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²⁷To account for the measured average $\partial\chi/\partial T$ for pure

titanium using Eq. (6), E_F must be situated at a minimum in $n(E)$ of "width" of the order 5×10^{-3} Ry.

²⁸A representative $n(E)$ curve for body-centered iron is given by E. P. Wohlfarth and J. F. Cornwell, *Phys. Rev. Letters* **7**, 342 (1961).

²⁹E. W. Collings and J. C. Ho, in *The Science Technology and Application of Titanium*, edited by R. Jaffee and N. Promisel (Pergamon, New York, 1970), p. 331. $\partial\chi_{\text{total}}/\partial T$ for pure Ti, Ti-Al (3 at. %) and Ti-Al (10 at. %) were, respectively, 10, 9, and 8% per 300°.

³⁰With mean free path ~ 100 Å and a Fermi velocity of 10^8 cm/sec we find $\tau \sim 10^{-14}$ sec, leading to $\Delta E \sim \hbar/\tau \sim 5 \times 10^{-3}$ Ry.

New Potential Function for Atomic and Solid-State Calculations*

David A. Liberman

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

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An expression for the potential energy of an isolated atom or a solid as a functional of the electron density is proposed. A one-electron potential function is derived from it by means of the variational principle. It has the correct asymptotic form at large radii in the case of atoms and ions. It also gives the correct total energy of the low-density electron gas. Calculations of binding energies of electrons in negative ions and of the bulk properties of some simple solids are given as examples of applications.

INTRODUCTION

The free-electron approximation for exchange¹⁻⁴ has been much used in recent years for atomic and band-structure calculations. The variational formulation,² which we want to consider here, consists in approximating the potential energy of the interelectron interaction with the classical Coulomb energy of the electron charge distribution and an exchange term based on the Hartree-Fock theory of the degenerate electron gas:

$$\begin{aligned} \frac{e^2}{2} \int |\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 \sum_{i \neq j} \frac{1}{r_{ij}} d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \\ + \frac{e^2}{2} \iint \frac{\rho(\vec{x}_1)\rho(\vec{x}_2)}{|\vec{x}_1 - \vec{x}_2|} d\vec{x}_1 d\vec{x}_2 \\ - \frac{3e^2}{4\pi} \int \rho(\vec{x}) [3\pi^2 \rho(\vec{x})]^{1/3} d\vec{x}, \end{aligned} \quad (1)$$

$$\begin{aligned} \text{where } \rho(\vec{x}) = \int |\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)|^2 \\ \times \sum_i \delta(\vec{x} - \vec{r}_i) d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \end{aligned} \quad (2)$$

is the electron density. Then variation of the (approximate) total energy, subject to the usual

normalization condition, gives an equation for the wave function

$$\sum_i h(\vec{r}_i) \psi = E \psi, \quad (3)$$

with $h(\vec{r}) = -\hbar^2 \nabla^2 / 2m - Ze^2/r$

$$+ e^2 \int \rho(\vec{r}') / |\vec{r} - \vec{r}'| d\vec{r}' - e^2 [3\pi^2 \rho(\vec{r})]^{1/3} / \pi, \quad (4)$$

which may be solved by separation of variables. By this means, a set of one-electron equations,

$$h(r) \varphi_n(\vec{r}) = \epsilon_n \varphi_n(\vec{r}), \quad (5)$$

is obtained. One recognizes in $h(\vec{r})$ the potential of the nucleus (for the moment we consider only the isolated atom), the potential of the electron charge distribution, and the free-electron exchange potential.

For the ground states of neutral atoms this prescription works very well^{4,5} giving orbital functions very close to those obtained by the much more complicated Hartree-Fock method. It is clear, however, that cases will arise in which the same good results will not be obtained as the potential function has the wrong asymptotic form at large radii, going to zero exponentially rather than as $1/r$ as it should. To remedy this situation, the

potential function is usually modified at large radii^{6,7} to give it the required form. It is our purpose here to suggest an alternative procedure to this somewhat arbitrary one.

