi$'s, which vary with lattice constant on account of the normalization of the wave functions, this term has quite an important effect on lattice constant and compressibility. The term Q was expected for the same reason to have an appreciable effect on the compressibility; numerical calculation however showed it to be almost negligible. The neglected terms with three and four $\Delta\varphi$'s are smaller still.

We shall now specialize to the case of beryllium, and with the aid of a few approximations which are safe in this case it will be possible to put the fourth, fifth, and sixth terms of (13) into a form which can be used for numerical calculation. The exchange energy $A_{ij}(\psi)$ of a valence electron state ψ_j with a core state ψ_i may be evaluated by expanding ψ_j into spherical harmonics about the nucleus on which ψ_i is localized. The part involving each spherical harmonic gives a contribution to $A_{ij}(\psi)$ which can be expressed as a double integral containing the radial coefficient of that spherical harmonic.[12] We shall retain only the terms $l=0$ and 1, writing

$$\psi_j = \varphi_j + \Delta\varphi_j = R_0(r) + \sum_{m=-1}^{1} R_{1m}(r)P_1^m(\cos\theta)\exp(im\varphi) \tag{14}$$

plus terms in higher harmonics which we neglect. Now the negative potential near the nucleus is practically spherically symmetrical, and is large compared with the width of the valence electron band and large compared with the variation of the potential with lattice constant. It is therefore reasonable to expect that near the nucleus the s part of φ_j can be well approximated by a constant

[12] The method of calculating these exchange terms has been described by J. C. Slater, Phys. Rev. **34**, 1293 (1929).

times a fixed function φ_{00} independent of j and of lattice constant. For φ_{00} we shall choose the eigenfunction of the lowest valence electron state, for the observed value of the lattice constant; in the approximation of Wigner and Seitz, which we use in Section 4, this wave function is simply a $2s$ function whose radial derivative vanishes on the boundary of the s sphere. Since the quantity $a_j(\nu)$ occurring in (7) depends only on the s part of φ_j around the νth atom, and since in all cases the $a_j(\nu)$ are so small that the second term of the denominator of (7) is $\lesssim 0.01$, we may set in (14)

$$R_0(r)=\frac{\varphi_j(0)}{\varphi_{00}(0)}\psi_{00}(r), \tag{15}$$

where ψ_{00} is the function obtained by putting $\varphi_j=\varphi_{00}$ in (7). Numerical calculations have shown that the error in the approximation (15) affects the contribution of R_0 to $A_{ij}(\psi)$ in the most unfavorable cases by only a few percent. We may approximate to R_{1m} near the nucleus by a similar expression:

$$R_{1m}(r)=\left[\lim_{r'\to 0}\frac{R_{1m}(r')}{R_p(r')}\right]R_p(r), \tag{16}$$

where $R_p(r)$ is the radial part of some standard solution, with $l=1$, of the wave equation in the central field which approximates the field around the nucleus. We shall choose for R_p the radial part of the p function calculated in the same central field used for φ_{00} with an energy parameter so chosen that the boundary condition $R_p'=0$ is satisfied on the surface of the s sphere for the observed lattice constant; the scale of R_p will be made definite by assuming that

$$2N/3\int_0^{r_s}4\pi r^2R_p^2dr=1$$

for $r_s=2.37$ Bohr units, corresponding to the observed lattice constant. This corresponds roughly to assuming that a function defined in each atomic cell as $R_p\cos\theta$ is normalized to 1 over Ω.

If the higher harmonics as in (14) are neglected, the approximations (15) and (16) yield,[12] for any valence electron state j,

$$\sum_{\substack{i\ \text{core}\\ \text{spin}\,\|\,j}}A_{ij}(\psi)=2s_jG_0+\tfrac{2}{3}p_jG_1. \tag{17}$$

Here

$$s_j=\text{average on }\nu\text{ of }\left|\frac{\varphi_j(\mathbf{R}_\nu)}{\varphi_{00}(\mathbf{R}_\nu)}\right|^2; \tag{18}$$

$$p_j=\text{average on }\nu\text{ of }\sum_{m=-1}^{1}\left|\lim_{\mathbf{r}\to\mathbf{R}_\nu}\frac{R_{1m}(|\mathbf{r}-\mathbf{R}_\nu|)}{R_p(|\mathbf{r}-\mathbf{R}_\nu|)}\right|^2, \tag{19}$$

where $R_{1m}(|\mathbf{r}-\mathbf{R}_\nu|)$ is meant to refer to the p part of ψ_j near the νth nucleus; and

$$G_0=\int_0^\infty\int_0^\infty\frac{P_{1s}(r)P_{2s}^{\,0}(r')P_{1s}(r')P_{2s}^{\,0}(r)}{r_b}drdr', \tag{20}$$

$$G_1=\int_0^\infty\int_0^\infty P_{1s}(r)P_{2p}(r')P_{1s}(r')P_{2p}(r)\frac{r_a}{r_b^{\,2}}drdr', \tag{21}$$

where r_a and r_b are, respectively, the smaller and larger of r and r', and where

$$P_{1s}(r)=r(4\pi)^{\frac{1}{2}}\varphi_{1s}(r),\quad P_{2s}^{\,0}(r)=r(8\pi N)^{\frac{1}{2}}\psi_{00}(r),$$

and

$$P_{2p}(r)=r(8\pi N/3)^{\frac{1}{2}}R_p(r)$$

are the radial s and p functions. Thus

$$\int_0^\infty P_{1s}^2 dr = 1;$$

P_{2s}^0 and P_{2p} are normalized to

$$\int_0^{2.37} P^2 dr = 1$$

and the former has been orthogonalized to P_{1s}.

An approximation of the same nature as (15) may also be used in the fifth term of (13). If we neglect the second term in the denominator of (7),

$$\Delta\varphi_j = -\sum_\nu a_j(\nu)\,\varphi_{1s}(\mathbf{r}-\mathbf{R}_\nu), \tag{22}$$

and if the s part of φ_j is nearly a constant multiple of φ_{00} near each nucleus,

$$a_j(\nu) = \frac{\varphi_j(\mathbf{R}_\nu)}{\varphi_{00}(\mathbf{R}_\nu)}(\varphi_{1s\nu},\ \varphi_{00}).$$

If we set

$$a/(2N)^{\frac{1}{2}} = (\varphi_{1s\nu},\ \varphi_{00}) \tag{23}$$

and use (18), the fifth term of (13) becomes (neglecting of course overlap of core functions on different atoms)

$$a^2 \sum_{j\ \text{valence}} s_j(\varphi_{1s},\ \{-\nabla^2 + U_0 - E_j\}\varphi_{1s}). \tag{24}$$

We shall assume φ_{1s} to be localized about an atom at the origin, and shall use the approximate expression (3) for U_0,[13] with

$$v(r) = -2Z/r + 2\mathrm{v}_{1s},$$

where v_{1s} is the potential due to one $1s$ electron on the free Be^{++} ion. If $-\epsilon$ is the Hartree $1s$ energy parameter for the free ion, we have

$$(-\nabla^2 + U_0 - E_j)\varphi_{1s} = (-\nabla^2 - 2Z/r + \mathrm{v}_{1s} + \epsilon + \mathrm{v}_{1s} - \epsilon + 6/r_s - 2r^2/r_s^3 - E_j)\varphi_{1s}.$$

Since φ_{1s} is the Hartree eigenfunction for the free ion, the first four terms in the parenthesis operate on it to give zero. The integral of $\mathrm{v}_{1s}|\varphi_{1s}|^2$ is just twice the quantity $F_0(1s, 1s)$ calculated by Hartree and Hartree,[6] and the integral of $2r^2/r_s^3|\varphi_{1s}|^2$ is so small that it can be neglected. Therefore

$$\text{Fifth term of (13)} \approx a^2 \sum_{j\ \text{valence}} s_j(-\epsilon - E_j + 2F_0 + 6/r_s). \tag{25}$$

The small sixth term of (13) can be transformed by using approximations of the same nature as those which we have described for the two preceding terms. As the term is unimportant we shall give only the result:

$$Q = 16Na^2\bar{s}^2B, \tag{26}$$

where

$$\bar{s} = 1/4N \sum_{j\ \text{valence}} s_j$$

is the average of s_j over all occupied states, and where

$$B = 2\int_0^{r_s}\left[\frac{\int_0^r (P_{1s}P_{2s} - 3ar_1^2/r_s^3)dr_1}{r}\right]^2 dr, \tag{27}$$

[13] This approximation gives rise to only a very small error. Cf. Wigner and Seitz, reference 1, Appendix II.

with P_{1s} as defined under (20) and (21), while $P_{2s}(r)=r(8\pi N)^{\frac{1}{2}}\varphi_{00}$ is the radial $2s$ wave function *not* orthogonalized to P_{1s}.

We are now ready to combine the expressions for the various terms of (13). The most useful way of grouping the terms would be to find out how much the energy is changed by removal of an electron from each state j, and then to express the total energy as a sum of these "ionization" energies plus whatever additional terms are necessary. If this has been done one can for example find the location of the Fermi surface from the requirement that the ionization energies of all electrons on the Fermi surface must be the same, and the requirement that the number of quantum states with ionization energies below that of the Fermi surface must equal the number of electrons. Now to find the precise ionization energies of the different states the change in the second and third terms of (13) due to removal of a particular electron would have to be calculated. To a good approximation the second term of (13) is zero, because it is the self-energy of the almost uniform charge distribution of the valence electrons minus its average value.[14] So it will not do much harm to neglect the change of this term when an electron is removed. But the third term of (13) is more troublesome. If the electron wave functions were plane waves and the filled region a sphere in momentum space, the change of this term on removal of an electron could be calculated rather easily: it is a function of the momentum of the electron, which has been given explicitly by Brillouin.[15] It will be shown in Section 8, however, that the exchange contributions to the ionization energies of the various electrons probably differ quite appreciably from these free electron values, and the differences are hard to calculate. We shall therefore leave untouched the third term of (13), as well as the second, and shall define a quantity η_j as the contribution of all the other terms of (13) to the ionization energy of the jth electron. From (13), (17), (25), and (26) we find

$$W_H=\sum_{j\text{ valence}}\eta_j-\tfrac{1}{2}\sum_{i,j\text{ valence}}C_{ij}(\varphi)-\tfrac{1}{2}\sum_{\substack{i,j\text{ valence}\\ \text{spins }||}}A_{ij}(\psi)-16Na^2\bar{s}^2B+\tfrac{1}{2}\sum_{\mu\neq\nu}\frac{8}{D(\mathbf{R}_\mu-\mathbf{R}_\nu)}+24N/5r_s \quad (28)$$

where

$$\eta_j=E_j+s_j[a^2(-\epsilon-E_j+2F_0+6/r_s+8B\bar{s})-2G_0]-\tfrac{2}{3}p_jG_1. \quad (29)$$

Of the quantities occurring in (28) and (29), five are independent of the lattice constant and of which quantum states are occupied, and it will be convenient to list their numerical values here; ϵ and F_0 are given by Hartree and Hartree,[6] and the others are calculated from the $2s$ and $2p$ wave functions of Section 4:

$$a=0.096 \qquad F_0=2.278$$
$$\epsilon=11.344 \qquad G_0=0.0284$$
$$G_1=0.0364.$$

To obtain the binding energy we must first subtract from W_H the "correlation energy"[16] due to the fact that the electrons tend to avoid one another in a way not taken into account by the Hartree or Fock approximation; the binding energy per atom of the crystal is then the difference between the resulting total energy, divided by $2N$, and the energy of a neutral beryllium atom relative to the doubly ionized state. Now it would not be correct to take for this energy difference between Be^{++} and Be the value given by a Hartree field calculation, if we include the correlation term in the energy of the crystal, since the tendency of the two valence electrons to avoid each other is not taken into account in the Hartree calculation for the atom. On the other hand, the correlation term is much too important to be omitted from the energy of the crystal. We shall therefore take for the energy difference between Be^{++} and Be the experimental value 2.024 rydbergs. This will tend to make our calculated binding energy too small, since it includes, in addition to correlation between the valence electrons, the effect of all other imperfections in the Hartree method.

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[14] The deviation of this term from zero is roughly estimated in Appendix II.
[15] L. Brillouin, J. de phys. et rad. **5**, 413 (1934).
[16] E. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

TABLE I. *The potential due to an ion and an s sphere.*

r	$-U_1(r, 2.37)$	r	$-U_1(r, 2.37)$	r	$-U_1(r, 2.37)$
0.04	182.7	0.28	15.44	0.92	2.067
0.08	83.14	0.36	10.46	1.08	1.446
0.12	50.48	0.44	7.59	1.40	0.667
0.16	34.59	0.60	4.556	1.72	0.256
0.20	25.35	0.76	3.008	2.04	0.057
				2.36	0.000

TABLE II. *Values of $E_0(r_s)$ and α.*

r_s	$E(U_1, r_s)$	$E_0(r_s)$	γ	α
2.07	0.167	0.333	1.154	0.422
2.37	0.100	0.102	1.124	0.616
2.67	0.067	−0.017	1.104	0.697

3. THE FIELD

If we define $v(\mathbf{r})$ to be $-4/D(\mathbf{r})$ for $r \gtrsim r_s$, instead of $-4/r$ as before, the potential U_0 defined by (4) may be written

$$U_0 = \sum_\nu v(\mathbf{r}-\mathbf{R}_\nu) - \frac{6}{5r_s} + \mathrm{v}_{\mathrm{val}}, \tag{30}$$

where $\mathrm{v}_{\mathrm{val}}$ is the neutralized potential due to the valence electron distribution. It would undoubtedly be sufficiently accurate to assume $\mathrm{v}_{\mathrm{val}}=0$ in (30), since the charge distribution of the valence electrons is almost uniform; if necessary, a first-order perturbation correction could be applied to the energies calculated using this assumption.

