1983

Vibrational frequencies and structural properties of transition metals via total-energy calculations

Chong-Long Fu
Iowa State University

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VIBRATIONAL FREQUENCIES AND STRUCTURAL PROPERTIES OF TRANSITION METALS VIA TOTAL-ENERGY CALCULATIONS

Iowa State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106

Ph.D. 1983
Vibrational frequencies and structural properties of transition metals via total-energy calculations

by

Chong-Long Fu

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

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In Charge of Major Work
Signature was redacted for privacy.

For the Major Department
Signature was redacted for privacy.
For the Graduate College

Iowa State University
Ames, Iowa
1983
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CHAPTER 1. INTRODUCTION

Modern band theoretical methods coupled with ever-advancing development of computer technology have obtained a new capability in electronic structure calculations. Recent applications within local-density-functional theory (1) have been remarkably successful in accounting for the ground state properties of crystals. The central quantity of local-density-functional theory is the total energy, which is a variational minimum for the proper ground state charge density. By accurately evaluating the ground state total energy self-consistently as a function of atomic position (crystal distortions caused by compression, stress, phonon, etc.), various physical quantities such as equilibrium bulk properties (2-13), lattice dynamical properties (11-18), temperature and pressure for phase transitions (11,19,20), and various surface geometries (21-25) can be accurately determined. The calculations also allow an intensive investigation into the microscopic electronic causes of the physical properties. In this thesis, we will present microscopic studies based on local-density-functional theory of the equilibrium bulk properties and lattice dynamics of selected phonon modes in transition metals Mo, Nb, and Zr using the self-consistent pseudopotential approach.

Because the energy scales we are interested in are of the order of a few millirydbergs per atom, whereas the total energies of the atoms are several thousand rydbergs, extreme numerical precision is
required. We have made the frozen core approximation to make our calculations more precise. In this approximation, we consider the nuclei plus the core electrons as rigid ions which are assumed to be unresponsive to the change in their chemical environment. This has the advantage of dealing with the reactive valence electrons only and, therefore, the corresponding total energy is three orders of magnitude smaller than that of the all-electron approach. The interaction of the cores and the valence electrons is then simulated by the angular-momentum-dependent (non-local) pseudopotentials, which are generated using the "Norm Conserving" scheme (26).

Because of the localized nature of the d-electrons, the electronic wave functions are represented by a mixed basis set of plane waves and Bloch sums of localized Gaussian type orbitals which permits an accurate description of both the localized and the itinerant features of d-band transition metals (27). The advantage of the pseudopotential approach is that the core states are eliminated from the problem. Unlike the real wave functions, the pseudowavefunctions are quite smooth with no radial nodes. One consequence of this is that the localized part of the mixed basis function is quite simple since it, together with the plane waves, is only required to reproduce the behavior of a pseudoatom near the atomic core. These features greatly simplify the self-consistent band calculations. In addition, the calculation of total energy is greatly facilitated by the use of a momentum space representation (28) with fast convergent reciprocal lattice sums.
The properties of the ab initio pseudopotentials used in our calculations are described in Chapter 2. The fitting procedures used in generation the pseudopotentials are given in Appendix A.

In Chapter 3, the formulation for the calculation of total energies in solids (28) is reviewed and a brief description of the mixed basis approach (27) to self-consistent band structure calculations is given. In Chapter 4, we apply these methods to study the ground state bulk properties of transition metals Mo, Nb, and Zr; we also include the details of calculational procedures and the scheme developed in carrying out the Brillouin zone sums (Gaussian smearing scheme). These calculations yield equilibrium lattice constants, cohesive energies, and bulk moduli which agree well with the measured values. The bcc band structure and charge densities obtained in the calculation are then briefly discussed.

In Chapter 5, the use of total energy calculations to study the lattice dynamics of transition metals is presented. The lattice dynamics of transition metals and transition-metal compounds with their abundance of phonon anomalies and lattice instabilities have been the subject of extensive experimental and theoretical studies (see Reference 29 for a review). For transition metals, the calculation of the phonon spectrum has typically required some inputs from experiments to fix empirical parameters, while the two most tractable methods used to obtain electron-phonon matrix elements employ approximations involving the rigid movement of localized wave functions or potentials. Here we
utilize a totally first principles method (frozen phonon technique) for calculating phonon frequencies at a few selected wavevectors which not only allows the determination of model parameters but also yields detailed information about non-rigid displacements of the charge density. This approach relies on the adiabatic principle. The method involves the calculation of the total energy of the crystal as a function of lattice displacements for a particular wavevector. From the calculated potential well, one can obtain the phonon frequency as well as the anharmonic terms which become important for soft modes and lattice instabilities. The method has also been extended to evaluate interplanar force constants from which the entire dispersion curves along a particular direction may be obtained (16). Here we demonstrate the applicability of this method for studying transition metals. We have performed frozen phonon calculations for the longitudinal \( \tilde{q} = (2/3, 2/3, 2/3) \) phonon of Mo, Nb, and the high temperature phase of Zr, as well as the H-point phonon in Nb and Mo. The calculated phonon frequencies are in good agreement with the measured values, moreover we are able to show that the bcc phase of Zr is unstable with respect to the \( \omega \)-phase transformation. The microscopic electronic response to the lattice distortions subjected to these phonon modes are also discussed. Specifically, we discuss the charge fluctuations when the lattice is distorted by the longitudinal \( \tilde{q} = (2/3, 2/3, 2/3) \) phonon, and the energy bands splitting effect in Mo caused by the distortion associated with the H-point phonon.
In Chapter 6, we consider possible significant corrections to the frozen phonon method. In particular, we have examined the non-adiabatic correction and the electron-phonon renormalization effect on the electronic states near the Fermi level. We find that in the presence of the second effect, the absolute magnitude of the Kohn anomaly (30) in the frozen phonon approach must be reduced, and this correction accounts for most of the discrepancy between the calculated and experimental value of the H-point phonon frequency in Mo. The derivation of this renormalization effect on the phonon frequency shift and the line width due to electron-phonon interaction is given in Appendix B, and the numerical calculations of the Fermi surface contribution to the phonon frequency for the Mo H-point phonon are outlined in Appendix C.

In Chapter 7, we describe the application of the Hellmann-Feynman theorem (31) to the study of longitudinal \( \vec{q} = (2/3, 2/3, 2/3) \) phonon in Mo, Nb, and bcc Zr. The analysis shows that the directional bonding nature of the d-electrons is responsible for the increase of the phonon frequency as one goes from Zr to Mo. The bcc-\( \omega \) transformation is discussed in terms of details of the bands near the Fermi level.

The calculations presented in this thesis are totally first principles, in which the only input information consists of atomic numbers, crystal structures, and the atomic masses of the constituent elements. The only approximations involved are local-density-functional theory (1) and the validity of the frozen core approximation (32).
This is the first time the phonon frequencies of selected phonons in transition metals have been evaluated from first principles.
CHAPTER 2. NORM-CONSERVING PSEUDOPOTENTIALS

Concepts

The pseudopotential has its origin in the Orthogonalized Plane Wave (OPW) method for band structure calculations introduced by Herring in 1940 (33). The idea is that the wave functions of valence electrons are plane wave-like except in the core region where they must have enough oscillations in order to be orthogonal to the core-state wave functions. Phillips and Kleinman (34) showed that the removal of the oscillations can be accomplished by an effective repulsive potential which cancels the real potential in the core region, resulting in a weak pseudopotential. In general, the pseudopotentials are not unique and are non-local operators. In the past, applications of pseudopotentials to the electronic structure in solids have utilized either parameterized model pseudopotentials (see Reference 35 for a review) or the first principles pseudopotentials obtained from self-consistent atomic calculations (36,37). However, these early pseudopotentials have one common deficiency, that is, the valence wave functions are not well described in the valence region due to the empirical form of the model pseudopotential and the orthogonalization hole problem (35) in the OPW method. Besides, the pseudopotentials based on the OPW method are still strongly repulsive at the origin, making it difficult to employ the Fourier analysis in solids because of the large number of basis functions required.
Since the pseudopotential is a device to eliminate the core states from the problem, the pseudowavefunctions which are suitable to our purpose need only reproduce the true valence wave functions in the valence region. There is no need to refer to the core states and the pseudowavefunctions need not be orthogonal to the core-state wave functions. This is the idea of the "Norm-Conserving" pseudopotential developed by Hamann, Schlüter, and Chiang (26), which enables one to construct the pseudopotentials from atomic calculations.

The "Norm-Conserving" properties for each valence state are:

1. The pseudopotential must reproduce the corresponding eigenvalues from an all-electron calculation.

2. The nodeless pseudowavefunction, after normalization, must be identical to the true valence wave function outside the core region, i.e., the corresponding charge distribution has the following relation (Norm-Conserving):

\[ \int_0^r \rho_{ps}(r) dr = \int_0^r \rho_{el}(r) dr , \quad \text{for } r \geq r_c \]  

(2.1)

where \( \rho_{ps} \) and \( \rho_{el} \) indicate the pseudo-charge and true charge distribution, respectively, and \( r_c \) is the core radius. Then through this property, the electrostatic Coulomb potential produced by these two kinds of charge distributions will be identical in the valence region.

The pseudopotential thus obtained from inverting the Schrodinger
equation converges identically to the atomic Coulomb potential outside
the core region for each valence state provided these two constraints
are satisfied.

In order that the frozen core approximation be valid in
solids, these properties should also be satisfied for various atomic
configurations above the ground state.

Applications to Mo, Nb, and Zr

The non-local ionic pseudopotentials used in our calculations
were generated using the "Norm-Conserving" scheme (26). These angular-
momentum-dependent potentials are determined from atomic calculations
by constraining the pseudowavefunction to match the ground state all-
electron wave function exactly outside some "core radius" as well as
reproducing the same atomic eigenvalues for the valence electrons
(see Appendix A for details, 38,39). The pseudopotentials and pseudowave-
functions we obtained for Mo, Nb, and Zr are shown in Figures 1 to 6.
The full lines represent the pseudopotential results while the dotted
lines indicate the all-electron valence wave functions and the Coulomb
potential. The quality of the pseudopotentials is examined by
comparing the excitation energies (defined as the total energy
differences between the excited configuration and the ground state
configuration) for various atomic valence configurations with the
corresponding all-electron values. The results are listed in Tables 1,
2, and 3. It is seen that the pseudopotential results (eigenvalues
Figure 1. Core pseudopotential of Mo generated using the reference valence configuration of $4d^5s^1$. The letters s, p, and d denote the non-local pseudopotential for angular momenta $\ell = 0, 1, \text{ and } 2$, respectively. Dashed line denotes the Coulomb potential of a (fictitious) point-like atomic core.
Figure 2. Comparison of the pseudowavefunctions (solid lines) and the corresponding all-electron valence wave functions (dotted lines) for the ground state (4d⁵5s¹) of Mo.
Figure 3. Similar to Figure 1 showing the core pseudopotential of Nb generated using the reference valence configuration of $4d^45s^1$. 
Figure 4. Comparison of the pseudowavefunctions (solid lines) and the corresponding all-electron valence wave functions (dotted lines) for the ground state (4d⁵s¹) of Nb
Figure 5. Similar to Figure 1 showing the core pseudopotential of Zr generated using the reference valence configuration of $4d^35s^1$. 
Figure 5. Comparison of the pseudowavefunctions (solid lines) and the corresponding all-electron valence wave functions (dotted lines) for the ground state \((4d^35s^1)\) of Zr.
Table 1. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations for Mo (in atomic units)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Eigenvalues</th>
<th>Excitation energy</th>
<th>$\Delta E_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>s</td>
<td>p</td>
</tr>
<tr>
<td>$4d_{5s}^1$</td>
<td>-0.3116</td>
<td>-0.3017</td>
<td>-0.0909</td>
</tr>
<tr>
<td></td>
<td>(0.0011)$^a$</td>
<td>(0.0010)</td>
<td>(0.0008)</td>
</tr>
<tr>
<td>$4d^6$</td>
<td>-0.1904</td>
<td>-0.2536</td>
<td>-0.0645</td>
</tr>
<tr>
<td></td>
<td>(-0.0021)</td>
<td>(0.0020)</td>
<td>(0.0027)</td>
</tr>
<tr>
<td>$4d_{5s^2}$</td>
<td>-0.4729</td>
<td>-0.3601</td>
<td>-0.1224</td>
</tr>
<tr>
<td></td>
<td>(-0.0058)</td>
<td>(0.0025)</td>
<td>(0.0006)</td>
</tr>
<tr>
<td>$4d_{5p^1}$</td>
<td>-0.3984</td>
<td>-0.3628</td>
<td>-0.1417</td>
</tr>
<tr>
<td></td>
<td>(0.0015)</td>
<td>(0.0018)</td>
<td>(-0.0004)</td>
</tr>
<tr>
<td>$4d_{5s^1}5p^1$</td>
<td>-0.5594</td>
<td>-0.4173</td>
<td>-0.1686</td>
</tr>
<tr>
<td></td>
<td>(-0.0057)</td>
<td>(0.0031)</td>
<td>(0.0009)</td>
</tr>
<tr>
<td>$4d^5$</td>
<td>-0.7956</td>
<td>-0.7152</td>
<td>-0.4431</td>
</tr>
<tr>
<td></td>
<td>(0.0050)</td>
<td>(0.0021)</td>
<td>(-0.0012)</td>
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<tr>
<td>$4d_{5s^1}$</td>
<td>-0.9903</td>
<td>-0.8033</td>
<td>-0.5103</td>
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<tr>
<td></td>
<td>(-0.0028)</td>
<td>(0.0043)</td>
<td>(0.0015)</td>
</tr>
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<td>$4d_{5p^1}$</td>
<td>-1.0645</td>
<td>-0.8517</td>
<td>-0.5544</td>
</tr>
<tr>
<td></td>
<td>(-0.0022)</td>
<td>(0.0357)</td>
<td>(0.0024)</td>
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$^a$The values in parentheses denote the deviations from the corresponding all-electron results.
Table 2. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations for Nb (in atomic units)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>d</th>
<th>s</th>
<th>p</th>
<th>$\Delta E_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb $4d^{4}5s$</td>
<td>-0.2554</td>
<td>-0.2944</td>
<td>-0.0944</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>(0.0013)$^a$</td>
<td>(0.0011)</td>
<td>(0.0003)</td>
<td></td>
</tr>
<tr>
<td>$4d^{5}5s^2$</td>
<td>-0.3922</td>
<td>-0.3467</td>
<td>-0.1225</td>
<td>0.0010</td>
</tr>
<tr>
<td></td>
<td>(-0.0044)</td>
<td>(0.0022)</td>
<td>(0.0008)</td>
<td>(0.0029)</td>
</tr>
<tr>
<td>$4d^{5}5p^1$</td>
<td>-0.1591</td>
<td>-0.2553</td>
<td>-0.0744</td>
<td>0.0698</td>
</tr>
<tr>
<td></td>
<td>(0.0020)</td>
<td>(-0.0015)</td>
<td>(0.0022)</td>
<td>(0.0018)</td>
</tr>
<tr>
<td>$4d^{4}5p^1$</td>
<td>-0.3338</td>
<td>-0.3500</td>
<td>-0.1411</td>
<td>0.2039</td>
</tr>
<tr>
<td></td>
<td>(0.0027)</td>
<td>(0.0029)</td>
<td>(0.0011)</td>
<td>(-0.0014)</td>
</tr>
<tr>
<td>$4d^{3}5s^15p^1$</td>
<td>-0.4723</td>
<td>-0.4000</td>
<td>-0.1659</td>
<td>0.2299</td>
</tr>
<tr>
<td></td>
<td>(-0.0041)</td>
<td>(0.0029)</td>
<td>(0.0011)</td>
<td>(0.0016)</td>
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<tr>
<td>$4d^{4}$</td>
<td>-0.7126</td>
<td>-0.6879</td>
<td>-0.4315</td>
<td>0.4881</td>
</tr>
<tr>
<td></td>
<td>(0.0053)</td>
<td>(0.0030)</td>
<td>(0.0000)</td>
<td>(-0.0002)</td>
</tr>
<tr>
<td>$4d^{3}5p^1$</td>
<td>-0.9552</td>
<td>-0.8162</td>
<td>-0.5369</td>
<td>0.8332</td>
</tr>
<tr>
<td></td>
<td>(0.0001)</td>
<td>(0.0066)</td>
<td>(0.0031)</td>
<td>(-0.0031)</td>
</tr>
</tbody>
</table>

