PHYSICAL REVIEW VOLUME 181, NUMBER 3 15 MAY 1969

Variation of Lattice Constant in Augmented-Plane-Wave Energy-Band Calculation for Lithium*

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(Received 25 November 1968)

Two series of self-consistent energy-band calculations in lithium by the augmented-plane-wave (APW) method are reported. The first used the exchange approximation proposed by Slater; the second used two-thirds of this quantity, as proposed by Gaspar, Kohn, and Sham. In each series, the lattice constant was varied, and the total energy was found as a function of this parameter. From this, the equilibrium lattice constant, the cohesive energy, and the compressibility were found. These quantities differ markedly for the two exchange approximations used, and roughly bracket the experimental values. A virial theorem is derived which is valid for Hartree-Fock-Slater calculations in solids, and it is shown that the numerical results in fact satisfy the virial expression.

I. ENERGY-BAND CALCULATION

THE augmented plane wave (APW) method[1] has been used for self-consistent energy-band calculations in body-centered-cubic (bcc) lithium. One-electron states were found at five points in the first Brillouin zone. At the end of each iteration, the resulting charge density was used to find a new potential, and the process was repeated until there was no significant change in the potential from one iteration to the next. Only the "muffin-tin" parts of these functions were considered, that is, those parts which are spherically symmetric inside the APW sphere about each atomic site, and constant in the plane-wave region outside the spheres. The lattice constant was varied over 10 values, ranging from $a=5.47$ to 8.84 a.u. (from about 0.83 to 1.34 times the experimental value), and also to $a=17.83$ and $a=72.44$. (2.7 and 11.0 times the experimental value). For all practical purposes, $a=72.44$ is equivalent to an infinite separation, or isolated atoms, and has been used numerically in place of $a=\infty$. At each of these 12 lattice constants, calculations were done using the average free-electron-exchange approximation proposed by Slater[2] ($f_B=1$) and also using two-thirds of this quantity, as proposed by Gaspar[3] and by Kohn and Sham[4] ($f_B=\frac{2}{3}$). f_B is that factor in the one-electron Schrödinger's equation which multiplies Slater's exchange, as discussed in the Appendix.

For the self-consistent potentials found at every third lattice constant, a number of excited states were calculated. The resulting one-electron energies are shown in Fig. 1. This figure is a schematic, since there is a break in the scale between $a=8.84$ and $a=17.83$. No points were calculated in this region, and the lines drawn are merely smooth extensions of the curves drawn on the left. For core and conduction states, the curves pass through 10 calculated points between $a=5.47$ and $a=8.84$. For the excited states, however, the points were calculated only at $a=5.47$, 6.60 (the experimental value), 7.72, and 8.84, so that these curves, as well, can only be taken to be schematic at points in between.

The energies plotted have been shifted so that the average of the energies of the occupied conduction states is always zero. The change in this shift, going from $a=5.47$ to $a=72.44$, is about 0.6 Ry. The slope in the graphs would have been steeper, if the shifts had not been made.

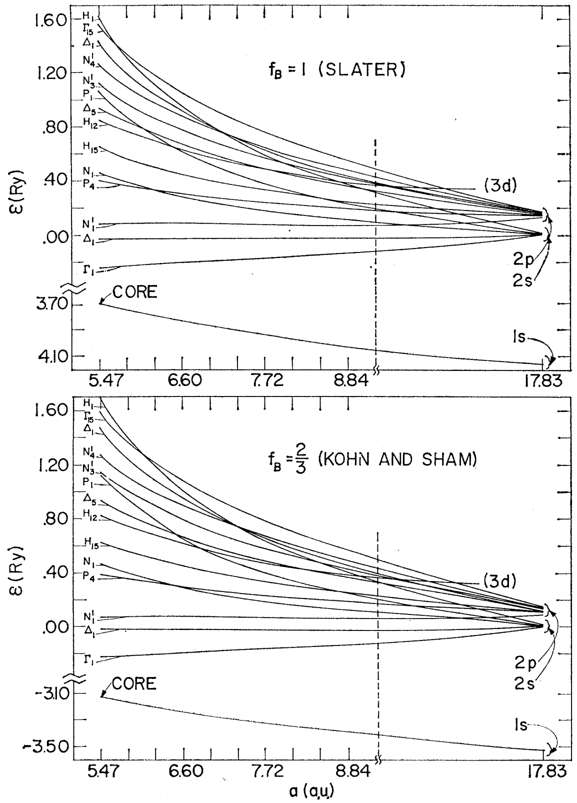

FIG. 1. One-electron energies in lithium versus lattice constant for two exchange potential approximations (schematic).