Before doing so, the reasons why the approximation (1) fails at large radii in atoms are worth noting. One is that the expression for the interelectron potential energy in the form used is an application of the semiclassical approximation as in the Thomas-Fermi model. This assumes that electron wavelengths are small compared to the distance in which the potential has a substantial fractional change.⁸ In atoms this requirement breaks down at large radii (and also close to the nucleus which does not concern us here). Another reason for the failure of the approximation is that, in using the Hartree-Fock expression for the exchange energy, one assumes that the antisymmetry of the wave function is more important than electrostatic repulsion in keeping electrons apart. As is well known, this is true for high electron densities but not for low densities.

Keeping in mind these objections to the approximation used above for the interelectron potential energy, we will now try to construct a better one. We imagine an atom divided into two parts by a sphere centered on the nucleus. The sphere is to separate the high-density region from that of low density. We fix its radius R so that on the average there is one electron outside the sphere,

$$\int_{x>R} \rho(\vec{x}) d\vec{x} = 1. \quad (6)$$

The potential energy of electrons inside the sphere interacting with other electrons inside the sphere is approximated as before by a classical Coulomb term and a Hartree-Fock free-electron exchange term

$$\begin{aligned} & \frac{e^2}{2} \iint_{x_1, x_2 < R} \frac{\rho(\vec{x}_1)\rho(\vec{x}_2)}{|\vec{x}_1 - \vec{x}_2|} d\vec{x}_1 d\vec{x}_2 \\ & - \frac{3e^2}{4\pi} \int_{x < R} \rho(\vec{x}) [3\pi^2 \rho(\vec{x})]^{1/3} d\vec{x}. \end{aligned} \quad (7)$$

Since, on the average, there is only one electron outside of the sphere, there is no contribution to the interelectron potential energy from charge outside the sphere interacting with itself. Finally, there is the potential energy of the interaction of charge outside the sphere with that inside,

$$e^2 \iint_{x_1 < R < x_2} \frac{\rho(\vec{x}_1)\rho(\vec{x}_2)}{|\vec{x}_1 - \vec{x}_2|} d\vec{x}_1 d\vec{x}_2. \quad (8)$$

There can be no exchange term here because the "hole" in the two-electron distribution function has been "used up" in assuming no self-interaction of

the charge outside the sphere.

The sum of the two contributions to the interelectron potential energy, (7) and (8), is then to be used instead of (1). The variational method is used as before, but now there is an additional constraint (6), which may be introduced with a second Lagrange parameter. Also, variations of the sphere radius R must be considered. One gets equations similar to (3) and (4):

$$\sum_i h'(\vec{r}_i) \psi = E' \psi \quad (9)$$

and

$$\begin{aligned} h'(\vec{r}) = & -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + e^2 \int_{r' < \infty} \frac{\rho(r')}{|\vec{r} - \vec{r}'|} d\vec{r}' \\ & - \frac{[3\pi^2 \rho(r)]^{1/3}}{\pi} + \lambda, \quad r < R \\ = & -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + e^2 \int_{r' < R} \frac{\rho(r')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad r > R \end{aligned} \quad (10)$$

where

$$\lambda = - \int_{r' > R} \frac{\rho(r')}{|\vec{R} - \vec{r}'|} d\vec{r}' + \frac{3[3\pi^2 \rho(R)]^{1/3}}{4\pi}. \quad (11)$$

Again a set of one-electron equations is obtained from (9) by separation of variables. The operator in them is now h' which contains the new potential function, the main result of this paper. [It may be noted that E' is not the Lagrange parameter associated with the normalization condition on the wave function but also contains the constant λ . Also, we have assumed the electron density is spherically symmetric. Without this assumption the constant λ would be determined by a somewhat more complicated expression than (11).]

The potential function in (10) will in general have a small discontinuity at the sphere radius. In the case of lithium metal at normal density the discontinuity is $0.059e^2/a_0$ at the radius $R = 1.43a_0$ (see Fig. 1). The potential at radii greater than R is seen to be $(-Z+N)e^2/r$, where N is the number of electrons inside the sphere.

