

Total energy of metallic lithium

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Procedures are presented for the accurate calculation of the total energy of a solid within the framework of the local-density approximation. The starting point is a self-consistent band calculation using a basis of localized orbitals. The method is applied to study the total energy of metallic lithium as a function of lattice spacing. Good results are obtained for the cohesive energy, equilibrium lattice constant, and bulk modulus. A transition to a magnetically ordered state is predicted for large lattice spacings.

I. INTRODUCTION

Early studies of the cohesive energies of metals¹ were based on semiempirical potentials fitted to reproduce atomic spectra, and included an essential assumption that each electron moves in the field of an ion. In modern terms, this assumption is that the exchange-correlation hole is restricted to the particular atomic cell in which the electron whose wave function is being calculated is found. Rather good results were obtained for the alkali metals. Computational complexities limited progress in regard to more complicated systems.

Modern band calculations are generally based on density-functional theory² in a local-density approximation. In these calculations an exchange-correlation potential determined by the local charge and spin densities is added to the electrostatic potential of the entire electron distribution (a neutral system). In nearly-free-electron-like systems, results of quality equivalent to the original Wigner-Seitz calculations should be obtained. Moreover, it is possible to make rather accurate calculations of cohesive properties for systems as complex as transition metals.³

One purpose of this paper is to report the development of procedures whereby a total-energy calculation can be made accurately starting from a self-consistent energy-band calculation using a local-orbital basis (specifically, Gaussian orbitals are used here). A persistent problem with studies of the total energy, once one abandons the spherical approximations of Wigner-Seitz calculations, is that computations of the Coulomb energy become cumbersome. We will discuss our method of handling this problem which, we believe, yields essentially exact results for this contribution, and is a substantial improvement over previous efforts of this group.⁴

An example was needed to test our developments. We chose lithium. Although this is a thoroughly studied metal, we believe we have something worth adding to recent results.³⁻⁸ We do obtain better agreement with experiment in regard to the total energy, equilibrium lattice constant, and bulk modulus than other recent papers. In addition, we have investigated the behavior of the total energy for large lattice constants. Since the free lithium atom has a ground state with nonzero spin, we expect a transition from the normal paramagnetic state to some spin-polarized state to occur for sufficiently large atomic separations. While we do not know what form of magnetic order may exist under these conditions, we believe that the difference in energy between different forms should be quite small (presumably decreasing exponentially with the distance between atoms). Our computer programs permit calculations for a ferromagnetic state, and we have investigated this case. Calais and Sperber⁶ have considered possible antiferromagnetic order; however, apparent calculational inadequacies make it impossible to extract reliable conclusions from that work. We find the ferromagnetic state to have lower total energy than the paramagnetic state for values of the lattice constant greater than about 10.5 a.u. as will be discussed in more detail below. A similar result was obtained for vanadium by Hattox *et al.*⁹

II. PROCEDURES

We have presented elsewhere¹⁰ the formulas employed in our calculation of the total energy. Only a brief summary will be given here.

The total energy of a crystal is, in density-functional theory, related to the sum of the one-electron eigenvalues by

$$\begin{aligned}
NE_T = & \sum E_{i\sigma} - \frac{e^2}{2} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r' \\
& + \frac{e^2}{2} \sum_{\substack{\mu,\nu \\ (\mu \neq \nu)}} \frac{Z_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|} + E_{xc} \\
& - \sum_\sigma \int \rho_\sigma V_{xc\sigma}(\vec{r}) d^3r, \quad (1)
\end{aligned}$$

where N is the number of atoms, E_T is the total energy per atom; $E_{i\sigma}$ is the energy of the i th occupied state of spin σ , ρ is the electron number density (ρ_σ is the spin density), the atomic nuclei of charge Z_μ are located at lattice sites \vec{R}_μ , E_{xc} is the exchange-correlation energy, and $V_{xc\sigma}$ is the exchange-correlation potential for electrons of spin σ .

