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Chemically Motivated Pseudopotential for Sodium*

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A local pseudopotential of the form $V=V_0\cos kr+C$, $r<r_c$, $V=-1/r$, $r>r_c$, is used to fit the experimental ground-state energy of atomic sodium. This form is chosen so as to mirror as closely as possible the actual valence charge distribution of Na. This is important in the calculation of chemical properties such as bonding and cohesion. Electrostatic calculations of the cohesive energy of the bcc metal from the virial theorem and from the electrostatic self-energy of the lattice are performed and the results compared. The results bear on the accuracy of electron-gas calculations in metals and the techniques of pseudopotential calculations. The phonon spectrum is calculated and all results are compared to those obtained with a Shaw-type flat-bottom pseudopotential.

I. INTRODUCTION

Pseudopotential theory has proven to be of great use both to experimentalists, as a framework within which to report their results, and to theoreticians, as a computationally facile way to approach solid-state calculations. By far the most extensive applications of the theory have been to the calculation of the one-electron properties of solids in a nearly-free-electron viewpoint. Previous pseudopotentials have been designed to reproduce the optical spectrum of the solid or the energy levels of the atom. Little attention has been given to the importance of matching the correct charge distribution as well. We present here several calculations with a potential that models not only the atomic energy levels but also the valence charge distribution. The purpose of this choice is the calculation of properties relevant to binding. The results will be compared with a potential designed to fit only the energy levels. We present two different calculations for the cohesive energy: from the virial theorem and from the electrostatic self-energy of the lattice. As these are in principle identical calculations, if customary approximations and interpolations are valid, the results should be the same. Discrepancies between these results suggest the scale of errors in the present understanding. The phonon spectrum is also calculated.

In order to calculate the cohesive energy, a necessary (although perhaps not sufficient) prerequisite is a pseudopotential which accurately predicts charge distributions in the bonding region, i. e., outside the ion cores. The most convenient class of pseudopotentials are the local, or energy and angular-momentum-independent, pseudopotentials. In this paper we present a local pseudopotential whose form is chosen to reproduce the atomic valence charge distribution as well as the ground-state energy. A theorem useful in doing this is rereviewed in the Appendix. We also require that this potential be continuous at the core boundary, and that the slope be continuous as well. This condition has been inserted to reduce spurious "ringing" effects of abrupt changes in $V(r)$. Previous local pseudopotentials have suffered from several defects, the most important of which, from our point of view, being that although the ground-state atomic energy could be fit, the excited states could not. Further, the elimination of the core oscillations causes an arbitrary alteration of the amplitude of the pseudo wave function in the tail region.[1] Because in the long run the pseudo wave function normally is treated as the real wave function in the tail region, it is precisely this region which is important in the calculation of chemical properties such as bonding. If the pseudoatoms are viewed as the basis for the calculations of real chemistry, it is essential to get the correct wave-function normalization in the bonding region. Finally, all present pseudopotentials have discontinuous slopes at the core radius, and most have discontinuous values as well. This leads to unphysically high Fourier coefficients in the reciprocal space, which in turn slows convergence of sums over reciprocal-lattice vectors and may produce spurious effects. Indeed it is found that in order to obtain reasonable fits to phonon and band structures in metals, reciprocal-space pseudopotentials must be truncated after $4k_F$.[2] Shaw has suggested "optimizing" a potential that is constant inside some radius and Coulomb outside by making the potential continuous at the core radius.[3] However, this still leads to an emphasized oscillating tail in reciprocal space.

In the following sections we present calculations of several atomic and metallic properties of sodium using the potential chosen to improve the valence charge density. The calculations are repeated with a Shaw-type potential for comparison. Both potentials involve parameters which are varied to fit the experimental 3s level of atomic Na.

Sodium has been chosen because we expect that the core will be well represented by a local (angular-momentum-independent) potential. A local approximation is computationally simpler and has some interesting normalization properties (Appendix). In lithium there are only s states in the core so that a potential would have to represent orthogonalization of the valence s wave, but not the p wave, to the core. In potassium it is expected that the low-lying d levels will complicate the chemistry. In either case the local approximation will be less valid. Further, the potentials for either Li or K will be stronger than that for Na, and thus less amenable to the free-electron treatment we have used to check the charge distributions.

II. ATOMIC SODIUM

The pseudopotential we used in this paper consists of a cosine with greater than one-half period in the core, joined smoothly to a Coulomb potential outside:

$$\begin{aligned} V(r) &= V_0 \cos(kr) + C\,, \qquad & r \leqslant r_c \\ &= -1/r\,, & r \geqslant r_c\,. \end{aligned} \tag{1}$$

This form contains four variables, V_0, C, k, and r_c. Two of the first three are used to assure continuity of the potential and its first derivative at the core radius. The third is used to fit the experimental atomic 3s level of Na. The variable r_c is relatively unimportant in real space and might be varied to fit any property dependent on the reciprocal-space potential, although we have not done so here. (We did find, however, that the phonon spectrum was not noticeably affected by varying r_c.) Varying the core radius will vary the point at which $V(q)$ crosses zero in reciprocal space.