What was actually done was to get a rough approximation to $\mathrm{v}_{\mathrm{val}}$ for $r_s=2.37$, and for other values of r_s to assume $\mathrm{v}_{\mathrm{val}}$ to vary in the same way near each ion as for $r_s=2.37$. More explicitly, for $r_s=2.37$ the valence electron distribution in a given s sphere was assumed to consist of a charge of one electron distributed with a density proportional to $|\varphi_{00}|^2$, plus a charge of one electron with a density proportional to $|R_p|^2$, where φ_{00} and R_p are the functions mentioned in the preceding section. The potential due to an ion and an s sphere containing the charge distribution just described will be called $U_1(r, 2.37)$. This function, values of which may be found from Table I, was determined so that the φ_{00} and R_p calculated from it were the same as those used in it: in this sense it is "self-consistent." If we define v_1 as the difference between $U_1(r, 2.37)$ and the neutralized potential due to a sphere of radius 2.37 containing a charge of two electrons uniformly distributed, we have

$$\begin{aligned} v_1(\mathbf{r}) &= U_1(r, 2.37) - 6/2.37 + 2r^2/2.37^3 \quad \text{for } r \lesssim 2.37 \\ &= -4/D(\mathbf{r}) \quad \text{for } r \gtrsim 2.37. \end{aligned} \tag{31}$$

The potential U which was actually used in calculating[17] the valence electron φ_j and E_j is now defined for all values of r_s by

$$U(\mathbf{r}) = \sum_\nu v_1(\mathbf{r}-\mathbf{R}_\nu) - \frac{6}{5r_s}, \tag{32}$$

and we have for the zeroth Fourier coefficient

$$U[0] = \frac{1}{(4/3)\pi r_s^3}\int_\alpha \left[v_1(r) + \frac{4}{r}\right] d\tau \approx c = U_0[0], \tag{33}$$

as a comparison with (5) shows. Since (32) differs slightly from (30), especially when $r_s \neq 2.37$, there will be a correction to the total energy resulting from the first-order perturbation corrections to the E_j; this is roughly estimated along with the Coulomb energy in Appendix II.

4. DETERMINATION OF E_0 AND α

Wigner and Seitz[1] have shown that the energy parameter E_0 for the lowest valence electron state in a metal can be determined with remarkable accuracy by integrating the radial wave equation

[17] The potential (32) is used directly in Sections 5 and 6; in Section 4 the wave functions are calculated in the field $U_1(r, 2.37)$ and their energies then corrected for the difference between this and (32).

for an s function in a single atomic cell, and finding the energy for which the radial derivative of the wave function vanishes at the radius r_s. Accordingly, s functions φ_0 were determined for several energies by numerical integration, in the field $U_1(r, 2.37)$ of the preceding section, and the energies for which the radial derivative vanished at $r_s=2.07$, 2.37, and 2.67 were found by graphical interpolation. These energies are listed in Table II in the column headed $E(U_1, r_s)$.

The desired energy parameter $E_0(r_s)$ is rather accurately given by $E(U_1, r_s)$ plus the average over an atomic cell of $|\varphi_0|^2U$ minus the average over an s sphere of $|\varphi_0|^2U_1(r, 2.37)$. As it will be of interest in Section 6 to have a rather precise value of E_0 to compare with the value calculated by the orthogonalized plane wave method, we shall evaluate this energy correction with greater accuracy than is needed for the other purposes of this paper. In analogy to (31) let us define for $r \leqslant r_s$

$$U_1(r, r_s)=v_1(r)+6/r_s-2r^2/r_s^3. \tag{34}$$

By (33) the average of U over an atomic cell then equals the average of $U_1(r, r_s)$ over an s sphere. Also

$$\text{spherical average of } U=U_1(r, r_s)+\left[\sum_\nu{}'v_1(\mathbf{R}_\nu)-\frac{36}{5r_s}\right], \tag{35}$$

the constant term in brackets being small (it is calculated numerically in Section 9). If φ_0 is normalized over an s sphere we can now write

$$E_0(r_s)=E(U_1, r_s)+\int_{\text{atomic cell}}[|\varphi_0|^2-|\varphi_0(r_s)|^2]Ud\tau + |\varphi_0(r_s)|^2\int_{\text{atomic cell}}Ud\tau-\int_{s\text{ sphere}}|\varphi_0|^2U_1(r, 2.37)d\tau.$$

The region of integration in the second term can be changed to the s sphere without much harm, since the integrand is nearly zero in the region between the cell and the sphere; then (35) can be used. In the second integral we may replace U by $U_1(r, r_s)$ and change the region of integration to the s sphere. The result is

$$E_0(r_s)=E(U_1, r_s)+\int_{s\text{ sphere}}|\varphi_0|^2[U_1(r, r_s)-U_1(r, 2.37)]d\tau+(\gamma-1)\left[\sum_\nu{}'\frac{4}{D(\mathbf{R}_\nu)}+\frac{36}{5r_s}\right] \tag{36}$$

where

$$\gamma=|\varphi_0(r_s)|^2\cdot\frac{4\pi}{3}r_s^3$$

is the ratio of the square of the wave function at r_s to its mean value. The quantity

$$\left[\sum_\nu{}'\frac{4}{D(\mathbf{R}_\nu)}+\frac{36}{5r_s}\right]$$

depends on the c/a ratio of the crystal. The observed c/a ratio for beryllium is 1.58; however, no appreciable error in any of the quantities being calculated in this paper is apt to result from using the value 1.63 (corresponding to ideal close packing of spheres), and as some of the numerical work is simpler if this value is used, all the calculations of this paper have been made assuming $c/a=1.63$. For this case

$$\left[\sum_\nu{}'\frac{4}{D(\mathbf{R}_\nu)}+\frac{36}{5r_s}\right] \text{ has the value } \frac{0.0317}{r_s}.$$

The integral in (36) was evaluated numerically for $r_s=2.07$ and 2.67. The resulting values of $E_0(r_s)$ are given in the third column of Table II; γ, which appears also in the expression (38) for α, is given in the fourth column.

The general form for an electron eigenfunction in the trebly periodic potential field of a crystal is[9]

$$\varphi_{\mathbf{k}} = \exp(i\mathbf{k}\cdot\mathbf{r})u_k, \tag{37}$$

where the function u_k possesses the same translational periodicity as the crystal; $\mathbf{k}$ is called the wave vector of the eigenfunction φ_k. The assignment of a wave vector to a given wave function is unique only to within 2π times an arbitrary vector of the reciprocal lattice; to make it unique one may define the "reduced wave vector" as the shortest wave vector which can be associated with the given eigenfunction. Also, an infinite number of eigenfunctions can be found for any value of $\mathbf{k}$. The energy E_0 which we have just calculated is the third lowest of those going with wave vector zero (the lowest belong to the functions of the $1s$ core band, and there are two such orbitals because there are two atoms in the unit cell).

For wave vectors close to zero there exist energies close to E_0, whose expansion in powers of k for a hexagonal crystal is of the form

$$E_k = E_0 + \alpha_\perp(k_x^2 + k_y^2) + \alpha_{\parallel} k_z^2 + 0(k^4).$$

Here k_z is the component of $\mathbf{k}$ along the hexagonal axis, and k_x and k_y are the components along any axes perpendicular to this. It can be shown that $\alpha_\perp$ and $\alpha_{\parallel}$ must be very nearly the same when the c/a ratio for the crystal is 1.63, which, as described above, is the value assumed in the present calculations.

With $\alpha_{\parallel} = \alpha_\perp = \alpha$, the value of α can be calculated from the formula

$$\alpha = \gamma\left[\frac{r}{f}\frac{df}{dr} - 1\right]_{r=r_s} \tag{38}$$

given in the first paper of Bardeen.[2] Here $f(r)$ is the radial p function obtained by outward integration in the field $U_1(r, r_s)$ using the energy E_0. This formula, though an approximation, seems to be a very good one, both for the absolute value of α and for the manner of its variation with r_s. The values of α listed in Table II were calculated from the field $U_1(r, 2.37)$ for all values of r_s, but only a negligible correction would result from changing the field to $U_1(r, r_s)$.

5. Excited Energies

Because of the fact that the occupied region of $\mathbf{k}$ space extends in beryllium out to and beyond the first planes of energy discontinuity, the parabolic approximation $E_k = E_0 + \alpha k^2$, which usually suffices for monovalent metals, is quite inadequate as a representation of the energies of most of the occupied quantum states. In fact, the calculations of Section 9, (3) show that with this approximation no stable state of the crystal exists anywhere near the observed lattice constant. We therefore calculate in this section the energy parameters of a number of states near the Fermi surface, using the orthogonalized plane wave method. An approximation to the energy parameter of such a state is obtained by solving a secular equation

$$\det(\chi_k, H\chi_{k'}) - E(\chi_k, \chi_{k'}) = 0, \tag{39}$$

where the functions χ_k are defined by Eq. (4) of reference 5. It is obvious that by taking a sufficient number of rows and columns in (39) a very good approximation to the desired energy could be obtained; it will be shown in this section and the next that fairly accurate energy values result even if only a few rows and columns are used. The matrix elements occurring in (39) are given by (13) and (14) of reference 5. For our case these take the form

$$\begin{aligned}(\chi_k, H\chi_{k'}) = {} & k^2\delta_{kk'} + U(\mathbf{k}'-\mathbf{k}) - \{E_{1s} - F(0,0)\}A_{1s}(k)A_{1s}(k')\{1+\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{t}]\} \\ & - \{A_{1s}(k)I_{1s}(\mathbf{k}') + A_{1s}(k')I_{1s}^*(\mathbf{k})\}\{1+\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{t}]\} \\ & + A_{1s}(k)A_{1s}(k')\sum_{\nu'\neq\nu}\sum_{\nu}^{\text{cell}}\{E_{1s}S(\nu,\nu') + F(\nu,\nu')\}\exp[-i\mathbf{k}\cdot\mathbf{R}_\nu + i\mathbf{k}'\cdot\mathbf{R}_{\nu'}]\end{aligned} \tag{40}$$

and

$$(\chi_k, \chi_{k'}) = \delta_{kk'} - A_{1s}(k)A_{1s}(k')\{1+\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{t}] - \sum_{\nu'\neq\nu}^{\text{cell}}\sum_{\nu} S(\nu,\nu')\exp[-i\mathbf{k}\cdot\mathbf{R}_\nu + i\mathbf{k}'\cdot\mathbf{R}_{\nu'}]\}, \quad (41)$$

where $\mathbf{t}$ is a vector joining the atom at the origin of coordinates to one of its nearest neighbors in the layer above or below it when the hexagonal axis is vertical. To use (40) and (41) we need to know values of the coefficients $A_{1s}(k)$, the Fourier coefficients $U[\mathbf{K}]$ of the potential (32), and the various overlap integrals.

For the field which was called $V(r)$ in reference 5 we chose the field $U_1(r, 2.37)$. The $1s$ eigenfunction was determined by numerical integrations, and its energy was found to be $E_{1s} = -4.55$ rydbergs. The integral which gives $\Omega_0^{\frac{1}{2}}A_{1s}(k)$ (Eq. (5) of reference 5) was calculated numerically for $k=0$ and two other values of k; for values of k smaller than the larger of these $A_{1s}(k)$ was determined graphically, and for greater values of k it was assumed that $A_{1s}(k)$ could be represented by an expression of the type of (29) of reference 5, which would be exactly correct for a hydrogenic core function. It was found, in fact, that by properly choosing the value of b in this expression, the three directly calculated values of $A_{1s}(k)$ could be fairly well represented.

To calculate the Fourier coefficients $U[\mathbf{K}]$, an integral similar to that in (18) of reference 5 was calculated numerically for eight values of $\mathbf{K}$, so spaced that the value of the integral for any other value of $\mathbf{K}$ could be fairly accurately estimated graphically. Table III contains the Fourier coefficients of U for the case $c/a=1.63$. The argument of each U in the first column is a vector of the reciprocal lattice, designated by four indices according to the Bravais-Miller notation.[18] Not all the Fourier coefficients of U are real, and for those which are complex only the absolute magnitude is given. The phase of each Fourier coefficient $U[\mathbf{K}]$ is that of the quantity[19] $-[1+\exp(i\mathbf{K}\cdot\mathbf{t})]$ where $\mathbf{t}$ is as described under (40) and (41), and where the minus sign is due to the fact that $U(r)$ is everywhere negative.

