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Lattice dynamics of metals from density-functional perturbation theory

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The density-functional perturbation theory approach to lattice-dynamical calculations is extended to metallic systems. The smearing technique is used to deal with the Fermi surface and its variational formulation is restated. First-principles phonon dispersions of Al, Pb and of the transition metal Nb are in good agreement with available experimental data. In particular an accurate description of the anomalies observed in lead and niobium is obtained.

Lattice dynamics is a key concept for understanding several physical properties of metals, such as electrical and thermal conductivity and, of course, superconductivity. Phonon dispersions in metals are also interesting on their own due to the anomalous electronic screening that can occur when the periodicity of the involved lattice distortion connects different portions of the Fermi surface, as pointed out by Kohn.[1]

The density-functional[2] linear-response approach to lattice dynamics[3] is by now a common and well established tool for studying, from first principles, vibrational and related properties of simple[4] and complex[5] semiconductor or insulating materials. In this work I extend the original linear-response method to metallic systems where the (Gaussian) smearing technique[6,7] is used to deal with the Brillouin zone (BZ) integration in the presence of a Fermi surface. Note, however, that a tetrahedron-based[8] calculation has been recently presented in Ref. 9.

The smearing approach to metallic systems is very general and simple to use. Unlike the tetrahedron method, it does not require to decompose the BZ into symmetry-breaking elemental volumes and to connect energy bands in neighboring **k** points in arbitrary ways. This is an important drawback of the tetrahedron method since, unless complete convergence in the BZ sampling is achieved, different results are obtained studying the same system in different geometries.[10] In the smearing approach, on the contrary, the results are independent of the assumed crystal geometry, as long as equivalent sampling points are used. Moreover, it is easy, albeit it has been somewhat controversial,[11–13] to define the energy functional in a variational form, thus allowing the use of the Hellmann-Feynman theorem[14] to compute forces or other energy derivatives.[15] This makes the smearing technique the method of choice in the first-principles molecular-dynamical simulations of metals.[13,16]

In the smearing approach the local density of states is convoluted with a smearing function, $f(\varepsilon)=(1/\sigma)\tilde{\delta}(\varepsilon/\sigma)$, which is an approximation to the Dirac's δ function that becomes exact for vanishing linewidth, σ. Many kinds of smearing functions can be used: Fermi-Dirac broadening, Lorentzian, Gaussian,[6] or Gaussian combined with polynomials,[7] to recall only some of them. After convolution the (modified) local density of states can be computed accurately on a discrete grid of points in the BZ, provided the average energy separation between neighboring computed eigenvalues is small with respect to the linewidth, σ:

$$n(\mathbf{r},\varepsilon)=\sum_i \frac{1}{\sigma}\,\tilde{\delta}\left(\frac{\varepsilon-\varepsilon_i}{\sigma}\right)|\phi_i(\mathbf{r})|^2, \tag{1}$$

where the sum refers both to the discrete **k**-vector index and to the band one. From this basic quantity the electron density follows:

$$n(\mathbf{r})=\int_{-\infty}^{\varepsilon_F} n(\mathbf{r},\varepsilon)\,d\varepsilon=\sum_i \tilde{\theta}\left(\frac{\varepsilon_F-\varepsilon_i}{\sigma}\right)|\phi_i(\mathbf{r})|^2, \tag{2}$$

where $\tilde{\theta}(x)=\int_{-\infty}^{x}\tilde{\delta}(y)dy$ is a smooth approximation to the step function and the Fermi energy is determined from the normalization to the total number of particles:

$$N=\int_{-\infty}^{\varepsilon_F} n(\varepsilon)\,d\varepsilon=\sum_i \tilde{\theta}\left(\frac{\varepsilon_F-\varepsilon_i}{\sigma}\right). \tag{3}$$

Given the definition in Eq. (1), the consistent way to define the Kohn-Sham (KS) kinetic energy functional is through the single-particle energy integral:

$$\begin{aligned} T_s[n]&=\int_{-\infty}^{\varepsilon_F}\varepsilon\, n(\varepsilon)\,d\varepsilon-\int V^{\mathrm{KS}}(\mathbf{r})\;n(\mathbf{r})\,d\mathbf{r}\\ &=\sum_i\left[-\frac{\hbar^2}{2m}\,\tilde{\theta}\left(\frac{\varepsilon_F-\varepsilon_i}{\sigma}\right)\langle\phi_i|\nabla^2|\phi_i\rangle+\sigma\tilde{\theta}_1\left(\frac{\varepsilon_F-\varepsilon_i}{\sigma}\right)\right], \end{aligned} \tag{4}$$

where $\tilde{\theta}_1(x)=\int_{-\infty}^{x}y\,\tilde{\delta}(y)dy$. With this definition the usual KS equations follow from the minimization of the total energy and forces can be computed in the usual way:

