Influence of Conduction-Band–Core Electron Exchange and Correlation on Pseudopotential Calculations*

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Using the Harrison first-principles nonlocal pseudopotential theory, an investigation was made to determine the influence of conduction-band-core electron exchange and correlation in the phonon dispersion relations in metallic lithium. The results of this study, together with previous results for the simple hcp divalent metals, indicate that (i) the phonon spectrum is extremely sensitive to the choice of an effective potential to approximate this interaction, and (ii) there is still no single *a priori* "best" choice for this approximation.

I. INTRODUCTION

A number of papers[1-3] have been published in recent years advocating different forms of the local approximation to the nonlocal exchange and correlation interactions in the electron gas. To test the appropriateness of some of the more popular approximations of these operators in describing conduction-band–core electron exchange and correlation, we calculated phonon dispersion relations for metallic lithium with the Harrison first-principles (HFP) nonlocal pseudopotential formalism.[4] This is a first-principles theory, based upon the orthogonalized-plane-wave pseudopotential of Phillips and Kleinman.[5] We used this formalism to construct pseudopotentials differing *only* in the approximation used for the conduction-core exchange.

Lithium was chosen for this study because, of the simple alkali metals, its Fermi surface and density of state[6] have the greatest relative departure from free-electron behavior, although the actual deviations are thought small. In fact, Schneider and Stoll[7] recently estimated that deviations of the Fermi surface from the free-electron sphere are at most 2%. Therefore, lithium should provide the most severe test of the HFP theory for the simple alkali-metal series. Since successful phonon spectra calculations require pseudopotentials that are accurate over large regions of q space, the phonon dispersion curves provide a better test of a theory than would calculations of most other physical properties. A second related purpose of this investigation, alluded to above, is to provide additional insight into problems surrounding conduction-band–core electron exchange approximations.

To test the validity and accuracy of a theory, it is necessary to know whether calculated results describe the actual physical phenomena or simply reflect some peculiarities of the theoretical model. To minimize such ambiguities, the model should contain as few arbitrary parameters and assumptions as possible. Of all the pseudopotential and model-potential formalisms in use, the nonlocal HFP theory comes closest to satisfying these criteria. In principle, the input to the HFP theory need only consist of the lattice constants, atomic number, and fundamental constants. Because of our incomplete understanding of some of the physical processes involved, however, some assumptions become necessary in any practical calculation. These include the magnitude of the core shift, the form of the screening function, and, of course, the conduction-band–core electron exchange approximation. When compared to the empirically fitted pseudopotentials and model potentials often used in the calculation of atomic and electronic properties, however, the minimal parametrization in the HFP theory lends itself ideally to testing the effect of varying such approximations as the conduction-band–core electron exchange operator.

A brief review of the conduction-band–core electron exchange problem is given in Sec. II A; the lattice dynamics and the pseudopotential are discussed in Sec. II B. Results and discussion of the phonon calculations are presented in Sec. III.

II. THEORY

A. Conduction-Band-Core Electron Exchange

Most of the papers suggesting an improved or more correct form for the electron exchange approximation usually begin with the Slater approximation,[8] show why it is or is not appropriate to the case at hand, and then proceed to suggest the proper modification to improve the approximation. To better understand the origin of these various and sometimes conflicting approximations, it is instructive to look at Slater's original results, in

which he obtained an effective exchange potential given by

$$X_S = -2e^2(3\rho/\pi)^{1/3}B(\eta),\qquad(1)$$

where η is the ratio of the electron momentum k to k_F, the value at the Fermi surface, and $\rho(\vec{r})$ is the nonuniform electron density. The function $B(\eta)$, defined by

$$B(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta^2}\ln\frac{1+\eta}{1-\eta}\,,\qquad(2)$$

equals $\frac{1}{2}$ for $k = k_F$ and 1 at the bottom of the Fermi distribution. Slater then averaged Eq. (2) over all occupied states to obtain $B(\eta) = \frac{3}{4}$. When this value is substituted into Eq. (1), it yields the usual form of the Slater-exchange approximation