The second and third terms in (1) are the Coulomb terms. Each, separately, is divergent but their sum converges. We evaluate these terms as follows. We add and subtract a term representing one-half of the interaction energy of the electrons and nuclei. Let

$$\begin{aligned}
U + D = & \frac{e^2}{2N} \sum_{\substack{\mu,\nu \\ (\mu \neq \nu)}} \frac{Z_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|} \\
& - \frac{e^2}{2N} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r', \quad (2)
\end{aligned}$$

in which

$$\begin{aligned}
U = & \frac{e^2}{2N} \sum_\nu Z_\nu \int \frac{\rho(\vec{r})}{|\vec{r}-\vec{R}_\nu|} d^3r \\
& - \frac{e^2}{2N} \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r d^3r', \quad (3a)
\end{aligned}$$

$$\begin{aligned}
D = & \frac{e^2}{2N} \sum_{\substack{\mu,\nu \\ (\mu \neq \nu)}} \frac{Z_\mu Z_\nu}{|\vec{R}_\mu - \vec{R}_\nu|} \\
& - \frac{e^2}{2N} \sum_\nu Z_\nu \int \frac{\rho(\vec{r})}{|\vec{r}-\vec{R}_\nu|} d^3r. \quad (3b)
\end{aligned}$$

These quantities are evaluated by the Fourier-transform method of Harris and Monkhorst.¹¹ This calculation leads to the results (here we specialize to a monatomic cubic lattice),

$$D = \frac{Z}{2} \left[\frac{Ze^2}{2\pi^2} - V_T(0) - \sum_s V_e(\vec{K}_s) \right], \quad (4a)$$

$$U = -\frac{\Omega}{2} \sum_s V_T(\vec{K}_s) \rho_e(\vec{K}_s), \quad (4b)$$

in which \vec{K}_s is a reciprocal-lattice vector, $V_T(\vec{K}_s)$ is

a Fourier coefficient of the total electrostatic potential energy (electron plus nucleus), and V_e and ρ_e refer to the electron distribution only. The quantity $V_T(0)$ is the $\vec{K}_s \rightarrow 0$ limit of $V_T(\vec{K}_s)$ as discussed, for example, in Ref. 12. Ω is the volume of the unit cell. Finally C is a finite constant given by

$$C = \frac{8\pi^3}{\Omega} \sum_{\substack{s \\ (s \neq 0)}} \frac{1}{K_s^2} - \int \frac{d^3q}{q^2}. \quad (5)$$

The evaluation of this quantity is discussed by Harris and Monkhorst,¹¹ but they do not give results for the body-centered-cubic lattice. Our value for this case is

$$C = -11.432877(2\pi/a). \quad (6)$$

The last two terms in (1) come from the exchange-correlation function. We combine them in the form

$$\begin{aligned}
E_{xc} - \sum_\sigma \int \rho_\sigma V_{xc\sigma}(\vec{r}) d^3r \\
= - \sum_\sigma \int \rho_\sigma(\vec{r}) W_\sigma(\vec{r}) d^3r, \quad (7)
\end{aligned}$$

where

$$W_\sigma(\vec{r}) = \rho(\vec{r}) \frac{\partial \epsilon_{xc}}{\partial \rho_\sigma}, \quad (8)$$

and ϵ_{xc} is the exchange-correlation energy per particle.

We have obtained an explicit result for an exchange-correlation potential having the functional form used by von Barth and Hedin.¹³ This result is given in Ref. 10.

III. METHODS OF CALCULATION

We have carried out the procedure described above for metallic lithium. The exchange-correlation potential employed was that of Rajagopal, Singhal, and Kimball,¹⁴ which has the same

TABLE I. Orbital exponents for the s, p, d -type orbitals used in the Gaussian basis set.

s -type	p -type	d -type
10 000.0	100.0	2.5
800.0	11.0	0.36
90.0	2.5	0.14
16.0	0.7	
4.0	0.29	
1.4	0.15	
0.46		
0.24		
0.13		

TABLE II. Total energy of lithium atom in the local-density approximation (SLD is the spin-unpolarized local-density calculation; LD is the spin-unpolarized local-density calculation; JMW are Janak, Moruzzi, and Williams, Ref. 16; GLW are Gunnarson, Lundquist and Wilkins, Ref. 17; Expt. is as quoted in Ref. 18).