The extension of the above results to simple solids is straightforward. Each atom or ion occupies a cell and within each cell a spherical surface is defined so that the part of the cell outside the sphere contains the charge of just one electron. Within a cell the potential energy of the electron interactions is defined as above. The interactions between charges in different cells are assumed to involve only the classical Coulomb term as in (8) above. For monatomic solids, where each cell may be regarded as neutral, the additional terms will usually be very small and can be neglected. When the cells are not neutral, the potential function will contain a Madelung term.

APPLICATION TO NEGATIVE IONS

Our experience has been that solutions do not

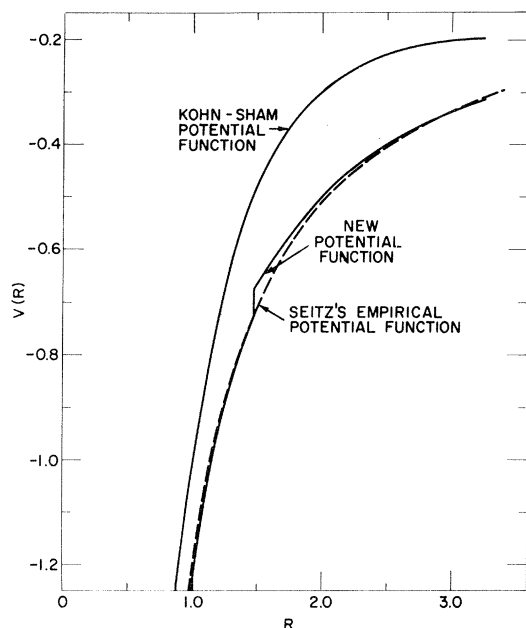


FIG. 1. Potential functions for lithium metal at normal density. The energy unit is the Hartree (e^2/a_0) and the radius is given in Bohr radii (a_0). The Kohn-Sham potential function and the new potential function are from our self-consistent field calculations. The empirical potential function is that of Seitz (Ref. 10).

exist to the self-consistent field equations for negative ions when the unmodified free-electron exchange potential [i. e., the one in (4)] is used. The usual way of dealing with this is to truncate the potential function where it starts going positive, setting it equal to zero beyond this point. The potential function developed here does much the same thing but in a more systematic manner. One test of how well this is done is to compare calculated and measured electron affinities for atoms which form negative ions. This is done in Table I. Self-consistent field calculations were done for both the neutral atoms and the corresponding negative ions and the differences of the total energies are tabulated. It should be noted that the total energies were computed using expressions (7) and (8) for the interelectron potential energy and *not* the expectation value of $\sum e^2/2r_{ij}$.

A couple of comments may be made. One is that the relatively poor results for hydrogen are probably connected with the failure of the statistical expression for exchange in the 1s orbital near the nucleus. The other is that for loosely bound electrons the method of this paper seems to do about as well as, and in a few cases rather better than, the Hartree-Fock method in computing binding energies.

ELECTRONIC STRUCTURE CALCULATIONS FOR SOLIDS

The problem of defining potential functions for solids is one that is receiving a good deal of attention at the present. Many of the early calculations were done with potential functions adapted from atomic calculations and had the $1/r$ form at large radii which is a feature of the prescription developed here. Since Slater introduced¹ the statistical exchange potential, it has been much favored, partly for theoretical reasons and partly as a matter of convenience: It offers, in principle and usually in fact, a simple way of obtaining a potential function for any atom or ion in a crystal.

In order to make a comparison of the usual statistical exchange potential with the one developed here, we have done self-consistent field calculations for lithium metal at normal density. One set of calculations was done with the potential function of Eq. (4) (usually referred to as that of Kohn and Sham) and the other set with the one in (10). A brief description of the methods of calculation will appear elsewhere.⁹

The potential functions obtained are shown in Fig. 1 along with the empirical one of Seitz.¹⁰ The close agreement between the new potential function and the empirical one is obvious. The Kohn-Sham potential function is much flatter in the outer parts of the atomic cell and will not bind electrons as strongly as the other two. This becomes more obvious if a constant ($0.23e^2/a_0$) is subtracted from it so that all three potentials coincide at small radii. Then the Kohn-Sham potential will lie below the others at larger radii.

