

Electronic Energy Bands in Metallic Lithium

J. MILLMAN, *Massachusetts Institute of Technology*

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The extension of Wigner and Seitz's method developed by Slater is applied to metallic lithium. Calculations corresponding to those of Slater for sodium have been made and the results discussed. One essential difference between these metals is that the conduction electrons in lithium are much more tightly bound than those of sodium.

INTRODUCTION

WIGNER, Seitz and Slater¹ have developed a method for calculating the electronic properties of metals and have applied this method to sodium. In this paper are presented the results of the application of their theory to the case of metallic lithium. Briefly, the method may be summarized as follows: Each ion in the metallic lattice is considered at the center of a polyhedral cell, the cells being so formed that the whole metal is obtained by tightly packing them together. In the case of a body centered lattice, which is the structure of all the alkali metals, these cells are truncated octahedrons formed by the intersections of planes which perpendicularly bisect lines joining an ion with its eight nearest and its six next nearest neighbors. Within each of these cells the potential is assumed to have spherical symmetry. In a simple translation from a point on one face of the polyhedron to the perpendicularly opposite point on the opposite face the wave function of an electron, according to a general theorem of Bloch,² will have become multiplied by $e^{2\pi i\mathbf{p}\cdot\mathbf{n}/h}$, where \mathbf{p} is the momentum which the electron would have if it were free and where \mathbf{n} is this lattice translation. The problem thus reduces to one of spherical symmetry within each cell together with the boundary conditions that the wave function and its gradient at a point on one face be equal to their value at the corresponding point of the opposite face multiplied by $e^{2\pi i\mathbf{p}\cdot\mathbf{n}/h}$. Then the wave function at any point of another cell is obtained by considering a point within

the primary cell such that the distance between these two points is an integral number of lattice translations and then applying the Bloch theorem.

In order to satisfy the boundary conditions at every point on the surfaces of the polyhedrons it would be necessary to choose a wave function which is a linear combination of all the solutions of the spherically symmetric Schrödinger equation. As a first approximation we fit the boundary conditions only at the midpoints of the faces between an ion and its eight nearest neighbors. We then use a linear combination of eight s , p , d and f functions which do not vanish at all the midpoints in question and are led to a set of linear homogeneous algebraic equations from which the constants are to be determined. In order that these have a nonvanishing solution the secular determinant must equal zero and this yields the relation between p_x , p_y , p_z and the one electron energies E .

I. ENERGY BANDS FOR LITHIUM

The potential field employed for lithium was that for the free atom.³ The use of such a potential at the actual internuclear distance is justifiable only as an approximation. In the immediate neighborhood of the nuclei the real potential and that for the free atom should be very nearly identical, but at larger distances there will be considerable difference. In fact the normal derivative of the potential must vanish at the boundary surface between two cells, since on the average the net charge within each cell is zero and hence the force on an electron at this boundary must vanish. The true potential

¹ Wigner and Seitz, *Phys. Rev.* **43**, 804 (1933); J. C. Slater, *Phys. Rev.* **45**, 794 (1934); *Rev. Mod. Phys.* **6**, 210 (1934).

² For a direct proof of this theorem see Sommerfeld and Bethe, *Handb. d. Physik* **XXIV**/2, p. 370.

³ I wish to express my thanks to Dr. F. Seitz who kindly supplied me with this potential.

thus lies lower than that for the free atom and the error made by neglecting this difference increases with decreasing internuclear distances. A better approximation would be to employ essentially the potential for the free atom rounded off and depressed so as to join smoothly with the potential of a neighboring cell.