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* Based in part on a thesis submitted in partial fulfillment of the requirements for a Ph.D. degree from the Department of Physics at the Massachusetts Institute of Technology. Further details are given in an expanded version of this paper, IBM Research Report No. RJ 539 (unpublished), available from the author.

[1] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[2] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[3] R. Gaspar, Acta Phys. Hung. **3**, 263 (1954).

[4] W. Kohn and L. J. Sham. Phys. Rev. **140**, 1133 (1965).

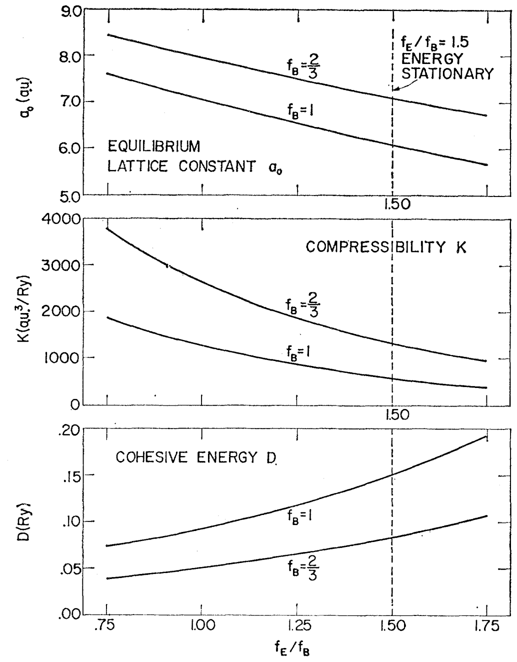

FIG. 2. Morse curve parameters for fitting total energy as a function of lattice constant in lithium.

It is instructive to note how the energy bands in the crystal go into the atomic energy levels. The $2s$ level in the atom, is, because of the energy shift introduced, at zero energy. The separation between the $2s$ and $2p$ levels in the atom has not been calculated, but the experimental value of about 0.136 Ry is consistent with the labels on Fig. 1. The figure shows that the s-like states Γ_1, Δ_1, N_1, P_1, and H_1 all go into the $2s$ atomic level, while the p-like states Γ_{15}, Δ_1, Δ_5, N_1', N_3', N_4', P_4, and H_{15} go into the $2p$ atomic level. The d-like state H_{12} has not been followed into the atom, but presumably goes into the atomic $3d$ level.

A spherical Fermi surface was assumed throughout this set of calculations. To test the validity of this assumption, the surfaces were found for some of the potentials. For $a=5.47$, the maximum deviation from sphericity was found to be 4.74% for $f_B=1$, and 5.84% at $f_B=\frac{2}{3}$. For $a=8.84$, the deviations were 0.33% for $f_B=1$, and 0.57% for $f_B=\frac{2}{3}$. It was found that the error in limiting the sum over the first Brillouin zone to five points is greater than the error introduced by assuming a spherical Fermi surface.

TABLE I. Comparison of equilibrium lattice constant a_0, compressibility K, and cohesive energy D for two calculations ($f_B=\frac{2}{3}$ and $f_B=1$, both with $f_E/f_B=\frac{3}{2}$) with experimental results.

	a_0 (a.u.)	K (a.u.³/Ry)	D (Ry/unit cell)
$f_B=\frac{2}{3}$	7.11	1343	0.084
Expt.	6.60	1200	0.12
$f_B=1$	6.09	577	0.15

It is noted that at some point between $a=8.84$ and $a=17.83$, the states N_1 and N_1' will become degenerate, and then reverse their relative positions. The Fermi surface probably becomes more and more spherical, until this point is reached.