TABLE III. *Fourier coefficients of U for c/a = 1.63.*

r_s	2.07	2.37	2.67
$U[000, 0]$	−0.6624	−0.5634	−0.4893
$U[000, 2]$	−0.3759	−0.3197	−0.2779
$U[000, 4]$	−0.1106	−0.0940	−0.0782
$\lvert U[1\bar{1}0, 0]\rvert$	0.2087	0.1783	0.1557
$\lvert U[1\bar{1}0, 1]\rvert$	0.2898	0.2459	0.2135
$\lvert U[1\bar{1}0, 2]\rvert$	0.1046	0.0900	0.0781
$\lvert U[1\bar{1}0, 3]\rvert$	0.1438	0.0974	0.0845
$\lvert U[1\bar{1}0, 4]\rvert$	0.047	0.039	0.034
$U[2\bar{1}\bar{1}, 0]$	−0.1552	−0.1398	−0.1138
$U[2\bar{1}\bar{1}, 2]$	−0.120	−0.100	−0.085
$\lvert U[2\bar{2}0, 0]\rvert$	0.0611	0.0514	0.0446
$\lvert U[2\bar{2}0, 1]\rvert$	0.100	0.085	0.071
$\lvert U[2\bar{2}0, 2]\rvert$	0.050	0.042	0.035

A number of the higher Fourier coefficients not listed in Table III occur in the expressions for the energies of some of the states which perturb the ones we are interested in. As the energies of the occupied states are rather insensitive to these Fourier coefficients, they were estimated by a rough extrapolation from the coefficients in the table.

The small overlap integrals given by (10), (11) and (12) of reference 5 could have been calculated with fair accuracy by methods similar to those mentioned there. However, we did not feel that the accuracy aimed at in this work was great enough to require a complete and accurate inclusion of overlap terms. It was considered sufficient to make use of an estimate of the overlap terms in (40) which is almost certainly too great. A comparison of the energies of the eigenfunction calculated with and without these overestimated overlap terms shows whether or not the uncertainty due to our ignorance of correct values of the overlap integrals is dangerous. In making this "overestimate" we shall neglect the $S(0, \nu)$, and the $F(0, \nu)$[20] for $\nu\neq 0$. For the eigenfunctions considered in this section this neglect does very little harm, because the quantities are small and, for the $\mathbf{k}$ vector we shall use, their coefficients in (40) turn out to

[18] Cf. N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936), p. 159.

[19] Cf. Eq. (18), reference 5.

[20] In Section 6 a calculation of E_0 is given from more accurate values of the overlap terms, and values for $S(0\nu)$ are given.

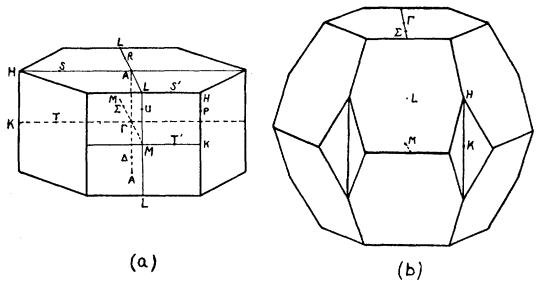

FIG. 1. First and second Brillouin zones for the close-packed hexagonal lattice.

be small. Since the chief contribution to the integral for $F(0, 0)$ comes from near the nucleus, we shall assume that $(U-V)$ is constant in this integral and equal to its value at the nucleus. This gives

$$F(0, 0) \approx (U-V)_{r=0} = 6\left(\frac{1}{r_s} - \frac{1}{2.37}\right). \quad (42)$$

The quantity $I_{1s}(\mathbf{k})$ is more difficult to approximate adequately. If we make the same assumption regarding the constancy of $(U-V)$ we have

$$I_{1s}(\mathbf{k}) = 6\left(\frac{1}{r_s} - \frac{1}{2.37}\right) A_{1s}(k). \quad (43)$$

More accurately calculated values for $I_{1s}(0)$ are given in the next section, and a comparison shows that the expression (43) is numerically too large by a factor 1.6 for $r_s=2.07$, and a factor 1.3 for $r_s=2.67$. For large values of $\mathbf{k}$, the contribution to the $I_{1s}(\mathbf{k})$ integral from the region close to the nucleus is relatively more important, however, since at a distance from the nucleus the phase of the exponential is different in different directions. So we may expect the approximation (43) to be a little less bad for the wave vectors to be considered in this section, than for $\mathbf{k}=0$. If (42) and (43) are inserted into (40) and the $S(0, \nu)$ and $F(0, \nu)$ for $\nu \neq 0$ are neglected, the resulting expression for $(\chi_k, H\chi_{k'})$ has the form which would be obtained by replacing E_{1s} by $(E_{1s}+6/r_s-6/2.37)$ and disregarding all the overlap terms. The energies E which will be given later on in Table V are obtained by calculating all matrix elements of the Hamiltonian in this way.

Before beginning on the detailed calculation of the energies of the various states, it will be worth while to consider what the occupied states for beryllium would be like in the approximation of almost free electrons.[21] In this approximation $\mathbf{k}$-space is divided up into Brillouin zones, across the boundaries of which discontinuities in energy occur. The boundaries of the various Brillouin zones are the planes which bisect perpendicularly the vectors from the origin to the various points of the reciprocal lattice, each multiplied by 2π. The first Brillouin zone is, in general, the space which can be reached from the origin by crossing just one plane, etc. We shall adhere to this definition here, although on account of the presence of a twofold screw axis in the space group there is no discontinuity in energy across the top and bottom boundaries of the first Brillouin zone.[22] The first and second Brillouin zones are shown in Fig. 1, and a number of wave vectors are indicated by letters.[23] Since there are just enough electrons present to fill the first two zones, we may expect that a Fourier analysis of the true crystal eigenfunction of a state near the Fermi surface would show it to be composed principally of one or more plane waves of wave vectors near the boundary of the second Brillouin zone.

Now the eigenfunctions in a crystalline field can be classified according to symmetry types, corresponding to the various irreducible repre-

TABLE IV. *Symmetry types for each lettered point in Fig. 1.*

POINT	NO. OF PLANE WAVES OF SAME KINETIC ENERGY AND SAME REDUCED WAVE VECTOR	SYMMETRY TYPES
M	2	M_1^+, M_2^-
L	4	L_1, L_1
K	3	K_1, K_5
H	6	H_1, H_2, H_3
Σ	2	Σ_1, Σ_3
Γ	2	Γ_3^+, Γ_4^-

[21] See the article of Sommerfeld and Bethe, *Handbuch der Physik* (Berlin, 2nd ed., 1933), Vol. 24/2, p. 385.

[22] That there cannot be a discontinuity in energy across these planes was first shown by F. Hund, Zeits. f. Physik **99**, 119 (1936); cf. also C. Herring, Phys. Rev. **52**, 361 (1937).

[23] It will be noted that the second zone in Fig. 1 differs from the zone (there designated as the "first zone") in Fig. 65 of Mott and Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936), in that we have included wedge-shaped pieces around the sides. The volume of these wedge-shaped pieces is just sufficient to make the whole zone hold exactly two electrons per atom.

sentations of the space group.[24] Suppose we take all the plane waves which have the same reduced wave vector, and the same kinetic energy, as the one corresponding to a particular lettered point in Fig. 1; with the aid of character tables for the irreducible representations of the close-packed hexagonal space group[25] we can find all the symmetry types which occur among the linear combinations of these plane waves. These symmetry types are listed, for each lettered point, in Table IV, the notation being that of reference 25. In the approximation of almost free electrons the symmetry types of those eigenfunctions at the lettered points which belong to the first and second zones must of course be among the listed types. It is reasonable to expect that the same holds true for the actual crystal eigenfunctions, i.e., that if we select the two valence electron states nearest the Fermi surface which have reduced wave vector corresponding to a given one of the lettered points, the symmetry types of these states will be among those listed for the given point in Table IV. It turns out that this is indeed the case, although it is of course necessary to investigate eigenfunctions of other symmetry types, which arise in the free electron approximation from higher energy plane waves, and to make sure that none of these have energies near the Fermi level.

For each symmetry type in Table IV the appropriate plane wave combination was set up. Similarly out of plane waves of higher energies

TABLE V. *Hartree energy parameters of the crystal eigenfunction.*

STATE	$r_s=2.07$ E_j	ΔE_j	2.37 E_j	E_j	2.67 ΔE_j	No. CONSTITUENT χ-FUNCTIONS
(s) M_1^+	0.764	0.006	0.547	0.401	−0.004	4
(s) M_2^-	1.010	−0.012	0.702	0.492	−0.016	4
(s) L_1	0.888	−0.003	0.650	0.489	0.001	3
K_1	0.967		0.712	0.537		5
(s) K_5	1.197	−0.008	0.852	0.623	−0.009	4
K_6	1.878		1.377	1.049		4
H_1	1.231		0.913	0.696		5
H_2	1.117		0.810	0.604		6
(s) Σ_1	1.419	0.011	1.012	0.726	−0.035	4
Σ_3	0.975		0.713	0.537		5
Γ_3^+	0.721		0.507	0.370		6
(s) Γ_4^-	1.45	0.05	1.00	0.68	−0.04	3

[24] L. P. Bouckaert, R. Smoluchowski and E. Wigner, Phys. Rev. **50**, 58 (1936).
[25] C. Herring, to be published in another place.

TABLE VI. *Values of E_0 calculated by the orthogonalized plane wave method. $\bar{E}_0$ is the average energy of the wave function χ_0 with inclusion of all overlap terms except the $F(0\nu)$ for $\nu\neq 0$. The four perturbations listed, and $E_0^{(1)}$, are calculated with inclusion of overlap terms and assuming $I_{1s}(\mathbf{k})/A_{1s}(k)=I_{1s}(0)/A_{1s}(0)$. $E_0^{(2)}$ is calculated with inclusion of overlap terms, using (42), and (43) for $\mathbf{k}\neq 0$, but using correct $I_{1s}(0)$. $E_0^{(3)}$ is calculated including only the $I_{1s}(\mathbf{k})$ and $F(0, 0)$ overlap terms, and assuming (42) and (43) for all $\mathbf{k}$. $E_0^{(4)}$ is calculated omitting all overlap terms. E_0^{WS} is taken from Table II.*

r_s	2.07	2.37	2.67
$I_{1s}(0)$	0.076	−0.0027	−0.049
$F(0, 0)$	0.342	0.0000	−0.269
$S(0, \nu)$	0.00159	0.00051	0.00016
$\bar{E}_0$	0.3771	0.1208	−0.0065
pert. $(1\bar{1}0, 0)$	0.004_2	0.0005	0.0002
$(1\bar{1}0, 1)$	0.024_4	0.0085	0.0017
$(000, 2)$	0.005_7	0.0015	0.0000
$(1\bar{1}0, 2)$	0.002_4	0.0017	0.0034
$E_0^{(1)}$	0.340	0.108	−0.012
$E_0^{(2)}$	0.355	0.109	−0.014
$E_0^{(3)}$	0.307	0.110	0.001
$E_0^{(4)}$	0.382	0.110	−0.028
E_0^{WS}	0.333	0.102	−0.017

linear combinations were formed having each of these symmetry types. These linear combinations of plane waves were then made orthogonal to the core functions, just as was done for a single plane wave in (4) of reference 5. Such a linear combination of plane waves, orthogonalized to the cores, will be referred to as a "constituent χ state" of the eigenfunction of the same symmetry type.

For certain symmetry types of Table IV it happens that the plane wave combination is itself orthogonal to the 1s core functions, so that no multiples of the core functions need to be added to get the constituent χ-state. This is the case for all symmetry types except those (labeled (s) in Table IV) which occur among the Bloch waves formed from the core functions. For each symmetry type we chose the several constituent χ-states of lowest average energy, and using (40) and (41) evaluated the scalar products of these with each other and the matrix of the Hamiltonian relative to them. The lowest root of a secular equation gave an approximate value for the Hartree energy parameter of the crystal eigenfunction.

The energy parameters so obtained are the quantities E_j listed in Table V. We have included

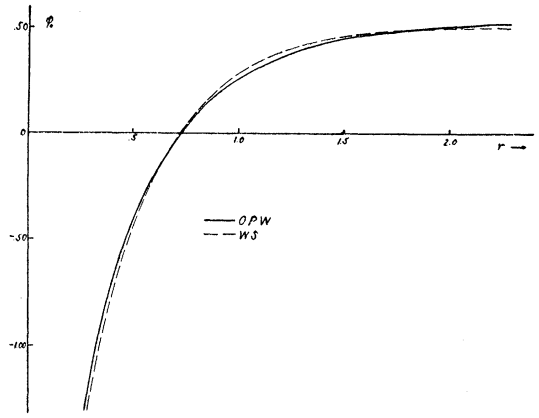

FIG. 2. Comparison of the orthogonalized plane wave and Wigner-Seitz wave functions for $\mathbf{k}=0$, $r_s=2.37$. The former (*OPW*) goes at $r=0$ to the value -4.21, the latter (*WS*) to -4.01.

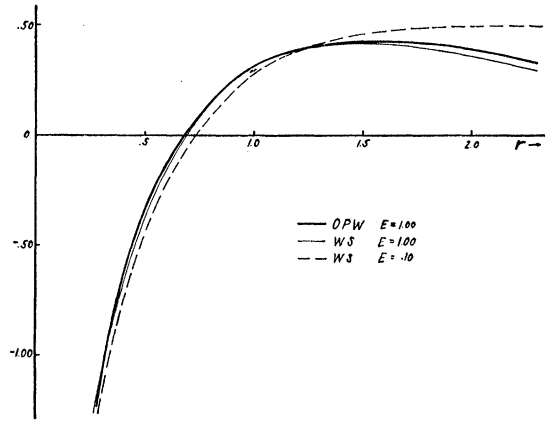

FIG. 3. Comparison of the s part of the orthogonalized plane wave function for Γ_4^- with central field functions, for $r_s=2.37$. The former (*OPW*) curve goes at $r=0$ to the value -4.4, the $E=0.10$ curve to -4.01, and the $E=1.00$ curve to -3.8.

here the lowest energy state of symmetry K_6 in addition to the states listed in Table IV. The quantities ΔE_j were obtained by subtracting the listed value of E_j from the value which resulted when all the overlap terms in (40) and (41) were neglected. Thus we may expect the solution of the correct secular equation to lie between E and $E+\Delta E$; probably about halfway. The last column of Table V gives for each symmetry type the number of constituent χ-functions used in the secular equation; we have neglected the perturbations due to the small matrix elements of the Hamiltonian connecting the constituent χ-functions with the core functions.