$^a$The values in parentheses denote the deviations from the corresponding all-electron results.
Table 3. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations for Zr (in atomic units)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Eigenvalues</th>
<th>Excitation energy</th>
<th>( \Delta E_{\text{tot}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>s</td>
<td>p</td>
</tr>
</tbody>
</table>
| Zr
| 4d\(^3\)s\(^1\) | -0.1980\(^a\) | -0.2841            | -0.0999                  | 0.0 |
|               | (0.0027)    | (0.0014)          | (-0.0016)               |               |
| 4d\(^2\)s\(^2\) | -0.3068     | -0.3298           | -0.1233                  | -0.0564       |
|               | (0.0035)    | (0.0029)          | (-0.0015)               | (-0.0001)     |
| 4d\(^4\)     | -0.1282     | -0.2545           | -0.0870                  | 0.1080        |
|               | (0.0027)    | (0.0005)          | (-0.0044)               | (0.0026)      |
| 4d\(^3\)p\(^1\) | -0.2682     | -0.3337           | -0.1416                  | 0.1877        |
|               | (0.0035)    | (0.0029)          | (0.0015)                | (-0.0041)     |
| 4d\(^2\)s\(^1\)p\(^1\) | -0.3832     | -0.3802           | -0.1640                  | 0.1548        |
|               | (-0.0018)   | (0.0018)          | (-0.0008)               | (-0.0025)     |
| 4d\(^3\)     | -0.6245     | -0.6535           | -0.4171                  | 0.4660        |
|               | (0.0073)    | (0.0050)          | (-0.0001)               | (-0.0030)     |
| 4d\(^2\)s\(^1\) | -0.7750     | -0.7328           | -0.4757                  | 0.4711        |
|               | (0.0031)    | (0.0047)          | (0.0024)                | (-0.0031)     |
| 4d\(^2\)p\(^1\) | -0.8466     | -0.7788           | -0.5177                  | 0.7799        |
|               | (-0.0010)   | (0.0038)          | (0.0018)                | (-0.0051)     |

\(^a\)The values in parentheses denote the deviations from the corresponding all-electron results.
and excitation energies) reproduce the all-electron energies with an error less than 0.005 Ry for all excited configurations with total energy less than 1 Ry above the ground state.
CHAPTER 3. GENERAL FORMALISM FOR TOTAL ENERGY IN SOLIDS

Local-density-functional Theory

At present, the most satisfactory approach to the one-electron description of the ground state properties of crystals is based on the local-density-function (LDF) formalism (1), which states that the total ground state energy of electrons in the presence of an applied potential (in the present case, a collection of valence electrons in the presence of ionic potentials) is a unique functional of electron density only. In this approach, the total energy can be expressed as

\[ E_T[\rho(\vec{r})] = E_{\text{KIN}} + E_H + E_{\text{xc}}[\rho(\vec{r})] + E_{\text{e-c}} + E_{\text{c-c}} \]  

(3.1)

where the individual terms represent electronic kinetic energy, electronic Hartree energy, exchange-correlation energy, electron-core interaction energy, and core-core interaction energy, respectively. Within the LDF framework, the exchange-correlation functional is expressed as

\[ E_{\text{xc}}[\rho(\vec{r})] = \int d\vec{r} \epsilon_{\text{xc}}(\vec{r}) \rho(\vec{r}) \]  

(3.2)

where \( \epsilon_{\text{xc}} \), the exchange-correlation energy per electron, is approximated by the expression appropriate for a uniform electron gas. The kinetic energy is defined to be the kinetic energy of non-interacting particles
with the same density and is given by

\[ E_{\text{Kin}} = \sum_i n_i \langle \psi_i | -\nabla^2 | \psi_i \rangle \]  

(3.3)

where \( n_i \) is the occupation number of state \( i \), and \( \psi_i \) is the solution of the one-particle Schrodinger equation derived variationally from Equation (3.1)

\[ (-\nabla^2 + V_{\text{eff}}[\rho(\mathbf{r})])\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \]  

(3.4)

The effective potential, \( V_{\text{eff}} \), is given by

\[ V_{\text{eff}}[\rho(\mathbf{r})] = V_C(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{XC}}[\rho(\mathbf{r})] \]

\[ = V_C(\mathbf{r}) + \int d\mathbf{r'} \frac{2\rho(\mathbf{r'})}{|\mathbf{r}-\mathbf{r'}|} + \frac{\delta(E_{\text{XC}}[\rho(\mathbf{r})])}{\delta \rho(\mathbf{r})} \]  

(3.5)

Equation (3.5) depends on the charge density \( \rho(r) \) given by

\[ \rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2 \]  

(3.6)

In Equation (3.5), \( V_C \) is the core potential, \( V_H \) and \( V_{\text{XC}} \) are the Hartree and exchange-correlation potential, respectively. The dependence of the effective potential on the charge density requires that Equation (3.4) and (3.6) be solved iteratively.
Total Energy of Solids

The total energy of the crystal in a form appropriate for the pseudo-potential approach using the LDF formalism was first derived by Ihm, Zunger, and Cohen (28). Assuming non-overlapping ion cores, Equation (3.1) can be rewritten in atomic units as

\[ E_T = \sum_i n_i \langle \psi_i \mid -\nabla^2 \mid \psi_i \rangle + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' + \int e_{xc}[\rho(\vec{r})] \rho(\vec{r}) \, d\vec{r} + \sum_{\vec{R}_s, \vec{t}} [\int \rho(\vec{r}) \psi_{ps}^L(\vec{r} - \vec{R}_s - \vec{t}) \, d\vec{r}] + \frac{1}{2} \sum_{\vec{R}_s, \vec{R}_s', \vec{t}, \vec{t}'} \frac{2Z_v^2}{|\vec{R}_s + \vec{t} - \vec{R}_s' - \vec{t}'|} \]

where the prime in the summation means the \(|\vec{R}_s + \vec{t} - \vec{R}_s' - \vec{t}'| = 0\) term is excluded; \(\vec{R}\) denotes the lattice vector; \(\vec{t}\) denotes the basis vector; \(Z_v\) is the effective ionic charge (e.g., 5 for Nb); and \(\psi_{ps}^L\) is the local part of pseudopotential which acts equally on all the angular momentum components of the wave function. The non-local part is then defined as

\[ \psi_{ps,\ell}^{NL} (\vec{r}) = \psi_{ps,\ell} (\vec{r}) - \psi_{ps}^L (\vec{r}) \]

(3.8)
where $V_{ps,\ell}$ and $P_{\ell}$ are the core pseudopotential and the projection operator for angular momentum $\ell$, respectively.

Thus, the long range part (singular part) of the pseudopotential has been isolated into the local part, making $V_{ps,\ell}^{NL}$ short range. Because of the long range nature of the Coulomb potential, $E_H$ and $E_{C-C}$ are also divergent quantities. They all have an infinite zero momentum component when expressed in reciprocal space. However, because of charge neutrality, the summation of these divergent terms is a finite quantity which can be evaluated using the Ewald method (40). Thus, Equation (3.7) can be rewritten symbolically as (per primitive cell)

$$E_T = E_{KIN} + E_H(|\vec{c}|=0) + E_{xc} + E_{e-e}^{\perp}(|\vec{c}|=0) + E_{e-e}^{NL} + \gamma_{\text{Ewald}} +$$

$$+ \alpha_1 Z_V \quad ,$$

(3.9)

where $\gamma_{\text{Ewald}}$ and $\alpha_1 Z_V$ are terms obtained by summing the divergent terms in the electrostatic interaction of the system, and $\gamma_{\text{Ewald}}$ is the Coulomb interaction energy of the positive ion cores together with the neutralizing homogeneous background which can be evaluated using the Ewald method (40). $\alpha_1$ is given by

$$\alpha_1 = \frac{N_a}{\Omega_{at}} \int (V_{ps}(\vec{r}) + \frac{2\pi}{r}) d\vec{r} \quad ,$$

(3.10)

where $N_a$ is the number of atoms per primitive cell and $\Omega_{at}$ is the atomic volume.
The corresponding one-electron Schrödinger equation derived variationally from Equation (3.7) is

\[ (-\nabla^2 + V_{\text{eff}}(\mathbf{r}))\psi_i(\mathbf{r}) = e\psi_i(\mathbf{r}) \quad , \]  

with \( V_{\text{eff}} \) given by Equation (3.5), in which \( V_C(\mathbf{r}) \) is expressed as

\[ V_C(\mathbf{r}) = \sum_{\mathbf{R}, \mathbf{\tau}} \left( V_{\text{ps}}^L(\mathbf{r}-\mathbf{R}, -\mathbf{\tau}) + \sum_{\mathbf{k}, \mathbf{\tau}} V_{\text{ps}}^N(\mathbf{r}-\mathbf{R}, -\mathbf{\tau}) \mathbf{\hat{e}}_{\mathbf{\tau}} \right) . \]  

(3.11a)

Using the resulting eigenvalues, we can simplify Equation (3.7), which can be expressed in reciprocal space as (per primitive cell)

\[ E_T = \sum_{n=1}^{\text{occ.}} \frac{1}{2} \sum_{\mathbf{k}, \mathbf{\tau}} \left[ \frac{1}{2} \sum_{\mathbf{G}} \sum_{\mathbf{\tau'}} \rho(\mathbf{\bar{G}})(\mathbf{\bar{G}}) - V_{\text{xc}}(\mathbf{\bar{G}}) \right] + \sum_{\mathbf{k}, \mathbf{\tau}} \frac{1}{2} \sum_{\mathbf{R}, \mathbf{\tau}, \mathbf{\tau}'} \frac{2Z^2}{|\mathbf{R}+\mathbf{\tau}-\mathbf{\tau}'|} . \]  

(3.12)

The first term is the sum of the occupied band energies, \( w_\mathbf{k} \) is the weight of each sampled \( k \)-point, and \( n \) is the band index. \( \Omega_{\text{cell}} \) is the primitive cell volume, and \( \mathbf{\bar{G}} \) denotes the reciprocal lattice vector. In order to eliminate the divergent terms in Equation (3.12), according to Equation (3.9), we can first solve the eigenvalue problem by setting \( V_H(|\mathbf{\bar{G}}|=0) \) and \( V_{\text{ps}}^L(|\mathbf{\bar{G}}|=0) \) to zero (this corresponds to a constant shift of the energy), then adding \( \gamma_{\text{Ewald}}^{\mathbf{k}} \alpha \gamma Z_V \) to the total energy expression. The final expression is
\[ E_T = 2 \sum_{nk} \text{occ.} \left( \omega \mathbf{k}_n \mathbf{k}_n - \Omega_{\text{cell}} \right) \left[ \frac{1}{2} \sum_{\mathbf{G} \neq 0} \frac{8\pi}{|\mathbf{G}|^2} |\rho(\mathbf{G})|^2 \right. \\
+ \sum_{\mathbf{G}} \rho(\mathbf{G})(\varepsilon_{xc}(\mathbf{G}) - v_{xc}(\mathbf{G})) \right] + \gamma_{\text{Ewald}} + \alpha_1 Z_V \cdotp \]  

(3.13)

Because of the smooth pseudopotential used in place of the real potential, the convergence of the summation in Equation (3.13) is very fast. But one word of caution should be made: because the kinetic energy and the electrostatic energy are mixed in a complicated manner for pseudoatoms, these terms have no direct relationship with the all-electron counterpart.

Mixed Basis Approach

In order to treat the system whose electronic wave functions contain both localized atomic-like character as well as extended plane wave-like character, an energy independent basis set containing both plane waves and a Bloch sum of localized orbitals is used to represent the electronic wave function (27)

\[ \psi_{nk}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \alpha_n(\mathbf{k}+\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} + \sum_{jm} \beta_j(\mathbf{n}, \mathbf{k}) \phi_j(\mathbf{k}, \mathbf{r}), \]  

(3.14)
In these equations, \( \Omega \) is the crystal volume, \( N \) is the number of atoms, and \( m \) is the label for the orbital on the \( j \)-th atom. The localized functions \( f_{jm}(\vec{r}) \) are here chosen as Gaussian local orbitals of the form

\[
\phi_{jm}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_j)} f_{jm}(\mathbf{r} - \mathbf{R} - \mathbf{r}_j).
\]

(3.14a)

In these equations, \( \Omega \) is the crystal volume, \( N \) is the number of atoms, and \( m \) is the label for the orbital on the \( j \)-th atom. The localized functions \( f_{jm}(\mathbf{r}) \) are here chosen as Gaussian local orbitals of the form

\[
f_{m}(\mathbf{r}) = N' r^2 e^{-\lambda r^2} Y_{2m}(\mathbf{r}),
\]

(3.15)

to represent the localized part of the d electronic wave function, where \( N' \) is the normalization constant, and \( \lambda \) is the Gaussian exponent.

The wave functions and the eigenvalues are determined by the variational method. This leads to the standard eigenvalue problem

\[
\sum_{j} (H - S \epsilon_{nk})_{ij} \Lambda_{nj}(\mathbf{k}) = 0,
\]

(3.16)

where \( H \) is the Hamiltonian matrix, \( S \) is the overlap matrix, and \( \Lambda \) is the column vector with elements corresponding to the expansion coefficients in Equation (3.14). The localized nature of the Gaussian orbitals enables us to make the "on-site" approximation (27) when evaluating the matrix elements involving the local orbitals.
The valence charge density is then calculated from

$$\rho(\mathbf{r}) = 2 \sum_{nk} \theta(\varepsilon_f - \varepsilon_{nk} \varepsilon_{nk})|\psi_{nk}(\mathbf{r})|^2,$$

(3.17)

and the Fermi energy is determined from the number of electrons per primitive cell, \(z\), by

$$z = 2 \sum_{nk} \theta(\varepsilon_f - \varepsilon_{nk}).$$

(3.18)

\(\theta(x)\) is the step function in Equations (3.17) and (3.18).