As might be expected from the potential functions, the bulk properties (lattice parameter, cohesive energy, and bulk modulus) calculated with the new potential function are close to Seitz's¹⁰ early calculation (and to experimental values) while those obtained with the Kohn-Sham potential

TABLE I. Electron affinities in electron volts.

Atom	New potential	Hartree-Fock ^a	Experiment ^b
H	-0.78	-0.33	0.75
O	1.92	0.56	2.41
F	3.20	1.36	3.45
Cl	2.94	2.58	3.61
Br	2.82	2.58	3.36
I	2.61	2.6	3.06

^aHartree-Fock calculations by J. Mann (unpublished).

^bExcept for hydrogen and oxygen the experimental values are those quoted by B. L. Moiseiwitsch, *Advan. Atomic Mol. Phys.* **1**, 61 (1965). For hydrogen the more accurate theoretical value is given. The oxygen value is based on the experimental value given by Moiseiwitsch but is adjusted to represent the average of the configuration so as to be directly comparable to the calculations.

TABLE II. Bulk properties of solids at zero pressure and temperature.

		Lithium	Beryllium	Aluminum	Iron
Wigner-Seitz cell radius (Bohr radii)	Calc	3.18	2.40	3.06	2.69
	Expt ^a	3.24	2.35	2.99	2.66
Cohesive energy (kcal/mole)	Calc	40	59	61	160
	Expt ^b	38	78	77	182
Bulk modulus (kbar)	Calc	131	1040	930	1750
	Expt ^c	123	1100	780	1690

^aLithium cell radius is from C. A. Swenson, J. Phys. Chem. Solids **27**, 33 (1966). The others are from *Crystal Data*, edited by J. D. H. Donay (American Crystallographic Association, New York, 1963).

^bJANAF Thermochemical Tables, edited by D. R. Stull (Dow Chemical Co., Midland, Michigan, 1965). Available from the Clearinghouse for Federal Scientific Information as report number PB168370, Springfield, Va. The experimental cohesive energy of iron has been increased by 83 kcal/mole so as to represent the value relative to the average over the ground-state configuration for the iron atom as the calculation of the iron atom is for this average. This value is based partly on observed energy levels in iron and partly on a configuration-splitting calculation by R. D. Cowan (unpublished).

^cLithium bulk modulus is Swenson's (Ref. a). The others are from velocities of sound quoted in the *Handbook of Chemistry and Physics*, edited by R. C. Weast (The Chemical Rubber Co., Cleveland, Ohio, 1967), 48th ed.

function show insufficient binding in the solid. Thus the new potential function gives a calculated pressure of -9 kbar at normal density while the Kohn-Sham potential function gives $+105$ kbar. Since the bulk modulus is about 120 kbar, it is probable that the Kohn-Sham potential function would give a zero-pressure density about half the observed one. Commonly used correlation corrections are too small by a factor of 5 to 10 to correct this.

Similar calculations to those for lithium have been done for beryllium, aluminum, and iron to see whether as good results could be obtained in cases of more complex electronic structure. The computed bulk properties are given in Table II and are indeed about as good as could be hoped for.

CORRELATION ENERGY

Wigner¹¹ has pointed out that the degenerate electron gas at low density should crystallize into

TABLE III. Cell radius and cohesive energy of aluminum calculated with, *A*, and without, *B*, the Gell-Mann-Brueckner correlation correction inside the sphere.