The Schrödinger equation was integrated numerically for a series of energy values. In this way the radial functions s , p , d and f (for $l=0, 1, 2$ and 3 , respectively) were obtained, and from these Fig. 1 was constructed. The energy is plotted as a function of half distance between nearest neighbors, the curves shown being those for which $s=0$, $s'=0$, $p=0$, $p'=0$, etc., where s , p , d and f denote the values of the radial functions at the surface of the cell and s' , p' , d' , f' the corresponding derivatives. The half distance between nearest ions is experimentally found to be 2.86 atomic units (indicated on the diagram by the dotted vertical line) and it is seen that the minima of the lowest $s'=0$ and $p'=0$ curves occur at just about this point. One very significant difference between these curves and the corresponding ones for sodium is that the minimum of the $p'=0$ curves is much lower than for sodium. This causes this curve to cross the lowest curve at about 2.0 atomic units whereas for sodium this crossing does not occur until we get to much smaller internuclear distances. It is just this difference which explains

the abnormal pressure coefficient of resistance of lithium.⁴

By restricting ourselves to the x - y plane of momentum space ($p_z=0$) we can explicitly obtain the allowed types of wave functions. Slater showed that for this case the eight linear equations break up into two sets of four each so that solutions are possible by placing the determinant of one set equal to zero and also equating the constants of the other set equal to zero. We call the two possibilities Case I and II, respectively. For Case I we have real propagations for some directions provided that either $ps'/p's$ or $pd'/p'd$ is negative. These two cases are labeled Ia and Ib, respectively. Similarly real propagation of type IIa and IIb is possible providing that $pd'/p'd$ or $fd'/f'd$ is negative. The regions in which the different types of propagation enumerated above can occur are indicated in Fig. 1. Of course, one can find such regions by seeing what sign s , s' , p , p' , d , d' , f , f' have for each energy and internuclear distance, but it is simpler to proceed as follows: For very large distances the energy bands degenerate into the energy levels of the free atom and therefore in the neighborhood of these levels are regions in which propagation is not possible in any direction. In other words, here $ps'/p's$, $pd'/p'd$ and $fd'/f'd$ are all positive. Such a region is seen in Fig. 1 surrounding the $2s$ level. Now, as we cross the line $s'=0$, $ps'/p's$ must change sign and is now negative, allowing type Ia. As we pass from this region across the $p'=0$ curve $ps'/p's$ and $pd'/p'd$ must change sign, so that $ps'/p's$ now becomes positive again whereas $pd'/p'd$ is now negative and only types Ib and IIa are allowed. By similar reasoning we can assign the other regions of Fig. 1 to the various cases as indicated. The regions which are not marked are those for which we have no real propagation in any direction. However, even for the other regions there are certain directions for which we have no propagation. For a detailed discussion of how these gaps come about we refer to Slater's paper. The following example will serve as an illustration. Consider the normal distance of separation and a momentum vector ending at the edge of the first zone in the 110 direction. Then an inspection of Slater's equations tells us that the corresponding energies

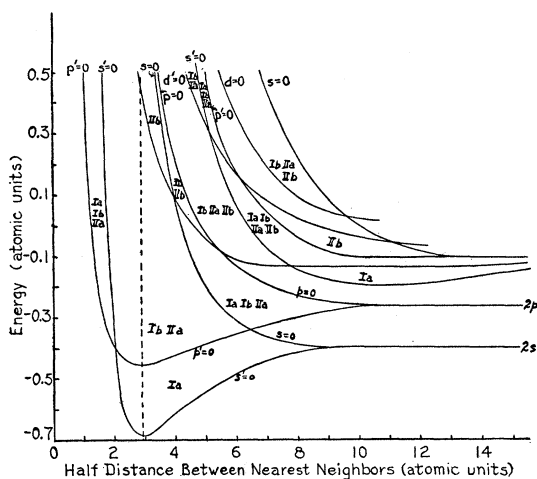


FIG. 1. Energy plotted against half distance between nearest neighbors for lithium.

⁴ See the preceding paper.