$$\frac{\partial E_{\mathrm{tot}}}{\partial \mathbf{u}_s}=\int n(\mathbf{r})\,\frac{\partial V^0(\mathbf{r})}{\partial \mathbf{u}_s}+\frac{\partial E_{\mathrm{ion}}}{\partial \mathbf{u}_s}, \tag{5}$$

where $\mathbf{u}_s$ is the atomic position, E_{ion} is the ionic electrostatic energy, V^0 is the bare ionic (pseudo-)potential of the crystal, and n is the ground-state electron density. Notice that the *free energy* introduced in Refs. 13 and 16, where electronic occupation numbers are considered as independent variables and an entropy contribution to the total energy is added to fix their value, is just the total energy originally defined in Ref. 6, and used here, where occupation numbers are a function of the single-particle energies, determined through the Kohn-Sham effective potential by the charge density of the system.

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The two schemes are strictly equivalent and the last term in Eq. (4) corresponds to the entropy correction in Refs. 13 and 16.

The price to be paid for the computational simplicity of the smearing approach is that the computed total energies depend on the chosen linewidth. Let us investigate this dependence before proceeding with the linear-response formulation. The first-order derivative of the total energy with respect to the width of the smearing function is simply related to the Fermi energy correction in the band-energy integral. All other contributions cancel due to the variational properties of the functional and the conservation of the number of particles. Calling $\hat{n}_\sigma(\varepsilon)$ the *presmearing* density of states of the system and assuming a power series expansion near the Fermi level one obtains

$$\frac{dE_{\rm tot}}{d\sigma}=\sum_i \tilde{\theta}_1\left(\frac{\varepsilon_F-\varepsilon_i}{\sigma}\right)=\int_{-\infty}^{\infty} d\varepsilon\, \hat{n}_\sigma(\varepsilon)\int_{-\infty}^{(\varepsilon_F-\varepsilon)/\sigma} y\tilde{\delta}(y)dy$$

$$=-\sum_{k=0}^{\infty}\sigma^{2k+1}\frac{c_{k+1}}{(2k+1)!}\left.\frac{d^{2k}\hat{n}_\sigma}{d\varepsilon^{2k}}\right|_{\varepsilon_F}, \qquad (6)$$

where $c_k=\int x^{2k}\tilde{\delta}(x)dx$ and $\tilde{\delta}(x)$ is taken to be an even function of its argument. From this equation, it is easily seen that, unless the second moment of the smearing function vanishes, the leading term in $E_{\rm tot}$ is quadratic in σ (proportional to the density of states at the Fermi level). This dependence is physically sound and is responsible for the linear temperature dependence of the specific heat in real metal (the Fermi-Dirac thermal broadening is appropriate in this case). Due to limitations in the affordable computational effort one is forced to use a smearing width corresponding to very high temperatures and the quadratic term may induce large errors in the calculation. Notice, however, that using a nonpositive-defined δ approximant it is possible to eliminate the quadratic term and make the leading dependence on σ (at least) quartic. This is the case when using the Hermite-Gaussian approximation of first (or higher) order proposed in Ref. 7. An alternative way to correct for the large quadratic dependence on σ has been developed in Refs. 16 and 17.

Let us come now to lattice dynamics. The force-constant matrix, in the adiabatic approximation, is defined by the second-order derivatives of the crystal total energy with respect to the atomic displacements from equilibrium. Taking the derivative of the Hellmann-Feynman force, Eq. (5), one easily obtains

$$\mathbf{\Phi}_{s,s'}=\int\frac{\partial n(\mathbf{r})}{\partial\mathbf{u}_s}\frac{\partial V^0(\mathbf{r})}{\partial\mathbf{u}_{s'}}+\int n(\mathbf{r})\frac{\partial^2V^0(\mathbf{r})}{\partial\mathbf{u}_s\partial\mathbf{u}_{s'}}+\frac{\partial^2E_{\rm ion}}{\partial\mathbf{u}_s\partial\mathbf{u}_{s'}}. \qquad (7)$$

Straightforward perturbation theory gives the density variation induced by the displacement of an atom:

$$\frac{\partial n(\mathbf{r})}{\partial\mathbf{u}_s}=\sum_{i,j}\frac{\tilde{\theta}_{F,i}-\tilde{\theta}_{F,j}}{\varepsilon_i-\varepsilon_j}\phi_i(\mathbf{r})^*\phi_j(\mathbf{r})\left\langle\phi_j\left|\frac{\partial V^{\rm KS}}{\partial\mathbf{u}_s}\right|\phi_i\right\rangle, \qquad (8)$$

where we have defined $\tilde{\theta}_{i,j}=\tilde{\theta}((\varepsilon_i-\varepsilon_j)/\sigma)$ and $\partial V^{\rm KS}/\partial\mathbf{u}_s$ is the first-order variation of the KS potential with respect to atomic displacement, self-consistently dependent on $\partial n/\partial\mathbf{u}_s$. To avoid the double sum over occupied and unoccupied states let us use the relation $\tilde{\theta}(x)+\tilde{\theta}(-x)=1$ and the symmetry between i and j to get