It was found that a small core radius slightly improved the fit to the excited s-like states, while a larger radius improved the fit to the p-state energies. A compromise fit appeared to be at $r_c = 3.0$ a. u. For comparison we calculated the energy levels of the ground and excited states of both the cosine and flat-bottom (Shaw) potentials. The potentials determined by fitting the ground-state energy are

$$\begin{aligned} \text{cosine:}\quad V(r) &= 0.1790\cos(1.224r) - 0.179\,, \quad & r \leqslant 3.0 \text{ a.u.} \\ &= -1/r\,, & r \geqslant 3.0 \text{ a.u.}; \\ \text{Shaw:}\quad V(r) &= -1/3.26\,, & r \leqslant 3.26 \text{ a.u.} \end{aligned}$$

TABLE I. Energy levels of the ground state and the first two excited states of the pseudoatom found with the Shaw and cosine pseudopotentials (both potentials were fit to the ground state) compared with experimental values.

Level(pseudo)	Experiment[a,b]	Cosine[a]	Shaw[a] (a.u.)
3S (1S)	−0.1888	−0.1888	−0.1888
4S (2S)	−0.0716	−0.0729	−0.0741
3P (2P)	−0.1116	−0.1098	−0.1076

[a] Units are $e^2=1$ and $\hbar^2/2m=\frac{1}{2}$.

[b] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 1, p. 203.

$$= -1/r, \qquad r \geqslant 3.26 \text{ a.u.}$$

The energy levels are shown in Table I and compared with experiment.

It may be shown (Appendix) that a fit to not only the ground-state energy but also the excited s-state energies is essentially necessary and sufficient to give a fit to the correct atomic valence charge distribution in the tail region. Further, all the excited states (p, d, f, etc.) must be fit before the charge density in the solid will be matched. Although both potentials fit the ground state, the cosine potential gives much better agreement with the excited states. Thus it is expected to give the wave function in the tail region more accurately. That this is so may be seen in Table II, where the wave functions for the ground state are compared at several points with a Hartree–Fock 3s function.

It may be seen that the deepening of the well just inside the core increases the binding of both s-like and p-like states which have high density here. The increase in the s-like states can be offset by the introduction of a repulsive core near the origin where only the s states penetrate. In this manner a certain amount of effective nonlocality may be introduced into a local potential. The deep-core region may be tailored to the $L=0$ states because the $L\neq 0$ states do not penetrate to the nucleus. The outer-core region may be tailored to the $L\neq 0$ states. The result is a much better over-all fit to the atomic spectrum. Physically, the repulsive core forces the ground-state charge density away from the nucleus and generates the charge deficit produced in reality by the "orthogonality hole." The cosine potential models much more closely atomic sodium than does the Shaw potential.

TABLE II. Wave function amplitude of the ground-state pseudowave calculated with the Shaw and cosine potentials compared to the Hartree–Fock 3S function of Clementi[a] at selected points in the tail region.

Radius (a.u.)	Hartree–Fock[a] (a.u.$^{-3/2}$)	Cosine (a.u.$^{-3/2}$)	Shaw (a.u.$^{-3/2}$)
3.01	0.1666	0.1676	0.1645
3.25	0.1568	0.1561	0.1526
3.51	0.1454	0.1432	0.1404
4.01	0.1227	0.1184	0.1162
5.01	0.0823	0.0783	0.0768

[a] E. Clementi, Tables of Atomic Functions, IBM, 1965 (unpublished).

While the cosine potential has larger low Fourier components, which reflects in some sense a stronger potential, the unphysical high Fourier coefficients are absent because of the smoothness of the potential. The Fourier transform $V(q)$ is plotted vs q in Fig. 1(b) for both the Shaw and cosine pseudopotentials, while $V(r)$ vs r is plotted in Fig. 1(a). The damping of the oscillations at large q should both speed convergence and improve the accuracy of calculations dependent on sums in reciprocal space.

An interesting atomic property that may be calculated using the pseudowave of the sodium model is the atomic polarizability. This is related to the second-order change in the energy due to an