The differences between the E_j's in the table and the average energies $\bar{E}_j$ for the lowest constituent χ-state are quite small, of the order 0.03 to 0.06 Ry, for the states not designated (s). The corresponding differences for the (s) states are as high as 0.20 Ry. Because of the rough perturbation method used the energy parameters are probably inaccurate to 0.01 Ry or more. However, the third figure listed in the table is significant in taking the differences δE_j and $\delta^2 E_j$, between the E_j's for the three values of the lattice constant, which are used in computing the lattice constant and compressibility. The quantities $\delta^2 E_j - \delta^2 \bar{E}_j$ are only a few thousandths of a Rydberg unit for all the non-(s) states except K_6. For the (s) states these quantities may be as high as 0.05 Ry.

6. TESTS OF THE ORTHOGONALIZED PLANE WAVE METHOD

Since our results will depend considerably upon the calculations of the preceding section, and since these calculations are the first to be published using the orthogonalized plane wave method, a check on the accuracy of the method is desirable. The most obvious test to make is to calculate E_0 by the orthogonalized plane wave method, and compare the result with the value obtained by the method of Wigner and Seitz. Another kind of test which can be made is to calculate the wave function for any state by the orthogonalized plane wave method, and then to compare the s and p parts of this wave function with the s and p functions for the same energy obtained by integrating the wave equation with the spherically symmetric potential $U_1(r, r_s)$ of

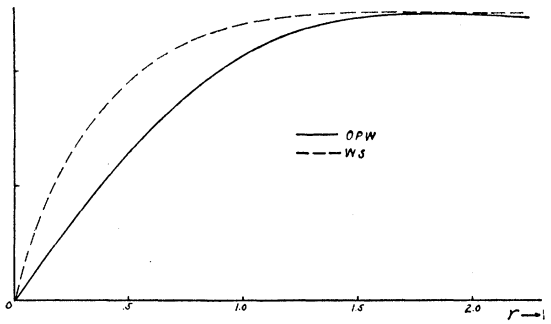

FIG. 4. Comparison of the p part of the orthogonalized plane wave function for Γ_3^+ with the central field function of the same energy, $r_s=2.37$.

Section 3. The radial functions obtained by these two methods should be the same to within a constant factor as long as r is sufficiently small so that the deviation of the true field U from spherical symmetry is negligible.

The results of the calculation of E_0 by the orthogonalized plane wave method are given in Table VI. As it is of interest to see how well E_0 can be calculated when all the overlap terms in (40) and (41) are taken accurately into account, values of $I_{1s}(0)$ and of $S(0, \nu)$ for nearest neighbors were calculated from (23), (24), (25), and (26) of reference 5; these are given in the first three rows of Table VI, along with accurate values of $F(0, 0)$ which were used here instead of the approximation (42).

Of the energies $E_0^{(1)} \cdots E_0^{(4)}$ calculated in various ways, one would expect $E_0^{(1)}$ to be the most accurate, with $E_0^{(2)}$ next. The energies $E_0^{(3)}$, and $E_0^{(4)}$ are calculated with the same approximations which were used for E and $E+\Delta E$, respectively, in Table V; the differences are much larger here because most of the (s) functions in Table V are rather smaller near a nucleus than the wave function φ_0 of Table VI, and also because $A_{1s}(k)$ is smaller for larger k values. The deviation of $E_0^{(1)}$ from E_0^{WS} is of the same order of magnitude as the uncertainty in the energies due to the uncertainty in the extrapolated values of $A_{1s}(k)$. The second differences of $E_0^{(1)} \cdots E_0^{(4)}$ and E_0^{WS} with respect to r_s, which are important for the compressibility, are, respectively, 0.112, 0.123, 0.088, 0.134 and 0.112. The perturbations listed in Table VI are the second-order perturbations due to the χ-states corresponding to the listed indices and other plane waves of the same kinetic energy.

Figure 2 shows a comparison for $r_s=2.37$ of the wave function φ_0 of Section 4 with the s part of the wave function calculated with the matrix elements used for $E_0^{(1)}$ in Table VI (omitting, however, the small perturbation by the (1–10, 0) waves). The two wave functions are drawn with the same normalization. It will be noted that the close agreement between the two functions persists even to $r=0$. The perturbations have a rather small effect on the wave function in this case, and even the unperturbed wave function χ_0 agrees fairly closely with the Wigner-Seitz function. Figure 3 shows a comparison, also for $r_s=2.37$, of the s part of the orthogonalized plane wave function for the state Γ_4^- with the s function of energy 1.00 in the field $U_1(r, 2.37)$. Since the eigenfunction cannot be accurately approximated by an s function alone, we cannot introduce a normalization requirement: the two curves have therefore been arbitrarily given the same ordinate at $r=1.24$. For comparison the Wigner-Seitz function from Fig. 2 is drawn in also, fitted to the same value at 1.24. It will be seen that the orthogonalized plane wave function resembles the central field function for $E=1.00$ much more closely than the one for $E=0.10$, although the agreement is not so good as in

TABLE VII. *Values of s_j and p_j and the derivatives of these quantities.*

STATE	s_j			p_j			η_j			w_j'	w_j''
	$r_s=2.07$	2.37	2.67	2.07	2.37	2.67	2.07	2.37	2.67		
M_1^+	0.164	0.141	0.121	1.5	0.8	0.5	0.713	0.514	0.378	0.1314	0.1651
M_2^-	0.555	0.511	0.462	1.4	0.6	0.3	0.924	0.636	0.438	0.1168	0.0734
L_1	0.007	0.009	0.014	1.7	1.0	0.5	0.847	0.625	0.476	0.2189	0.2752
K_1	0	0	0	3.2	1.9	1.2	0.888	0 666	0.509	0.0876	0.1101
K_5	0.344	0.292	0.280	0.9	0.5	0.4	1.142	0.810	0.586	0.0876	0.0184
K_6	0	0	0	2.6	1.5	1.0	1.82	1.34	1.02	0.0073	0
H_1	0	0	0	3.1	1.6	1.0	1.156	0.873	0.672	0.0876	0.1101
H_2	0	0	0	3.1	1.9	1.2	1.041	0.764	0.576	0.1460	0.1284
Σ_1	0.850	0.765	0.746	1.5	0.7	0.3	1.300	0.918	0.641	0.0146	0.0092
Σ_3	0	0	0	1.7	1.0	0.6	0.935	0.690	0.522	0.0438	0.0551
Γ_3^+	0	0	0	1.6	1.1	0.7	0.682	0.481	0.352	0.0438	0.0550
Γ_4^-	1.61	1.25	1.00	0	0	0	1.29	0.87	0.58	0.0146	0
Γ_1^+	1.617	1.000	0.654	0	0	0	0.186	0.007	−0.081		
$\left[\frac{d}{d(k^2)}\right]_{k=0}$	−2.11	−1.42	−1.00	1.69	1.16	0.81	0.563	0.714	0.769		
$\bar{s}$	0.58	0.40	0.29								
B	0.161	0.163	0.165								

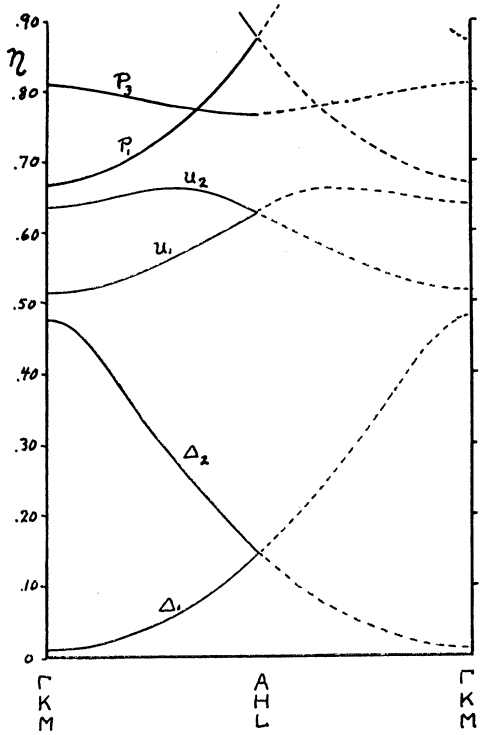

FIG. 5. η *vs.* **k** along lines of Fig. 1 parallel to the hexagonal axis, for $r_s=2.37$. The representation P_3 is two-dimensional. (The horizontal scale is different from that of Figs. 6 and 7.)

Fig. 2, especially for $r=0$. The poorer agreement is to be expected, since only three constituent χ-states were used, the smallest number for any of the states in Table V. One might expect the orthogonalized plane wave functions for the (s) states of Table V to be considerably more in error for $r_s=2.07$ or 2.67 than for 2.37, because of the crude treatment of the overlap terms. To test this curves similar to Fig. 3 were constructed for the state M_2^-, for $r_s=2.07$; the agreement with the central field function of the same average energy was found to be slightly worse for large r than in Fig. 3, but slightly better for small r.

It was pointed out in reference 5 that one would expect the orthogonalized plane wave functions to resemble the true eigenfunctions more closely in their s parts (and also in their d and higher parts) than in their p parts. This expectation is confirmed by Fig. 4, where the p part of the orthogonalized plane wave function for the Γ_3^+ state of Table V, for $r_s=2.37$, is compared with the central field p function of the same energy. The ordinates of the two curves correspond to values of the p part along a line in the direction of the hexagonal axis, and are arbitrarily chosen equal at $r=1.88$. In spite of the apparently poor agreement of the wave function here, however, the energies of the states not labeled (s) in Table V are probably accurate to 0.01 Ry. A similar plot for the H_2 wave function shows even worse agreement, which can perhaps be attributed to the fact that this function is far from a pure p function: the more of the higher harmonics there are in the wave function, the less the effect on the energy of an inaccuracy in the p part.

7. Distribution of States in Energy

As has been remarked previously, the quantities η_j defined by (29) are of more physical interest than the E_j. To obtain them we need to know the quantities s_j and p_j. The s_j defined by (18) can be calculated in a straightforward way from the approximate wave functions which correspond to the energies E in Table V. The p_j could be calculated similarly from their definition (19); however, since the p parts of these approximate wave functions differ considerably from the p parts of the true eigenfunctions near a nucleus (as shown by Fig. 4), the values of the p_j calculated in this way would be very bad. So instead, each p_j was estimated from the magnitude of the p part of the approximate wave function at a distance of 1.5 Bohr units from each nucleus. Such estimates are very

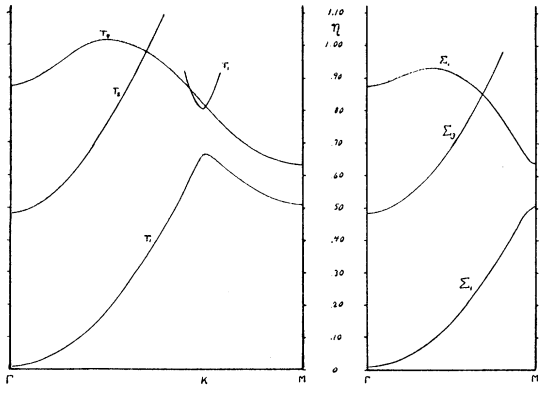

FIG. 6. η *vs.* **k** along lines in the central plane of the first Brillouin zone, for $r_s=2.37$.

rough, but are good enough for our purposes. The first two sections of Table VII give the values of the s_j and the p_j. Also given are the derivatives of these quantities with respect to k^2 at $k=0$, which can be calculated by an analysis similar to that used by Bardeen[2] to obtain α. This analysis is given in Appendix III.

The next to the last line of Table VII gives roughly estimated values of $\bar{s}$, the average of the s_j of the occupied states, which appears in (28) and (29) with a very small coefficient. The quantity which multiplies $\bar{s}$ is given in the last line. The values of the η_j, which can now be calculated from (29), are given in the third section of Table VII.

As the first step in the determination of the distribution of states in η, graphs were drawn of η against reduced wave vector along a number of lines in **k**-space. Reduced wave vectors (lying always in the first Brillouin zone) were used because the wave functions of the higher energy states did not resemble single plane waves closely enough to justify assigning unique wave vectors to them outside the first Brillouin zone. These graphs were constructed for $r_s=2.07$, 2.37, and 2.67; those for $r_s=2.37$ are reproduced in Figs. 5, 6 and 7. The symmetry types belonging to the various curves are written in, using the notation of reference 25; use has been made of the fact, pointed out there, that the line ΓK when prolonged reaches a point equivalent to M, and that similarly AH prolonged reaches a point equivalent to L.