II. MORSE CURVE FIT OF TOTAL ENERGY VERSUS LATTICE CONSTANT: COMPRESSIBILITY AND COHESIVE ENERGY

The total energy of the crystal was found at each lattice constant, for $f_B=1$ and $f_B=\frac{2}{3}$, and for a range of f_E from 0.75 to 1.75, using expression (1) in the Appendix. f_E is an arbitrary factor multiplying Slater's exchange in the expression for the total energy. In order to analyze the results, it is convenient to fit each of these curves, E versus a, with a curve with the form of the Morse potential

$$E(a)=E_A-D\left[2e^{-b(a-a_0)}-e^{-2b(a-a_0)}\right],$$

where $b=\frac{3}{2}(a_0/DK)^{1/2}$. This curve was originally used by Morse to approximate interatomic potentials, but as seen below, it also serves well in the present application. $E_A=E(a=\infty)$ is the total energy of an isolated atom, $D=E(a=\infty)-E(a_0)$ is the cohesive energy of the crystal per unit cell, a_0 is the equilibrium lattice constant, so that

$$\left.\frac{dE}{da}\right|_{a=a_0}=0.$$

The bulk modulus of a solid is defined to be $B=-Vdp/dV$, where V is the volume of the solid, and p is the pressure on it. Since entropy is constant at absolute zero, it is possible to write $p=-dU/dV$, where $U=NE$ is the total energy of a crystal with N atoms. The volume, for a bcc crystal, is $V=\frac{1}{2}Na^3$. Then, at equilibrium, it is found that K is the reciprocal of the bulk modulus, and hence is the compressibility.

The three parameters describing the Morse curve are then the equilibrium lattice constant a_0, the compressibility K, and the cohesive energy D. Taking the fourth parameter E_A to be fixed at the calculated value for an isolated atom, the first three parameters were found by finding a least-squares fit of the Morse curve to the 12 calculated points. The values so found are shown graphically in Fig. 2. The variational principle for total energy is satisfied only for $f_E/f_B=\frac{3}{2}$, as indicated by a vertical dashed line. The results for that case are shown in Table I, along with the experimental results. Each experimental value lies between the two calculated values. On these strictly empirical grounds, it is suggested that $\frac{2}{3}<f_B<1$ would be a better choice for the exchange potential. The Morse curves using these parameters have been plotted in Fig. 3. The calculated points fall on the curve, to the scale drawn. An enlarged detail of the minimum for each case, with the energy scale multiplied by ten, has been included to show the calculated points. The dashed line through each calculated point is the computed tangent to the curve at that point, using the result of the virial theorem for dE/da. The figure shows that the virial theorem is very well satisfied for $f_E/f_B=\frac{3}{2}$. If this ratio is changed to $f_E/f_B=1.45$ or 1.55, the slope predicted by the virial theorem (which of course is no longer applicable) is incorrect by a factor of 2 or more, showing that the theorem depends critically on the correctness of the ratio f_E/f_B.

All four of the Morse curve parameters (a_0, K, D, and E_A) can be chosen by the least-squares procedure, but when this is done, the rms error is reduced only by a small amount, and the resulting parameters are not significantly different from the ones given above.

APPENDIX

The total energy of a crystal may be written in terms of a spin-independent Hamiltonian for the system and a determinantal wave function, made up of one electron functions $u_i(\mathbf{r})$. If this is done, a troublesome exchange integral appears. This may be replaced by a factor f_E, as yet undetermined, multiplied by the average exchange integral for a free-electron gas with the same local charge density. If the variational method is applied to minimize this energy, the result is known as the Hartree-Fock-Slater equations.

