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# Dynamic pseudopotential theory of phonon spectra in metals

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Electron clouds of large atoms undergo significant distortion during lattice vibration. The shell model, which divides each ion into an inner core and a last-filled electron shell, is combined with the pseudopotential method to provide a theory of phonon spectra. The conduction electrons screen all of the following interactions: core-core, core-shell, and shell-shell. An important feature of the theory is inclusion of exchange interactions of shell electrons with the conduction-electron sea. As a consequence three different dielectric functions appear in the theory (appropriate to core-core, core-shell, and shell-shell interaction energies). The pseudopotential of each ion has two parts: one for the core and one for the shell. The new features of the theory are expected to be important in heavy metals.

## I. INTRODUCTION

The purpose of this paper is to construct a dielectric theory of phonon spectra in metals which combines conventional pseudopotential methods[1] with the shell model of Dick and Overhauser.[2] The motivation is to allow for ionic distortions (during lattice vibration) which may sometimes be important, especially in heavy metals.

The shell model has been used extensively[3] in lattice dynamics of insulators and semiconductors. Coupling between the outermost filled shell of an atom and its inner-ion core is usually described by adjustable ("spring") constants. Our intention here is to treat *all* interactions as Coulombic, but screened by the dielectric functions of the conduction-electron sea.

Ordinarily, pseudopotential models of metals treat each pseudo-ion charge density $\bar{\rho}(\mathbf{r}-\mathbf{L})$ as rigid, i.e., the shape of $\bar{\rho}$ does not change when the ion is displaced from its equilibrium lattice site $\mathbf{L}$. Interactions between ions are screened by the electron-gas dielectric function $\epsilon(q)$, which in this paper we shall call the test-charge—test-charge or core-core dielectric function

$$\epsilon(q)\equiv\epsilon_{cc}(q)=1+\frac{Q_0(q)}{1-G_+(q)Q_0(q)} . \tag{1}$$

Here $Q_0(q)$ is the Lindhard function,

$$Q_0(q)=\frac{me^2}{\pi\hbar^2k_Fx^2}\left[\frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\left|\frac{1+x}{1-x}\right|\right|\right] , \tag{2}$$

where $x\equiv q/2k_F$ and $k_F$ is the radius of the Fermi sphere. $G_+(q)$ is the spin-symmetric, exchange and correlation local-field factor.[4]

Standard theory considers the ion as a rigid "test charge." Here we introduce an important distinction. The inner-ion core will be treated as a test charge, but the outermost-filled shell will be recognized as an assembly of electrons. Consequently, there will be exchange corrections to the shell interaction with the conduction-electron sea. A consequence of shell-conduction exchange is that core-shell and shell-shell interactions will be screened by two "new" dielectric functions: $\epsilon_{cs}(q)$ and $\epsilon_{ss}(q)$. The theory of these new functions will be presented in Sec. IV. For the present we will consider these functions as known. However, before developing the deformable-ion theory we shall review the rigid-ion version in a formulation that allows immediate generalization to the new model.

## II. RIGID-ION PSEUDOPOTENTIAL THEORY

The simplest derivation[5] of the phonon spectrum of a simple metal requires only a few steps. (In Appendix A we prove its equivalence to published formulations.) The total pseudo-ion charge density of a monatomic metal (having unit volume) is

$$\rho(\mathbf{r})=\sum_{\mathbf{L}}\bar{\rho}(\mathbf{r}-\mathbf{L}) . \tag{3}$$

Its Fourier transform $\rho(\mathbf{Q})$ is zero unless $\mathbf{Q}=\mathbf{G}$, a reciprocal-lattice vector. For this case

$$\rho(\mathbf{G})=n\bar{\rho}(\mathbf{G}) , \tag{4}$$

where $\bar{\rho}(Q)$ is the Fourier transform of the pseudo-ion charge density $\bar{\rho}(\mathbf{r})$, and $n$ is the atomic density. The Fourier coefficient of each electrostatic potential component is

$$\phi(\mathbf{Q})=4\pi\rho(\mathbf{Q})/Q^2\epsilon(Q) . \tag{5}$$

Consequently, the potential energy of the equilibrium lattice is

$$U_0={\sum_{\mathbf{G}}}'\frac{2\pi\,|\,\rho(\mathbf{G})\,|^2}{G^2\epsilon(G)} . \tag{6}$$

(The prime indicates omission of the term for $\mathbf{G}=0$, which is a requirement of overall charge neutrality.) It should be appreciated that $U_0$ is a fictitious energy (devoid of physical significance) since it includes the electrostatic self-energy of the pseudo-ions. Only changes in potential energy relative to $U_0$ will influence lattice dynamics.