It will be noticed that some of the curves have horizontal tangents at the symmetry points and

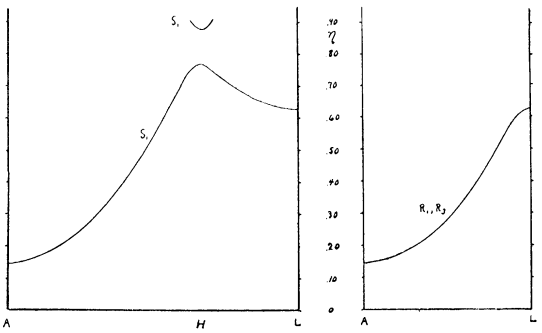

FIG. 7. η *vs.* **k** along lines in the top plane of the first Brillouin zone, for $r_s=2.37$. The representation S_1 is two-dimensional; R_1 and R_3 are one-dimensional but coincide in energy because of time-reversal symmetry.

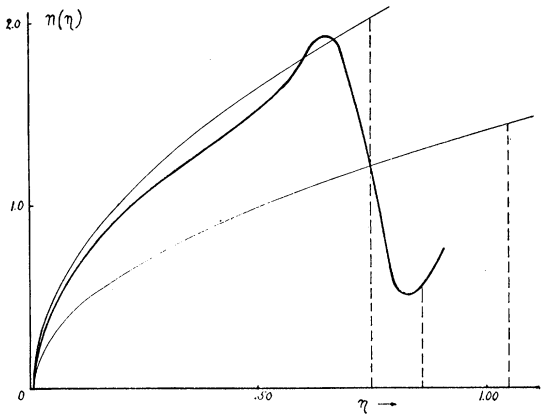

FIG. 8. Distribution of states in the energy parameter η, for $r_s=2.37$, with the scale such that $\int_{\eta_0}^{\eta_{\max}} n(\eta)d\eta=1$.

that others do not, and that in the latter cases the slopes of the two curves which intersect at the point in question are equal and opposite. These facts can be deduced from the space group and time-reversal symmetry of the problem. It will be noticed also that there is a very sharp curvature at the points Γ_3^+, Γ_4^- in Fig. 5, M_1^+, M_2^-, K_1, K_5 in Fig. 6, and H_1, H_2 in Fig. 7. In each case this curvature is due to the perturbation of the curve in question by others which have the same symmetry at the general point of the line; the curvature is sharp because the chief perturbing influence comes from a curve which comes very close to the one in question. For these cases the curvature β at the symmetry point depends chiefly on the energy interval between the curves at that point, and can be calculated roughly.[26] Each of the lower curves of Figs. 5 and 6 was drawn by plotting a number of points on the parabola

$$\eta_k=\eta_0+\left[\frac{d\eta}{d(k^2)}\right]_{k=0}k^2$$

and then drawing a curve osculating this parabola at the bottom and osculating another parabola of curvature β at the top. The other curves were drawn in what seemed to be the most plausible manner, using the various β values.

With the aid of Figs. 5, 6, and 7 secondary

[26] The reasoning involved in such calculations of curvatures is discussed in more detail in Appendix IV.

graphs similar to Fig. 6 and Fig. 7 were drawn in planes $\frac{1}{3}$ and $\frac{2}{3}$ way between the plane of Fig. 6 and that of Fig. 7. In these planes none of the curves will intersect,[27] and use was made of the fact that the energy separation of two bands varies linearly with the distance in **k**-space from a "line of contact" in a plane of symmetry.[27] From all these graphs contours of constant η were drawn, and from their areas the number of states per unit range of η could be roughly determined. Figure 8 shows this distribution function, for $r_s=2.37$. The Fermi surface is represented by a vertical dotted line at $\eta=0.872$, and the distribution function is normalized to

$$\int_{0.007}^{0.872} n(\eta)d\eta=1.$$

For comparison two parabolas are also shown: the lower one shows what the distribution function would be for free electrons ($\eta_k=\eta_0+k^2$), and the upper one shows what it would be if η_k were

$$\eta_0+\left[\frac{d\eta}{d(k^2)}\right]_{k=0}k^2.$$

The Fermi surface appropriate to each of these cases is represented by a dotted line.

Table VIII gives, for three values of r_s, the energies $\eta_{\max}$ of the Fermi surface, and the average energies $\bar{\eta}$ of all occupied states, as determined by the graphical method just described. The differences $\delta\bar{\eta}$ and $\delta^2\bar{\eta}$ are also shown. However, one may very well doubt the accuracy of a second difference computed from three separate graphical calculations. To get an independent estimate of $\delta\bar{\eta}$ and $\delta^2\bar{\eta}$, one may try averaging the differences of the η_j, with appropriate weights w_j (such a procedure neglects the effect on $\delta^2\bar{\eta}$ of the change of the shape of the Fermi surface with lattice constant). For a choice of weights to be "reasonable," it should assign to each of the lower energy levels listed in Table VII a weight approximately proportional to the number of *distinct* wave functions belonging to the listed energy value, and to each of the higher levels a weight smaller than this number, to take account of the fact that levels near and above the Fermi surface affect the average energy of the filled region less than the lower levels. It is less easy to decide how much weight should be given to $[d\eta/d(k^2)]_{k=0}$. Figure 9 illustrates the difficulty.

TABLE VIII. *The energies of the Fermi surface and the average energies of all occupied states for three values of r_s.*

	$r_s=2.07$	2.37	2.67
$\eta_{\max}$ from graphs	1.18	0.87	0.64
$\bar{\eta}$ from graphs	0.701	0.480	0.337
$\delta\bar{\eta}$ from graphs		−0.221	−0.143
$\delta^2\bar{\eta}$ from graphs		0.078	
$\delta\bar{\eta}$ from w_j'		−0.257	−0.176
$\delta^2\bar{\eta}$ from w_j'		0.081	
$\delta\bar{\eta}$ from w_j''		−0.241	−0.165
$\delta^2\bar{\eta}$ from w_j''		0.076	
parabolic $\delta\bar{\eta}$		−0.193	−0.156
parabolic $\delta^2\bar{\eta}$		0.037	

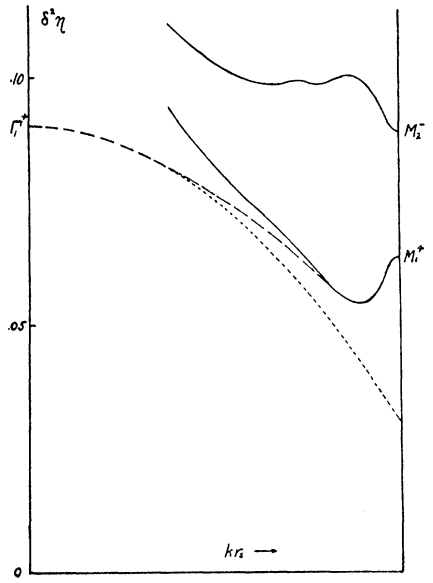

FIG. 9. Variation of $\delta^2\eta$ with kr_s.

Here $\delta^2\eta_k$ is plotted against kr_s along the line ΓM. If η_k were simply $\eta_0+k^2[d\eta/d(k^2)]_{k=0}$, the graph for the lower band would be the dotted parabola. Actually it must end at the value belonging to the M_1^+ state. The value of $\delta^2\bar{\eta}$ will depend quite seriously on whether or not the true curve follows the parabola nearly to the end, so it is important to decide just how the curve should be drawn. The rough β-values calculated in Appendix IV yield a sharp downward curvature at the M_1^+ end. Now β is the second-order part of a root of a second-degree secular equation; if the energy gap at the right hand end is sufficiently small, the exact solution

[27] See C. Herring, Phys. Rev. **52**, 365 (1937).

of this secular equation can be shown to yield a curve of $\delta^2\eta_k$ against k of the rather complicated form shown by the lower full curve. The true curve must deviate from this one by an amount which varies smoothly near the M_1^+ end, since it comes from matrix elements of $\partial/\partial x$ connecting the M_1^+ state with states a considerable distance from it. From the other end, it can be shown (see Section 9, Part (7)) that the curve of $\delta^2\eta_k$ against k must deviate from the parabola in the upward direction by a fairly appreciable amount if we neglect the perturbations due to the Fourier coefficients of the potential. We may therefore expect the true curve to look something like the dashed curve. Except for the dip near the end this is very much the type of curve we would draw if we were given the $\delta^2\eta$ values for Γ_1^+ and M_1^+, and knew nothing about $d\eta/d(k^2)$ or about any of the fine points just discussed. It should be noted, moreover, that in the next higher band the curve (upper full curve) has sharp variations which are almost the mirror image of those of the lower band, and if a small region near M_2^- in the higher band is occupied, $\delta^2\bar{\eta}$ will have about the same value as if the curves for both bands had been drawn smoothly.

Accordingly we may conclude that $\delta^2\bar{\eta}$ is probably about equal to the "reasonably weighted" average of the $\delta^2\eta_j$, to within the accuracy with which this average can be determined. In the last two columns of Table VII are given two sets of weights, w_j' and w_j''; the w_j'' are less "reasonable" than the w_j', having been chosen so as to give a value of $\delta^2\bar{\eta}$ which may be regarded as a lower limit. The $\delta\bar{\eta}$ and $\delta^2\bar{\eta}$ calculated from the w_j', from the w_j'', and from the parabolic assumption $\eta_k=\eta_0+k^2[d\eta/d(k^2)]_{k=0}$, are given in Table VII.

8. Error in Assuming Free Electron Exchange

The term $\frac{1}{2}\sum A_{ij}(\psi)$ in (28) is the exchange energy of the valence electrons. Order-of-magnitude calculations made by Seitz[1] have indicated that for alkali metals it is a rather good approximation to set this exchange energy per electron equal to $0.916X^{\frac{1}{3}}/r_s$, which is the exchange energy, per electron, of a perfect free electron gas whose density equals the density of valence electrons in the metal. For beryllium with $r_s=2.37$, this would give 0.482 rydberg per electron, or 304 kilocalories per gram atom. The largeness of this term, and the fact that the higher energy eigenfunctions for beryllium differ considerably from single plane waves, give us good reason to worry about the legitimacy of using the free electron value. As the actual exchange energy is very hard to calculate, however, we shall in this section merely give two lines of reasoning from which the limiting behavior of the exchange energy for low and high electron densities can be calculated; these make possible an estimate of the order of magnitude of the deviation from the free electron value for the actual case of beryllium.

The integral $A_{ij}(\psi)$ may be interpreted as twice the neutralized self-energy of the charge distribution $\psi_i^*\psi_j$ (if $j\neq i$ the neutralizing charge is zero). Let

$$\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})=\sum_{\mathbf{K}}\gamma_K(i,j)\exp\left[i(\mathbf{k}_j-\mathbf{k}_i+\mathbf{K})\cdot\mathbf{r}\right], \tag{44}$$

where $\mathbf{k}_i$ and $\mathbf{k}_j$ are the reduced wave vectors of ψ_i and ψ_j, and where $\mathbf{K}/2\pi$ runs over all vectors of the reciprocal lattice. Then the neutralized potential due to $\psi_i^*\psi_j$ is, if $i\neq j$,

$$4\pi\sum_{\mathbf{K}}\frac{\gamma_K(i,j)}{|\mathbf{k}_j-\mathbf{k}_i+\mathbf{K}|^2}\exp\left[i(\mathbf{k}_j-\mathbf{k}_i+\mathbf{K})\cdot\mathbf{r}\right] \tag{45}$$

(if $i=j$ the term $\mathbf{K}=0$ must be omitted). Since the $i=j$ term contributes only an amount of order $1/N$ to the energy per atom, it may be neglected; we then have from (45),

$$\tfrac{1}{2}\sum_{\substack{i,j\ \text{valence}\\ \text{spins}\ \|}}A_{ij}(\psi)=8\pi\Omega\sum_{\mathbf{K}}\sum_{\substack{i\neq j\\ \text{orbitals}}}\frac{|\gamma_K(i,j)|^2}{|\mathbf{k}_j-\mathbf{k}_i+\mathbf{K}|^2}, \tag{46}$$

where in the summation on the right i and j run over the orbital wave functions only, states with different spins being no longer distinguished.