E_T^{atom}	Present	JMW	GLW	Expt.
SLD	-14.787	-14.709	-14.766	-14.956
LD	-14.768	-14.682	-14.741	

functional form as used by von Barth and Hedin,¹³ but with slightly different parameters. The basic band calculation was carried out using the linear combination of Gaussian orbitals (LCGO) method.¹⁵ The basis set consisted of 42 independent Gaussian orbitals including angular dependences. There are nine *s*-like Gaussians, six *p*-like functions, and three *d*-like functions. The parameters of this set are those used in Ref. 15, and are contained in Table I. It seems to yield well-converged results.

It would be necessary to extend this basis in order to make calculations for other than first-row atoms. As the atomic number increases, it is necessary to

TABLE III. Total energies of solid lithium for nonmagnetic and magnetic states as a function of lattice spacing. Above 11.3 a.u. the magnetic insulator state prevails.

a (a.u.)	$E_{T,\text{nonmag}}^{\text{solid}}$ (Ry per atom)	$E_{T,\text{mag}}^{\text{solid}}$ (Ry per atom)
5.8	-14.905 07	
6.0	-14.909 74	
6.2	-14.912 63	
6.3	-14.913 50	
6.4	-14.914 02	
6.45	-14.914 17	
6.5	-14.914 25	
6.55	-14.914 24	
6.597	-14.914 17	
6.7	-14.913 82	
6.8	-14.913 25	
6.9	-14.912 44	
7.0	-14.911 44	
7.5	-14.904 04	
8.0	-14.893 69	
8.5	-14.881 00	
10.0	-14.811 21	
10.5	-14.789 75	
10.7	-14.7854	-14.7857
11.0	-14.7772	-14.7853
11.3	-14.7715	-14.7859
12.0	-14.7653	-14.7896
13.0	-14.7664	-14.7916
13.5	-14.7665	-14.7912
14.0	-14.7667	-14.7908

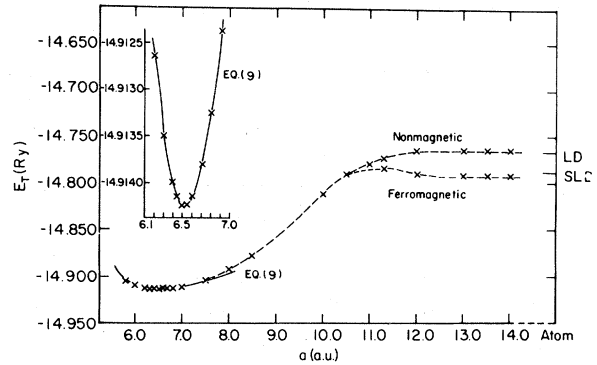


FIG. 1. Total energy as a function of lattice spacing for lithium. The solid lines result from fits to Eq. (9). For the atom, LD and SLD refer, respectively, to spin-unpolarized and spin-polarized results.

add additional rapidly decaying Gaussians to describe the variation of the wave function near the nuclear site. We estimate that 60 functions would be needed to achieve equivalent accuracy for sodium and perhaps 75 for potassium.

A separate calculation was made using the same basis set to obtain the total energy of the free lithium atom in the configuration $(1s)^2(2s)$. Both spin-polarized and -unpolarized states were considered. The results of this calculation are given in Table II.

IV. RESULTS: COHESIVE PROPERTIES

The total energy was calculated for lattice spacings from 5.8 to 14.0 a.u. For lattice constants greater than 10.5 a.u. we were able to obtain a self-consistent ferromagnetic solution which had lower total energy. This solution will be discussed subsequently. Numerical values for the total energy are listed in Table III and shown in Fig. 1.