	Experimental values	Calculated values	
		<i>A</i>	<i>B</i>
Wigner-Seitz cell radius (Bohr radii)	2.99	3.00	3.06
Cohesive energy (kcal/mole)	77	76	61

a close-packed lattice with one electron per cell. The present model can be easily applied to this case and gives Wigner's result for the low-density limit to the correlation energy. It seems probable that the success of the present method in solid-state calculations is due to approximate account of correlation being taken in the regions of a crystal with low electron density. Even better results might be obtained by also using a further correction for correlation in the high-density region.

Tong and Sham⁵ have tried this for atoms by adding a correlation term to the right-hand side of (1). We have used it in the parts of an atom inside the radius *R* as an added term in (7). The correlation term used by us was the one derived by Gell-Mann and Brueckner.¹² Aluminum was recalculated with the results shown in Table III. The improvement due to the added correlation term is probably in part fortuitous as there is some uncertainty about the correct correlation energy in the important density region.

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⁹D. A. Liberman, in Proceedings of the International Colloquium on the Properties of Solids Under Pressure at Grenoble, 1969 (unpublished). The solid-state calculations were done in the same way as the atomic calculations. Both core and valence-band electrons were treated self-consistently. The eigenvalues and eigen-

functions in the bands were obtained from a Green's-function band-structure program. Pressures from which the quoted bulk moduli were obtained were calculated from the flux of momentum of the electrons on the boundaries of the Wigner-Seitz cell. A cohesive energy was obtained by taking the difference of two total energies, one from a solid-state calculation for a Wigner-Seitz cell and the other for an isolated atom (e.g., for iron the total energies were, respectively, -2518.326 and -2517.814 Ry). It was possible to subtract these large numbers and obtain a significant result because the solid-state calculation was designed to be virtually the same as the atomic one.

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Pseudopotential and the Phonon Dispersion in Aluminum

H. C. Gupta and B. B. Tripathi

Physics Department, Indian Institute of Technology, Hauz Khas, New Delhi-29, India

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The phonon-dispersion curves, binding energy, and compressibility of aluminum have been calculated using the pseudopotential approach involving two adjustable parameters in the model pseudopotential. An exponential term of the type $e^{-\rho a}$ is introduced in the repulsive part of the pseudopotential so that it vanishes rapidly outside the ion core. The exchange and the correlation effects in the Hartree dielectric function have been adequately considered. Comparison with the experimental data shows good agreement.

The phonon-dispersion relations for metals have been calculated from basic principles by several workers.¹⁻³ Recently, a method based on a pseudopotential concept was developed by Sham.² Using a local as well as a nonlocal pseudopotential, calculations were made for sodium. Harrison³ used it in a slightly different way, with one adjustable parameter to compute the dispersion relations for aluminum, sodium, and magnesium, with very little success. He therefore adopted a model pseudopotential containing two adjustable parameters, which resulted in limited success in the case of aluminum and lead. The same method has been used by Wallace^{4,5} for the calculation of phonon frequencies in sodium, potassium, and lithium.

In the present paper, we report calculations on phonon-dispersion relations for aluminum using a modified form of the model pseudopotential. The bare (unscreened) pseudopotential of Harrison³ has been modified by introducing an exponential term

$e^{-\rho a}$. The new form now becomes

$$\omega_b(q) = \frac{1}{\Omega_0} \left(-\frac{4\pi Ze^2}{q^2} + \frac{\beta e^{-\rho a}}{(1+q^2\gamma_c^2)^2} \right), \quad (1)$$

where β , ρ , and γ_c are the adjustable parameters. β is the strength of repulsion, and ρ and γ_c are constants of the order of the Bohr radius. Taking into account the effect of screening, we obtain the relation for the energy wave-number characteristic

$$E(q) = -\frac{\Omega_0 q^2}{8\pi Ze^2} \omega_b^2(q) \frac{\epsilon(q) - 1}{\epsilon(q)}. \quad (2)$$

The symbols in these expressions carry the same meaning as those given by Harrison.⁶ It is evident from Eq. (1) that for large q , the pseudopotential $\omega_b(q)$ drops to zero as demanded by theory. This condition was not fulfilled by the basic $E(q)$ of Harrison³ where it approached a constant β for large values of q . The computation of the