Suppose now that we have a fictitious metal, for which the wave functions ψ_j of the various quantum states are the same as for the actual metal, but for which the number of valence electrons to occupy these states is less than for the actual metal by a factor ξ^3; the actual metal corresponds to $\xi=1$. Thus as $\xi\to 0$ the radius of the occupied region of k space is asymptotically proportional to ξ. The $\mathbf{K}=0$ term in (46) is of order ξ^4, while all the terms for which $\mathbf{K}\neq 0$ are of order ξ^6. For small ξ we can expand the wave function of any occupied state in a series in powers of the three rectangular components of its wave vector:

$$\psi_k=\exp(i\mathbf{k}\cdot\mathbf{r})[\psi_0+\sum_{\mu=1}^{3} ik_\mu v_\mu+\sum_{\mu,\nu=1}^{3}(ik_\mu)(ik_\nu)w_{\mu\nu}\cdots]. \tag{47}$$

We may choose ψ_0 real: then the v_μ, $w_{\mu\nu}$ will be real. This gives

$$\gamma_0(i,j)=\frac{1}{\Omega}\int_\Omega[|\psi_0|^2+i\psi_0\sum_{\mu=1}^{3}(k_{j\mu}-k_{i\mu})v_\mu+\sum_{\mu,\nu=1}^{3}k_{j\mu}k_{i\nu}v_\mu v_\nu-\psi_0\sum_{\mu,\nu=1}^{3}(k_{j\mu}k_{j\nu}+k_{i\mu}k_{i\nu})w_{\mu\nu}\cdots]d\tau. \tag{48}$$

Now the normalization of ψ_k requires that v_μ be orthogonal to ψ_0 and that

$$2\int_\Omega \psi_0 w_{\mu\nu}d\tau=\int_\Omega v_\mu v_\nu d\tau.$$

For cubic crystals

$$\int_\Omega v_\mu v_\nu d\tau=\lambda\delta_{\mu\nu}, \tag{49}$$

where

$$\lambda=\int_\Omega v_\mu^2 d\tau=\tfrac{1}{3}\int_\Omega[\sum_{\mu=1}^{3}v_\mu^2]d\tau; \tag{50}$$

it is probably a good approximation to assume that this is also true for hexagonal crystals with c/a close to 1.63 (this is similar to the assumption $\alpha_{||}=\alpha_\perp$ made in Section 4). Using these relations, (48) becomes

$$\gamma_0(i,j)=\frac{1}{\Omega}\left[1-\frac{\lambda}{2}|\mathbf{k}_j-\mathbf{k}_i|^2+0(\xi^4)\right]. \tag{51}$$

The $\mathbf{K}=0$ term of (46) is therefore

$$\frac{8\pi}{\Omega}\sum_{\substack{i\neq j\\ \text{orbitals}}}\left[\frac{1}{|\mathbf{k}_j-\mathbf{k}_i|^2}-\lambda+0(\xi^2)\right]. \tag{52}$$

If the filled region of $\mathbf{k}$-space is asymptotically spherical, as is always the case for cubic crystals, and as we are assuming for beryllium, it can easily be shown that

$$\frac{8\pi}{\Omega}\sum_{\substack{i\neq j\\ \text{orbitals}}}\frac{1}{|\mathbf{k}_j-\mathbf{k}_i|^2}=NnX\xi^3\left[\frac{0.916\xi}{r_e}\right]+0(\xi^8). \tag{53}$$

Here $NnX\xi^3$ is just the number of electrons in Ω, for our fictitious crystal, and

$$\frac{r_e}{\xi}=\left(\frac{3}{4\pi NnX\xi^3}\right)^{\frac{1}{3}}.$$

is the radius of a sphere whose volume equals the volume per electron. The first term of (53) is just the exchange energy, in rydbergs, of a free electron gas.[28] If the filled region of **k**-space were asymptotically ellipsoidal instead of spherical, the leading term in (53) would of course be different, and the remaining terms would be $0(\xi^6)$ instead of $0(\xi^8)$. In the terms of (46) with $\mathbf{K}\neq 0$ we have, using (47),

$$\gamma_K(i,j)=\gamma_K(0,0)+\sum_{\mu=1}^{3}(k_{j\mu}-k_{i\mu})f_{K\mu}+0(\xi^2),$$

where $f_{K\mu}$ is a Fourier coefficient of $i\psi_0 v_\mu$. Also,

$$\frac{1}{|\mathbf{k}_j-\mathbf{k}_i+\mathbf{K}|^2}=\frac{1}{K^2}-\frac{2(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{K}}{K^4}+0(\xi^2).$$

Inserting these in (46), the terms linear in $(\mathbf{k}_j-\mathbf{k}_i)$ drop out on summation, and we have

$$8\pi\Omega\sum_{\mathbf{K}\neq 0}\sum_{\substack{i\neq j\\ \text{orbitals}}}\frac{|\gamma_K(i,j)|^2}{|\mathbf{k}_j-\mathbf{k}_i+\mathbf{K}|^2}=8\pi\Omega\left(\frac{NnX\xi^3}{2}\right)^2\sum_{\mathbf{K}\neq 0}\frac{|\gamma_K(0,0)|^2}{K^2}+0(\xi^8). \tag{54}$$

We may note that

$$8\pi\Omega\sum_{\mathbf{K}\neq 0}\frac{|\gamma_K(0,0)|^2}{K^2}=C_{00}(\psi)$$

is just twice the neutralized self-energy of the charge distribution $|\psi_0|^2$. Combining (46), (52), (53), and (54) gives finally

$$\tfrac{1}{2}\sum_{\substack{i,j\ \text{valence}\\ \text{spins}\ ||}}A_{ij}(\psi)=NnX\xi^3\left[\left(\frac{0.916}{r_e}\right)\xi+\left(\frac{NnX}{4}C_{00}(\psi)-\frac{3\lambda}{2r_e^3}\right)\xi^3+0(\xi^5)\right]. \tag{55}$$

The bracketed quantity in (55) is the exchange energy per electron; for small values of ξ the second term gives the correction to be applied to the free electron value represented by the first term.

To calculate this correction numerically for beryllium we may note that the functions v_μ occurring in (47) are the same as those occurring in the corresponding expansion of φ_k in powers of the k_μ. Bardeen[2] has shown that in each atomic cell it is a good approximation to set

$$v_\mu=-x_\mu\varphi_0+\frac{x_\mu}{r^2}\left(\frac{r_s^2\varphi_0(r_s)}{f(r_s)}\right)f(r), \tag{56}$$

where f is the radial p function calculated in the same field used for φ_0, with the same energy E_0. We have already calculated f for use in (38). If we replace each atomic cell by an s sphere, the integral on the right of (50) can thus be expressed in terms of a radial integral of a known function. The resulting values of λ are given in the first line of Table IX. The second line of Table IX gives the values of $\frac{1}{4}NnXC_{00}(\psi)$, which can be calculated by radial integrations of the sort used in Appendix II. The third line represents the correction to the exchange energy per electron which would obtain if the $0(\xi^5)$ in (55) could be neglected even for $\xi=1$. The second derivative of this term with respect to r_s is quite appreciable, as is to be expected from the occurrence of r_e^3 in the denominator. Actually, of course, the $0(\xi^5)$ in (55) becomes appreciable (for beryllium) when ξ is still rather smaller than 1, and we cannot trust the last line of Table IX to give anything more than the order of magnitude of the correction to be added to the free electron exchange energy. For monovalent metals, however, (55) might give a good approximation.

[28] Cf. Wigner and Seitz, reference 1.

To get an expression valid for larger values of ξ, one might try to evaluate higher terms in the expansion of the exchange energy in powers of ξ, just as the first two were obtained above. This does not seem impossible, although the next term would be much harder to calculate than the first two. However, when the Fermi surface extends beyond the first planes of energy discontinuity in **k**-space, we can no longer expect such a formal power series to be valid for $\xi=1$.

Two other possible lines of attack suggest themselves, but they both appear even less valid than the preceding. One is to start from a free electron gas, and treating the potential U as a small perturbation, to find the second-order change in the exchange energy. This second-order change can be expressed as a rapidly convergent series of terms containing the squares of the Fourier coefficients $U[\mathbf{K}]$. But the rapidity of the convergence is misleading: it can be shown that each term is positive, so that in the second order the perturbation increases the exchange energy, for any value of ξ; this does not agree with the result obtained for beryllium above (Table IX) that for small ξ the exchange energy is less than for free electrons. This is not surprising, since the wave functions obtained by applying a small perturbation to plane waves do not resemble the true wave functions at all in the regions near nuclei.

The second possibility is to use a Fermi-Thomas model, assuming a large number of electrons to be present in a region in which U changes only slightly (ξ very large). For this model the exchange energy per electron in a given region of space is $0.916/\rho_e(\mathbf{r})$ where $(4\pi/3)[\rho_e(\mathbf{r})]^3$ is the reciprocal of the electron density at the point $\mathbf{r}$. Multiplying this by the electron density and integrating give the total exchange energy. The final result is

$$\text{Average exchange energy per electron}=\frac{0.916\xi}{r_e}\left\{\frac{\frac{1}{\Omega}\int_\Omega (E_m-U)^2 d\tau}{\left[\frac{1}{\Omega}\int_\Omega (E_m-U)^{3/2}d\tau\right]^{4/3}}\right\}, \tag{57}$$

where E_m is the energy of the highest occupied state, which is of order ξ^2 as $\xi\to\infty$. The coefficient of $0.916\xi/r_e$ is always >1, so here again the exchange energy is greater than for free electrons. If (57) were assumed to hold for $\xi=1$, this coefficient would be roughly 1.9; however, most of the contribution to this value comes from regions within a few tenths of a Bohr unit from each nucleus, where for $\xi=1$ the Fermi-Thomas model is completely inapplicable.

9. Results and Discussion

(1) Binding energy

If we insert in (28) the free electron values for the Coulomb and exchange energies, use the precise value (see Part (6) of this section) for the electrostatic interaction energy of the ions, and then add to (28) the free electron value of the correlation energy, for which Wigner[16] has given the expression $1.16/(r_e+5.1)$ rydbergs per electron, we obtain for the energy per atom of the crystal

$$\frac{W}{2N}=2\bar{\eta}-\frac{7.077}{r_s}-\frac{1.46}{r_s+6.4}-0.074\bar{s}^2B. \tag{58}$$

Inserting in (58) the observed value of 2.37 for r_s and the graphically determined value of $\bar{\eta}$ from Table VIII, and subtracting the observed energy -2.024 rydbergs of the neutral Be atom, there results a binding energy of 0.170 rydberg per atom, or 53 kilocalories per gram atom. If we were to assume the deviation from the free electron value of the exchange energy per electron to be as given by the last line of Table IX, this correction would decrease the above value

Table IX.

	$r_s=2.07$	2.37	2.67
λ	0.165_0	0.135_2	0.109_5
$\frac{NnX}{4}C_{00}(\psi)$	0.003	0.002	0.002
$\left(\frac{NnX}{4}C_{00}(\psi)-\frac{3\lambda}{2r_e^3}\right)$	−0.053	−0.028	−0.015

TABLE X. *Values of r_s and $1/\kappa$ as obtained in various ways.*

	r_s	$(1/\kappa)\times10^{-12}$
from graphs	2.23	0.87
from w_i'	2.57	1.32
from w_i''	2.45	1.00
experimental[29]	2.37	1.25

of the binding energy to 36 kilocalories. However, there seems to be both theoretical and empirical evidence (see Part (5) below) that the exchange energies of electrons near the Fermi surface are numerically greater than the free electron values, so that the average deviation from the free electron exchange energy is probably less than that given in Table IX, perhaps even of the opposite sign. The deviation of the Coulomb energy from the free electron value, whose order of magnitude is estimated in Appendix II, increases the binding energy by about 2 kilocalories.

(2) The experimental value of the binding energy

The only direct determination of the binding energy of beryllium is that of Baur and Brunner.[30] These authors by measuring the slope of a vapor pressure curve find 53.5 kcal./g-atom for the heat of sublimation at around 2000°K; the heat of sublimation at 0°K, which is to be compared with the binding energy calculated above, should be at most a few kilocalories greater than this. Such a value would agree nicely with the theory, but we feel that it cannot be correct. For it is possible to calculate the heat of sublimation from the vapor pressure at a single temperature, if the latent heat of fusion is known, together with specific heats of the solid and liquid phases over the entire temperature range. To obtain a heat of sublimation as small as 53.5 kcal. at any of the temperatures at which Baur and Brunner measured the vapor pressure one would have to assume a specific heat for molten beryllium of nearly 20 cal./g-atom/°C. If instead a value of 8 cal. is assumed the heat of sublimation at 2111°K is around 80 kcal./g-atom if the Baur and Brunner value of the vapor pressure at this temperature is used. This would mean a value of about 85 kcal./g-atom at 0°K which value we feel is nearer the truth. This is also more in line with the estimate of 75 kcal./g-atom given by Bichowsky and Rossini.[31]

(3) Lattice constant and compressibility

The energies given by (58) for the three values 2.07, 2.37, and 2.67 of r_s can be fitted to a parabola, whose minimum gives the theoretical equilibrium value of r_s. The compressibility in c.g.s. units is given by

$$\frac{1}{\kappa}=\frac{3.88\times10^{12}}{r_s}\left[\frac{d^2}{dr_s^2}\left(\frac{W}{2N}\right)-\frac{2}{r_s}\frac{d}{dr_s}\left(\frac{W}{2N}\right)\right], \quad (59)$$

where r_s is still to be measured in Bohr units, $W/2N$ in rydbergs. The second term vanishes at the equilibrium lattice constant. We shall calculate $1/\kappa$ for $r_s=2.37$, and since this is not the theoretical equilibrium lattice constant, there will be a small contribution from the second term.

Table X gives the values of r_s and $1/\kappa$ resulting from (58) and (59) for each of the estimates of $\delta\bar{\eta}$ and $\delta^2\bar{\eta}$ in Table VIII. No values of r_s and $1/\kappa$ are given corresponding to the parabolic assumption, because when the resulting $\delta\bar{\eta}$ and $\delta^2\bar{\eta}$ are used the curve of W against r_s is concave downward. If the last line of Table IX were used for the deviation from the free electron value of the exchange energy, the values of $1/\kappa$ would be increased by about 0.3. The deviation from the free electron value of the Coulomb energy will introduce a correction of only a few percent into the calculated values of $1/\kappa$, and will have a negligible effect on r_s.

Bardeen[2] has pointed out that a relation

$$W=A(r_0/r_s)^3+B(r_0/r_s)^2-C(r_0/r_s) \quad (60)$$

suggested by some work of Fröhlich,[32] holds rather well for alkali metals. Bardeen chose the constants A, B, C, to fit the observed binding energy, lattice constant, and compressibility at zero pressure; he then calculated the variation of compressibility with volume and found it in good agreement with experiment. The same procedure applied to beryllium gives a pressure coefficient of compressibility about two-thirds

[29] At room temperature. Compressibility from P. W. Bridgman, Proc. Am. Acad. Arts and Sciences **68**, 27 (1937).