Consider now a sinusoidal displacement $\mathbf{u}(\mathbf{L})$ of the ions from their lattice sites (for a peak amplitude $A$):

$$\mathbf{u}(\mathbf{L})=A\hat{\boldsymbol{\alpha}}_{\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{L}) \ , \tag{7}$$

where $\hat{\alpha}_q$ is the (unit) polarization vector of the phonon having wave vector $\mathbf{q}$ and frequency $\omega_q$. Instead of Eq. (3) the charge density of the ions is now

$$\rho(\mathbf{r})=\sum_{\mathbf{L}}\rho(\mathbf{r}-\mathbf{L}-A\hat{\boldsymbol{\alpha}}_{\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{L}) \ . \tag{8}$$

The nonzero Fourier coefficients (to relevant order in $A$) are,

$$\begin{aligned}\rho(\mathbf{G})&=n\bar{\rho}(\mathbf{G})\left[1-\frac{A^2}{4}(\mathbf{G}\cdot\hat{\boldsymbol{\alpha}})^2\right] \ ,\\ \rho(\mathbf{G}\pm\mathbf{q})&=\tfrac{1}{2}in\bar{\rho}(\mathbf{G}\pm\mathbf{q})(\mathbf{G}\pm\mathbf{q})\cdot\hat{\boldsymbol{\alpha}} \ .\end{aligned} \tag{9}$$

The change $\Delta U$ in electrostatic energy (relative to $U_0$) can be obtained using Eq. (5). Now, for any harmonic oscillator the peak value of $\Delta U$ equals the peak value of the kinetic energy. Since the displacement amplitude varies as $A\cos\omega_{\mathrm{q}}t$, we must set

$$\Delta U=\tfrac{1}{4}nM\omega_{\mathrm{q}}^2A^2 \ , \tag{10}$$

where $M$ is the ionic mass. Equations (6), (9), and (10) determine the phonon spectrum:

$$\omega_{\mathrm{q}}^2=\frac{4\pi n}{M}\left[\sum_{\mathbf{G}}\frac{|\bar{\rho}(\mathbf{G}+\mathbf{q})|^2|(\mathbf{G}+\mathbf{q})\cdot\hat{\mathbf{a}}_{\mathrm{q}}|^2}{|\mathbf{G}+\mathbf{q}|^2\epsilon(\mathbf{G}+\mathbf{q})}-\sum_{\mathbf{G}}{}'\frac{|\bar{\rho}(\mathbf{G})|^2\mathbf{G}\cdot\hat{\boldsymbol{\alpha}}_{\mathrm{q}}|^2}{G^2\epsilon(G)}\right] . \tag{11}$$

This simple result follows from our assumption that the phonon polarizations $\hat{\boldsymbol{\alpha}}_{\mathrm{q}}$ are known (as is usually the case for $\mathbf{q}$ along symmetry axes). For an arbitrary $\mathbf{q}$ one obtains, instead of Eq. (11), a $3\times3$ dynamical matrix. Eigenvalues and eigenvectors of this matrix give the phonon frequencies and polarizations. Equation (11) has taken the compact form shown by assuming spherical ions, i.e., $\bar{\rho}(\mathbf{Q})=\bar{\rho}(-\mathbf{Q})$, and by realizing that the sum over $\mathbf{G}$ is the same as the sum over $-\mathbf{G}$. Note that Eq. (11) involves the test-charge—test-charge dielectric function, Eq. (1).

## III. DYNAMIC PSEUDOPOTENTIAL MODEL

The ansatz of the new model is that the pseudo-ion charge density $\bar{\rho}(\mathbf{r})$ can be divided into two parts. For an ion in equilibrium,

$$\bar{\rho}(\mathbf{r})=\rho_c(\mathbf{r})+\rho_s(\mathbf{r}) \ , \tag{12}$$

where $\rho_c(\mathbf{r})$ arises from the inner-ion core and $\rho_s(\mathbf{r})$ from the outermost-filled electron shell. During a lattice vibration the core displacements will still be given by Eq. (7), but the shell displacements $\mathbf{v}(\mathbf{L})$ will differ:

$$\mathbf{v}(\mathbf{L})=B\hat{\boldsymbol{\beta}}_{\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{L}) \ . \tag{13}$$