In actual practice, the \(\mathbf{k}\) summation is restricted to the irreducible part of the Brillouin zone determined by symmetry and only the part of the charge density invariant under all the space group operations is retained.

Iteration to self-consistency is carried out until the total energy is stable to \(10^{-5}\) Ry or less, corresponding to a self-consistency error of \(10^{-4}\) Ry or less between the input and output screening potentials in reciprocal space.
CHAPTER 4. STRUCTURAL PROPERTIES
VIA TOTAL ENERGY CALCULATIONS

Since the introduction of norm-conserving pseudopotentials (26) three years ago, total-energy calculations using these potentials have been very successful in determining theoretically the structural properties of a number of materials. Using no other input than the atomic number, physical properties such as lattice constants, cohesive energies, bulk moduli (6-9,11,13), and phonon frequencies (11,13,15-18) have been calculated accurately to within a few percent of experimental values. Successful applications to determine phase transition pressures (11,19,20) and atomic geometries of surfaces (21-25) have also been reported. However, except for one investigation on Al (6,17), all of these investigations have been restricted to semiconductors. We have applied these methods to study the static structural properties and phonon modes of the bcc transition metals Nb and Mo as well as the structural properties of hcp Zr. In this chapter, we will outline some of the calculational details and report the calculated results for the static structural properties. The results on the phonon calculations will be described in the next chapter.

There are two main difficulties that have to be overcome before these methods can be applied to calculate the microscopic properties of transition metals. First, the localized nature of the d-electrons in transition metals makes expansion of the wave function in plane waves
uneconomical. This is solved by using a mixed basis set of plane waves and Bloch sums of localized orbitals to give an efficient representation of the wave function. Secondly, unlike semiconductors, transition metals are characterized by partially filled bands with complicated Fermi surfaces, making it difficult to carry out integrations over the occupied portion of the energy bands in the Brillouin zone. We have tested several weighting schemes and developed a Gaussian integration scheme which is able to take into account the variation of band occupancies near the Fermi level in a convenient and efficient way.

In this chapter, we first describe the calculational procedures used in the self-consistent band calculations. Then we discuss the convergence properties (Fermi surface weighting schemes, the size of the basis functions, and the k-points sampled in the Brillouin zone). Results on the equilibrium bulk properties are then presented and discussed.

Calculational Procedures

Step 1

Solve for the eigenvalues and the wave functions via Equation (3.16) in the mixed basis approach. Our basis contains plane waves with energy $|k+q|^2$ up to $E_{\text{cut}} = 10.5$ Ry. The Gaussian exponent $\lambda$ in Equation (3.15) is varied to optimize the convergence of the wave function. For our $E_{\text{cut}}$ of 10.5 Ry, we find that values of $\lambda$ of 1.3 a.u., 1.2 a.u., and
1.12 a.u. give optimal convergence for Mo, Nb, and Zr, respectively. The energy eigenvalues and the wave functions are evaluated at 55 points (105 points) in irreducible Brillouin zone for bcc structure (hcp structure).

**Step 2**

Determine band occupancy for each sampled k-point in the irreducible Brillouin zone (IBZ) and Fermi energy using Equation (3.18).

**Step 3**

Calculate the total pseudo-valence charge density via Equation (3.17). The charge density is expanded in reciprocal space with approximately 1500 plane waves per atom in unit cell. From the charge density, the Hartree screening potential and the exchange-correlation energy (Hedin-Lundqvist form (39) has been used) of the electrons are calculated. At each iteration step n, a new input potential \( V_H \) and \( v_{xc} \), \( V_{in}^{n+1} \), for the \((n+1)\)th iteration is obtained by mixing the old input potential \( V_{in}^n \) and the output potential \( V_{out}^n \) as follows:

\[
V_{in}^{n+1}(\vec{r}) = CV_{in}^n(\vec{r}) + (1-C)V_{out}^n(\vec{r}), \quad 0 < C < 1
\]  

(4.1)

where the mixing coefficient, \( C \), is a function of \( \vec{r} \) which corresponds to screening the charge density oscillation by a Fermi-Thomas type dielectric function (41). The new input potential is then added to the ionic potential to form the new total input potential for the next
iteration. The whole process is repeated iteratively toward self-consistency until the difference between the input and output screening potentials (for each \( G \)-component in the momentum space) is less than \( 10^{-4} \text{ Ry} \).

**Step 4**

Calculate total ground state energy using Equation (3.13), which can be rewritten as

\[
E_T = \sum_{\mathbf{k}} f_{\mathbf{n}\mathbf{k}} E_{\mathbf{n}\mathbf{k}} - \Omega \text{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) v_{\text{sc}}^{\text{in}}(\mathbf{G}) + \Omega \text{cell} \sum_{|\mathbf{G}|=0} \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} \\
+ \Omega \text{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) \varepsilon_{xc}(\mathbf{G}) + \alpha_1 Z_V + \gamma \text{Ewald} ,
\]

(4.2)

where \( f_{\mathbf{n}\mathbf{k}} \) in the first term is the weight of each state, and \( V_{\text{sc}}^{\text{in}} \) in the second term is the reciprocal space component of the input screening potential for the self-consistent band calculation given by

\[
V_{\text{sc}}^{\text{in}}(\mathbf{G}) = \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + v_{xc}(\mathbf{G}) .
\]

(4.3)

The first two terms in Equation (4.2) together contain the kinetic energy of the electrons and the interaction of the electrons with the ions through the pseudopotential.
Convergence Tests

**Fermi surface weighting scheme**

For metals, the bands crossing the Fermi level are partially occupied, and a large number of k-points in the IBZ will be needed to account for the Fermi surface. To accelerate the convergence of the total energies with respect to the number of k-points sampled, it is necessary to weight each state near the Fermi level by the occupied portion of the reciprocal space volume it represents. Several schemes for determining these weights have been tested. The one that we found most effective and most convenient is the Gaussian smearing method. In this scheme, the energy of each state calculated is broadened by a Gaussian whose width is chosen to be roughly equal to the dispersion of the energy bands between neighboring grid points near the Fermi surface. The Fermi energy is then determined from the Gaussian smoothed density of states given by

$$z = \sum_{nk} w_k \frac{E_F}{n_k} \int_{-\infty}^{E_F} \frac{1}{\sqrt{\pi\delta}} e^{-\frac{(\varepsilon - E_n)^2}{\delta}} d\varepsilon, \tag{4.4}$$

$\delta$ is the Gaussian smearing width (see also Equation (3.18)). The weight of each state is determined by the portion of its Gaussian distribution which lies under the Fermi level. The sum of the occupied band energies over the Brillouin zone is evaluated by integrating the product of the density of states with the energy up to the Fermi level ($\int_{0}^{E_F} N(\varepsilon) \varepsilon d\varepsilon$).
This scheme is convenient to use since the evaluation of band velocities are not necessary and there is no restriction on the k-point mesh. We have also investigated schemes based on the traditional Gilat-Raubenheimer (GR) method (42).

Figure 7 shows the calculated total energy for bulk Nb as a function of size of the k-point grid sampled in the IBZ for the various weighting schemes. The crosses indicate the results obtained using the Gaussian weighting scheme with Gaussian widths of 0.025 eV (x symbols) and 0.10 eV (+ symbols), respectively. The convergence with the number of k-points is quite rapid and the results are quite insensitive to the value of the Gaussian widths. In our final results, we used a Gaussian width of 0.05 eV and a mesh of 55 points in the IBZ. The convergence of the total energy with respect to the size of the k-point mesh is estimated to be better than 0.5 mRy per atom. Also shown are the results obtained with two schemes based on the GR method. In the GR method, both the band energies and band velocities are calculated on a cubic grid and the occupied portion of a particular cube element is found analytically assuming a linear band dispersion inside the small cube with the band velocity determined at the cube center. For the upper curve (o symbols), the sum over the occupied band energies is performed by adding together the calculated band energies on the grid points at the cube center with weights equal to the occupied portion of the cube element. In the lower curve (Δ symbols), the contribution from each cube is obtained by the product of the occupied volume times the energy at the centroid of the
Figure 7. The calculated total energy for bcc Nb at equilibrium lattice constant as a function of the number of grid points sampled in IBZ for various weighting schemes (see text for details).
occupied portion assuming again linear band dispersion. The latter method corresponds to integrating $\int_{0}^{E_F} eN(e)de$. We found that the convergence of the total energy with respect to the number of k-points in the IBZ is rather slow using the GR method. This is due to the curvature of the bands at the Fermi level. We have performed tests of these schemes on model bands in a cubic unit cell where we can do the integrals analytically to obtain the exact answers. While the GR method gives the exact answer for the case of linear bands, the Gaussian method gives better results for the case of spherical bands. We have also considered schemes similar to the tetrahedron method (43) which use the energies of neighboring grid points to estimate the band velocities. We found that the convergence for the bulk is intermediate between the Gaussian and the GR schemes. However, schemes which rely on interpolating between neighboring k-points have a disadvantage when investigating small distortions about the bulk structure as is the case when one wants to study phonons. What happens is that unless a very fine mesh is used, the interpolation will open up fictitious gaps at the Fermi level near band crossings even for zero distortions and, as a result, the total energies for systems with small distortions will not approach the bulk value when the distortion goes to zero. Such methods are inconvenient for studies of lattice dynamics.
Convergence of the basis set

To test the convergence of our results with respect to the basis set, we have calculated the total energies of bulk Nb with two basis sets with cutoff energies for the plane waves equal to 10.5 Ry and 14.5 Ry. In the mixed basis approach, for a given cutoff energy, the Gaussian exponent of the local orbitals is varied until the band structure energy (estimated by the position of the d-states) is minimized. The optimal $\lambda$ values are found to be 1.20 a.u. and 1.25 a.u. for $E_{\text{cut}}$ equal to 10.5 Ry and 14.5 Ry, respectively. We found that increasing the plane wave cutoff from 10.5 Ry to 14.5 Ry lowers the calculated total energy by roughly 4 mRy. As shown in Figure 8, this is essentially a constant shift of the energy-volume curve which changes the calculated lattice constant and bulk modulus by less than 0.1%. Thus, in our calculations, we have used 10.5 Ry as the cutoff energy for the plane waves in our basis set which corresponds to five local orbitals and approximately 60 to 70 plane waves per atom in the unit cell.

Results and Discussion

bcc structure

Total energies were calculated for bcc Nb and Mo at 10 different lattice volumes ranging from $0.8 V_o$ to $1.2 V_o$, where $V_o$ is the equilibrium unit cell volume. The calculated total energies are then fitted with the Murnaghan's equation of state (44)
Figure 8. The calculated total energy for bcc Nb as a function of primitive cell volume for different plane wave cutoff kinetic energies (E_{cut}): (a) E_{cut} = 10.5 Ry (+ symbols); (b) E_{cut} = 14.5 Ry (Δ symbols). The solid lines represent the fitted curve using Equation (4.5).
\[ E_T(V) = E_T(V_0) + \frac{B_0 V}{B_0'} \left[ \frac{(V_0/V)B_0'}{V_0 - 1} + 1 \right] - V_0 \left( B_0 - \frac{B_0'}{V_0 - 1} \right) \] 

where \( V_0 \) is the volume, \( B_0 \) and \( B_0' \) are the bulk modulus and its pressure derivative at the equilibrium volume \( V_0 \). The energy versus volume curves for Nb and Mo are shown in Figures 9 and 10, respectively, together with the fitted curves. The rms value of the fit is \( 10^{-4} \) Ry. To obtain the cohesive energies, the energies of the isolated atoms are needed. These are obtained by taking the ground state total energy of the corresponding pseudoatom calculated using a Herman-Skillman like program (38) and adding a spin-polarization correction obtained from the total energy difference between spin-polarized and unpolarized all-electron atomic calculations (2). It is important to note that for the case of transition metals where there is an appreciable overlap of the d-state with the core states, estimation of the spin-polarization energy from calculations on the pseudoatom can give rise to large errors because of the non-linearity of the exchange-correlation function (2). For Nb, we found the spin-polarization energy to be 0.223 Ry, whereas calculations on the pseudoatom give a result which is too large by a factor of two. The spin-polarization energy for Mo is 0.326 Ry.

The static structure properties thus obtained, together with the comparisons with experiments, are shown in Table 4. The calculated results for the equilibrium lattice constants, bulk moduli, and cohesive
Figure 9. The calculated total energy for bcc Mo as a function of primitive cell volume. Calculated values are denoted by + symbols, the solid line representing the fitted curve using Equation (4.5)
Figure 10. Similar to Figure 9 showing the calculated results for bcc Nb
energies agree with experimental values (45-48) to within 1%, 10%, and 3%, respectively, for both Mo and Nb. We have also performed parabolic fits of the calculated results with volumes limited to be within 10% of $V_0$ with very similar results.\(^1\) Prior to our calculation, there were a number of successful calculations on the transition metals based on the other methods (2,5,14). They are also summarized in Table 4.

The calculated band structures along symmetry directions are plotted in Figures 11 and 12. They agree very well with previous self-consistent calculations (2,27).