[30] E. Baur and R. Brunner, Helv. Chim. Acta **17**, 958 (1934).

[31] F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold, 1936).

[32] H. Fröhlich, Proc. Roy. Soc. **A158**, 97 (1937).

the observed value.[33] This is sufficiently close so that we can use (60) to estimate the amount of error in the assumption, used above, that W varies parabolically with r_s. In this way it can be concluded that the r_s values given in Table X are too large by something like 0.05 Bohr unit, and that the $1/\kappa$ values are too large by ten or fifteen percent.

(4) Diamagnetism

Beryllium is known to be rather strongly diamagnetic,[34] whereas magnesium and calcium, the two metals which ought to resemble it most closely in electronic structure, are paramagnetic. The chief cause of this may very well be the low density of electronic states near the Fermi surface, which is shown by the heavy curve in Fig. 8. This abnormally low density causes the paramagnetic contribution which the spins of the electrons make to the total susceptibility to be only a fraction of the value it would have if the electrons were free.

(5) Work function

The work function ϕ is the change in the energy of the crystal when one electron is removed; if starting from (28) we follow the line of reasoning used by Wigner and Bardeen,[3] and include the correlation energy as in (58) above, we obtain

$$-\phi=\eta_{\max}-\frac{4}{3}\frac{(2)^{\frac{1}{3}}0.916}{r_s}-\frac{0.73}{r_s+6.4}-\frac{0.73r_s}{3(r_s+6.4)^2}-D, \quad (61)$$

where D is the discontinuity in the potential energy of an electron (measured in rydbergs) which occurs at the surface of the crystal because of the double layer, and where the exchange energy per electron has been assumed to have the free electron value $0.916/r_e=(2)^{\frac{1}{3}}0.916/r_s$. Inserting 2.37 for r_s in (61) and taking $\eta_{\max}$ from Table VIII, we find

$$\phi=-0.14+D.$$

Now experimentally ϕ is about 3.9 volts,[35] or 0.29 rydberg. There is thus 0.43 rydberg to be accounted for by the double layer and by the deviation from the free electron values of exchange and correlation energy. The correlation terms in (61) are rather small, so it is reasonable to put most of the blame on the double layer and the exchange. For the alkali metals D is known to be small, of the order of a few hundredths of a rydberg.[3] For beryllium it should be larger, because there are two electrons per atom and because the electrons move faster; but a value as large as 0.43 rydberg would be very unreasonable. Probably, therefore, one must assume that the exchange energies of electrons at the Fermi surface are considerably greater than the corresponding free electron values. This is not unreasonable, although a very large effect is needed to remove the discrepancy on the work function. For the wave functions considered in Section 8, for example, some of the terms $A_{ij}(\psi)$ can become quite large, although the large part tends to cancel out on summation. Of course, the possibility should not be entirely eliminated that a pure beryllium surface would have a very low work function, and that in spite of careful precautions the observed values are due to oxygen contamination.

(6) Electrostatic energy of the ions and its variation with c/a.

The quantity $\sum_\nu{}'4/D(\mathbf{R}_\nu)$ which occurs in (28) and (36) represents the neutralized potential, at the position of an ion at the origin, due to all the other ions. The deviation of this quantity from $-36/5r_s$ was needed in Section 4. Moreover, the success of the theory of Fuchs[36] in predicting the elastic constants of the alkali metals leads one to suspect that the behavior of this electrostatic term may be important in determining the equilibrium value of the ratio c/a, and possibly in determining the relative stability of different lattice types.[37] In Fig. 10 the ratio of $\sum_\nu{}'1/D(\mathbf{R}_\nu)$ to $1/r_s$, as calculated

[33] P. W. Bridgman, reference 31, corrected for the improved pressure-volume relation for iron, which was used as a reference material, Phys. Rev. **57**, 235 (1940).

[34] M. Owen, Ann. d. Physik **37**, 657 (1912).

[35] M. M. Mann and L. A. DuBridge, Phys. Rev. **51**, 120 (1937).

[36] K. Fuchs, Proc. Roy. Soc. **A153**, 622 (1936) and Proc. Roy. Soc. **A157**, 444 (1936).

[37] H. B. Huntington, Phys. Rev. **57**, 60 (1940), has shown that the elastic constants of divalent hexagonal metals as determined from electrostatic energy of the ions do not agree nearly so well with experiment as do those for the alkali metals. So the electrostatic energy of the ions is probably only one of a number of factors determining the equilibrium c/a for beryllium.

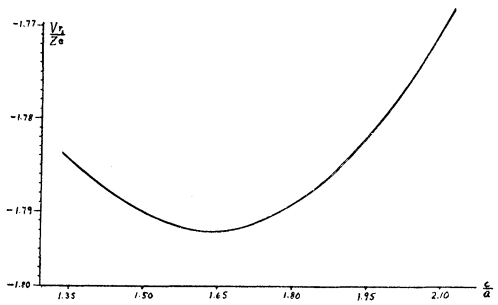

FIG. 10. Variation with c/a of the neutralized potential $\bar{V}$ produced at an ionic position by all other ions.

by the method of Ewald,[8] is plotted against c/a. The minimum electrostatic energy comes very close to $c/a=1.63$, although there seems to be no symmetry requirement which would cause the minimum to occur at exactly this point. At $c/a=1.63$,

$$\sum_{\nu}{}'\frac{4}{D(\mathbf{R}_\nu)}+\frac{36}{5r_s}=\frac{0.031_7}{r_s};$$

for the face-centered and body-centered cubic lattices this quantity has the values $0.03312/r_s$ and $0.03256/r_s$, respectively.[36] The differences between these quantities represent the differences in rydbergs per atom, between the electrostatic energies of the three lattice types; the electrostatic energy for the hexagonal lattice is thus lower than for either of the cubic types, but by an amount which is probably too small to be significant in determining the stable type.

(7) Remarks on the calculations

Apart from the deviation of the exchange and correlation energies from the free electron values, the principal uncertainties in the calculations of the above quantities arise from the use in Section 5 of an insufficient number of constituent χ-states and of a very crude estimate of the overlap integrals. The neglect of the perturbation of the valence electron states by the matrix elements connecting them with the core states ((16) and (17) of reference 5) is less serious. From Fig. 4 one can estimate that the energy given in Table V for the Γ_3^- state is too high by something like 0.01 Ry; this has been confirmed by a more accurate solution of the secular equation for this state. The other energies may be expected to be in error by a similar amount. This would account for a part, but probably only a part, of the difference between our calculated binding energy and the probable true value. The overlap uncertainty, whose order of magnitude is indicated by the ΔE's in Table V, is negligible for $r_s=2.37$, so it does not affect the binding energy. Its effect on the lattice constant and compressibility may be appreciable, but we do not think it can be very great, as some of the ΔE's in Table V are positive and some negative. Moreover, the lattice constant and compressibility will not be much affected by the neglect of the higher constituent χ-states, since most of the contribution to the variation of the E's with r_s in Table V comes already from the unperturbed $\bar{E}$'s. Combining these facts with what has been said in (1), (3), and (6) above, and in Section 8, it may be concluded that the exchange correction is probably fairly important for the binding energy, lattice constant, and compressibility, and apparently very important for the work function. The correlation energy probably differs from the free electron value by only a fraction of the latter, and probably varies less rapidly with r_s than does the exchange. The comparison of theory with experiment cannot make possible any stronger assertions about correlation than these, since for beryllium exchange is larger relative to correlation than for the alkalis and deviates so strongly from the free electron value that it largely masks the behavior of the correlation energy. However, *a priori* one might expect the polarization of the core by the valence electrons to have a serious effect, especially for the compressibility. The approximate agreement between theory and experiment tends to show that this effect must be small.

The orthogonalized plane wave method of calculating energy values provides an illuminating interpretation of the way in which E_k varies with $\mathbf{k}$. If $\mathbf{k}$ is not too near the boundary of the Brillouin zone, the principal term in E_k is the average energy of the wave function χ_k obtained by orthogonalizing a plane wave to the core functions. For beryllium, if we neglect overlap effects, this term is

$$\bar{E}_k=\frac{k^2+U[0]+9.1A_{1s}{}^2(k)}{1-2A_{1s}{}^2(k)} \quad \text{(cf. (40) and (41))}. \quad (62)$$

Now $A_{1s}^2(k)$ is $1/r_s^3$ times a function of k which decreases monotonically toward zero as k increases. So (62) shows why α is less than 1, why α decreases with decreasing r_s, and why the curve of E_k against k tends to deviate in the upward direction from the osculating parabola $E_k=E_0+\alpha k^2$. This upward deviation is of course often nullified by the influence of Bragg reflections.

In conclusion the authors wish to express their thanks to Professors J. C. Slater, E. Wigner and F. Seitz for discussions of various parts of this paper.

Appendix I

A rough upper limit to the interaction energy of two beryllium ion cores can be obtained quickly by considering a pair of fictitious atoms, each consisting of a nucleus of charge $2e(Z/2)^{\frac{1}{2}}$, and two "electrons" each of mass m and charge $e(Z/2)^{\frac{1}{2}}$. The fictitious atom is thus simply a helium atom with the electronic charge increased by $(Z/2)^{\frac{1}{2}}$, making the potential energy of an electron in the field of the nucleus the same function of r for the fictitious atom as for the actual ion core. Since the electrons in the fictitious atom repel each other more strongly than those in the ion core, we may expect the electron distribution of the former to be more spread out than that of the latter, hence the repulsive exchange force at large distances will be greater for the fictitious atoms than for the ion cores. The increased interaction of the electrons will also cause the van der Waals attraction between the fictitious atoms to be greater than that between the ion cores. Therefore, if both types of force are negligible for the fictitious atoms, the interaction of the ion cores can be neglected.

If $w(r)$ is the interaction energy of two helium atoms a distance r apart, dimensional considerations show that the interaction energy of a pair of our fictitious atoms must be $\frac{1}{4}Z^2w(\frac{1}{2}Zr)$. Now for $r_s=2.07$ Bohr units, nearest neighbor atoms in the beryllium lattice are 3.74 Bohr units apart, and at twice this distance the van der Waals term for helium predominates over the repulsive one. Using the expression for w given by Margenau[38] we have

$$4w(2\times 3.74)=-0.00007 \text{ rydberg},$$

which is quite negligible.

Appendix II

The Coulomb energy correction to the total energy values used in Section 9 consists of two parts: the sum

$$\frac{-1}{2Nn}\sum_{i,j \text{ valence}} C_{ij}(\varphi),$$

and the correction to $2\bar{\eta}$ required by the fact that we have calculated the η's using the potential (32) instead of (30). Thus to the energy values we have used should be added

$$\frac{\Delta W_H}{nN}=-\tfrac{1}{2}\int_{\text{atomic cell}}\rho v_{\text{val}}d\tau+\int_{\text{atomic cell}}\rho(\mathbf{r})\sum_\nu[v(\mathbf{r}-\mathbf{R}_\nu)-v_1(\mathbf{r}-\mathbf{R}_\nu)]d\tau+\int_{\text{atomic cell}}\rho v_{\text{val}}d\tau,$$

where ρ is the charge density of valence electrons.

Since $[v-v_1]$ differs from zero only inside the radius r_s,

$$\frac{\Delta W_H}{nN}=\tfrac{1}{2}\int_{\text{atomic cell}}\rho v_{\text{val}}d\tau+\int_{\text{atomic cell}}\rho[v-v_1]d\tau. \tag{A}$$

In the regions between a cell and an s sphere ρv_{val} is nearly constant and $[v-v_1]$ is negligible, so in both integrals the region of integration may be changed to the s sphere without sensible error.

To obtain ρ and v_{val} accurately, it would be necessary to calculate the charge distributions due to all the various eigenfunctions, and average them. However, the order of magnitude of the cor-

[38] H. Margenau, Phys. Rev. **56**, 1000 (1939), Eq. (20).

rection can be estimated for $r_s=2.37$ by using as a rough approximation to ρ a distribution ρ_1 consisting of a charge of two electrons distributed with a density proportional to $|\varphi_{00}|^2+\frac{1}{3}R_p^2$. As described in Section 3, the neutralized potential due to this distribution is just $[v-v_1]$. For $r_s=2.37$ we have therefore

$$\frac{\Delta W_H}{nN}\approx -\tfrac{1}{2}\int_{s\text{ sphere}}\rho_1[v_1-v]d\tau=-\tfrac{1}{2}\int_{s\text{ sphere}}(\rho_1-\bar{\rho}_1)[v_1-v]d\tau, \tag{B}$$

where $\bar{\rho}_1=3/2\pi r_s^3$ may be introduced because $[v_1-v]$ has average value 0. If we define $Z_0(r)$ as $4\pi\int_0^r(\rho_1-\bar{\rho})r^2dr$, the right of (B) becomes

$$-\tfrac{1}{2}\int[v_1-v]dZ_0=\tfrac{1}{2}\int Z_0d[v_1-v]=-\int_0^{r_s}\left(\frac{Z_0}{r}\right)^2dr. \tag{C}$$

Evaluation of this integral gives $\Delta W_H/nN\approx -0.0063$. A rough upper bound for the rate of variation of this correction with r_s can be obtained by noting that if the contributions to the integral on the right of (C) are almost entirely from small values of r, the first integral on the right of (A) will be roughly proportional to r_s^{-6}, the second to r_s^{-3}. If this were assumed we should have

$$\frac{\Delta W_H}{nN}\approx 0.0063\left(\frac{2.37}{r_s}\right)^3\left[\left(\frac{2.37}{r_s}\right)^3-2\right]. \tag{D}$$

Direct calculations of $C_{00}(\varphi)$ and $C_{00}(\psi)$ which were made for different lattice constants showed that the former is roughly proportional to r_s^{-6}, but that the latter varies much less rapidly (see Table IX). It is likely that (A) also varies rather less rapidly than (D).