The total energy may then be written as

$$E=V_{\rm nn}+\sum_i\int d^3\mathbf{r}_1u_i^*(\mathbf{r}_1)[-\nabla_{r_1}^2+V_{ne}(\mathbf{r}_1)+\tfrac{1}{2}V_{ee}(\mathbf{r}_1)+\tfrac{1}{2}f_EV_{\rm ex}(\mathbf{r}_1)]u_i(\mathbf{r}_1)\,,\quad(1)$$

where V_{nn} is the nuclear-nuclear interaction, $V_{ne}(\mathbf{r})$ and $V_{ee}(\mathbf{r})$ are the nuclear-electron and electron-electron Coulomb potentials, $\rho(\mathbf{r})$ is the total electron density, and the average free-electron exchange is

$$V_{\rm ex}(\mathbf{r}_1)=-3[(3/\pi)\rho(\mathbf{r}_1)]^{1/3}.$$

In the same terms, the Hartree-Fock-Slater equations can be written

$$[-\nabla_{r_1}^2+V_{ne}(\mathbf{r}_1)+V_{ee}^0(\mathbf{r}_1)+f_BV_{\rm ex}^0(\mathbf{r}_1)]u_i(\mathbf{r}_1)=\epsilon_iu_i(\mathbf{r}_1)\,,\quad(2)$$

where $f_B=\frac{2}{3}f_E$ if the variational principle is satisfied. At this point, however, it is convenient to leave f_B unspecified. The self-consistent solution of this set of equations is to be found by an iterative procedure, for instance, by using the APW method. The superscript 0 on the potentials indicates that these are derived from the charge density of the previous iteration. The explicit kinetic energy operator ∇_r^2 may be eliminated from (1) by using (2), which in turn can be used to find a practical expression to calculate the total energy per unit cell, E/N.

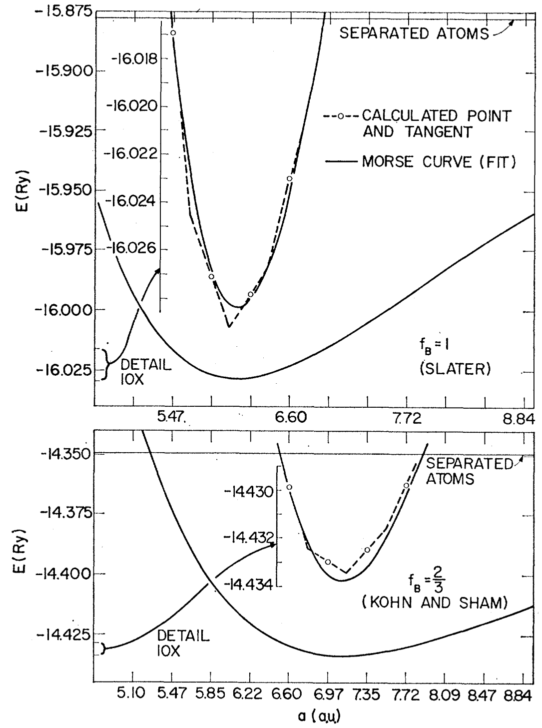

FIG. 3. Total energy versus lattice constant near minimum of curve, showing calculated points and slopes (dashed lines) predicted by the virial theorem, and Morse curve fit. Note that vertical scale is magnified 10 times in insert to show detail.

The Virial theorem has been discussed by Slater[5] in the context of the Born-Oppenheimer and Hartree-Fock approximations. From Slater's more general result, the form of the virial theorem

$$\partial E/\partial a=-(1/a)[2(\mathrm{KE})_{\rm av}+(\mathrm{PE})_{\rm av}]=-(1/a)[E+(\mathrm{KE})_{\rm av}]\quad(3)$$

follows quite simply. Further, it can be shown from (1) and (2) that this same expression for $\partial E/\partial a$ holds in the Hartree-Fock-Slater approximation, provided that $f_E/f_B=\frac{3}{2}$.

The conclusions of this Appendix can be generalized without difficulty to include also the more general exchange potential proposed by Lindgren.[6] In that case a third factor arises, weighting the contribution of the exchange to the average potential energy in (3) in a way depending simply on Lindgren's parameters. The ratio f_E/f_B is in general then not equal to $\frac{3}{2}$ to satisfy the variational principle.

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[5] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), Vol. 1.

[6] I. Lindgren, Arkiv Fysik **31**(4), 59 (1966).