For later studies of lattice dynamics, we have also calculated the equilibrium lattice constant and bulk modulus for bcc Zr. The calculation yields values of 3.47 Å for the equilibrium lattice constant which agrees well with the measured value (45) to within 3%, and 0.98 Mbar for the bulk modulus. In order to understand qualitatively the variation of the bulk properties among these three elements with bcc structure, a plot of the Nb valence charge density in the (110) plane for states in four increasing energy intervals corresponding to four major peaks in the density of states (49) is shown in Figure 13. For Mo, the states in the energy interval corresponding to Figure 13(a) to Figure 13(c) are occupied and give a clear density maxima along the nearest neighbor (111) direction. Thus, as the number of valence electrons increases (Zr-Nb-Mo),

\(^{1}\)There is no change for the equilibrium lattice constant and cohesive energy. In contrast, the bulk modulus has a variation of about 5%.
Table 4. Comparison of the calculated and measured values for the static bulk properties of Mo, Nb, and Zr

<table>
<thead>
<tr>
<th></th>
<th>Lattice constant (Å)</th>
<th>Cohesive energy (eV/atom)</th>
<th>Bulk modulus (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mo</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moruzzi et al.(^a)</td>
<td>3.12</td>
<td>6.73</td>
<td>2.51</td>
</tr>
<tr>
<td>Harmon et al.(^b)</td>
<td>3.17</td>
<td>6.28</td>
<td>2.57</td>
</tr>
<tr>
<td>Zunger and Cohen(^c)</td>
<td>3.15</td>
<td>6.68</td>
<td>3.05</td>
</tr>
<tr>
<td>Present calculation</td>
<td>3.14(^d)</td>
<td>6.64</td>
<td>2.85</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.14(^e)</td>
<td>6.82(^e)</td>
<td>2.62(^f)</td>
</tr>
<tr>
<td><strong>Nb</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moruzzi et al.(^a)</td>
<td>3.28</td>
<td>7.50</td>
<td>1.68</td>
</tr>
<tr>
<td>Harmon et al.(^b)</td>
<td>3.34</td>
<td>6.63</td>
<td>1.62</td>
</tr>
<tr>
<td>Present calculation</td>
<td>3.26(^d)</td>
<td>7.55(^e)</td>
<td>1.82</td>
</tr>
<tr>
<td>Experiment</td>
<td>3.29(^d)</td>
<td>7.57(^e)</td>
<td>1.735(^g)</td>
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<td><strong>Zr</strong></td>
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<tr>
<td>Present calculation</td>
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<td>3.14(^h)</td>
<td>1.605(^h)</td>
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<tr>
<td>Experiment</td>
<td>5.14143(^h)</td>
<td>3.2294(^h)</td>
<td>1.5921(^h)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 2.
\(^b\)Reference 14.
\(^c\)Reference 5.
\(^d\)Reference 45.
\(^e\)Reference 46.
\(^f\)Reference 47.
\(^g\)Reference 48.
\(^h\)Reference 50.
\(^i\)Reference 51.
Figure 11. Calculated electronic band structure for bcc Nb along symmetry directions
Figure 12. Calculated electronic band structure for bcc Mo along symmetry directions
Figure 13. The Nb valence charge density in the (110) plane for states in four increasing energy intervals corresponding to the four major peaks in the density of states (49). For each plot, the density has been normalized to one electron per unit cell. For Mo, the states in the energy interval corresponding to (a), (b), and (c) are occupied.
one would expect a relative increase in the magnitude of the attractive partial pressure due to the directional bonding developed within the d-bonding bands. The s-electron contribution to the partial pressure has to become more repulsive for Mo in order to counter this attractive d-pressure to achieve equilibrium. As a result, the equilibrium atomic volume for Mo is the smallest among these three elements. On the other hand, the bulk modulus is determined from the slope of the pressure at equilibrium position. Because of the rapid increase of the s-pressure as one moves closer to smaller radius, this will be reflected in a larger bulk modulus for Mo. The directional bonding behavior of d-electrons in Mo will be important for the discussion of the phonon anomaly for the longitudinal $\mathbf{q} = (2/3, 2/3, 2/3)$ mode in the next chapter.

hcp structure

Total energies were calculated for hcp Zr at different c/a ratios as well as different volumes. Sixty k-points in the IBZ are sufficient to achieve the convergence in total energy, but 105 k-points in IBZ are necessary to account for the small variation in total energy for different c/a ratios at constant volume.

The calculated total energies are also fitted with the Murnaghan's equation of state. The energy versus volume curves for c/a = 1.633 (+ symbol) and c/a = 1.605 (Δ symbol) are shown in Figure 14. Then, at the calculated equilibrium primitive cell volume (290 a.u.), a plot of energy versus c/a ratio is shown in Figure 15. The equilibrium c/a
Figure 14. Similar to Figure 9 showing the calculated results for hcp Zr at different c/a ratios: (a) $c/a = 1.633$ (+ symbols); (b) $c/a = 1.605$ (Δ symbols)
Figure 15. The calculated total energy as a function of c/a ratio at the calculated equilibrium unit cell volume (290 a.u.). The calculated values are denoted by + symbols, the solid line represents the fitted curve using polynomial equation up to third order.
ratio in our calculation is 1.605 which compares well with the experimental value 1.5921 (50). The results on the static structural properties are also summarized together in Table 4. The spin-polarization energy for Zr is 0.143 Ry.

Summary

We have applied first principles total energy calculations using ab initio pseudopotentials to study the static structural properties of the transition metals Mo, Nb, and Zr. The calculated results for the equilibrium lattice constants, bulk moduli, and cohesive energies agree very well with experimental values. These calculations show that our method has the accuracy required for calculating the properties of transition metals and enable us to proceed with confidence to investigate the lattice dynamical properties in transition metals. We have extended these calculations to study phonon modes of Mo, Nb, and the occurrence of phase transitions in Zr. Details of these studies will be presented in the following chapters.
CHAPTER 5. VIBRATIONAL FREQUENCIES VIA TOTAL ENERGY CALCULATIONS

Introduction

Until very recently, the phonon dispersion curves of transition metals have been interpreted in terms of the Born-von-Karman (52) and numerous phenomenological models (see Reference 29 for a review). In order to fit the observed dispersion curves, a large number of parameters is required and it is difficult to judge the physical significance of the various models. Recently, Varma and Weber (53), using a perturbative approach involving an empirical non-orthogonal tight-binding description of the electronic states and electron-phonon matrix elements (54), have been very successful in correlating anomalies in the phonon spectra of several transition metals and transition metal compounds with features of the band structure near the Fermi level. However, not all of the features in the phonon spectra of transition metals can be related to features of the Fermi surface, and as Varma and Weber note in their paper (53), the parameters required in their theory to describe the short range forces are still not well-understood. In this chapter, we utilize an alternative approach which involves the precise evaluation of the total energy of the crystal as a function of the lattice displacement associated with a particular phonon mode. These are known as frozen phonon calculations. The phonon frequency can then be obtained from the resultant potential energy curve. Unlike previous methods, this method requires no experimental input to obtain
the phonon frequency, the only approximations made are the local-density approximation (1) for evaluating the total energies and the Born-Oppenheimer approximation (52). Because of its non-perturbative nature, this approach also yields information on phonon anharmonicity and possible lattice instability. It is complementary to the other methods since we focus on a few particular modes and examine the microscopic response and trends among several systems, while others try to model the whole phonon branch at a time. Recently, successful applications of the frozen phonon approach to study the phonons in semiconductors (11,12,15,16) and metals (13,14,17,18) have been reported. In this chapter, we demonstrate the applicability of this method for studying transition metals: we have performed the frozen phonon calculations for the longitudinal $\vec{q} = (2/3,2/3,2/3)$ phonon mode in Mo, Nb, and the high temperature bcc phase of Zr as well as the H-point phonon in Mo and Nb. We find, in general, that the frozen phonon approach yields phonon frequencies within a few percent of the measured values. The only exception is the Mo H-point phonon where severe Fermi-surface nesting causes errors in the Born-Oppenheimer approximation.

We begin with the experimental results and the motivations of our calculations. The frozen phonon method is covered next, followed by the total energy results. We then analyze the charge response when the lattice is distorted by the longitudinal $\vec{q} = (2/3,2/3,2/3)$ phonon, and the energy band splitting effect in Mo caused by the distortion associated with the H-point phonon.
Experimental Results and Motivation

Figure 16 shows the phonon dispersion curves for the longitudinal (111) branch measured by inelastic neutron scattering experiments for Mo (55), Nb (56), and the high temperature (1400 K) bcc phase of Zr (57). Our motivation for studying the longitudinal \( \mathbf{q} = (2/3,2/3,2/3) \) mode (L(2/3,2/3,2/3), in abbreviation) and the H-point phonon in Nb and Mo is the marked difference in the phonon spectra of the two metals at these wavevectors. For Nb, the longitudinal (111) phonon branch exhibits a dip at the (2/3,2/3,2/3) position, whereas the same branch in Mo is flat near (2/3,2/3,2/3) but shows a dip at the zone boundary (H-point).

Of particular interest is the \( L(2/3,2/3,2/3) \) phonon of bcc Zr. This element undergoes a phase transformation to the hcp structure at a temperature of \( \sim 1100 \) K. However, there is a competing transformation to the so-called \( \omega \)-phase by alloying (58,59) or upon the application of high pressure (60,61). From a lattice dynamic point of view, the \( \omega \)-phase can actually be formed from the bcc phase through the softening of the \( L(2/3,2/3,2/3) \) mode. The experimental phonon dispersion curves for the high temperature bcc phase (57) indicate a huge dip in the (111) longitudinal branch with the minimum at (2/3,2/3,2/3) and a corresponding peak in the quasi-elastic scattering at this wavevector.
Figure 16. Phonon dispersion curves for the longitudinal (111) branch measured by inelastic neutron scattering for Mo (55), Nb (56), and the high temperature (1400 K) bcc phase of Zr (57)
Method of Calculation

Frozen phonon

In the Born-Oppenheimer approximation (52), the motions of the ions are assumed to be so much slower than the motions of the electrons that at each instant the electrons are always in the ground state defined by the instantaneous ionic configuration. The total ground state energies for the various positions of the ions then form the effective potential for the ionic motions. When the crystal is distorted with displacements corresponding to a particular phonon mode with a wave-vector commensurate with the bulk reciprocal lattice vectors, the resultant lattice can be viewed as a new crystal structure with lower symmetry. In the frozen phonon approach, we carry out self-consistent band calculations for the distorted lattice to obtain the total energies for various frozen ionic displacements. For small displacement, the distortion energy per atom caused by the phonon mode \( \mathbf{q} \) can be expressed in the harmonic approximation as

\[
\Delta E_q = \frac{1}{2} \sum_{i} \left[ \frac{M_{i} \omega_{q}^{2}}{2} U_{iq}^{2} \right] \cdot \cos^{2}(\mathbf{q} \cdot \hat{R}_{i} + \delta_{q})
\]

(5.1)

In these equations, \( \hat{R}_{i} \) is the equilibrium position at the i-th atom, \( U_{iq} \) is the amplitude of the phonon wave, \( \delta_{q} \) is the phase factor, \( N \) is the number of atoms in the crystal, \( M \) is the atomic mass, and \( \omega_{q} \) is the phonon frequency.
For a zone boundary phonon, Equation (5.1) gives

\[ \Delta E^\pm_q = \frac{1}{2M} \omega_q^2 u_q^{\pm2} \]  

(5.2)

and for a phonon mode of arbitrary \( \vec{q} \) (except for zone boundary phonons)

\[ \Delta E^\pm_q = \frac{1}{4M} \omega_q^2 u_q^{\pm2} \]  

(5.3)

Thus, from Equations (5.2) and (5.3), phonon frequencies can be evaluated from the curvature of the calculated energy versus displacement curve for small displacement.

To keep the size of the Hamiltonian matrix manageable, the new unit cell size is restricted to 10 atoms or less. In this aspect, the frozen phonon approach can only be effectively employed for a restricted number of wavevectors at high symmetry points, and in the present study the calculations are limited to the most interesting phonons at \( L(2/3,2/3,2/3) \) and the H-point.

**Geometry**

\( L(2/3,2/3,2/3) \) phonon. In the presence of such a phonon, the distorted bcc crystal can be described by a unit cell consisting of three atoms. In Figure 17(a), three neighboring atomic planes normal to [111] direction of the bcc structure are shown, the phonon distortion corresponds to moving a pair of such adjacent planes (labeled as plane 2 and plane 3) toward each other (or apart)
Figure 17. Geometry for the distorted bcc crystal in the presence of $L(2/3,2/3,2/3)$ phonon:
(a) The bcc lattice and three neighboring (111) planes
(b) Spacing of (111) planes in the bcc phase, the fully collapsed, $\omega$-phase and the phonon-distorted crystal pattern corresponding to the $L(2/3,2/3,2/3)$ phonon
and leaving every other third plane (labeled as plane 1) unmoved. When plane 2 and plane 3 collapse together as depicted in Figure 17(b), the configuration of this structure is known as the $\omega$-phase.

The distorted bcc crystal can be described with a hexagonal primitive cell with $A = 2a$ and $C = \frac{\sqrt{3}}{2}a$, where $a$ is the lattice constant of the bcc crystal. With the phonon, the crystal belongs to trigonal system with space group $D_{3d}^*$. For the $\omega$-phase, the space group is $D_{6h}^*$.

**H-point phonon** In the present study, $\mathbf{q} = (0,0,1)2\pi/a$ has been chosen. The primitive cell of the phonon-distorted lattice is a simple cubic with two atoms, and the space group is $D_{4h}$ (non-symmorphic).

**Grid points**

Since the Brillouin zone of the phonon-distorted bcc lattice is commensurate with that of the bulk bcc crystal, it is possible to choose a grid common to both the distorted and undistorted crystal when evaluating the eigenvalues and wave functions. This ensures a maximum cancellation of errors in subtracting energies to find the distortion energy. It is also essential to make sure that the grid chosen for the distorted crystal has the full cubic symmetry of the bulk lattice, otherwise there will be charge distortions and transfers even when the atomic displacements go to zero unless an extremely fine mesh is used.

Cubic grid points have been used in the present calculations and are chosen to avoid sampling points along high symmetry lines. Fifty-
seven k-points for the L(2/3, 2/3, 2/3) phonon and 126 k-points for the H-point phonon in their individual phonon irreducible Brillouin zones (IBZ) have been used through this study, which corresponds to 55 and 112 k-points, respectively, in the bulk bcc IBZ.

**Procedures**

The calculations proceed in analogy to that of the bulk bcc structure, except for the larger real space unit cell and lower symmetry for the phonon-distorted structure. Our calculations were made using a first principles pseudopotential method employing a mixed basis of Gaussian localized orbitals and plane waves. The details of the calculational procedures have already been discussed in the previous chapter. For small phonon displacements (∼1% of the lattice constant), about equilibrium the distortion energies involved are of the order 0.001 Ry per atom and numerical precision is extremely important. The calculations are feasible because we require only energy differences so that the major errors associated with the local-density approximation (1) and k-point sampling cancel in the subtraction.

Before attempting any calculations for the displaced lattice, we have calculated various structural properties for the bulk. The results are in excellent agreement with the measured values (see Chapter 4). For each phonon mode, in order to assure good convergence, the total energies of the distorted and undistorted crystal are calculated with the same cutoff energies for the plane wave expansion of the wave
function and charge density (e.g., for the \( L(2/3, 2/3, 2/3) \) mode, about 200 plane waves for the wave function and 4500 for the charge density were used).

In dealing with the lattice distortion in metals, it is necessary to consider changes in the Fermi surface and band occupancies. To handle this, the same Gaussian smearing scheme described in the previous chapter was used to take into account the partial occupation of the bands near the Fermi level. We have tested the convergence of our results with respect to the size of the sampling grid in the IBZ. Table 5 lists the results for the phonon frequency of the \( L(2/3, 2/3, 2/3) \) mode of Nb obtained from calculations with different sampling grids and different values of the Gaussian smearing used in the Fermi-surface-weighting. We have also carried out one calculation for a plane wave cutoff energy of 14.5 Ry with a Gaussian orbital exponent of 1.25 a.u., and obtained a shift of 1% in the calculated phonon frequency. Grids of up to 196 points in the phonon IBZ have been tested for the Mo H-point phonon. For comparison, we have also applied the empirical tight-binding (TB) method (12, 62-64) to find the weight of each state near the Fermi level for the Mo H-point phonon. In this method, the IBZ is divided into a number of large tetrahedrons (up to 96 in the phonon IBZ have been tested) and the center of mass k-point of each tetrahedron was used as a sample grid point. At each iteration, the band structure is fitted with empirical TB parameters obtained from
Table 5. The convergence of the frequency of the L(2/3,2/3,2/3) phonon in Nb as the size of the sampling grid in the phonon IBZ and the value of the Gaussian smearing width (δ) used in the Fermi-surface-weighting are varied.