The (unit) polarization vector $\hat{\boldsymbol{\beta}}_{\mathrm{q}}$ of the shell displacements will usually have an in-phase and out-of-phase component in crystals having two or more atoms per primitive cell. For simplicity we consider here only metals with one atom per cell. Exchange (and correlation) corrections to the interaction between shell electrons and conduction electrons lead to three distinguishable dielectric functions: $\epsilon_{cc}(q)$, $\epsilon_{ss}(q)$, and $\epsilon_{cs}(q)$. The first of these is the same as Eq. (1). The equilibrium potential energy is, instead of Eq. (6),

$$U_0=2\pi n^2\sum_{\mathbf{G}}\left[\frac{|\rho_c(\mathbf{G})|^2}{G^2\epsilon_{cc}(G)}+\frac{|\rho_s(\mathbf{G})|^2}{G^2\epsilon_{ss}(G)}+\frac{2\rho_c(\mathbf{G})\rho_s(\mathbf{G})}{G^2\epsilon_{cs}(G)}\right] . \tag{14}$$

The dynamical matrix (for a monatomic lattice) is $6\times6$ instead of $3\times3$. The core mass is $M$ and the shell mass is $zm$, where $z$ is the number of electrons in the outermost-filled shell. Derivation of the equations of motion is straightforward. The result is,

$$\begin{bmatrix}D(cc) & D(cs)\\ D(sc) & D(ss)\end{bmatrix}\begin{bmatrix}A\hat{\boldsymbol{\alpha}}\\ B\hat{\boldsymbol{\beta}}\end{bmatrix}=\begin{bmatrix}nM\omega^2A\hat{\boldsymbol{\alpha}}\\ znm\omega^2B\hat{\boldsymbol{\beta}}\end{bmatrix} . \tag{15}$$

Each $D$ is a $3\times3$ matrix, given below, and $\hat{\boldsymbol{\alpha}},\hat{\boldsymbol{\beta}}$ are three-dimensional (unit length) column vectors.

$$D_{ij}(cc)=4\pi n^2\left[\sum_{\mathbf{G}}\frac{|\rho_c(\mathbf{G}+\mathbf{q})|^2(\mathbf{G}+\mathbf{q})_i(\mathbf{G}+\mathbf{q})_j}{|\mathbf{G}+\mathbf{q}|^2\epsilon_{cc}(\mathbf{G}+\mathbf{q},\omega)}-\sum_{\mathbf{G}}{}'\left[\frac{|\rho_c(\mathbf{G})|^2}{\epsilon_{cc}(\mathbf{G},\omega)}+\frac{\rho_c(\mathbf{G})\rho_s(\mathbf{G})}{\epsilon_{cs}(\mathbf{G},\omega)}\right]\frac{\mathbf{G}_i\mathbf{G}_j}{G^2}\right] . \tag{16}$$

We have indicated here an explicit frequency dependence of the dielectric functions. Since the three lowest eigenfrequencies of Eq. (15) are phonon modes, the $\omega=0$ limits can be used because $\omega \ll \omega_P$, the conduction-electron plasma frequency. The three remaining eigenfrequencies are collective shell excitons. Their frequencies correspond to 15—90 eV. For these modes one would use $\epsilon\approx1-\omega_p^2/\omega^2$ (for all three $\epsilon$'s). $D(ss)$ can be obtained from Eq. (16) by interchanging $c$ and $s$. Finally,

$$D_{ij}(cs)=4\pi n^2\sum_{\mathbf{G}}\frac{\rho_c(\mathbf{G}+\mathbf{q})\rho_s(\mathbf{G}+\mathbf{q})(\mathbf{G}+\mathbf{q})_i(\mathbf{G}+\mathbf{q})_j}{(\mathbf{G}+\mathbf{q})^2\epsilon_{cs}(\mathbf{G}+\mathbf{q})} \ , \tag{17}$$

and $D(sc)$ is the transpose of $D(cs)$.

It is easily verified that the foregoing theory reverts to the rigid-ion pseudopotential model if $B\hat{\boldsymbol{\beta}}$ is forced to equal $A\hat{\boldsymbol{\alpha}}$ and if the three $\epsilon$'s are equal to Eq. (1). Application of this theory to specific metals will be published separately. However, we note here that allowance for the shell vibration (relative to the core) can, in heavy metals, reduce the zone-boundary frequencies by 15—60%. Neglect of shell conduction-electron exchange interactions can lead to further errors of a factor of 2. In the past these hidden omissions have been compensated by adjustments in phenomenological, pseudopotential parameters.