The self-energy $\frac{1}{2}C_{00}(\psi)$ of ψ_0 is needed in Section 8. This may be reduced to an integral like that on the right of (C), a rough evaluation of which yielded the values listed in Table IX.

Appendix III

To find s_k and p_k for small values of k, let us set

$$\varphi_k=e^{i\mathbf{k}\cdot\mathbf{r}}[\varphi_0+\sum_{\mu=1}^{3}ik_\mu v_\mu+\sum_{\mu,\nu=1}^{3}(ik_\mu)(ik_\nu)w_{\mu\nu}+\cdots], \tag{A}$$

$$E_k=E_0+\alpha k^2+\cdots. \tag{B}$$

Inserting (A) and (B) in the Schrödinger equation and setting to zero each term of the resulting power series in the components of $\mathbf{k}$, we have a sequence of wave equations, the first three of which are

$$(-\nabla^2+U-E_0)\varphi_0=0, \tag{C}$$

$$(-\nabla^2+U-E_0)v_\mu-2\partial\varphi_0/\partial x_\mu=0, \tag{D}$$

$$(-\nabla^2+U-E_0)w_{\mu\nu}-\left(\frac{\partial v_\mu}{\partial x_\nu}+\frac{\partial v_\nu}{\partial x_\mu}\right)+(\alpha-1)\delta_{\mu\nu}\varphi_0=0. \tag{E}$$

The boundary conditions are that φ_0, v_μ, and $w_{\mu\nu}$ must all have the periodicity of the lattice. Bardeen has shown[2] that a good approximation to v_μ in each atomic cell is

$$v_\mu=\frac{x_\mu}{r}\left[-r\varphi_0+\frac{r_s^2\varphi_0(r_s)}{f(r_s)}\frac{f}{r}\right], \tag{F}$$

where f is a radial p function satisfying $d^2f/dr^2+[E_0-2/r^2-U]f=0$. The first term of (F) is a particular solution of (D); the second is a solution of the associated homogeneous equation, so

chosen as to make v_μ vanish on the surface of the s sphere. Expanding the exponential in (A) and using (F), we have

$$p \text{ part } \varphi_k = \frac{i\mathbf{k}\cdot\mathbf{r}}{r}\left[\frac{r_s^2\varphi_0(r_s)}{f(r_s)}\frac{f}{r}+0(k^3)\right]. \tag{G}$$

From (19) therefore

$$p_k = k^2\left[\frac{r_s^2\varphi_0(r_s)}{f(r_s)}\right]^2\cdot\frac{4\pi}{3}\frac{f^2}{P_{2p}^2}+0(k^4). \tag{H}$$

Putting (A) into (18), s_k is defined for small k by

$$s_k = \left|\frac{\varphi_0(0)-\sum_{\mu,\nu=1}^{3}k_\mu k_\nu w_{\mu\nu}(0)}{\varphi_{00}(0)}\right|^2+0(k^4) \tag{I}$$

$$= \frac{\varphi_0(0)^2-\frac{2}{3}\varphi_0(0)w(0)k^2}{|\varphi_{00}(0)|^2}+0(k^4),$$

where

$$w=\sum_{\mu=1}^{3}w_{\mu\mu}.$$

An approximate expression for w can be obtained by steps similar to those used in obtaining (F). It can readily be verified that a particular solution of (E) is

$$w_{\mu\nu}^{(0)} = -\frac{(x_\mu v_\nu+x_\nu v_\mu)}{2}-\frac{x_\mu x_\nu}{2}\varphi_0-\frac{\alpha}{2}\delta_{\mu\nu}\frac{\partial\gamma}{\partial E}\Big]_{E=E_0}, \tag{J}$$

where in the last term $\gamma(E, \mathbf{r})$ may be any function which satisfies the wave equation (C) with E_0 replaced by E, and which varies continuously with E in such manner that $\gamma(E_0, \mathbf{r})=\varphi_0$. We shall take for γ the $2s$ function obtained by outward integration starting from the value $\varphi_0(0)$. The general solution of (E) is thus $w_{\mu\nu}^{(0)}+w_{\mu\nu}^{(1)}$, where $w_{\mu\nu}^{(1)}$ satisfies the homogeneous equation. We must choose $w_{\mu\nu}^{(1)}$ so that this sum satisfies the boundary conditions and the normalization condition

$$\int_{\Omega_0}[v_\mu v_\nu-2\varphi_0 w_{\mu\nu}]d\tau=0. \tag{K}$$

We are here interested only in the function w which occurs in (I). Let us set

$$w^{(0)}=\sum_{\mu=1}^{3}w_{\mu\mu}^{(0)}, \quad w=w^{(0)}+w^{(1)}.$$

It can be verified that $w^{(0)}$ is almost spherically symmetrical, and almost satisfies the boundary conditions. Therefore w will be almost spherically symmetrical and so if we take the trace of Eq. (K) it will be permissible to change the region of integration in the resulting equation from a cell to an s sphere:

$$\int_{s \text{ sphere}}[\sum_{\mu=1}^{3}v_\mu^2-2\varphi_0 w]d\tau=0. \tag{L}$$

We need only the s part of w in (I), and this can now be determined from (L). Since $w^{(1)}$ satisfies the same wave equation as φ_0,

$$s \text{ part of } w^{(1)}=b\varphi_0$$

and b can be determined by substituting $w=w^{(0)}+w^{(1)}$ in (L). The result is most conveniently

expressed if φ_k is considered to be normalized to 1 over an atomic cell, instead of over Ω as in the text. It is

$$2b=3\lambda+\int_{s\text{ sphere}}\varphi_0\left\{2\sum_{\mu=1}^{3}x_\mu v_\mu+r^2\varphi_0+\alpha\frac{\partial\gamma}{\partial E}\right]_{E=E_0}\Bigg\}d\tau, \tag{M}$$

where

$$\lambda=\int_{s\text{ sphere}}v_\mu^2 d\tau$$

is the same as the quantity defined by (50). The integration in (M) can easily be reduced to a radial integral and evaluated numerically. Since $w(0)=w^{(1)}(0)=b\varphi_0(0)$, we have from (I)

$$\frac{d}{d(k^2)}\left(\frac{s_k}{s_0}\right)\Bigg]_{k=0}=-\tfrac{2}{3}b. \tag{N}$$

Appendix IV

A direct calculation of the variation of η_k with $\mathbf{k}$ near a symmetry point of Fig. 1 would be rather involved, since to the calculated variation of E_k would have to be added that of all the other terms in (29). These other terms may change quite considerably in a short distance from the symmetry point, since the form of the wave function varies rapidly with k near a small energy gap. However, a fair approximation to the behavior of η_k near such a point can be obtained by noting that the η_k are roughly the energy parameters which would occur in the solution of a wave equation formed with some potential U', different from U, but independent of $\mathbf{k}$.

Let $\boldsymbol{\Theta}$ be one of the symmetry points in Fig. 1, and let $\varphi_{j\Theta}$, $\eta_{j\Theta}$ be the complete set of wave functions and energies going with reduced wave vector $\boldsymbol{\Theta}$. Let $j=1$ and $j=2$ correspond to the states of the two lowest valence electron bands, and suppose for simplicity that the levels $\eta_{1\Theta}$ and $\eta_{2\Theta}$ are nondegenerate, so that $\partial\eta_k/\partial\mathbf{k}=0$ at Θ for the bands 1 and 2. For any $\boldsymbol{\kappa}$ we can write for the wave function of band 1 the infinite series

$$\varphi_{\Theta+\kappa}=e^{i\boldsymbol{\kappa}\cdot r}\sum_j b_j\varphi_{j\Theta}. \tag{A}$$

The chief contribution to the summation in (A) will come from small values of j; if the separation of bands 1 and 2 at $\boldsymbol{\Theta}$ is small compared with the distance of band 1 from any other band, the terms $j=1$ and 2 will be much more important for small κ than any others. If (A) is substituted in the wave equation $(-\nabla^2+U'-\eta_{\Theta+\kappa})\varphi_{\Theta+\kappa}=0$, there results the secular equation

$$\det\left[2\boldsymbol{\kappa}\cdot\mathbf{F}_{ij}+(\eta_{j\Theta}+\kappa^2-\eta_{\Theta+\kappa})\delta_{ij}\right]=0, \tag{B}$$

where $\mathbf{F}_{ij}=-i(\varphi_{i\Theta},\nabla\varphi_{j\Theta})$. If κ is very small this can be solved by the Schrödinger perturbation method. When κ is so large that $\boldsymbol{\kappa}\cdot\mathbf{F}_{12}$ is of the same order of magnitude as $(\eta_{2\Theta}-\eta_{1\Theta})$, however, this procedure must be modified by first finding two functions φ_a, φ_b, which are orthogonal linear combinations of $\varphi_{1\Theta}$ and $\varphi_{2\Theta}$ and which diagonalize the part $i,j=1,2$ of the matrix in brackets in (B). After this has been done we may set up the secular equation relative to these two new functions and the remaining functions $\varphi_{3\Theta}$, $\varphi_{4\Theta}\cdots$, and solve this by the perturbation method. This procedure will work for values of κ which are an appreciable fraction of the diameter of the Brillouin zone, provided $\eta_{3\Theta}$, $\eta_{4\Theta}$ are separated from $\eta_{1\Theta}$ by amounts of the order of magnitude of those which would be encountered for almost free electrons. Let η_a, η_b be the energies corresponding to φ_a, φ_b: they are the roots of the second-degree secular equation obtained by taking only $i,j=1,2$ in (B). Thus $\eta_{\Theta+\kappa}$ for band 1 is η_a plus perturbations from the higher states.

The second-order perturbations from $\varphi_{3\Theta}$, $\varphi_{4\Theta}$, $\cdots$ may vary rapidly with κ, since φ_a and φ_b vary rapidly with κ when κ is small; however, the sum of these second-order perturbations will always be less than some function $c\kappa^2$, where c is of the order of 1. They can therefore

be neglected in rough calculations of the manner of variation of $\eta_{\Theta+\kappa}$ with κ for small κ, since as will be shown presently the variation of η_a with κ is on a rather larger scale than $c\kappa^2$. We have

$$\eta_a=\tfrac{1}{2}(\eta_{1\Theta}+\eta_{2\Theta}) +\kappa^2-\tfrac{1}{2}[(\eta_{2\Theta}-\eta_{1\Theta})^2+16|\boldsymbol{\kappa}\cdot\mathbf{F}_{12}|^2]^{\frac{1}{2}}, \quad (C)$$

while η_b has the same form with a plus sign before the radical. Successive differentiations of (C) with respect to K, and with respect to r_s holding Kr_s constant, establish the existence of the maxima and minima shown in Fig. 9, provided the difference $(\eta_{2\Theta}-\eta_{1\Theta})$ is sufficiently small.

The quantities

$$\beta_\Theta=\tfrac{1}{2}\frac{\partial^2\eta_{\Theta+\kappa}}{\partial\kappa^2}\Big]_{K=0}\approx\tfrac{1}{2}\frac{\partial^2\eta_a}{\partial\kappa^2}\Big]_{\kappa=0}$$

are easily obtained from (B) or (C). The required matrix elements $\mathbf{F}_{12}$ were calculated for several points Θ, using for the wave functions the best approximation which could be obtained from two constituent χ-functions (for most of the (s) states it turned out that the wave function could not be well approximated by a single constituent χ-function, but could be by two). These matrix elements were found to be within about 25 percent of the values they would have for almost free electrons.

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Design and Preliminary Performance Tests of the Westinghouse Electrostatic Generator

W. H. WELLS, R. O. HAXBY,* W. E. STEPHENS,* AND W. E. SHOUPP*
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

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Design and performance characteristics of the Westinghouse electrostatic generator are discussed. Steady voltages of 1.3 Mv at atmospheric pressure and up to a maximum to date of 3.7 Mv at about 75 lb./sq. in. have been used to accelerate hydrogen ions. The maximum steady voltage is limited mainly by sparking along the belts. The voltage remains constant to within 0.5 percent for observing times of several minutes, and at times to within 0.2 percent for a half-minute or so.

INTRODUCTION

DURING the past three years, a large electrostatic generator of the belt type, using compressed air insulation, has been constructed at the Westinghouse Research Laboratories in East Pittsburgh. It has been in satisfactory operation for nearly a year as a source of high energy protons for research in nuclear physics. This paper gives an account of the design features and a preliminary account of its performance. Details of the researches in nuclear physics carried out to date will be published soon in other papers.

The first successful utilization of air under high pressure as insulating medium for an endless-belt electrostatic generator was made by Barton, Mueller, and L. C. Van Atta[1] but they did not apply the potential to an accelerating tube. Herb, Parkinson, and Kerst,[2] using a somewhat similar generator successfully applied 400 kv to a vacuum tube to accelerate hydrogen ions. A larger generator was then constructed by them[3] and the performance of these generators indicated that further development to larger dimensions was a practical method of obtaining a beam of high energy ions having energy

* Westinghouse Research Fellow.

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