<table>
<thead>
<tr>
<th></th>
<th>Phonon frequency (THz)</th>
<th>δ = 0.025 eV</th>
<th>0.05 eV</th>
<th>0.1 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 k-points (20)</td>
<td></td>
<td>3.36</td>
<td>3.63</td>
<td>3.61</td>
</tr>
<tr>
<td>57 k-points (55)</td>
<td></td>
<td>3.57</td>
<td>3.61</td>
<td>3.63</td>
</tr>
<tr>
<td>124 k-points (112)</td>
<td></td>
<td>3.63</td>
<td>3.56</td>
<td>3.57</td>
</tr>
</tbody>
</table>

^The numbers in parentheses denote the corresponding number of grid points in the bcc IBZ.
fitting to the eigenvalues at the sample grid points with a typical rms fit error of less than 0.05 eV. The weight of a state is then represented by the occupied volume as determined by the TB fit using 64 small tetrahedrons inside each large one. The phonon frequency is then determined from comparing the distortion energies between two neighboring phonon displacements (since in this scheme the total energy of the distorted bcc crystal does not approach the bulk bcc values as the displacement goes to zero). We found that the convergence using the TB fit method is slow, 96 k-points in the phonon IBZ are necessary to approach the value obtained from the Gaussian smearing scheme using 75 k-points.

In the process towards self-consistency, the dielectric matrix scheme (65) has been used between iterations to accelerate the convergence. Self-consistency within $10^{-4}$ Ry on the screening potentials in reciprocal space can be achieved in four to five iterations for the $L(2/3,2/3,2/3)$ phonon.

**Total Energy Results**

The calculated total energy for Mo, Nb, and Zr as a function of lattice displacement corresponding to the $L(2/3,2/3,2/3)$ mode is shown in Figure 18. The curves for Mo and Nb indicate nearly harmonic behavior for small displacements and yield values of $3.6 \pm 0.05$ THz and $6.2 \pm 0.05$ THz, respectively, for the frequencies of the $L(2/3,2/3,2/3)$ phonon in Nb and Mo. These compare well with measured values of
Figure 18. The calculated total energy as a function of the displacement corresponding to the \( \mathbf{L}(2/3,2/3,2/3) \) phonon for Mo, Nb, and bcc Zr. The insert shows the displacement pattern for the (111) planes of the bcc crystal. Planes 2 and 3 coincide for the \( \omega \)-phase.
3.57 ± 0.06 THz (56) and 6.31 ± 0.04 THz (66) from inelastic neutron scattering experiments. Of particular interest is the result we calculated for bcc Zr also shown in Figure 18. The calculated potential well is strongly anharmonic; moreover, the minimum in energy does not occur at the undisplaced bcc phase but, rather, it occurs when two of the bcc (111) planes in the unit cell collapse together to form the ω-phase. The instability of the bcc phase towards the formation of the ω-phase at low temperature occurs in a wide variety of Ti, Zr, and Hf alloys (59,60) and also in pure Ti and Zr under pressure (61,62). The bcc-ω transformation has been studied extensively (67-69) because of its anomalous effects on the diffusion process and the mechanical properties of the metal. This is the first time that a potential energy curve has been calculated for this important transition. We obtain an energy difference of 0.045 eV (or 520 K) per atom between these two phases. It should be noted that the temperature effects have not been included in the calculations. The stability of the bcc phase at high temperature is due to its higher lattice vibrational entropy (70). Our results do suggest that the bcc-ω transition is first order in nature since we find the Zr bcc lattice has very low but non-zero restoring forces when subjected to the distortion of the L(2/3,2/3,2/3) phonon. Stassis et al. (57) have measured phonon dispersion curves for the bcc phase of Zr at high temperature and their results show that there is a sharp dip in the longitudinal mode at
the \((2/3,2/3,2/3)\) position (Figure 16) as well as quasi-elastic scattering at Bragg positions corresponding to the \(\omega\)-phase. As the temperature is lowered, the quasi-elastic scattering corresponding to \(\omega\)-phase grows\(^1\) but before a transition to the \(\omega\)-phase can occur, there is a first order transition to the hcp phase which is the stable phase at low temperature for Zr.\(^2\)

The calculated phonon frequencies for the H-point phonon of Mo and Nb, along with the experimental values (56,66,71), are summarized in Table 6, together with the results for the \(L(2/3,2/3,2/3)\) mode. The results are in good agreement with experiments.\(^3\)

Discussion

\(L(2/3,2/3,2/3)\) phonon (charge density analysis)

In the analysis of the phonon spectra of Nb and Mo using the traditional Born-von-Karman model, it is necessary to include interactions up to eight neighbors to obtain a good fit (56). With this

\(^1\)The magnitude of the quasi-elastic peak depends on oxygen impurities (57) which might serve as pinning centers of the soft phonon.

\(^2\)According to Reference 60, the energy difference between the hcp structure and the \(\omega\)-phase is about 1.5 mRy/atom. To our precision, it is difficult to resolve this energy difference when comparing different lattice structures, since the energy difference of core relaxation energy is also of the same magnitude (32).

\(^3\)Except for the 9% discrepancy for the Mo H-point phonon, the agreement is always within the error limit (~2%).
Table 6. Comparison of the calculated and measured values for the frequencies of the \( \frac{2}{3}, \frac{2}{3}, \frac{2}{3} \) phonon and the H-point phonon in Mo and Nb.

<table>
<thead>
<tr>
<th>Phonon frequency</th>
<th>Exp. Mo</th>
<th>Calc. Mo</th>
<th>Exp. Nb</th>
<th>Calc. Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{2}{3}, \frac{2}{3}, \frac{2}{3} )</td>
<td>6.31±0.04(^a)</td>
<td>6.2</td>
<td>3.57±0.06(^b)</td>
<td>3.6</td>
</tr>
<tr>
<td>H-point</td>
<td>5.51±0.05(^a)</td>
<td>5.0</td>
<td>6.49±0.10(^b)</td>
<td>6.4</td>
</tr>
</tbody>
</table>

\(^a\)Reference 66. These values were measured at 10.5 K.

\(^b\)Reference 56.
profusion of parameters, the physical significance of such a fit is questionable. Besides, the Born-von-Karman analysis may not be considered exact, since it does not consider the long-range force arising from the inter-ion interaction modulated by the valence electrons. General theories based on dielectric response were proposed and led to simplified models emphasizing charge fluctuations (72,73). Wakabayashi (74) and Allen (75) have used phenomenological models in which the phonons are coupled to the charge fluctuations in crystal. They were able to fit the phonon dispersion curve in Nb with considerably fewer parameters. Our investigations of the charge fluctuations caused by the L(2/3,2/3,2/3) phonon in Mo, Nb, and bcc Zr are shown in Figures 19 and 20. In these figures, $\Delta \rho$ indicates the monopolar charge ($\rho_{00}$) fluctuation defined as

$$\Delta \rho(r) = \rho^{\text{phonon}}_{00}(r) - \rho^{\text{bulk}}_{00}(r),$$

and $\rho_{00}$ of the $j$-th atom is given by

$$\rho_{00}(r) = \sum_{\mathbf{G}} \rho(\mathbf{G}) j_0(Gr)e^{i\mathbf{G}\cdot \mathbf{r} - \sigma_j},$$

where $\rho(\mathbf{G})$ is the component of charge density in reciprocal space, $j_0(x)$ is the spherical Bessel function of zero-order, $\sigma_j$ denotes the basis vector.

For small displacements about the bcc equilibrium position, the charge density fluctuations are similar in magnitude but very different
Figure 19. The spherical component of the charge density difference 
($\Delta \rho = \rho_{\text{phonon}} - \rho_{\text{bulk}}$) for a small displacement ($\delta = 0.5$ 
for a full displacement to $\omega$-phase). By symmetry, atoms 
in plane 3 are equivalent with those in plane 2. Charge 
density is in the unit of electrons per unit cell volume.
Figure 20. Similar to Figure 19 showing the character of the charge fluctuation for Zr with a displacement corresponding to \( \omega \)-phase. Charge is transferred from atoms in plane 1 to atoms in planes 2 and 3.
in character; the Δρ curves for Nb and Zr (Figure 19) indicate a transfer of d-like density from atoms in plane 1 to d-like density on the equivalent atoms in planes 2 and 3, whereas the Δρ curves for Mo show that there is a transfer of sp-like charge about atoms in planes 2 and 3. For Nb, the charge transfer character remains the same for large displacements, while for Zr there develops a transfer of d-like charge from plane 1 to sp-like charge in planes 2 and 3 (Figure 20) accompanied by a decrease in the kinetic energy; just the direct opposite to the charge transfer character for Mo. In the ω-phase of Zr, 0.14 e/atom in plane 1 are transferred to planes 2 and 3, an amount which should be detected by high resolution measurements of core level shifts.

The systematic development of the dip in the longitudinal phonon branch about the (2/3,2/3,2/3) position as the number of valence electrons decreases (Mo-Nb-Zr) suggests that this anomaly is not associated with a sharp feature of a particular Fermi surface. From a geometrical consideration of the bcc lattice, one would expect a relative decrease of the phonon frequencies of the L(111) branch in the vicinity of the (2/3,2/3,2/3) position of the phonon dispersion curves for monatomic bcc crystals, since for this vibrational mode the nearest neighbor distance between atoms in the (111) direction are preserved as the lattice is distorted (illustrated in Figure 21). Thus, the corresponding restoring force vanishes and the atomic displacements for this mode can be viewed as a shearing motion between chains of atoms along the (111) direction. In view of the above
Figure 21. Atomic displacements pattern corresponds to the $L(2/3,2/3,2/3)$ phonon in the cubic (110) plane of bcc lattice. Full circles, triangles, and open circles represent atoms in planes 1, 2, and 3, respectively. The dotted lines outline the diagonal plane of the bcc crystal, and the arrows indicate the directions of atomic displacements associated with the distortion caused by the $L(2/3,2/3,2/3)$ phonon.
discussion, the absence of the dip in Mo (also in isoelectronic Cr and W) must be due to some special aspects of the electronic structure. The increase in the frequency of the 1(2/3,2/3,2/3) phonon as one goes from Zr to Mo is accompanied by an increase in the bonding d-like charge density directed along the nearest neighbor (111) direction (see Figure 13). To assess the effect of the d-bonds, we have employed the Hellmann-Feynman theorem (31) to investigate the contribution to the electronic force from different electronic states. The analysis shows that the absence of the dip in Mo is due to the directional bonding behavior of the d-electrons which is responsible for stiffening the shearing force. Details will be presented in Chapter 7.

Contour plots of the valence charge density in the cubic (110) plane corresponding to the geometry in Figure 21 for different atomic displacements are shown in Figures 22, 23, and 24. In these figures, arrows indicate the directions of atomic displacements, and the charge density unit is \( e/\Omega \), where \( \Omega \) is the unit cell volume. Since the inter-atomic distances in the (111) direction (intrachain direction) remain unchanged when the lattice is distorted with this phonon mode, we will mainly concentrate on the charge density distribution between atoms of neighboring chains. With small displacements (Figure 22), the charge for Mo is mainly concentrated in a bonding d-like lobe between the neighboring atoms and gives a clear density maxima along these directions. For large displacements (Figure 23), two main features are discernible: first, the d-lobes in Mo (unlike Zr) do not show appreciable change in the
Figure 22. Contour plots of the valence charge density for (a) Mo, (b) Zr, in the cubic (110) plane, where atoms in planes 2 and 3 have been displaced by an amount $\delta = 0.05$ ($\delta = 0.5$ for a full displacement to $\omega$-phase). The black dots denote the atomic positions and arrows denote the directions of atomic displacements.
Figure 23. Similar to Figure 22 showing the contour plots of valence charge density for (a) Mo, (b) Zr, in the cubic (110) plane, where atoms in planes 2 and 3 have been displaced by an amount $\delta = 0.25$. 
Figure 24. Similar to Figure 22 showing the contour plots of valence charge density for (a) Mo, (b) Zr, in the cubic (110) plane, with a displacement corresponding to ω-phase.
orientation, which indicates the directional behavior of the d-bonds in Mo gives rise to forces which oppose the shearing motion between neighboring chains; second, d-bonds have developed in Mo between nearest neighbor atoms (between atoms in planes 2 and 3), whereas for Zr, the charge tends to spread into the low atomic density region as the atoms are brought closer. The second feature becomes more prominent for the \( \omega \)-phase configuration (Figure 24). For Mo, a plot of the charge density in the plane where planes 2 and 3 coincide together shows triangular-bonding behavior (Figure 25), whereas for Zr (Figure 26), the charge is more spread out and suggests that the d-like to sp-like charge transfer is a mechanism for stabilization of the \( \omega \)-phase.

**H-point phonon in Mo**

The sharp dip at the H-point in the phonon dispersion curve of Mo has been associated with features of the Fermi surface (52). An analysis of the distorted Mo band structure for displacements corresponding to this phonon confirms a large band splitting occurs at the Fermi level between bands with large and oppositely directed Fermi velocities. As shown in Figure 27, the solid lines represent the band dispersion for the bcc crystal along the \( k_z \) direction with \((k_x, k_y) = (1/8, 1/24)2\pi/a\), and the dotted lines are the corresponding distorted band structure with a displacement 1.5% of the lattice constant. With a displacement of this magnitude, the total energy changes by \( \approx 0.01 \) eV/atom while the band splitting is larger than 0.5 eV. Furthermore, for this wavevector
Figure 25. Contour plot of the valence charge density for Mo in the plane where two of the bcc (111) planes, planes 2 and 3, coincide for the $\omega$-phase.
Figure 26. Similar to Figure 25 showing the valence charge density for Zr in the plane where two of the bcc (111) planes, planes 2 and 3, coincide for the ω-phase.
Figure 27. Band structures along the $k_z$ direction, with $(k_x,k_y) = (1/8,1/24)2\pi/a$, for the bcc lattice (solid lines) and the phonon distorted lattice (dotted lines) associated with the distortion caused by the Mo H-point phonon.
the splitting occurs over a large volume of the Brillouin zone and significantly lowers the total energy of the crystal, thus accounting for the dip in the phonon dispersion curve. The large volume of the Brillouin zone affected and the size of the splitting for modest displacements allows convergence of total energy calculations with a reasonable number of k-points (75 points in IBZ) using the Gaussian smearing scheme. The convergence was, of course, tested for much larger sampling sets.