$$X_S = -3e^2(3\rho/8\pi)^{1/3}.\qquad(3)$$

Kohn and Sham (KS)[1] questioned the propriety of this approximation and proposed instead that the averaging of $B(\eta)$ be taken at the top of the Fermi distribution. Their derivation yielded the exchange function

$$X_{KS} = \tfrac{2}{3}X_S\,.\qquad(4)$$

In general, many of the effective local potentials which represent the nonlocal exchange operator X can be expressed as some simple scaling variant of the Slater approximation, given by

$$X \approx \alpha X_S,\qquad(5)$$

where α can take on values from $\frac{1}{2}$ to 2.

Depending upon the criteria one chooses to decide which exchange potential is "best," various calculations have been and are being produced to "confirm" the uniqueness and superiority of a particular selection. For example, free-atom calculations[9,10] with KS exchange have yielded one-electron energies in better agreement with Hartree-Fock results than those values obtained from the same calculations carried out with Slater exchange. If the criterion is to duplicate Hartree-Fock results, then in this case the KS approximation yields superior results. On the other hand, we have computed phonon dispersion relations and other properties of the simple hexagonal-close-packed (hcp) metals using the nonlocal HFP method with the conduction-band–core electron exchange operator approximated by (i) Hartree-Fock, (ii) Kohn-Sham, and (iii) Slater effective potentials.[11] No single best approximation emerged from these studies, although good results were obtained when a given exchange approximation was used for a specific metal in all cases. An interesting feature of these calculations was that physically plausible systematic trends were noted relating Fermi-surface characteristics to the choice of an exchange approximation. Also, as Payne[2] has pointed out,

the optimum value of α in Eq. (5) seems to depend upon the valence and crystal structure of the material under investigation, so that a universal value for α is not justified.

Overhauser[12] recently clarified some of the confusion surrounding this controversy by demonstrating the present futility of attempting to obtain a single universal best approximation to the (nonlocal) exchange operator by a local potential. He argues, for example, that in band-structure calculations the use of the Slater-exchange approximation severely underestimates the contribution of the off-diagonal elements of the exact exchange operator. Nevertheless, successful energy-band calculations are achieved with the use of X_S, which are attributed by Overhauser to compensation of this error by neglect of the correlation potential. He further questions the reliability of any local approximation because of the extreme nonlocality exhibited by X. However, in cases where one chooses to adopt such a local approximation, Overhauser emphasizes that the procedure used for averaging the matrix elements over $\vec{k}$ should be determined by what one ultimately intends to calculate. Highly significant are his conclusions that, as $q \to 0$, the exchange potential approaches $\ln\infty$ while the correlation potential approaches $-\ln\infty$ in such a way that their sum tends to the KS approximation. In a more recent paper, Duff and Overhauser[13] develop a microscopic theory of correlation, combine it with Overhauser's previous results for the exchange potential,[12] and determine the q dependence and nonlocal behavior of the exchange and correlation operator. One of their conclusions relevant to the present discussion is that, although correlation is singular and highly nonlocal, the sum of exchange and correlation, albeit still nonlocal, is significantly less singular than either individually.

Similar qualitative behavior, i.e., the absence of pronounced singularities, obtains when the exact exchange operator is replaced by any of the local approximation schemes such as Slater,[8] Kohn-Sham,[1] or Payne.[2] This significant result is a consequence of the averaging process used in these approximations which apparently smooths out the characteristically singular behavior. Thus, the omission of an explicit correlation contribution, when combined with the smoothing of singularities in local exchange approximations, yields results which will effectively take account of both the exchange and the correlation operators.