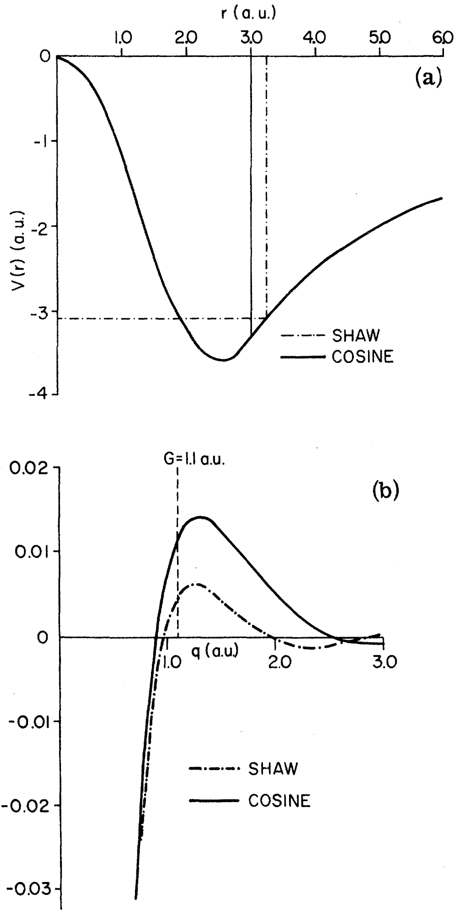

FIG. 1. Real space (a) and Fourier space (b) Shaw and cosine pseudopotentials in atomic units ($e^2=1$, $\hbar/2m=\frac{1}{2}$).

external electric field by

$$E_2 = -\tfrac{1}{2}\alpha |\vec{\mathrm{E}}|^2 , \qquad (2)$$

where α is the polarizability. Hirschfelder[4] has shown that in a perturbation expansion it is true that

$$E_2 \leqslant \langle \psi_1 | \mathcal{H}_0 - E_0 | \psi_1 \rangle + \langle \psi_0 | \mathcal{H}_1 - E_1 | \psi_1 \rangle + \langle \psi_1 | \mathcal{H}_1 - E_1 | \psi_0 \rangle \qquad (3)$$

for any ψ_1. In this case $E_1 = 0$ (no first-order energy shift) and $H_1 = Eer\cos\theta$ (field in $\hat{z}$ direction), so that

$$E_2 \leqslant \langle \psi_1 | \mathcal{H}_0 - E_0 | \psi_1 \rangle + 2 \langle \psi_1 | eEr\cos\theta | \psi_0 \rangle . \qquad (4)$$

We know the unperturbed Hamiltonian H_0 and the unperturbed energy E_0, for a good choice of ψ_1 we should be able to calculate E_2. Dalgarno and Lewis[5] have found an exact solution to the hydrogenic problem and by analogy we choose

$$\psi_1 = \frac{E}{e}\cos\theta \sum_n \frac{A_n}{(\pi n^3 a_0^3)^{1/2}} (n a_0 r + \tfrac{1}{2} r^2) e^{-r/n a_0} , \qquad (5)$$

where the A_n and a_0 are variable parameters. Inserting this into (4), and taking the partial derivatives with respect to the A_n set equal to zero, leads to a set of linear equations in A_n. The solution of these equations gives an upper bound on E_2 at a given a_0. Then a_0 may be varied to give the best upper bound. For both potentials the scale parameter $a_0 = 2.0$ a.u. gave the best bound. For the cosine potential this bound gave $\alpha = 155$ a.u.[3], while for the Shaw potential $\alpha = 146$ a.u.[3]

The cosine potential pseudoatom is more easily polarized or distorted and hence should have a lower activation energy towards reaction. The atomic energy levels and wave functions are more accurately modeled. It is expected that in order to be useful for the calculation of chemical properties of molecules, a pseudopotential must give the correct charge density in the region of chemical interaction, far from the nucleus. It is seen from the polarizability calculation that fitting the ground-state energy is not enough. If solid charge distributions, energy levels, and polarizabilities are calculated from the kind of pseudopotential that gives correct charge distributions outside the core, it is expected that correct results would be obtained. There is somewhat more of a question in this regard in molecules, where the low symmetry can emphasize certain aspects of the core region more than in solids. In Sec. III we investigate the importance of a correct charge distribution for the calculation of the cohesive energy by calculating this quantity with both the Shaw and cosine potentials.

III. COHESION

In this section we calculate the cohesive energy (defined as the difference between the total energy per atom of the metal and the atomic binding energy) of bcc sodium starting from the virial theorem and from the electrostatic self-energy of the lattice. The major ingredients of these calculations are the kinetic energy of the free gas $E_{\mathrm{ke}} = 1.105/r_s^2$, the exchange energy of the free gas $E_{\mathrm{ex}} = -0.458/r_s$, and the atomic binding energy -0.1888 a.u. The Nozières and Pines expression for the correlation energy will be used[6]:

$$E_{\mathrm{corr}} = 0.0575 + 0.0155 \ln r_s \text{ a.u.}$$

We will use Overhauser's[7] polynomial approximation to the (wave-number-dependent) dielectric function of Singwi *et al.*[8] to take into account the response of the electron gas to the lattice. This is a linear theory in which exchange and correlation effects have been included.