We need to mention a possible source of error in the calculation for the ferromagnetic state. This state tends to be completely polarized: The $2s$ electron and a $1s$ electron have spin "up," a single $1s$ electron has spin "down." So throughout most of the atomic volume the down-spin density is quite small. This complicates the self-consistency calculation in the following way. Our "band package" programs require us to calculate matrices representing derivatives of the potentials. As discussed by von Barth and Hedin,¹³ the derivative of the parametrized exchange-correlation potential with respect to x_σ ($x_\sigma = \rho_\sigma / \rho$) becomes singular for $x_\sigma \rightarrow 0$ as $x_\sigma^{-2/3}$, whereas the potential resulting from the "two-bubble" approximation goes to infinity as $x_\sigma^{-1/3}$. This large derivative has no effect in principle on the calculation since its contribution to the total energy would involve multiplication by factors of $\delta\rho_\sigma$ and ρ_σ . However, in our method, we

must calculate matrix elements of the derivative potential, and must cut off the singularity. For $x_\sigma < 0.2$, we replace the derivatives of the minority-spin exchange-correlation potential by their values at $x_\sigma = 0.2$. So it is not surprising that the uncertainty in the calculations for the ferromagnetic state is larger than for the nonmagnetic state. The estimate of the uncertainty in the total-energy calculation is 0.0005 Ry for lattice constants less than 10 a.u. This error increases to about 0.002 Ry in the magnetic-state calculations for lattice spacings larger than 10 a.u. due in part to the above-mentioned cutoff. These difficulties related to the large magnitude of $x_\sigma^{-2/3}$ are particularly pronounced for metallic lithium due to the small number of electrons atomic lithium possesses. Similar problems may arise for other light materials. The divergence problem is so far absent from ongoing computations for iron and nickel. The above described cutoff in x_σ is not needed in those cases.

To determine the equilibrium lattice constant, minimum total energy, and bulk modulus, we fit the calculated total energies of Table III in the region from 6.2 to 6.9 a.u. by a formula proposed by Bardeen.¹⁹ Our fitting formula is

$$E_T = -14.78680 + 1.441043/a - 35.01945/a^2 + 131.7412/a^3. \quad (9)$$

We find the following results. The minimum total energy occurs at 6.52 a.u. and has the value -14.914 Ry. The bulk modulus is obtained by differentiating E_T

$$B = \frac{1}{\Omega} \frac{d^2 E_T}{d^2 \Omega}.$$

We find from this $B = 0.138$ Mbar. Our results are summarized in Table IV. Results of other recent calculations are presented. The occupied bandwidth at the equilibrium lattice spacing is 3.55 eV. Our results seem to be quite satisfactory, and are an improvement over both previous calculations using a local-density potential³ and a limited-basis Hartree-Fock calculation.⁸ No minimum of the total-energy curve was reported in the Hartree-Fock calculation of Pack *et al.*⁸; their results for the total energy and bulk modulus given in Table IV refer to the experimental lattice constant. Those authors found an occupied bandwidth of 9.87 eV. The experimental value is about 4.0 eV. This exaggeration of the bandwidth is one of the characteristic defects of the Hartree-Fock approximation.

In order to calculate the cohesive energy, we add a small contribution

$$E_0 = \frac{9}{8} k_B \Theta_D$$

TABLE IV. Equilibrium lattice constant a , bulk modulus B , total energy E_T^{solid} and cohesive energy E_c for lithium (MJW are Moruzzi, Janak, and Williams Ref. 3; PMF are Pack, Monkhorst, and Freeman Ref. 8; Expt. are a , B , and E_T^{solid} values as quoted in Ref. 8. E_c value is as quoted in Ref. 16).