The validity of the adiabatic approximation as applied to this phonon mode is discussed in the next chapter. Specifically, we examine the non-adiabatic correction by including the time dependence of the ionic motions, and the correction to the phonon frequency due to the presence of the other virtual phonon modes which renormalize the electronic states near the Fermi level.
CHAPTER 6. RENORMALIZATION OF THE H-POINT PHONON ANOMALY IN MOLYBDENUM

Frozen phonon calculations provide an accurate first principles approach for the study of lattice dynamics. We have applied the method to transition metals using a self-consistent pseudopotential approach within the local-density formalism to evaluate the total electronic energy. We obtained excellent agreement with experiment for the equilibrium structural properties (e.g., the lattice constant and bulk modulus) of Nb and Mo and were able to show that at low temperatures the bcc phase of Zr is unstable with respect to \(\omega\)-phase transformation. For phonon frequencies, we made extensive tests of precision and convergence and found that, except for the H-point phonon in Mo, the agreement with experiment was always within the experimental and theoretical error limits (~2%). The 9% discrepancy for the Mo H-point phonon amounts to a 0.5 THz difference in frequency. This is larger than we would expect from the numerical precision of the calculations and the quoted experimental uncertainty. To investigate possible causes for the discrepancy, we have studied the approximations which are assumed in the frozen phonon method and examined the conditions under which there might be problems with these approximations. In particular, we have estimated the frequency shifts caused by non-adiabatic effects which we find to be negligible and many-body renormalization effects which we find to be significant.
The main difference between the Mo H-point phonon and the other phonons we have investigated is that this phonon is associated with a Kohn anomaly arising from the well known nesting feature of the energy bands near the Fermi level (53,55,66,71). In isoelectronic Cr, this same nesting feature gives rise to a spin density wave with a wavevector near H. In Mo, this causes a sharp dip in the phonon dispersion curves at the H-point (55,71). Measurements of the phonon dispersion curves as a function of temperature (66) show that this dip diminishes rapidly with increasing temperature indicating the importance of contributions of states near the Fermi level to the phonon frequency at the H-point. An analysis of the distorted band structure corresponding to the H-point phonon confirms that the anomaly is caused by large band splittings occurring at the Fermi level. The frozen phonon method relies on the adiabatic approximation which neglects the time dependence of the ionic motions. Since the adiabatic approximation is suspect when Fermi surface nesting features occur in the electronic band structure (76,77), we investigated the possible breakdown of this approximation. Another correction we have studied is the renormalization of electronic states near the Fermi level by excitation of virtual phonon modes (shown schematically in Figure 28(c)). Before giving our numerical results, we will briefly discuss each of these corrections.

According to standard lattice dynamical theory (78), the electronic contribution to the phonon frequency due to the electron-phonon (e-p)
Figure 28. Diagrams describing phonon self-energy in the presence of electron-phonon interaction:

(a) Dyson equation for the phonon propagator in the electron-phonon system. The heavy and light wavy line represent the bare and normalized phonon propagator, respectively, $g^0$ is the bare e-p interaction, and $\Pi$ is the proper phonon self-energy.

(b) Equations (6.1) and (6.2) in diagrammatic form. The heavy line is the dressed electron propagator. $V_C$ and $v_C$ represent the screened and bare Coulomb interaction, respectively, and $g^S$ is the screened vertex.

(c) Electron propagator with phonon renormalization.
interaction is given to lowest order by the real part of the diagram shown in Figure 28(b). In the Random-Phase-Approximation, this contribution can be represented in abbreviated notation by

$$\omega^{\text{el-ph}} = g^0 \frac{\chi^0}{\epsilon} g^0, \quad (6.1)$$

where $\chi^0$ is the electronic susceptibility, $g^0$ is the scattering matrix element between electronic states due to the e-p interaction, and

$$\epsilon = 1 - v_c \chi^0$$

is the dielectric matrix of the electron system which includes screening due to the electrons. Following References 53 and 78, Equation (6.1) can be regrouped into two terms which can be written as

$$\omega^{\text{el-ph}} = \left(\frac{g^0}{\epsilon}\right)^\dagger \chi^0 \left(\frac{g^0}{\epsilon}\right) - \left(\frac{g^0}{\epsilon}\right)^\dagger \left(\chi \frac{g^0}{\epsilon}\right) v_c \left(\chi \frac{g^0}{\epsilon}\right), \quad (6.2)$$

where $v_c$ is the Coulomb interaction between electrons including the exchange-correlation energy and $\chi = \chi^0/\epsilon$. The second term may be interpreted as a contribution from charge distortions caused by the phonon whereas the first term represents a band structure contribution (78). Since we are interested in the effects of band splitting near the Fermi level, in the following we will concentrate on the first term.

For most cases, the effects of renormalization on phonon frequencies are negligible and it is a good approximation to replace the dressed electron propagator in Figure 28(b) by the bare propagator.
However, when the electronic response contains a large contribution from electrons whose energies are in the range of the Debye energy \( \omega_D \) of the Fermi level, the dressing effects due to the phonon cloud becomes important (79). Taking into account this "renormalization" effect on the electrons (Figure 28(c)), the contribution to the phonon frequency from the band splitting effect (Kohn anomaly) is reduced by a factor of \( 1/(1+\lambda) \), where \( \lambda \) is the e-p coupling constant (see Appendix B for details, 80,81). This is the same factor that goes into the renormalization of the electron mass, expressions for the superconducting transition temperature, the enhancement of the electronic specific heat, and other electronic properties involving states at the Fermi surface.

In the frozen phonon calculations, only one phonon mode is present and the renormalization effect due to the virtual phonons which give rise to the \( 1/(1+\lambda) \) factor is missing. Thus, the frozen phonon calculations overestimate the effect of the Fermi surface band splitting and should have a correction given by

\[
\Delta \omega(\text{ren.}) \approx -\frac{\lambda}{1+\lambda} \sum_k \frac{|g^S(k+\tilde{q})|^2 (E^0_k - E^0_{k+\tilde{q}})}{E^0_k - E^0_{k+\tilde{q}}},
\]

(6.3)

where the summation is limited to the volume in the Brillouin zone and both \( E^0_k \) and \( E^0_{k+\tilde{q}} \) are within several Debye energies of the Fermi
level. In Equation (6.3), $E^0$ is the "bare" electron energy, $f^0$ is the Fermi-Dirac distribution function, and $g^s$ is the screened e-p matrix element.

The correction due to the time dependence of the ionic motions has previously been investigated in detail and is given by (76,77)

$$A(\text{adi.}) = \frac{1}{\hbar} \sum_k |g^s(k,\mathbf{q})|^2 \left( f^0_k - f^0_{k+\mathbf{q}} \right)$$

where $\omega_q$ is the phonon frequency.

Since both corrections involve electron states in a very narrow energy region about the Fermi energy, we can simplify the evaluation of Equations (6.3) and (6.4) by parameterizing our first principles band structure by the velocities and deviations from perfect nesting of the bands at the Fermi level. We can also obtain the fully screened electron-phonon matrix elements ($g^0/e$) for the bands of interest from the band splittings in our frozen phonon calculations. Using these procedures, we estimated the contribution from states near the Fermi level and the corrections that must be applied to the frozen phonon results for the Mo H-point phonon (see Appendix C for details). We find that the $\Delta\omega$ (adi.) correction is very small (amounting to less than 2% of the Fermi-surface contribution to the Kohn anomaly) even
though the nesting occurs in a relatively large portion of the Brillouin zone. However, the correction $\Delta \omega(\text{ren.})$ is not negligible. If we include only contributions from bands within five $\omega_D$ of the Fermi level, we obtain a depression of the H phonon frequency by 0.8 THz. According to our theory above, this contribution is overestimated in the frozen phonon calculation, and inclusion of phonon renormalization effects will cause a reduction in the size of the dip by a factor of $1/(1+x)$ (for Mo, $\lambda = 0.47$ (82)). Taking this correction into account, we find that the frequency of the H phonon as obtained from the frozen phonon calculations should be increased by $0.25 \pm 0.1$ THz. The renormalization correction is in the right direction to account for the discrepancy between our original theoretical result of $5.0 \pm 0.1$ THz and the experimental result of $5.5 \pm 0.1$ THz (55,66,71). Our method of estimating the renormalization effect is, of course, approximate and only indicates the magnitude and direction of the effect. The actual pieces of the Fermi surface responsible for the Kohn anomaly may have a $\lambda$ value which differs from the average, and more precise calculations would treat the electron-phonon matrix elements explicitly rather than assuming a constant value.

Since phonon renormalization affects only energy bands in a very narrow energy range near the Fermi level, its effect on the phonon

---

1The choice of cutoff energy is not very critical, since the main contribution ($\sim 50\%$) to the summation of Equation (4) comes from energies within $\omega_D$ of the Fermi level.
frequency can be neglected except in the case of a phonon anomaly where there is an appreciable contribution from electronic states right at the Fermi level. For this case, renormalization is a significant effect which is not included in frozen phonon calculations.
CHAPTER 7. MICROSCOPIC ANALYSIS OF INTERATOMIC FORCES OF THE LONGITUDINAL $\mathbf{q} = (2/3,2/3,2/3)$ PHONON IN Zr, Nb, AND Mo

Introduction

Recent progress in band structure techniques have permitted evaluation of the total energies of simple crystalline solids to such a precision that not only can static structural properties be calculated accurately but energy differences between distorted and ideal structures can be determined to an accuracy of 0.01 mRy or better. These advances have opened an entirely new approach on the study of phonons in solids. From the frozen phonon calculations, not only can the phonon frequency be obtained but also the electronic wave functions and charge density which allow detailed analysis of the microscopic response of the crystal to the lattice distortion in the presence of a phonon. Valuable insights into the physical origins causing anomalous behavior of the phonon spectra in these materials can thus be obtained. Previous investigations (15,17) have concentrated on the analysis of the energy differences between the bulk and the phonon-distorted lattice; however, it is difficult to obtain a clear physical picture from such an analysis because of the presence of large cancelling terms in the total energy and the difficulty of separating out contributions from various electronic states caused by the non-linear dependence of the total energy on the electronic charge density. We find that by employing
the Hellmann-Feynman theorem (31) we can obtain the forces on individual atoms in the distorted crystal in the form that allows easy physical interpretation of the results. In this chapter, we will describe the application of such an analysis to study the longitudinal $\mathbf{q} = (2/3,2/3,2/3)$ phonon mode in Mo, Nb, and bcc Zr.

The phonon spectra of simple bcc alkali metals all show a dip in the longitudinal (111) branch near the $(2/3,2/3,2/3)$ position. Perturbative pseudopotential calculations (83,84) have shown that this behavior is caused by a minimum in the ionic restoring force for the bcc lattice as a function of phonon wavevector. However, in transition metals, the presence of the d-electrons gives rise to screening effects which are radically different than the electron-gas type of screening in the alkali metals, and a different physical picture might be expected. Indeed, experimental investigations of the phonon dispersion curves of transition metals show that the phonons in these metals have a more complicated behavior. As shown in Figure 16, it can be seen that the behavior of the L($2/3,2/3,2/3$) mode is very different for the different metals. While the dispersion curve for Nb (56) shows a dip near the two-thirds position very much like the alkali metals, Mo (55) shows no dip near this position. If one goes to bcc Zr (57), the curve dips sharply at the two-thirds position indicating the instability of the lattice towards the formation of the $\omega$-phase. To understand the physical reasons behind this behavior, we have performed frozen phonon
calculations for the L(2/3,2/3,2/3) phonon in Mo, Nb, and bcc Zr, as described in Chapter 5. Our calculations yielded phonon frequencies for Mo and Nb to within 2% of the experimental values and, of more interest, our calculations for bcc Zr showed that the restoring force for the phonon distortion is very weak and highly anharmonic, and that if the distortion is big enough, the crystal will transform to the \( \omega \)-phase structure which we found to be energetically more stable than the bcc structure at low temperature.

In this chapter, we will present an analysis of our results making use of the calculated Hellmann-Feynman forces. It is found that the localized and directional character of the occupied d-states is responsible for the differences in behavior of the L(2/3,2/3,2/3) phonon in these metals. We will first present a simple derivation of the Hellmann-Feynman force expression. The results of the force analysis will then be employed to identify the physical origin of the differences in behavior of the L(2/3,2/3,2/3) mode found in the bcc transition metals, and to discuss the driving mechanism causing bcc-\( \omega \) transition.

**Hellmann-Feynman Force Analysis**

The Hellmann-Feynman theorem (31) provides a powerful method for calculating the forces on the individual atoms without having to calculate total energies for various neighboring geometries. First proved for the case of the exact all-electron problem (31), it has been
extended to the case where the $X_\alpha$ approximation is used (85) and recently derived for pseudopotential calculations where the ionic potentials are non-local in character (28). However, the proof in Reference 28 is quite intricate and we would like to present here a simpler version.

We start with the expression for the total energy per primitive unit cell, Equation (4.2), which we have used in our calculation:

$$E_T = \sum_{\mathbf{n}k} f_{\mathbf{n}k} \varepsilon_{\mathbf{n}k} \Omega_{\text{cell}} \left[ \sum_{\mathbf{G}} \rho(\mathbf{G}) V_{\text{sc}}^{\text{in}}(\mathbf{G}) + \frac{1}{2} \sum_{|\mathbf{G}| \geq 0} \frac{8\pi \rho(\mathbf{G})}{|\mathbf{G}|^2} \right]$$

$$+ \sum_{\mathbf{G}} \rho(\mathbf{G}) e_{\text{xc}}(\mathbf{G}) + a_1 Z_v + \gamma_{\text{Ewald}}$$

(7.1)

where the meaning of notations in Equation (7.1) are the same as those encountered in Chapters 3 and 4.