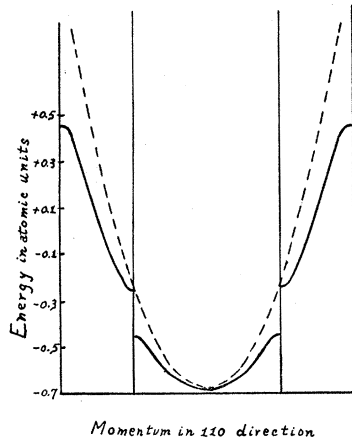


FIG. 2. Energy plotted as a function of momentum in the 110 direction.

occur at either $p' = 0$ or at $sd' + ds' = 0$. Since we have two energies corresponding to the same momentum at the edge of the zone this must mean that we have a gap in energy here. This is clearly seen in Fig. 2 where the energy is plotted as a function of the magnitude of momentum in the 110 direction. The first two zones are indicated and the gap comes at the vertical lines which represent the boundary between these zones. For lithium one finds that the $p' = 0$ condition comes for a lower energy than the $sd' + ds' = 0$ condition and hence $p' = 0$ corresponds to the top of the first band whereas $sd' + ds' = 0$ is the bottom of the second band. For sodium just the reverse is true.

If we plot curves of constant energy in the $p_x - p_y$ plane we obtain Fig. 3 for the first two Brillouin zones at the normal distance of separation. The center of the first zone comes at about $E = -0.68$ atomic units and the corner of the second at about $E = +0.46$ atomic units, a much wider range than is covered in sodium. The first zone goes to the $2s$ level of the free atom at infinite separation and the second goes to the $2p$ level. There is a marked difference in appearance between this figure and the corresponding one for sodium. Near the center of the diagram the curves are approximately circular, but they flatten out and become parallel to the edge of the first zone as we approach this edge. For sodium they stay more nearly circular (free-electron-like) all the way out except very close to the edge of the zone where there is the gap in

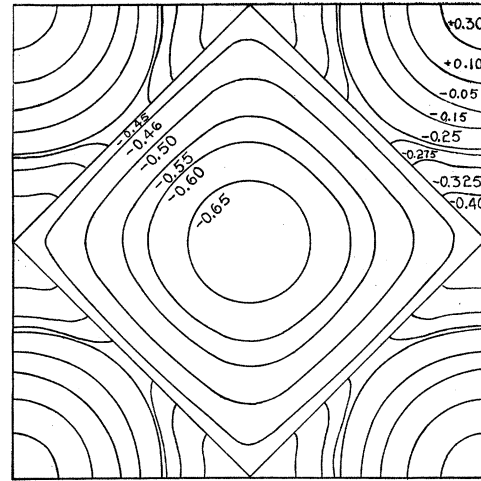


FIG. 3. Constant energy contours in x - y plane of momentum space.

energy spoken about above. The difference in the shapes of the constant energy curves for lithium and sodium is due mainly to the fact that the gap comes in the second zone for lithium whereas it occurs in the first zone for sodium.

Let us now examine Fig. 2 in more detail. The dashed curve is the free electron parabola ($E = p^2/2m$) and it is seen that the solid curves are much flatter than this, indicating that the conduction electrons in metallic lithium are none too "free." As a matter of fact, at the edge of the Fermi distribution the ratio of the slopes of the two curves (which measures the freedom of the electrons) is about $\frac{1}{2}$, whereas for sodium its ratio is very nearly 1. An inspection of the shape of the constant energy curves (Fig. 3) tells us that in any other direction the E vs. p curves will be even flatter than in the 110 directions and hence the electrons are even less free for these directions. Furthermore, whereas for sodium the energy gap extends only from -0.37 to -0.32 atomic units, for lithium it is from -0.45 to -0.26 atomic units, a jump almost four times as large.

Due to the periodicity of energy in momentum space the curves of Fig. 2 can be continued periodically along the axis of abscissas. Then the upper curve would have a maximum at the center of the first zone while the lower curve has a minimum there. This is what is usually found, the minima occurring for bands which go to

s-states at infinite separation and the maxima for bands which go to *p*-states.