A. Virial Theorem

We know[9] that for systems involving only two-body central forces it is true that

$$2\langle T \rangle = \langle r\, \partial V / \partial r \rangle . \qquad (6)$$

Now for a pseudopotential for which $V = V_m$ $(r \leqslant r_c)$ and $V = -1/r$ $(r \geqslant r_c)$,

$$2\langle T \rangle = \iiint_0^{r_c} \left(r \frac{\partial V}{\partial r} \rho \right) d\tau + \iiint_{r_c}^{\infty} \frac{1}{r} \rho \, d\tau , \qquad (7)$$

where ρ is the charge density. Adding and subtracting a term gives

$$2\langle T \rangle = \left\{ \iiint_0^{r_c} \left[\left(r \frac{\partial V}{\partial r} + V \right) \rho \right] d\tau \right\} - \left(\iiint_0^{r_c} V \rho \, d\tau + \iiint_{r_c}^{\infty} -\frac{1}{r} \rho \, d\tau \right) \qquad (8)$$

$$= \iiint_0^{r_c} \left[\left(r \frac{\partial V}{\partial r} + V \right) \rho \right] d\tau - \langle V \rangle , \qquad (9)$$

$$E = -\langle T \rangle + \iiint_0^{r_c} \left[\left(r \frac{\partial V}{\partial r} + V \right) \rho \right] d\tau , \qquad (10)$$

$$E_{\mathrm{coh}} = E - E_{\mathrm{atom}} \qquad (11)$$

To calculate the average kinetic energy, we take simply $\frac{3}{5} E_F$ plus a correction for the kinetic energy gained in electron-electron correlation. March[10] has shown that the many-body virial theorem gives

$$2\langle T \rangle + \langle V \rangle = -r_s \frac{\partial E}{\partial r_s} , \qquad (12)$$

so that if we write

$$E = E_F + E_{\mathrm{ex}} + E_{\mathrm{corr}} \qquad (13)$$

we find that

$$T = -E - r_s \frac{\partial E}{\partial r_s} \qquad (14)$$

$$= E_F - E_{\mathrm{corr}} - r_s \frac{\partial E_{\mathrm{corr}}}{\partial r_s} , \tag{15}$$

or that part of the correlation energy due to kinetic energy is

$$T_{\mathrm{corr}} = - E_{\mathrm{corr}} - r_s \frac{\partial E_{\mathrm{corr}}}{\partial r_s} \tag{16}$$

$$= 0.0575 - 0.0155 \ln r_s - 0.0155 , \tag{17}$$

so that

$$T = \tfrac{3}{5} E_F + 0.0575 - 0.0155 (\ln r_s + 1) . \tag{18}$$

For the integral over the core in (10) we need to know the charge distribution in the core. This may be found from the electrostatic response of a uniform electron gas to the lattice potential:

$$\rho = \rho_0 + \Delta\rho$$

$$= \frac{3e}{4\pi r_s^3} + \sum_{G\neq 0} \frac{G^2}{4\pi e^2} \left(\frac{1}{\epsilon_G} - 1 \right) V_G \cos \vec{G}\cdot\vec{r} , \tag{19}$$

where $\vec{G}$ is a reciprocal-lattice vector, V_G is the Gth Fourier coefficient of the potential, and ϵ_G is the zero-frequency wave-vector-dependent dielectric function. Calculating the right-hand side of Eq. (11) as a function of r_s, one obtains a function that equals the real cohesive energy at the equilibrium lattice position. (The virial theorem as used is incorrect except in the absence of external forces or pressure.) The results are shown in Fig. 2(a) for the cosine potential and in Fig. 2(b) for the Shaw potential.

B. Electrostatic Self-Energy

In calculating the lattice energy it is important to perform the calculation in such a way that the infinite self-energy terms of the electron gas and the positive lattice of ion cores exactly cancel. One way of doing this is to calculate the electrostatic self-energy of the assembly of charge composed of the ion lattice and a uniform electron gas of canceling charge:

$$W = \frac{1}{8\pi} \int_{\text{all space}} |\vec{E}|^2 d\tau , \tag{20}$$

where $\vec{E}$ is the sum of the fields due to the uniform electron gas and the lattice. It may be seen that if this is done, the infinite ($\vec{G}=0$) terms cancel and may be consistently ignored. Since the electron gas is uniform, it has no term other than $\vec{G}=0$ in a sum over reciprocal-lattice vectors and all that is left is that term due to the periodic part of the lattice field

$$\vec{E} = \sum_{G\neq 0} V_G \vec{G} \sin \vec{G}\cdot\vec{r} . \tag{21}$$

From this it is possible to find the total energy of the assembly, but we are interested in that part of the energy dealing with bonding or cohesion and so we must subtract the self-energy of the core charge distribution, which is the same in the solid or atom. Thus

$$W_{\mathrm{lat}} = \frac{1}{8\pi} \int_{\text{all space}} \left(\left| \sum_{G\neq 0} V_G \vec{G} \sin \vec{G}\cdot\vec{r} \right|^2 - \left| \frac{\partial V}{\partial r} \hat{r} \right|^2 \right) d\tau \tag{22}$$