Suppose the position of one of the atoms in the unit cell is changed by a displacement $\delta \mathbf{r}$. This will cause a change in the total energy given by

$$\delta E_T = \sum_{\mathbf{n}k} \left( \delta f_{\mathbf{n}k} \varepsilon_{\mathbf{n}k} + \delta f_{\mathbf{n}k} \varepsilon_{\mathbf{n}k} \right) - \Omega_{\text{cell}} \left[ \sum_{\mathbf{G}} \rho(\mathbf{G}) \delta V_{\text{sc}}^{\text{in}}(\mathbf{G}) \right]$$

$$+ \sum_{\mathbf{G}} \rho(\mathbf{G}) (-V_{\text{sc}}^{\text{in}}(\mathbf{G}) + \frac{8\pi \rho(\mathbf{G})}{|\mathbf{G}|^2} + V_{\text{xc}}(\mathbf{G})) + \delta \gamma_{\text{Ewald}}$$

(7.2)
The self-consistency criteria guarantees that

\[ V_{\text{sc}}^{\text{in}}(\mathcal{E}) = \frac{8\pi p(\mathcal{E})}{|\mathcal{E}|^2} + V_{\text{xc}}(\mathcal{E}), \]  

(7.3)

so the term involving the change in charge density drops out in Equation (7.2). To evaluate the change in band energies, we can use perturbation theory, then

\[ \sum_{nk} f_{nk}^+ \delta c_{nk} = \sum_{nk} f_{nk}^+ \psi_{nk}^\dagger \delta V_{\text{ion}} + \delta V_{\text{sc}}^{\text{in}} \psi_{nk} \]

\[ = \sum_{nk} f_{nk}^+ \psi_{nk}^\dagger \delta V_{\text{ion}} \psi_{nk} + \Omega_{\text{cell}} \sum_{\mathcal{E}} \rho(\mathcal{E}) \delta V_{\text{sc}}^{\text{in}}(\mathcal{E}), \]  

(7.4)

where \( \delta V_{\text{ion}} \) is the change in ionic potential.\(^1\) Combining Equations (7.2) and (7.4), we can decompose the total force on the atom into two terms. The first, we refer to as \( \mathbf{F}_{\text{ion}} \), is the ionic restoring force which can be evaluated very easily (40). The second, \( \mathbf{F}_{\text{el}} \), is the electronic force which is made up of contributions from all the occupied states. These can be expressed as

\[ V_{\text{ion}}(\mathbf{r}) = \sum_{\mathbf{R},\pi,\ell} V_{\text{ps},\pi,\ell} (\mathbf{\hat{r}} - \mathbf{\hat{R}} - \mathbf{\hat{r}}) \hat{p}_\ell, \]  

\(^1\) \( \mathbf{V}_{\text{ion}}(\mathbf{r}) \) is the superposition of atomic pseudopotentials.
where
\[
\dot{F}_{\text{ion}} = - \frac{\delta \gamma_{\text{Ewald}}}{\delta t}, \tag{7.5a}
\]

and
\[
\dot{F}_{\text{el}} = - \sum_{nk} (\hat{f}_{nk} < \psi_{nk} | \frac{\delta V_{\text{ion}}}{\delta t} | \psi_{nk} > + \frac{\delta f_{nk}}{\delta t} \epsilon_{nk}). \tag{7.5b}
\]

\(\delta \epsilon^0\) is the change in eigenvalue produced by the change in \(V_{\text{ion}}\) only.

Using Equation (7.5b), we can investigate how each of the states contribute to the response of the system under distortion. For the \(L(2/3, 2/3, 2/3)\) phonon in the metals we have studied, we found that the term due to the change in occupation of the states has a negligible effect, so we will concentrate on the first term of Equation (7.5b).

Within the mixed basis formalism (27), we can evaluate \(\delta \epsilon^0\) by treating the Schrodinger equation as a matrix eigenvalue equation:
\[
H\psi = \epsilon S\psi, \tag{7.6}
\]

then
\[
\delta \epsilon^0 = \psi^+(\delta H - \epsilon \delta S)\psi. \tag{7.6a}
\]
The $\delta S$ term indicates the change in the overlap matrix. The cause of the $\delta S$ term is that in the basis set, the local orbitals are centered on the atoms and thus would move with the atom. The use of such a basis set solves the problem of representing the rapid changes produced by the rigid motion of localized electrons that one encounters when a basis set that does not move with the atom in use. The $\delta H$ term indicates the change in the Hamiltonian matrix elements caused by moving the ionic potential with the atom while keeping the screening potential unchanged.

Results and Discussion

Using Equation (7.5b) and the electronic wave functions from frozen phonon calculations with small atomic displacements, we have calculated the total restoring force on the displaced atoms for Mo, Nb, and bcc Zr (see Table 7). From the results, we can calculate the phonon frequencies. We note that in order to get an accurate answer, it is essential to take the average of the forces for positive and negative displacements because the anharmonicity has a larger effect on the force than on the energy. This effect has already been noted in earlier force calculations on Si (15). The frequencies obtained from the force calculations are very close to those obtained from the total energy curves indicating the good convergence of our results. We have analyzed the contributions to the electronic force as a function of band

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2 The positive displacements are defined in the direction to form the $\omega$-phase.
Table 7. The total force and the separate ionic and electronic contributions for small atomic displacements associated with the \(L(2/3,2/3,2/3)\) phonon in Mo, Nb, and bcc Zr

<table>
<thead>
<tr>
<th>Displacement ((\delta))^a</th>
<th>Force (Ry/a_0)</th>
<th>Phonon frequency (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(F_{\text{ion}})</td>
<td>(F_{\text{el}})</td>
</tr>
<tr>
<td>(-0.05)</td>
<td>0.04768</td>
<td>-0.02171</td>
</tr>
<tr>
<td>Mo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>-0.03989</td>
<td>0.01219</td>
</tr>
<tr>
<td>Average</td>
<td>0.04379</td>
<td>-0.01675</td>
</tr>
<tr>
<td>(-0.05)</td>
<td>0.03061</td>
<td>-0.02225</td>
</tr>
<tr>
<td>Nb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>-0.02561</td>
<td>0.01624</td>
</tr>
<tr>
<td>Average</td>
<td>0.02811</td>
<td>-0.01925</td>
</tr>
<tr>
<td>(-0.05)</td>
<td>0.01744</td>
<td>-0.01463</td>
</tr>
<tr>
<td>Zr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>-0.01459</td>
<td>0.01208</td>
</tr>
<tr>
<td>Average</td>
<td>0.01602</td>
<td>-0.01336</td>
</tr>
</tbody>
</table>

^a\(\delta = 0.5\) for a full displacement to \(\omega\)-phase.
energy and as a function of different regions in the Brillouin zone for each of the metals.

Investigation of electronic force contribution as a function of band energy

In analogy to the density of states in ordinary band structure, we can define a force-weighted density of states (FDOS) defined by

\[ F_{\text{el}}(E) = \sum_{\mathbf{n}k} F_{\text{el},\mathbf{n}k} \delta(E - \varepsilon_{\mathbf{n}k}) \]  

(7.7)

\( F_{\text{el},\mathbf{n}k} \) is the magnitude of the electronic force along the (111) direction from electronic state \(|\mathbf{n}k\rangle\). The magnitude of the total electronic contribution to the force is then given by

\[ F_{\text{el}} = \int f(E) F_{\text{el}}(E) dE \]  

(7.8)

where \( f(E) \) is the Fermi-Dirac distribution factor.

In Figure 29, we show plots of the FDOS for Zr, Nb, and Mo. These plots show how the contribution to the electronic force varies as a function of band energy when the crystal is distorted by the \( L(2/3,2/3,2/3) \) mode with small atomic displacement in the positive direction. The FDOS being positive means the force contribution is in the same direction as the atomic displacement, while a negative FDOS means the force contribution is directed opposite to the atomic displacement. We see that the curves for the three metals are very similar except for the
Figure 29. The force-weighted density of states (FDOS) associated with the $L(2/3, 2/3, 2/3)$ phonon for small atomic displacement in the positive direction as a function of band energy for Zr, Nb, and Mo. The dotted lines indicate the positions of the corresponding Fermi level.
position of the Fermi levels. When an atom is displaced in the positive direction, the ionic restoring force will be in the negative direction. In a simple metal, the ionic force is reduced by the electron screening, thus one would expect the electronic force to be in the positive direction. From the plots, it can be seen that while the occupied states in Zr and Nb produce the expected screening effect, the extra states that are occupied in going from Nb to Mo behave anomalously. Instead of opposing the ionic force, these states give a negative contribution which enhances the ionic force. This anti-screening behavior increases the phonon frequency and is responsible for the rapid increase in the L(2/3,2/3,2/3) phonon frequency from Nb to Mo.

To understand the physical reason for this anomalous behavior, we investigated the charge density for states in this energy region. To highlight the states responsible for the anti-screening behavior, we have weighted the charge density of each state in the anti-screening region by its contribution to the total electronic force given by

\[ \hat{\rho}(\mathbf{r}) = \sum_{\mathbf{n}\mathbf{k}} |\psi_{\mathbf{n}\mathbf{k}}(\mathbf{r})|^2 F_{\mathbf{e}_\mathbf{l},\mathbf{n}\mathbf{k}} \]  

(7.9)

\[ ^3\text{The contributions to the electronic force from each state in the anti-screening region are of the same sign, thus, } F_{\mathbf{e}_\mathbf{l},\mathbf{n}\mathbf{k}} \text{ in Equation (7.9) has been treated as a scalar factor.} \]
A plot of this force-weighted charge density in the (110) plane for the states in the anti-screening region is given in Figure 30. The positions of the atoms are indicated by the filled circles, the dotted lines outline the diagonal plane of the bcc lattice, and the arrows indicate the directions of displacements of the atoms. This plot shows very clearly that the states responsible are those which form d-bonds directed towards nearest neighbors. These directional d-bonds give rise to forces which oppose the shearing motion between neighboring chains, in analogy to the bond-bending forces in covalent bonded materials. This directional bonding behavior of the d-states is also manifested in the rapid rise in the shear elastic constants as one goes from Nb to Mo (48).

Analysis of Zr

Figure 31 shows the total force and also the separate ionic and electronic contributions as a function of atomic displacement for bcc Zr. It can be seen that for positive displacement the total force is restoring (negative) for small displacements but changes sign at larger displacements. The position of the zero force coincides with the hump on the total energy curve (Figure 18). The ionic force is screened by a large electronic force which overcomes the ionic restoring force at larger displacements. This behavior drives the bcc lattice into the ω-phase structure. In order to understand the reasons for the sharp dip in the phonon spectra in bcc Zr, we have divided the irreducible Brillouin zone into four regions (see the insert in
Figure 30. Contour plot of the force-weighted charge density of states in the anti-screening region for Mo in the cubic (110) plane of bcc lattice.
Figure 31. The total force (solid line), electronic force (broken line), and ionic restoring force (broken and dotted line) as a function of atomic displacement associated with the L(2/3, 2/3, 2/3) phonon of bcc Zr.
Figure 32). When the lattice is distorted with the L(2/3,2/3,2/3) phonon, the Brillouin zone is folded from the bcc rhombohedron into the hexagonal prism (Figure 33). The irreducible part of the frozen phonon Brillouin zone is divided into four regions of roughly equal volume by the planes shown in the insert of Figure 32.

If we concentrate on the small displacement portion of the curves in Figure 31, we can see that the main part of the electronic screening forces comes from the occupied states in regions 1 and 2. We have analyzed the charge distribution of the electronic states which lies in these two regions. Figure 34(a) is a contour plot of the total occupied valence charge density in the (110) plane for states in the regions 1 and 2. The charge density is concentrated in d-bonds which run in chains along the (111) direction with very little interaction between neighboring chains. As shown in Figure 21, the atomic displacements in the presence of this phonon can be viewed as just a shearing motion between neighboring chains. If we examine the response of the charge density in regions 1 and 2 to these atomic motions, we find that the electronic charge just shifts rigidly with the chains (see Figure 34(b) for a plot of the charge density of regions 1 and 2 at large displacement). Since the charge is highly localized on the chain and shifts rigidly with it, this gives rise to a very effective screening mechanism which softens the L(2/3,2/3,2/3) phonon in bcc Zr.
Figure 32. The contribution to the electronic force for bcc Zr from different regions in the phonon Brillouin zone associated with the $L(2/3,2/3,2/3)$ phonon. The insert shows the division of the IBZ into four regions of roughly equal volume.
Figure 33. The bcc Brillouin zone (rhombohedron) and the phonon Brillouin zone (hexagonal prism) for the L(2/3,2/3,2/3) phonon
Figure 34. Contour plots of the valence charge density of occupied states in regions 1 and 2 in the cubic (110) plane of bcc lattice for Zr for (a) small atomic displacement $\delta = 0.05$ ($\delta = 0.5$ for a full displacement to $\omega$-phase), (b) large atomic displacement $\delta = 0.4$.
The bcc-ω transition in Zr

If we concentrate on the larger displacement portion of the curve in Figure 31, we can see that the force contribution from states in region 3 behaves rather anomalously. For small and negative displacements, these states give a negligible contribution to the total force. However, for atomic displacements between $\delta = 0.1$ and 0.3, ($\delta = 0$ for the bcc structure and $\delta = 0.5$ for the ω-phase structure), the force contribution increases sharply. This behavior causes an increase in the total electronic force (see Figure 30) which overbalances the ionic restoring force and makes the crystal unstable towards the formation of the ω-phase. In order to investigate the microscopic electronic cause of this behavior, we have examined the band structure of the distorted crystal in this region of the IBZ. Figures 35 and 36 show plots of the bands along the A-L-H-A directions for various atomic displacements. Of particular interest are the two bands labeled by arrows. These bands are predominantly d-like in character and nearly degenerate in the bcc structure. As the atomic displacements increase, they are separated by the changing crystal field (the arrows indicate the directions of motion of the bands with increasing atomic displacements), each giving a large but opposite contribution to the Hellmann-Feynman force. For small displacement, both bands are occupied and the total contribution to the electronic force is small. But for larger displacements, the upper band starts to be depopulated and the
Figure 35. Calculated band structure of Zr along the A-L-H-A direction of the phonon Brillouin zone for the L(2/3,2/3,2/3) phonon for (a) bulk bcc, (b) small atomic displacement $\delta = 0.05$. The arrows indicate the directions of motion of the energy bands as the atomic displacement increases.
Figure 36. Similar to Figure 35 showing the calculated band structures of Zr for larger atomic displacements: (a) $\delta = 0.20$; (b) $\delta = 0.40$
cancellation effect between the two bands decreases. This is the reason for the sharp rise in the force contribution from region 3. In fact, at displacements larger than \( \delta = 0.4 \), a gap opens up at the Fermi level over the entire A-H-L plane which accounts for the stability of the \( \omega \)-phase over the bcc phase.

**Summary**

First principle techniques have been developed which not only enable us to calculate accurately the phonon frequencies and interatomic forces in transition metals, but also permit detailed investigations leading to an understanding of the microscopic electronic causes of phonon behavior. Application of these techniques to the L(2/3,2/3,2/3) phonon in Mo, Nb, and bcc Zr revealed that the characters of the occupied d-states have a great influence on the behavior of the phonons in these metals. Directional bonding of the d-electrons is found to be responsible for the sharp increase in the frequency of the L(2/3,2/3,2/3) mode as one goes from Nb to Mo. The instability of the bcc phase towards the formation of \( \omega \)-phase is found to be caused by the opening up of a gap in the energy bands at the zone boundary A-H-L plane.
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APPENDIX A. FITTING PROCEDURES FOR
THE NORM-CONSERVING PSEUDOPOTENTIAL

In this appendix, we will outline the steps in our generation of the pseudopotentials for Mo, Nb, and Zr. The procedures used here are the same as those in Reference 26.

**Step 1**

Carry out the self-consistent all-electron calculation in local-density-functional approximation (1) via a Herman-Skillman like program (38), and retain both the wave functions\(^1 \psi_\lambda(r)\) and potential \(V(r)\). The Hedin-Lundqvist form has been used for the exchange-correlation potential (39).