II. THE WAVE FUNCTIONS

In Fig. 4 are plotted a number of typical wave functions in the first band. The dots represent nuclei along the 111 direction, this being the direction of closest packing. The wave normal is in the 110 direction ($p_x = p_y$, $p_z = 0$). The dashed curves are the wave functions of free electrons having the same *p* value as the actual curve. It is seen that, whereas near the nuclei the two do not agree at all, in the region between ions we have wave functions which are fairly free-electron like. This is our justification for using the metallic correspondence, that is, for assigning the 2*s* electrons rather than the bound 1*s* electrons to the first zone of momentum space. Physically, this is just what we should expect. The bound electrons are confined to regions of low potential around the nuclei and hence are traveling much faster than the free electrons. Therefore, their *p*-values must be larger than those of the 2*s* electrons.

A comparison with the wave functions for sodium again indicates that lithium is far less free-electron like than sodium. This means that the metallic correspondence is much better for sodium than for lithium. In other words, if we were to look at the momentum eigenfunctions for the 2*s* electrons of metallic lithium we would not find that they had simply a peak for one value of *p* in the first zone and were practically zero everywhere else, but rather that they had appreciable values for several cells of momentum space.

Let us examine the wave functions more closely. At the center of the first zone, ($p=0$, $\lambda = \infty$), we have a standing wave (that is, a real instead of a complex wave function) which is simply an *s* function repeated periodically throughout the lattice (Fig. 4a). It is interesting to note that for a large part of the volume the wave function is constant. (A free electron wave function with $\lambda = \infty$ would be constant everywhere.) As we decrease the wavelength we obtain successively the traveling waves Fig. 4b, c, d and e. Then at the edge of the first zone, where the wavelength is just twice the distance

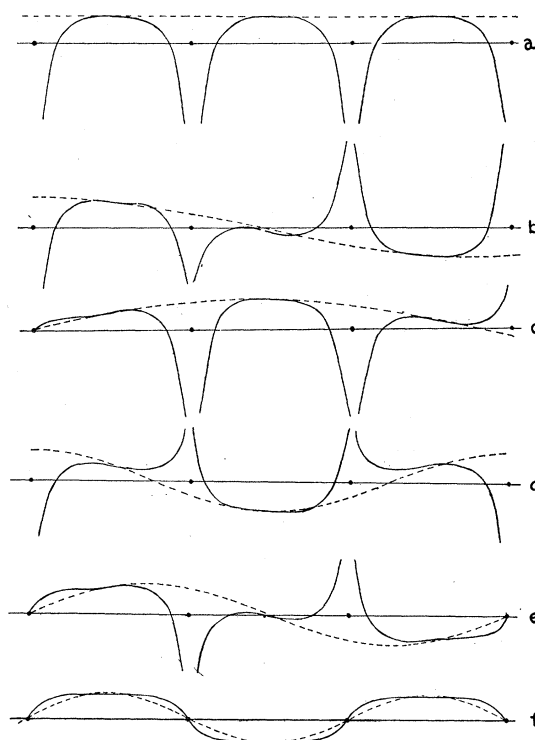


FIG. 4. Wave functions for free electrons for lithium as a function of distance along 111 direction, first band, type Ia. a. 2*s* function $E = -0.68$, $p = 0$, $\lambda = \infty$. Real function. b.c. Real and imaginary parts. $E = -0.65$, $\lambda = 31.8$ atomic units. d.e. Real and imaginary parts. $E = -0.55$, $\lambda = 17.1$ atomic units. f. 2*p* function. End of first zone $E = -0.45$. Wavelength is twice distance between nearest neighbors. The dashed curves indicate sinusoidal wave functions having the same wavelength as the actual function.

between nearest neighbors we obtain a standing wave, Fig. 4b. This means zero current, corresponding physically to Bragg reflection of the electron wave. One sees that whereas the lowest level of the first band is an atomic *s*-state (repeated periodically) and the highest an atomic *p*-state (repeated periodically) the intermediate levels are linear combinations of *s*, *p* and *d* functions. If one examines the nodes of the functions one observes that some come from the atomic states and some are due to the modulating sine and cosine functions.