Herman and Schwarz[14] have also recently commented that local approximations to the exact exchange operator take account of exchange and correlation interactions. In addition, they also note that approximations which attempt to include the effects of both exchange and correlation have been shown by other investigations[15–17] to "... lead to

theories that closely resemble one or another version of the XA" (i. e., exchange approximation).[14]

B. Lattice Dynamics and Pseudopotential

Critical in any nonlocal HFP calculation is the construction of the energy-wave-number characteristic $F(q)$. A detailed description of the method for this computation has been given elsewhere[4,18] and we need not repeat that discussion here. With $F(q)$, the band-structure energy can be calculated from

$$E_{bs} = \sum_{\vec{q}}' |S(\vec{q})|^2 F(q), \tag{6}$$

where $S(\vec{q})$ is the structure factor and the prime means the $\vec{q} = 0$ term is excluded from the sum. It is often more convenient to use the normalized energy-wave-number characteristic given by

$$F_N(q) = -q^2 \Omega_0 F(q)/2\pi e^2 Z^{*2}, \tag{7}$$

where Z^* is the effective valence, Ω_0 is the atomic volume, and the limit of $F(q)$ as $q \to 0$ is

$$F(q) \to -2\pi e^2 Z^{*2}/q^2 \Omega_0.$$

Within the framework of Born-von Kármán lattice dynamics and the adiabatic approximation, the phonon frequencies ω can then be calculated from

$$\det |D_{\alpha\beta}(\vec{Q}) - M\omega^2 \delta_{\alpha\beta}| = 0, \tag{8}$$

where M is the ionic mass and $\vec{Q}$ is the wave vector of the disturbance. The dynamical matrix $D_{\alpha\beta}(\vec{Q})$ is the sum of (i) the direct Coulombic in-

teraction between ions immersed in a uniform compensating negative charge and (ii) the ion-electron-ion interaction. An explicit expression for the former component can be obtained with methods due to Ewald[19] and Thompson,[20] while contribution (ii) can be derived from Eq. (6) by methods given by Harrison.[4] We found it unnecessary to include an additional contribution for the core-core repulsive interaction. As Vosko,[21] Borchi and DeGennaro,[22] and our previous calculations have indicated,[18,23] the often used Born-Mayer theory of ionic crystals[24] for the repulsive exchange potential between ions can yield contributions for metals which can be an order of magnitude too large.

III. CALCULATIONS AND DISCUSSION

The energy-wave-number characteristic was constructed with core states for the Li$^+$ ion. These wave functions were calculated with the Herman and Skillman[25] program for the Hartree-Fock-Slater wave functions with an unmodified potential. By setting α in Eq. (5) equal to $\frac{2}{3}$, 1, and 1.15, we calculated $F_N(q)$ for the three different values of the conduction-band-core electron exchange and correlation approximation corresponding, respectively, to Kohn-Sham,[1] Slater,[8] and Payne.[2] The resulting energy-wave-number characteristics are shown in Fig. 1.

To account for exchange and correlation among the conduction electrons, we used a modified dielectric function given by

$$\epsilon^*(q) = 1 + [1 - G(q)][\epsilon(q) - 1], \tag{9}$$

where $\epsilon(q)$ is the screening function in the Hartree or random-phase approximation. For the function $G(q)$, which describes the effects of exchange and correlation, we used the expression

$$G(q) = \frac{1}{2}[q^2/(q^2 + \xi k_F^2)], \tag{10}$$

with $\xi = 2$. This value of ξ, which is the same as that used in our previous calculations,[18,23,26,27] causes the effective exchange potential to approach (i) the Kohn-Sham[1] approximation as $q \to 0$, and (ii) the Hubbard[28] result as q becomes very large.

To be consistent, the compressibility computed from the long-wavelength limit of the dielectric function should equal the compressibility obtained from the second differentiation of the cohesive energy. Although the dielectric function obtained with Eq. (10) does not exactly satisfy this compressibility sum rule, we have found that the choice of response function, with its attendant approximation for exchange and correlation, is not a very critical factor for the calculation of atomic properties. For example, the exchange and correlation approximation suggested by Geldart and Vosko[29] has the same form as Eq. (10), with ξ equal to 1.85
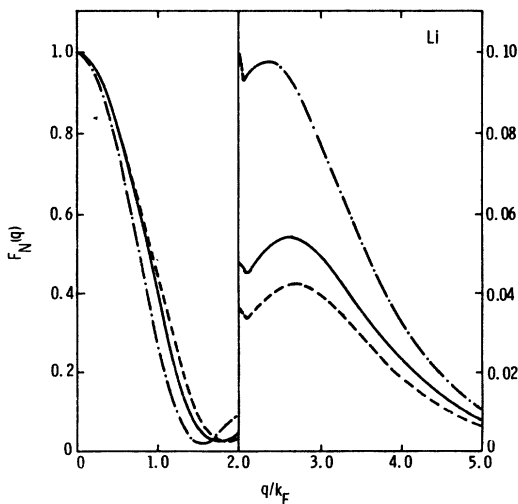