## IV. THE DIELECTRIC FUNCTIONS $\epsilon_{cs}(q)$ AND $\epsilon_{ss}(q)$

We will follow the method of Kukkonen and Overhauser to derive the two new dielectric functions which appear in the theory of the preceding section. One must recall that the effective potential experienced by a *conduction* electron from a test-charge Fourier component $\rho_q$ is

$$V_e^{\text{eff}} = -\frac{4\pi e}{q^2}[\rho_q - e\Delta n_q(1-G_+)] , \tag{18}$$

where $\Delta n_q$ is the Fourier component of the conduction-electron density response (caused by $V_e^{\text{eff}}$).

$$\Delta n_q = -\frac{q^2}{4\pi e^2} Q_0(q) V_e^{\text{eff}} , \tag{19}$$

where $Q_0(q)$ is given by Eq. (2). $G_+(q)$ is the spin-symmetric[4] exchange (and correlation) correction factor to a conduction electron's effective potential:

$$G_+(q) \approx \frac{1.1x^2}{1+1.7x^2} , \tag{20}$$

with $x \equiv q/2k_F$. This function is an interpolation between $x=0$ and $\infty$ limits, which are known from electron-gas theory.[6] (It does not include a possible peak[7] near $q=2k_F$.)

Equations (18) and (19) determine $V_e^{\text{eff}}$, which provides a definition of the electron-test-charge dielectric function:

$$V_e^{\text{eff}} \equiv -\frac{4\pi e \rho_q}{q^2 \epsilon_{\text{et}}(q)} . \tag{21}$$

Accordingly,

$$\epsilon_{\text{et}}(q) = 1 + (1-G_+)Q_0(q) . \tag{22}$$

This function differs substantially from $\epsilon(q)$, Eq. (1), which one can obtain from just the Coulomb contribution to $V_e^{\text{eff}}$. ($\epsilon_{\text{et}}$ will appear in the derivation of the rigid-ion theory presented in Appendix A.)

We now focus our attention on the effective potential $V_s^{\text{eff}}$ experienced by an electron in the (last-filled) shell. Its exchange interaction with the conduction-electron density $\Delta n_q$ is much smaller than that of a conduction electron—by a factor of $\sim 2$ to 4.[8] There is no reason why the $q$ dependence of this correction should be the same as $G_+(q)$. However, since Eq. (20) is heuristic anyway, we shall merely multiply it by a factor $\gamma_s < 1$. Consequently the effective potential of a shell electron (caused by $\rho_q$) is,

$$V_s^{\text{eff}} = -\frac{4\pi e}{q^2}[\rho_q - e\Delta n_q(1-\gamma_s G_+)] . \tag{23}$$

Equations (18), (19), and (23) can be solved simultaneously for $V_s^{\text{eff}}$. The result defines a shell-test-charge (or shell-core) dielectric function:

$$\epsilon_{cs}(q) = \frac{1+(1-G_+)Q_0(q)}{1-(1-\gamma_s)G_+ + Q_0(q)} . \tag{24}$$

This expression reverts (as it must) to $\epsilon(q)$ if $\gamma_s = 0$ and to $\epsilon_{\text{et}}(q)$ if $\gamma_s = 1$.

Derivation of the shell-shell dielectric function $\epsilon_{ss}(q)$ requires a modification to Eq. (18). The source $\rho_q$ of the "disturbance" arises now from shell electrons. Consequently the effective potential experienced by a *conduction* electron must include the correction $\gamma_s G_+$. Therefore,

$$V_e^{\text{eff}} = -\frac{4\pi e}{q^2}[\rho_q(1-\gamma_s G_+) - e\Delta n_q(1-G_+)] . \tag{25}$$

Equations (19), (23), and (25) may be solved for $V_s^{\text{eff}}$. The result defines the shell-shell dielectric function:

$$\epsilon_{ss}(q) = \frac{1+(1-G_+)Q_0(q)}{1-(1-2\gamma_s+\gamma_s^2 G_+)G_+ + Q_0(q)} . \tag{26}$$

This function also reverts to $\epsilon(q)$ when $\gamma_s = 0$.