Fig. 5 shows wave functions of type Ib in the second band, and it is seen that we again have standing waves at the beginning and end of the zone. 5a is formally related to 4f as the real and imaginary parts of a wave function, 5a resembling a sine curve and 4f a cosine curve. As mentioned above, for sodium the reverse is

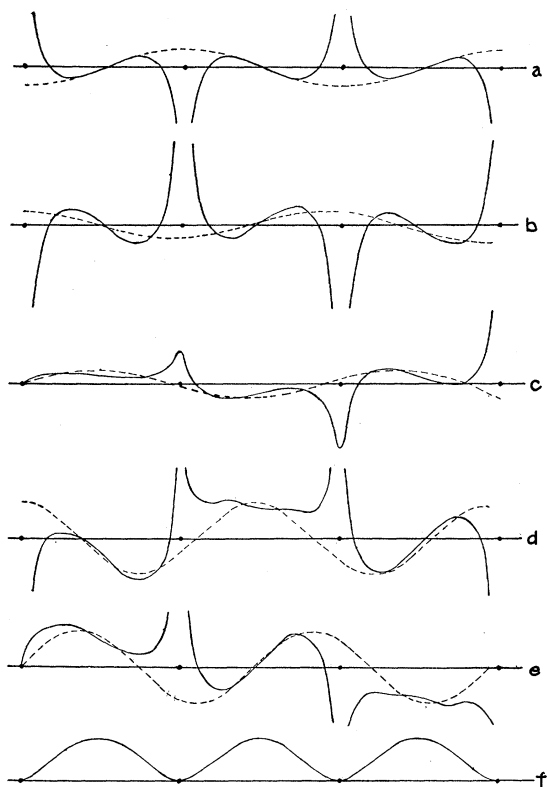


FIG. 5. Wave functions for free electrons for lithium as a function of distance along the 111 direction, second band, type Ib.

- a. Beginning of second band. $E = -0.26$, λ is twice distance between nearest neighbors.
 b.c. Real and imaginary parts, $E = -0.25$, $\lambda = 10.8$.
 d.e. Real and imaginary parts, $E = -0.05$, $\lambda = 8.40$.
 f. Standing wave at end of second zone. $E = +0.46$, λ is just the distance between nearest neighbors.

true, namely, the sine-like wave function (satisfying the condition $sd' + d's = 0$) comes at the end of the first zone and the cosine-like function (satisfying the condition $p' = 0$) at the beginning of the second. Now as we move away from the edge of the zone to higher energies we obtain the remaining curves of Fig. 5 and it is seen that the agreement with the free electron wave functions gets poorer and poorer. At the end of the zone, where the wave is simply a d -function

the agreement is so bad that no free electron curve is even indicated on 5f. At first this may seem strange since we should expect that as the energy of an electron was increased it would become more and more free. However, we must remember that we have assigned that part of momentum space about the origin to the $2s$ electrons and we have said that the $1s$ electrons are traveling faster than these and hence have momentum values further out from the origin. It is only for energies higher than those of the bound electrons that we can expect wave functions which closely resemble sinusoidal waves, that is, momentum eigenfunctions which have an appreciable value for only one cell lying relatively far from the origin.

We must therefore conclude from the wave functions as well as from the shapes of the constant energy curves in momentum space and the E vs. p diagram that the conduction electrons in lithium are much less free than those in sodium.

A few remarks about the approximations made should be added. The assumption of spherical symmetry around each ion has been discussed by Wigner, Seitz and Slater.¹ They show it to be a consistent one which should be very nearly the truth for the type of lattice involved. The worst approximation made, however, is the fitting of the boundary conditions at only eight points instead of all over the polyhedral surface with which we have surrounded each ion. It would be very interesting to fit the boundary conditions midway between second nearest neighbors also; that is, at the center of every face of the polyhedrons. Such a refinement will undoubtedly modify the shape of the energy contours of Fig. 3 near the edge of the zone. For example, we should no longer expect to find the boundary a surface of constant energy.

I should like to express my thanks to Professor J. C. Slater for suggesting this problem.