$$= \frac{1}{8\pi} \sum_{G,G'\neq 0} V_G V_{G'} \vec{G}\cdot\vec{G}' \times \int_{\text{all space}} \sin \vec{G}\cdot\vec{r} \sin \vec{G}'\cdot\vec{r}\, d\tau - \frac{1}{8\pi} \int_{\text{all space}} \left| \frac{\partial V}{\partial r} \hat{r} \right|^2 d\tau , \tag{23}$$

$$W_{\mathrm{lat}} = \frac{\omega_c}{8\pi} \sum_{G\neq 0} V_G^2 G^2 - \frac{1}{8\pi} \int_{\text{all space}} \left| \frac{\partial V}{\partial r} \hat{r} \right|^2 d\tau , \tag{24}$$

where $\omega_c = \frac{4}{3}\pi r_s^3$.

To this we must add the energy due to the redistribution of charge by the lattice

$$W_{\mathrm{redis}} = \tfrac{1}{2} \int_{\text{all space}} \Delta\rho V d\tau , \tag{25}$$

where $\Delta\rho$ is as in the previous section. Finally we must add the exchange, correlation, and kinetic energies of the electron gas and subtract the atomic binding energy to get the cohesive energy. This may be done as a function of r_s with the minimum of the curve giving the equilibrium lattice constant and the cohesive energy of the solid. The results are plotted with the results of the virial calculation in Figs. 2(a) and 2(b).

IV. PHONON SPECTRUM

While the cohesive properties depend on the value of the q-space potential, the phonon spectrum depends principally on the slope in q space. Moreover the phonon dispersion reflects the entire potential curve, while the cohesion only samples its values at the reciprocal-lattice vectors. Thus it might be expected that the phonon spectrum would be more difficult to fit than the cohesive energy.

The equation of motion for the crystal normal modes may be expressed as

$$(M\omega^2 \delta_{ij} - D_{ij}) \vec{A} = 0 , \tag{26}$$

where M is the ion mass, ω is the frequency, $\vec{A}$ is the polarization vector, and $\overleftrightarrow{D}$ is the dynamical matrix. There are two important parts to the dynamical matrix: that due to the ion-ion interaction and that due to the electronic response to the ionic motion, or the ion-electron-ion term.

The term involving the ion-ion interaction gives the frequencies which the lattice of unscreened point charges would have. Because of the long-range nature of the Coulomb interaction the lattice sums are divergent and a special technique due to Ewald[11] is necessary to do the sums. The lattice is split into a sum of two lattices. The first is a

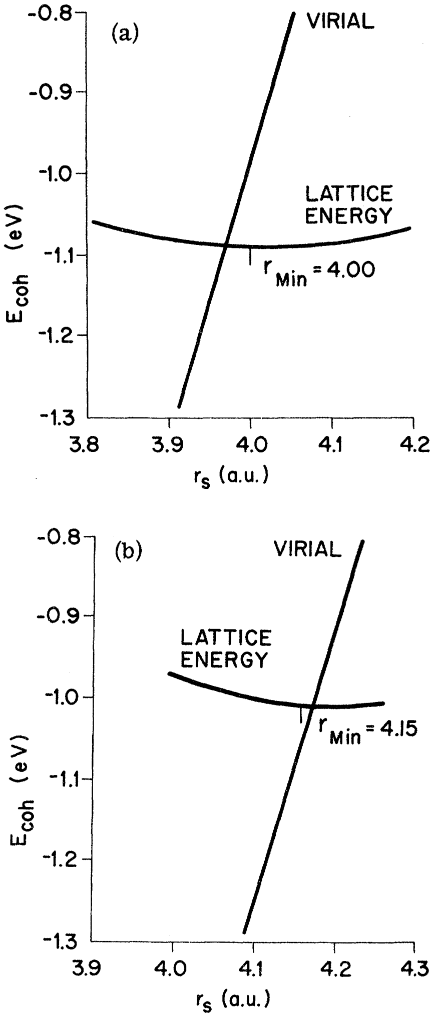

FIG. 2. Plots of cohesive energy vs electron density parameter r_s as calculated using the virial theorem and the electrostatic self-energy of the lattice for the cosine (a) and Shaw (b) pseudopotentials. Note the virial calculation is only correct at the equilibrium lattice point, but that the two curves do not cross at the minimum of the lattice energy curve, and that the crossing point is on different sides for the two potentials.

lattice of Gaussian charge distributions of same sign as the ions. The second is a lattice of Gaussian charge distributions of opposite sign added to point charges of the same sign as the ions. When this is done, it is found that both sums quickly converge. The appropriate expressions can be found in papers by Kellermann[12] or Wallace.[13]