**Step 2**

For each valence state, we then obtain the potential in the form

\[
V_{1,\lambda}(r) = (a_1 + a_2 r^2) e^{-a_3 r}, \quad \text{for } r < r_c
\]

(A.1)

where \(r_c\) is the core radius.\(^2\) We can adjust variables \(a_1, a_2,\) and \(a_3\) so that \(V_{1,\lambda}(r)\) joins smoothly onto \(V(r)\) for \(r > r_c\). The nodeless wave function \(W_{1,\lambda}(r)\) of the Schrodinger equation using \(V_{1,\lambda}(r)\) has eigen-

\(^1\)These are defined as \(r\) times the radial wave functions.

\(^2\)\(r_c\) is angular momentum dependent, which is chosen about 0.5 ~ 0.8 times the position of the outermost peak of \(U_\lambda(r)\).
value $E_\ell$ equal to the corresponding eigenvalue from all-electron calculation.

**Step 3**

Since for $r > r_C$ both the all-electron wave function $U_\ell^A(r)$ and the pseudowavefunction $W_{1,\ell}^P(r)$ satisfy the same radial Schrödinger equation, they are related by the following relation:

$$W_{1,\ell}^P(r) = \gamma_\ell U_\ell^A(r) \quad , \text{for } r > r_C \quad ,$$  \hspace{1cm} (A.2)

where $\gamma_\ell$ is a multiplicative constant. In order to satisfy the norm-conserving constraint, we have to modify $W_{1,\ell}^P(r)$ in such a way that the new pseudowavefunction $W_{2,\ell}^P(r)$, after normalization, is identical to the all-electron wave function $U_\ell^A(r)$ outside the core radius. We can form $W_{2,\ell}^P(r)$ as

$$W_{2,\ell}^P(r) = \gamma_\ell [W_{1,\ell}^P(r) + \delta_\ell g_\ell(r/r_C)] \quad .$$  \hspace{1cm} (A.3)

The function $g_\ell(X)$ in Equation (A.3) has to satisfy the following asymptotic forms:

$$g_\ell(X) \rightarrow 0 \quad , \text{for } X \geq 1 \quad ,$$

and

$$g_\ell(X) \rightarrow X^{1+\ell} \quad , \text{for } X \rightarrow 0 \quad ,$$
thus, the proper choice of \( g_\chi(x) \) is given by

\[
g_\chi(x) = x^{1+\frac{\rho}{4}} e^{-x^c} \quad . \tag{A.4}
\]

The coefficient \( c \) in Equation (A.4) is varied in the fitting to assure the new pseudowavefunction \( W_{2,\chi}(r) \) is a smooth function.\(^3\) The \( \delta_\chi \) in Equation (A.3) is determined from the normalization requirement of the wave function:

\[
\int_0^\infty dr \ |W_{2,\chi}(r)|^2 = 1 \quad . \tag{A.5}
\]

**Step 4**

From the radial part of the Schrodinger equation, the potential \( V_{2,\chi}(r) \) corresponding to the pseudowavefunction \( W_{2,\chi}(r) \) is related to the \( V_{1,\chi}(r) \) and \( W_{1,\chi}(r) \) through

\[
V_{2,\chi}(r) = V_{1,\chi}(r) + \left[ \frac{1}{W_{2,\chi}(r)} \frac{d^2}{dr^2} W_{2,\chi}(r) - \frac{1}{W_{1,\chi}(r)} \frac{d^2}{dr^2} W_{1,\chi}(r) \right]
\]

\[
= \frac{\delta_\chi g_\chi(r/r^c)}{W_{1,\chi}(r)} + \delta_\chi g_\chi(r/r^c) \left( E - V_{1,\chi}(r) - \frac{\rho(\rho+1)}{r^2} \right) + \frac{1}{g_\chi(r/r^c)} \frac{d^2 g_\chi(r/r^c)}{dr^2} + V_{1,\chi}(r) \quad . \tag{A.6}
\]

\(^3\)The typical values for \( c \) are 3.5 ~ 4.5.
Step 5

The atomic pseudopotential is obtained by unscreening the $V_{2,s}(r)$ and is given by

$$V_{ps,s}(r) = V_{2,s}(r) - (V_H(r) + v_{xc}(r))$$  \hspace{1cm} (A.7)

where $V_H(r)$ and $v_{xc}(r)$ are the Hartree and the exchange-correlation potential, respectively, which can be calculated from the pseudo-charge distribution.
APPENDIX B. ELECTRON-PHONON RENORMALIZATION

EFFECT ON THE PHONON FREQUENCY AND THE
PHONON LINE WIDTH

In this appendix, the effects on phonon frequencies caused by the renormalization of the electronic states near the Fermi level are derived with the methods of many body theory. Our results are an extension of the discussion found in standard references (80,81). The phonon self-energy obtained from Dyson's equation and shown diagrammatically in Figure 28(b) can be written in terms of temperature Greens functions as (here we only consider the band structure contribution)

\[
\pi_q^\pm = T \sum_{\epsilon} \sum_k |g^S(q,k)|^2 G(k-q,\epsilon-\omega_q^\pm) G(k,\epsilon),
\]

(B.1)

The real part of \(\pi_q^\pm\) represents the phonon frequency shift. Following Reference 80, it is given by

\[
\text{Re}\pi_q^\pm = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\epsilon \sum_k |g^S(q,k)|^2 \left[ \text{Im}G_R(k,\epsilon)\text{Re}G_R(k-q,\epsilon-\omega_q^\pm) \right. \\
+ \left. \text{Im}G_R(k-q,\epsilon)\text{Re}G_R(k,\epsilon+\omega_q^\pm) \right] \tanh \frac{\epsilon}{2T}.
\]

(B.2)

For electronic states with energies far from the Fermi level, the replacement of \(G_R\) by the bare propagator has a negligible effect. However, when \(E_k^0\) and \(E_{k-q}^0\) are within the range of \(\omega_D\) from the Fermi
level, there is a rapid variation of the electron self energy, $\Sigma$, and the electron Green's function can be expressed as

$$G_R(\varepsilon) = \frac{Z_k}{\varepsilon - \varepsilon_k + i \delta \text{sgn}(k-k_F)} , \quad \delta = 0^+ , \quad (B.3)$$

where

$$\varepsilon_k = Z_k \varepsilon_k^0$$

and

$$Z_k = (1 - \frac{\partial \varepsilon (\varepsilon)}{\partial \varepsilon} \mid_{\varepsilon_k} \right)^{-1} \equiv (1+\lambda)^{-1} . \quad (B.4)$$

Substituting Equation (B.3) into (B.2), we find that the Fermi surface (FS) contribution to $\Re \Pi_{q}^+ \omega_q$ is given by

$$\omega_q^\pm = \sum_k (FS) \frac{Z_k^2 |g^S(q,k)|^2 (f_k^0 - f_{k-q}^0)}{\varepsilon_k - \varepsilon_k^0 + \omega_q}$$

$$= \frac{1}{1+\lambda} \sum_k (FS) \frac{|g^S(q,k)|^2 (f_k^0 - f_{k-q}^0)}{E_k^0 - E_{k-q}^0 + \omega_q(1+\lambda)}$$

$$= \frac{1}{1+\lambda} \sum_k (FS) \frac{|g^S(q,k)|^2 (f_k^0 - f_{k-q}^0)}{E_k^0 - E_{k-q}^0} . \quad (B.4)$$
which is reduced by a factor \((1+\lambda)\) from the expression obtained without considering the renormalization. The last step is justified only when the correction for the time dependence of the ionic motion is small.

The summation in Equation (B.4) is over the region of Brillouin zone where \(E_k^0\) and \(E_k^0\) are of the order \(\omega_D\) from the Fermi level.

The \((1+\lambda)\) factor has a simple origin. In the frozen phonon calculation, the contribution to \(\omega_{k-q}^{e-p}\) is given symbolically as \(-\hat{N}(0)|g^S|^2\), where \(\hat{N}(0)\) is the portion of density of states at the Fermi level affected by band splittings. The inclusion of the virtual phonon processes renormalize the electronic states near the Fermi level. This effect will be reflected in the enhancement of the density of states and the reduction of the scattering matrix elements. Thus, in symbolic form

\[
\hat{N}(0)|g^S|^2 \xrightarrow{\text{phonon renormalization}} (1+\lambda)\hat{N}(0) \frac{1}{(1+\lambda)^2} |g^S|^2
\]

\[
= \frac{1}{1+\lambda} \hat{N}(0)|g^S|^2
\]

It is also interesting to see the renormalization effect on the phonon line width. The phonon line width due to the e-p interaction is expressed as (81)
\[ \delta_+ = \lim_{\xi \to 0} \frac{\omega_+ \text{Im}_q^+(\xi)}{q} \]  \hspace{1cm} \text{(B.5)}

In analogy to the \( \text{Re}_q^+ \) already discussed, the imaginary part is given by

\[ \text{Im}_q^+(\xi) = \frac{\pi}{1+\lambda} \sum_k |g^S(q,k)|^2 (E_k^0 - E_{k-q}^0) \delta(E_k^0 - E_{k-q}^0 - \xi(1+\lambda)) \]

for \( \xi < \omega_d \).  \hspace{1cm} \text{(B.6)}

Introduce a factor \( I = \int \text{d}\epsilon \delta(\epsilon - E_k^0) \int \text{d}\epsilon' \delta(\epsilon' - E_{k-q}^0) \) into the integrand of Equation (B.6), and define

\[ N(0)^2 I^2(\epsilon, \epsilon') \equiv \sum_k |g^S(q,k)|^2 \delta(\epsilon - E_k^0) \delta(\epsilon' - E_{k-q}^0) \]

then Equation (B.6) can be written as

\[ \text{Im}_q^+(\xi) = \frac{\pi}{1+\lambda} \int \text{d}\epsilon \text{d}\epsilon' N(0)^2 |I(\epsilon, \epsilon')|^2 (f^0(\epsilon) - f^0(\epsilon')) \delta(\epsilon - \epsilon' - \xi(1+\lambda)). \]

\[ \text{(B.7)} \]

For \( \xi \to 0 \), \( I^2(\epsilon, \epsilon') \) in Equation (B.8) varies slowly with \( \epsilon \) and \( \epsilon' \) (comparing with the other \( (\epsilon, \epsilon') \) dependent factors remaining in the \( \int \text{d}\epsilon \text{d}\epsilon' \) integrals). Therefore, we can replace \( I^2(\epsilon, \epsilon') \) by \( I^2(0,0) \equiv \langle I_q^2 \rangle \).

\[ \text{(B.8)} \]

\(^1\)Only the first diagram in the bottom line of Figure 28(b) has a contribution to the imaginary part.
Thus, Equation (B.8) becomes

\[
\lim_{\xi \to 0} \text{Im} \tau_+^q(\xi) = \frac{\pi}{1+\lambda} N(0)^2 <I_q^2> \int d\epsilon [f^0(\epsilon) - f^0(\epsilon + \xi(1+\lambda))] \\
= \frac{\pi}{1+\lambda} N(0)^2 <I_q^2> (1+\lambda)\xi \\
= \pi N(0)^2 <I_q^2> \xi
\]  

(B.9)

Substituting (B.9) into (B.5), the phonon line width is then given by

\[
\delta_q = \pi \omega_q N(0)^2 <I_q^2>
\]  

which is identical to the expression obtained without considering the renormalization effect. We are very grateful to Professor P. Allen for pointing out the steps in the derivation for the phonon line width.
APPENDIX C. EVALUATION OF THE
FERMI-SURFACE CONTRIBUTION TO THE PHONON
FREQUENCY FOR THE Mo H-POINT PHONON

In this appendix, we will give the details on the evaluation of
Equations (6.3) and (6.4). For the Mo H-point phonon, the phonon anomaly
is caused by the nesting bands (labeled as 1 and 2 in the following)
near the Fermi level. The Fermi surface contribution to the phonon
frequency without renormalization can be rewritten as

$$\omega_{\mathbf{q}}^{\pm} = \sum_{\mathbf{k}} |g^{\pm}(\mathbf{q}, \mathbf{k})|^2 \left[ \frac{f_{1,\mathbf{k}}^{0}(1-f_{2,\mathbf{k}+\mathbf{q}}^{0})}{E_{1,\mathbf{k}}^{0} - E_{2,\mathbf{k}+\mathbf{q}}^{0} + \omega_{\mathbf{q}}^{\pm}} \right]$$

$$+ \frac{f_{2,\mathbf{k}}^{0}(1-f_{1,\mathbf{k}-\mathbf{q}}^{0})}{E_{2,\mathbf{k}}^{0} - E_{1,\mathbf{k}-\mathbf{q}}^{0} - \omega_{\mathbf{q}}^{\pm}}.$$  \hspace{1cm} (C.1)

The adiabatic approximation corresponds to setting $\omega_{\mathbf{q}}^{\pm} = 0$ in Equation
(C.1).

Since we are only interested in a narrow energy range around the
Fermi level, we can assume linear bands in the $z$-direction:

$$E_{1,\mathbf{k}}^{0} = -V_{1}(k_{z} - k_{f})$$

and

$$E_{2,\mathbf{k}}^{0} = V_{2}(k_{z} - k_{f} - Q).$$  \hspace{1cm} (C.2)
where the linear velocity $V$ and the nesting wavevector $Q$ are functions of $k_x$ and $k_y$.

The e-p matrix elements can be obtained from the magnitude of the band splittings in the frozen phonon calculation. For an atomic displacement of $\sim 2\%$ of the lattice constant, we obtained splittings around the Fermi level ranging from 0.55 to 0.65 eV. Therefore, it is a good approximation to assume constant matrix elements over the Fermi surface to simplify the calculation. Also, we found that the linear velocities, $V_1$ and $V_2$, are essentially independent of $k_x$ and $k_y$ in the region of interest, thus, constant velocities have been used. Integration over $k_z$ in Equation (C.1) gives

$$\omega_q = -\frac{|q|^2}{\sqrt{V_1 V_2}} \frac{\Omega}{3} \int dk_x dk_y \ln \left| \frac{(V_1 + V_2)^2}{(V_1(q-Q)+\omega)(V_2(q-Q)-\omega)} \right| \Delta K_z$$

(C.3)

$\Delta K_z$ in Equation (C.3) represents the region where $E_1^0$ and $E_2^0$ are of the order of several $\omega_0$ from the Fermi level. However, the exact choice of $K_z$ is not critical since the contribution to the integral goes as $\ln(\Delta K_z)$ which changes slowly with $\Delta K_z$. The nesting vector $Q$ can be well-parameterized by the expression

$$Q = a + b (k_x - k_x^0)^2$$

(C.4)
where $a$ is a function of $k_y$, $k_x^0$ and $b$ are constant.

Substituting Equation (C.4) into (C.3), we can do the integration over $k_x$ analytically, it is then easy to perform the remaining integral over $k_y$ numerically.