FIG. 1. Normalized energy-wave-number characteristics for lithium calculated with three different approximations for conduction-band-core electron exchange and correlation: dot-dash, Kohn-Sham ($\alpha = \frac{2}{3}$); dash, Payne ($\alpha = 1.15$); solid, Slater ($\alpha = 1$).
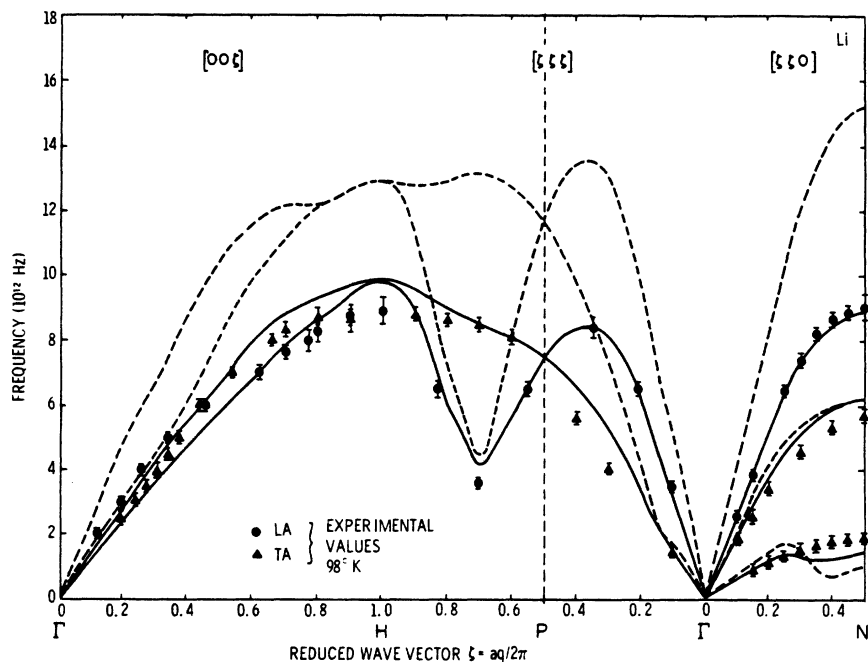
FIG. 2. Theoretical
phonon frequencies for
lithium calculated with ef-
fective potentials for con-
duction-band-core electron
exchange and correlation
given by Kohn-Sham (dashed
curves) and Payne (solid
curves with $\alpha = 1.15$). The
experimental points are 98 °K
measurements by Smith
et al. (Ref. 30).

for lithium. With this value, the expression then
satisfies the compressibility sum rule. The pho-
non spectrum resulting from the use of this $G(q)$
in the pseudopotential, however, differs so slight-
ly from the spectrum obtained with $\xi = 2$ that its
effect is at most second order. On the other hand,
a shift in the conduction-band–core electron ex-
change and correlation potential of the same mag-

nitude as this change in $G(q)$ produces much more
drastic changes in the atomic properties.