The ion-electron-ion term is quickly convergent because the screened reciprocal potential drops off much faster than the Coulomb. The contribution to the dynamical matrix is

$$D_{ij} = Q_i Q_j F(\vec{Q}) + \sum_{G \neq 0} (G_i + Q_i)(G_j + Q_j) F(\vec{G} + \vec{Q}) - G_i G_j F(\vec{G}), \tag{27}$$

where[14]

$$F(\vec{G}) = V_G^2 G^2 (\epsilon_G - 1)\omega_c / 4\pi\epsilon_G . \tag{28}$$

The two contributions are added and the matrix is diagonalized to solve for the eigenfrequencies ω. For propagation along symmetry directions the matrix is diagonal. The transverse and longitudinal modes for $r_s = 3.93$ a.u. are plotted for both potentials in Fig. 3 along with the experimental points of Woods *et al.*[15] It may be seen that, unlike in the other calculations, there is little to choose between the two potentials, and that errors are typically 5–10%. Repeating the calculation at the equilibrium lattice parameter $r_s = 4.00$ a.u. gives only marginal improvement. A much better fit can be obtained by varying as few as one parameter with a wise choice for the functional form of the reciprocal potential, and the present work represents no significant improvement over previous calculations.

To see why this is so, we need to look at a potential which accurately fits the phonon spectrum. The two q-space paramaters which characterize a pseudopotential are q_0, the point where it crosses zero, and the height of the first maximum after q_0. While the cosine and Shaw potentials have approximately the same value at their maxima as the empirical q-space potentials, giving reasonable results for the phonon spectrum, the crossing point is at about 0.08 a.u. rather than at 0.97 a.u. That this affects the phonon frequencies is obvious, if the crossing point is nearer to the first reciprocal-lattice vector $G_1 (= 1.1$ a.u.) the func-

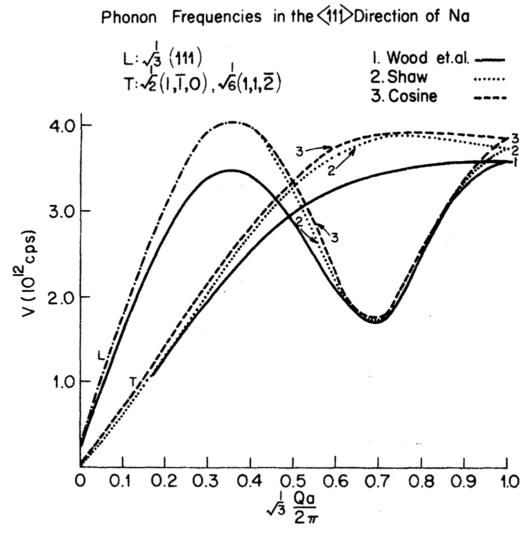

FIG. 3. Phonon dispersion curves calculated with the Shaw and cosine potentials in the (1, 1, 1) direction of sodium compared with the experimental work of Woods (Ref. 15).

tion will have a steeper slope at G_1, giving a larger contribution to the ion-electron-ion frequency. This is a canceling term which balances the ion-ion term, so that this will cause the phonon frequencies to decrease and bring them more nearly into agreement with experiment. It may be seen that while the magnitudes of the two q-space potentials are different their slopes for low-q values are very close; hence the similar spectra. In order to shift q_0 outward the core size would have to be increased, which is possible with the cosine potential, although the fit to the atomic and cohesive properties would be worse.

V. DISCUSSION

From the graphs of cohesive energy vs electron density parameter it may be seen that the pseudopotential giving the more accurate charge distribution also gives the more accurate cohesive energy and equilibrium lattice parameter. The experimental cohesive energy is 1.13 eV at $r_s = 3.93$ a.u. Although the charge density is grossly wrong near the ion cores and only marginally correct at the ionic radius, it is accurate in the tail region. Moreover, and perhaps more important, the ratio of charge in the chemically inert core to the charge in the bonding region is more nearly correct. It is the correlation of electrons in the bonding region that determines the cohesive properties of the system, and if there is sufficient charge in this region the bonding will be strong. The phonon spectrum, on the other hand, is not only a function of how charge is distributed at equilibrium but how charge is redistributed during small excursions from equilibrium as well, and the proper in-out normalization is not expected to be a sufficient condition for a good fit to the phonon spectrum. Apparently the calculation of the energy of a state of lower symmetry (containing a strain) does not work as well as that of the total energy.

While the calculated cohesive energy agrees well with experiment a slight discrepancy exists between the two calculations. If the electron gas approach is valid, or more exactly if the various expressions entering into this approach are correct, the two calculations should be consistent for a given potential. The virial calculation does not cross the total energy calculation at its minimum as would be expected. There are two possible reasons for this. One is the presence of errors in the understanding of the correlation energy or of the dielectric response of the electron gas. Because the correlation energy and the dielectric function enter in different ways in the two calculations, discrepancies will be introduced by errors in either. The other is the failure of linear-response theory to give an adequate description of the charge density for the pseudopotentials used. This latter is particularly important for the cosine potential, for which the charge in the core region is severely depleted. It is probably not important for the Shaw potential. An error in the correlation energy alone would produce crossing points on the same side of the minimum for the two model potentials because the correlation energy enters the calculation for the two problems in a virtually identical fashion. Thus there must be errors in ϵ_G or a failure of a linear response analysis (or both).