## V. DISCUSSION

Application of the foregoing theory to specific metals will be the subject of a separate study. Our intent here is to elaborate the formalism without making specific choices on how to model the pseudo-ion core and shell charge densities $\rho_c(\mathbf{r})$ and $\rho_s(\mathbf{r})$, Eq. (12). Each worker will naturally have his own preference in such matters.

Two important effects have been included in the present theory which have ordinarily been neglected in the lattice dynamics of metals: motion of the last-filled shell, relative to its inner-ion core, and the modified dielectric interaction of the last-filled shell with the conduction-electron sea. We have already remarked that a quantitative study of this latter effect indicates that $\gamma_s \sim 0.3$. For the filled shells of the inner-ion core the corresponding $\gamma$'s would be much smaller.[8] (Exchange integrals between conduction electrons and hydrogenic states are $\sim Z_{\text{eff}}^{-2}$). For this reason one can regard the inner-ion core (as we have done) as a test charge.

The theory developed here has application beyond lattice dynamics alone. For example, the theory of electron-phonon interaction (and its application to electronic transport phenomena) will be altered by the ion deformations and by exchange (and correlation) associated with the last-filled shells.

Finally, the lattice dynamics of magnetic metals will involve a spin-dependent generalization of $\epsilon_{ss}(q)$, Eq. (26), analogous to the Kukkonen-Overhauser interaction between conduction electrons.[4] This development would be of interest for studying the influence of magnetic order on phonon spectra.

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## APPENDIX A: THE RIGID-ION MODEL

A commonly used formalism[9] describing pseudopotential models of phonon spectra in metals divides the dynamical matrix $D_{ij}$ into two parts:

$$D^c_{ij}=\frac{n}{4\pi M}\left[\sum_{\mathbf{G}}(\mathbf{G}+\mathbf{q})_i(\mathbf{G}+\mathbf{q})_j\,|\mathbf{G}+\mathbf{q}|^2\,|V_c(\mathbf{G}+\mathbf{q})|^2-\sum_{\mathbf{G}}{}'\mathbf{G}_i\mathbf{G}_jG^2V_c(\mathbf{G})\right], \qquad \text{(A1)}$$

and

$$D^E_{ij}=\frac{n}{4\pi M}\left[\sum_{\mathbf{G}}(\mathbf{G}+\mathbf{q})_i(\mathbf{G}+\mathbf{q})_j g_0(\mathbf{G}+\mathbf{q})-\sum_{\mathbf{G}}{}'G_iG_jg_0(\mathbf{G})\right]. \qquad \text{(A2)}$$

In Eq. (A1), $V_c(\mathbf{q})\equiv 4\pi Ze/q^2$. $Z$ is the valence of the ion, so this term corresponds to the "bare" Coulomb interaction between the ions, which can be treated as point charges $Ze$. In Eq. (A2),

$$g_0(\mathbf{q})\equiv -q^2\frac{|V_M(\mathbf{q})|^2}{\epsilon_{\text{et}}(q)}\,\frac{(\epsilon_{\text{et}}-1)}{1-G_+(q)}\,. \qquad \text{(A3)}$$

This factor arises from the self-energy of the pseudo-ions immersed in the conduction-electron sea. $V_M(\mathbf{q})$ is the bare-ion pseudopotential which, in our notation, is $4\pi\bar{\rho}(q)/q^2$. Observe that the dielectric function in Eq. (A3) is the electron-test-charge dielectric function, Eq. (22). In the theory presented in Sec. II only the "true" $\epsilon(q)$, i.e., the test-charge—test-charge dielectric function appears. Nevertheless the two formulations are equivalent.

Each term of Eq. (11) can be divided into two by writing

$$\frac{1}{\epsilon}=1+\left[\frac{1}{\epsilon(q)}-1\right]. \qquad \text{(A4)}$$

The first term (on the right-hand side) describes bare Coulomb interactions between the ions, and corresponds to the contributions given in Eq. (A1). Now, the following identity can be verified easily from Eqs. (1) and (22):

$$\frac{1}{\epsilon(q)}-1=-\frac{1}{\epsilon_{\text{et}}(q)}\,\frac{\epsilon_{\text{et}}(q)-1}{1-G_+(q)}\,. \qquad \text{(A5)}$$

It follows by inspection of Eq. (A3) that the second term of (A4) corresponds to Eq. (A2).

Dielectric models of phonon spectra in metals depend sensitively on the exchange (and correlation) corrections to the various dielectric functions. Which $\epsilon$ is the relevant one depends on the theoretical approach.

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