	a (a.u.)	B (Mbar)	E_T^{solid} (Ry per atom)	E_c (Ry)
				0.124
Present work	6.52	0.138	-14.914	(0.121)
MJW	6.42	0.15	-14.832	0.121
PMF			-14.831	
Expt.	6.597	0.123	-15.072	0.122

from the zero-point energy of the lattice vibration to the total energy. (Θ_D is Debye temperature and k_B is Boltzmann's constant.) The Debye temperature for lithium is 334 K at the experimental lattice constant (6.597 a.u.). The Debye temperature varies with the crystal volume. At $a = 6.52$ a.u., we find

$$E_0 = 0.0026 \text{ Ry}.$$

However, we have neglected the small contribution from this term in calculating the equilibrium lattice constant and the bulk modulus. Then if we compare the total energy of the solid including E_0 with the spin-polarized local-density calculation (SLD) total energy of the atom from Table II we find a cohesive energy of 0.124 Ry per atom.

There are small differences in the total energy of the lithium atom which is used in the determination of the cohesive energy as obtained by the different calculations quoted in Table II. These are apparently due to different parametrizations of the exchange-correlation potential.

There is another way in which the cohesive energy may be calculated. We may use the atomic limit of the total energy of the solid in place of the calculated total energy of the atom. From Table III we see that this is -14.791 Ry, 0.004 Ry below the atomic calculations. The difference between these two calculations, small but not quite negligible, may be a basis-set effect associated with the influence of the tails of wave functions on neighboring atoms on the energy of a "central" atom. In any case, we regard this agreement as relatively satisfactory. If the cohesive energy is calculated in this way, the result is 0.121 Ry per atom.

The good agreement of calculation and experimental cohesive energies is probably the result in part of cancelation of errors. The energy of the atom is too large probably due in most part to the neglect of a needed self-interaction correction.²⁰ Such a correction, which current theory predicts to be zero for extended wave functions in a solid,

would lead to too small a cohesive energy. On the other hand, it is not unlikely that the current exchange-correlation functional underestimates the correlation energy of a solid, and the use of a more adequate exchange-correlation potential would tend to lower the total energy.

V. MAGNETIZATION OF EXPANDED LITHIUM

For lattice constants up to 10.5 a.u., we were unable to obtain a self-consistent solution to the energy-band problem corresponding to a ferromagnetic state. The self-consistent iterations converged to a state of negligible magneton number. At $a = 10.7$ or 11 a.u., a ferromagnetic state was found which has a lower total energy than the paramagnetic state. The magneton numbers at 10.7 and 11 a.u., were, respectively, found to be 0.907 and 0.969, indicating unsaturated ferromagnetism. In this region, our calculation describes a ferromagnetic metal. For $a = 11.3$ a.u. and greater, a saturated ferromagnetic state is stable. At this separation a gap appears, and persists for large separations, indicating that the system has become a (ferromagnetic) insulator. The calculation predicts a metal-insulator transition at this spacing. Moreover, we find an indication of a shallow minimum in the energy of this state (near $a = 13$ a.u.) indicating that this state is stable with respect to dissociation into separate neutral atoms.

Our calculations have not considered the possibility of other forms of magnetic order. In fact, we believe on the basis of general arguments, such as those of Herring,²¹ that an antiferromagnetic state

should have lower energy than a ferromagnetic state at large lattice constants.

This calculation indicates clearly a characteristic property of calculation based on density-functional theory; the system dissociates correctly at large interatomic spacing to separated, neutral atoms. This contrasts clearly with the situation in ordinary Hartree-Fock theory where the state found at large separations can contain a mixture of ionic configurations leading to an unacceptably high total energy. It will be seen that proper behavior at large separations is obtained for both the nonmagnetic and ferromagnetic states: The nonmagnetic state approaches the limit for non-spin-polarized atoms, the ferromagnetic state for spin-polarized atoms.

VI. CONCLUSIONS

This calculation furnishes another example of the ability of local-density theory to account for cohesive properties of metals. The total energy, equilibrium lattice constant, bulk modulus, and cohesive energy obtained are in good agreement with experiment, with values somewhat improved with respect to previous studies. Calculations made for large atomic separation show that a magnetically ordered state becomes stable in the neighborhood of a lattice constant of 10.5 a.u. The magnetic insulator state prevails above 11.3 a.u.

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