The terms due to the redistribution of charge are nearly an order of magnitude more important in the cosine potential calculations. The potential is more rapidly varying and contains portions both more attractive and more repulsive than the Shaw potential. Further the charge redistribution term in the virial calculation involves V_G multiplied by $1 - 1/\epsilon_G$, while in the self-energy calculation V_G enters as $V^2{}_G$ multiplied by $1 - 1/\epsilon_G$, so that if the screening function were altered, the two calculations would be differentially affected. A change towards a more responsive electron gas would both bring the crossing point to the same side as the Shaw calculation and improve the agreement with the experimental energy, of course, within the framework of a linear response. Alternatively, a nonlinear effect in the case of the cosine potential which decreases ρ_G for $G = [111]$ would also put the crossing points on the same side.

The errors in the phonon spectrum cannot be easily pinned down. The phonon spectrum is only partly a function of the charge distribution at equilibrium, and involves importantly the redistribution of charge for distortions away from equilibrium. It is probably not so sensitive to in-out normalization, but has great sensitivity to the response of the electron gas. Thus both errors in the dielectric response function of the electron gas or the supposition of linearity would have major effects on the phonon spectrum. Lacking at present an assessment of either of these problems, we cannot tell whether the cosine potential will be adequate for the phonon spectrum. This is an important question, for if it fails in such a simple case of lowered symmetry, it could not be expected to be an adequate basis for molecular calculations

VI. CONCLUSIONS

The addition of a repulsive core to a model potential introduces a degree of effective nonlocality and improves the fit to the excited states of the atom. From the theorem proved in the Appendix, this means that the valence charge distribution in the tail region is also correct. This can be understood physically as the wave function being excluded from the deep core by the repulsive center, thus reducing the orthogonality hole. As expected, the cohesive-energy calculations show that replicating the actual charge distribution in the region of chemical overlap is indeed necessary for the calculation of chemical properties such as binding energy and equilibrium lattice parameter. The Shaw-type potential which gives a poor charge distribution gives poor results for other chemical properties as well. However, no improvement was seen in the phonon spectrum, though it is not clear whether this represents a failure of the potential or of the calculational method.

The electron-gas approach, with minor exceptions, seems entirely consistent and very accurate indeed. The best cohesive energy calculated was 1.09 eV at $r_s = 4.00$ a.u., only slightly different from 1.13 eV at $r_s = 3.93$ a.u. One should remember, however, that the direct and virial calculations do not agree, and this error could be evaluated as 0.09 or 0.002 eV depending on the interpretation of Figs. 2(a) and 2(b). The interpolation scheme of Nozières and Pines is just that. The Padé approximation may prove useful in obtaining a more nearly correct interpolation. It is interesting to note that the Wigner–Seitz treatment of the cohesive energy, which involves a completely different approach to electron correlation, gives curves that have minima at almost exactly the minima of the lattice self-energy calculations but at lesser binding energies. Moreover, the quantities involving displacements such as the coefficient of thermal expansion and the compressability were given much more in agreement with experiment in the Wigner–Seitz approach than in our electron-gas calculation, for whatever reason. Thus it is possible that the linear screening broke down in the phonon calculation because the cosine potential is not weak enough.

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APPENDIX

In this appendix we first show that if a potential gives both the atomic ground-state energy and the energies of the excited states of the same symmetry correctly, it gives the correct in-out normalization of the wave function. The form of the wave function in the region outside the core is determined by the Coulomb tail to the potential. This, coupled with the correct in-out normalization, assures that we have the correct charge distribution in the tail region. We then generalize to the charge density in the unit cell of a solid.

Take an arbitrary potential such that

$$(-\tfrac{1}{2}\nabla^2 + V)\psi_E = E\psi_E\,, \tag{A1}$$

$$(-\tfrac{1}{2}\nabla^2 + V)\psi_{E+\Delta E} = (E + \Delta E)\psi_{E+\Delta E}\,. \tag{A2}$$

Cross multiply by $\psi^*_{E+\Delta E}$ and ψ^*_E, take the complex conjugate of (A1) and subtract it from (A2), and integrate over the core volume V ($d\tau$ is the volume element in spherical coordinates and da is the area):

$$\int\int\int_0^{r_c} [\psi^*_E(-\tfrac{1}{2}\nabla^2 + V)\psi_{E+\Delta E} - \psi_{E+\Delta E}(-\tfrac{1}{2}\nabla^2 + V) \times\psi^*_E]d\tau = \int\int\int_0^{r_c} \Delta E\psi^*_E\psi_{E+E\Delta}\, d\tau\,. \tag{A3}$$