Theoretical phonon dispersion relations for
three symmetry directions are shown in Fig. 2.
These results were obtained with an effective po-
tential for the conduction–core exchange and
correlation given by (i) the Kohn-Sham approxima-
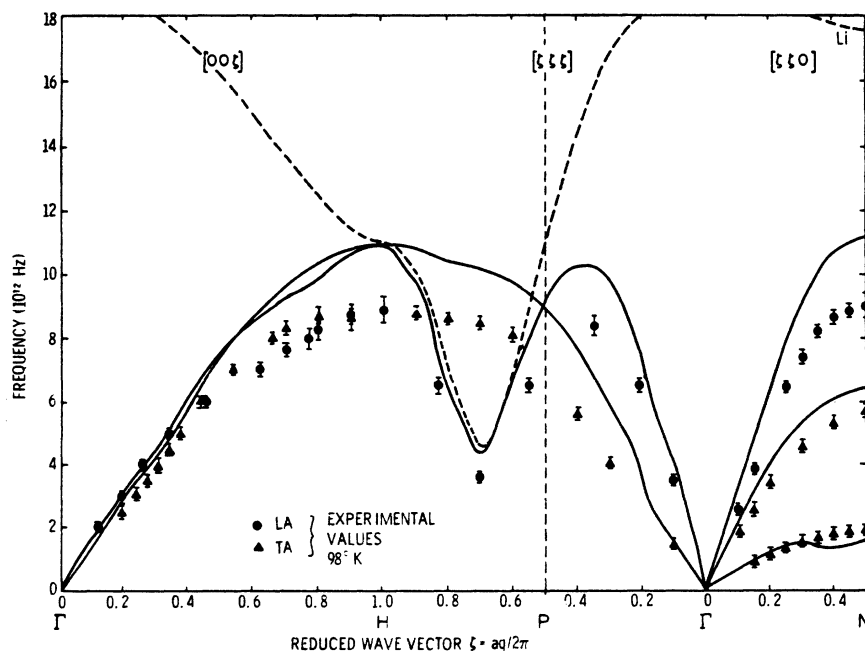tion ($\alpha = \frac{2}{3}$), and (ii) the Payne approximation (α

FIG. 3. Theoretical
phonon frequencies for
lithium calculated with (i)
an effective potential for
conduction-band-core elec-
tron exchange and correla-
tion from Slater (solid
curves) and (ii) the Cou-
lomb interaction by itself
(dashed curves). The ex-
perimental points are 98 °K
measurements by Smith
et al. (Ref. 30).

= 1.15). Our previous results for the simple hcp metals indicated that the KS potential yielded better results for very free-electron-like metals[23] (magnesium), while the Slater potential gave better results for metals that were less free-electron-like[18] (beryllium). On the basis of these calculations, we would not expect the KS approximation to yield the best results for lithium. The solid curves in Fig. 2, obtained with the Payne potential, give a much better quantitative fit to the experimental dispersion relations. Neither of these calculations, however, reproduces the experimentally observed crossing of the longitudinal and transverse branches in the [001] direction.[31]

Calculated results for the phonon frequencies with the Slater approximation for conduction–core exchange and correlation, i.e., with $\alpha = 1$, are shown in Fig. 3. Unlike the results in Fig. 2 and a number of other recent calculations,[31-34] these results do predict the crossing of the LA and TA branches in the [001] direction at almost the exact value of the wave vector measured by Smith et al.[30] Since the computed frequencies are generally higher than the observed values, better agreement could probably be obtained with a different value of the dielectric screening function. However, for reasons we have previously indicated, this would necessitate a larger change in the screening function $G(q)$ than can be obtained with any of the present approximations.

To exhibit explicitly the effects caused by using the different conduction–core exchange and correlation approximations, all other factors in these calculations were kept constant. If these restrictions were relaxed, then, for example, if plausible reasons could be found for choosing a different core shift in the calculation of the pseudopotential, improved agreement could result between the theoretical and experimental dispersion relations when using the Slater-exchange approximation. In this manner, but without justifying their choice of core shift, Schneider and Stoll[7] made use of a phenomenological approach to adjust the core state eigenvalue and eigenfunction parameter to fit the phonon spectrum for lithium. The magnitude of the core shift has a strong effect on the pseudopotential, and its value is much more critical to the calculation of the phonon frequencies than the choice of a particular dielectric function with its attendant approximation for exchange and correlation among conduction electrons.

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