If we assume $V \neq V(E)$, then Green's theorem gives

$$-\frac{1}{2}\oint\left(\psi^*_E\frac{2\psi_{E+\Delta E}}{2r} - \psi_{E+\Delta E}\frac{\partial\psi^*_E}{\partial r}\right)da = \iiint_0^{r_c} \Delta E\psi^*_E\psi_{E+\Delta E}\, d\tau\,. \tag{A4}$$

Multiplying through by ΔE^{-1} and taking the limit $\Delta E \to 0$ gives

$$-\frac{1}{2}\oint_{r=r_c}\left(\psi^*_E\frac{\partial^2\psi_E}{\partial E\partial r} - \frac{\partial\psi_E}{\partial E}\frac{\partial\psi^*_E}{\partial r}\right)da = \iiint_0^{r_c} \psi^*_E\psi_E\, d\tau \tag{A5}$$

or

$$-\tfrac{1}{2}r^2\psi^2_E\frac{d}{dE}\left(\frac{\partial\psi_E}{\partial r}\bigg/\psi_E\right)\bigg|_{r=r_c} = \iiint_0^{r_c} \psi^*_E\psi_E\, d\tau\,. \tag{A6}$$

If the eigenvalues for the ground and excited states for any given angular momentum are matched, the logarithmic derivatives at any point on or outside the core radius will be correct. The energy variation of the logarithmic derivative will then be correct, and by expression (A6) the amount of charge in the core will be determined within a constant (a scale factor multiplying ψ_E). Since the potential in the tail region is pure Coulomb, the amount of charge outside the core will be determined except for this *same constant*. Because we require that we have unit total charge, this constant must be equal to unity. Thus if a potential gives the ground- and excited-state energies of a given symmetry in agreement with experiment, it will give the correct wave function in the tail region as well.[16] We here presume that any reasonable potential will, if it gives the slope-to-value ratio correctly at a set of discrete energies, also give the slope-to-value ratio correctly at interpolated energy points.

The generalization to charge densities in the solid is straightforward. Assume that the Bloch function within the unit cell can be expanded in a series of partial waves:

$$\Psi_E = \sum_{l,m} a_{l,m}R_{E,l}(r)\,Y_{l,m}(\theta, \phi)\,. \tag{A7}$$

For an arbitrary potential V,

$$(-\tfrac{1}{2}\nabla^2 + V)\Psi_E = E\Psi_E\,, \tag{A8}$$

$$(-\tfrac{1}{2}\nabla^2+V)\Psi_{E+\Delta E}=(E+\Delta E)\Psi_{E+\Delta E}\,. \tag{A9}$$

Now cross multiply by $R^*_{E,l'}Y^*_{l'm'}$ and $R^*_{l',E+\Delta E}Y^*_{l'm'}$ and proceed as in the atomic problem. This gives

$$-\tfrac{1}{2}r^2R^2_{lE}\frac{d}{dE}\left(\frac{\partial R_{lE}/\partial r}{R_{lE}}\right)_{r=r_c}=\int_0^{r_c}R^*_{lE}R_{lE}r^2\,dr \tag{A10}$$

for every l. Thus in order that the charge density of the solid be properly represented between cores it is necessary to fit the ground and excited states of all symmetries.

It should be noted that this theorem is only valid if V is independent of the energy E, for then $[d/dE, V]=0$ and the potential terms in (A3) cancel.

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Forward-Scattering Approximation for Disordered Systems*

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Changes in the Fermi surface with disorder can be defined for only two cases: (a) when ordinary perturbation theory is applicable and (b) when the forward-scattering approximation is applicable. In the forward-scattering approximation (FSA) the perturbation is large in the vicinity of the forward direction or diagonal elements, but the average off-diagonal element is small, in contrast to the ordinary perturbation approximation where all perturbing matrix elements are small. The multiple scattering problem is solved for the FSA, and its close relation to ordinary perturbation theory is discussed. All the results of ordinary perturbation theory can be carried over to the FSA if proper account is taken of the self-energies of the states and interband mixing. The self-consistent condition on the potential imposed by shielding is given. The fact that the FSA can satisfy this self-consistency makes it a physically realistic approximation. All systems with a large concentration of disorder whose properties still can be approximated by the concepts of ordered systems, such as a Fermi surface, must be describable by either the FSA or ordinary perturbation theory.

I. INTRODUCTION

In the development of our understanding of a given subject, it is helpful to have models which are simple yet good approximations to physical reality. The field of disordered systems is such a developing subject, but its progress is being hampered by a scarcity of such simple models. One simple approximation that has proven to be successful is perturbation theory.[1] Both disordered alloys[2] and liquid metals[3] have examples which have been successfully described by perturbation theory. However, especially for disordered alloys, the most interesting and most numerous cases cannot be described in terms of perturbation theory.

Much effort has been expended on developing other approximations which can supplement perturbation theory. Perhaps the best known and most widely pursued one has been the coherent-potential approximation (CPA).[4–6] The CPA has the advantage that it is relatively simple if applied to the highly localized perturbation model where the random perturbations are localized to a single site and enter into only the diagonal elements of a