$$\frac{\partial n(\mathbf{r})}{\partial\mathbf{u}_s}=2\sum_{i,j}\frac{\tilde{\theta}_{F,i}-\tilde{\theta}_{F,j}}{\varepsilon_i-\varepsilon_j}\tilde{\theta}_{j,i}\phi_i(\mathbf{r})^*\phi_j(\mathbf{r})\left\langle\phi_j\left|\frac{\partial V^{\rm KS}}{\partial\mathbf{u}_s}\right|\phi_i\right\rangle, \qquad (9)$$

where the first index runs only over the partially occupied states and the second one only over those partially unoccupied. This expression can be further simplified, avoiding the sum over the unoccupied states, by writing

$$\frac{\partial n(\mathbf{r})}{\partial\mathbf{u}_s}=2\sum_i\phi_i(\mathbf{r})^*\Delta\phi_i(\mathbf{r}), \qquad (10)$$

where the $\Delta\phi_i$'s satisfy

$$[h^{\rm KS}+Q-\varepsilon_i]\Delta\phi_i=-[\tilde{\theta}_{F,i}-P_i]\frac{\partial V^{\rm KS}}{\partial\mathbf{u}_s}|\phi_i\rangle,$$

$$Q=\sum_k\alpha_k|\phi_k\rangle\langle\phi_k|,\quad P_i=\sum_j\beta_{i,j}|\phi_j\rangle\langle\phi_j|,$$

$$\alpha_k=\max(\varepsilon_F+3\sigma-\varepsilon_k,0), \qquad (11)$$

$$\beta_{i,j}=\tilde{\theta}_{F,i}\tilde{\theta}_{i,j}+\tilde{\theta}_{F,j}\tilde{\theta}_{j,i}+\alpha_j\frac{\tilde{\theta}_{F,i}-\tilde{\theta}_{F,j}}{\varepsilon_i-\varepsilon_j}\tilde{\theta}_{j,i},$$

and the Q operator is chosen in such a way to make the linear system nonsingular for all nonvanishing $\Delta\phi_i$. It can be easily checked that since α_k is taken to vanish when ϕ_k is unoccupied then also $\beta_{i,j}$ vanishes when any of its indices refers to unoccupied states. Therefore the Q and P operators involve only the small number of partially filled bands and the first-order variation of the wave functions and of the charge density can be computed avoiding explicit reference to the unoccupied states, in much the same way as was the case for insulating materials.[3]

Let us apply the present approach to the lattice dynamics of Al, Pb, and Nb elemental metals. While aluminum is a prototype of free-electron-like metals, lead and niobium are strongly coupled electron-phonon systems: their superconducting transition temperatures are the highest among elemental crystal and their phonon dispersions present dips and wiggles related to Kohn anomalies. They constitute a stringent test of the ability of our approach to deal with the metallic state.

Standard norm-conserving pseudopotentials from the compilation by Bachelet, Hamann and Schlüter[18] (BHS) are used, except for Al where a Von Barth–Car pseudopotential[19] already tested in many semiconductor physics applications is used. The kinetic-energy cutoffs considered in the plane-wave expansion are 16, 12, and 32 Ry for Al, Pb, and Nb, respectively. In all cases it was checked that increasing the cutoff energy produced negligible effects on the calculated properties.

Let us first discuss the choice of the smearing function and of its width, taking lead as example. In Fig. 1 the total energy per atom of fcc-Pb crystal, at a fixed lattice parameter (9.0 a.u.), is displayed as a function of the linewidth, σ, and for two different smearing functions: a Hermite-Gaussian

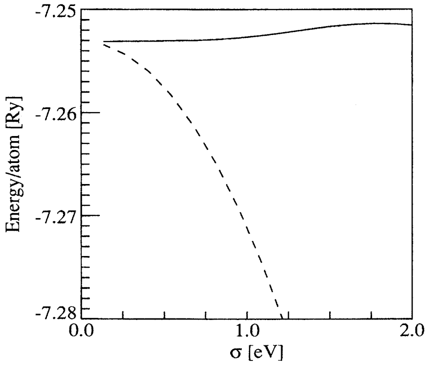

FIG. 1. Total energy per atom of fcc-Pb crystal as a function of the smearing linewidth and for two different smearing functions: the Hermite-Gaussian function of order 1 (solid line) and the simple Gaussian function (dashed line).

function of order 1 (HG1) (Ref. 7) and the simple Gaussian function. A very large number of sampling points in the BZ is used (408 in the irreducible wedge) to ensure converged results. It can be clearly seen that while the simple Gaussian function gives energies considerably far from the desired *zero-width* limit unless the linewidth is very small (it is easily recognized the quadratic dependence on σ), the slightly more sophisticated HG1 function gives convergence within 1 mRy/atom already for a broadening as large as 1 eV, which would allow to use a much lower number of points for the BZ integration. A careful analysis confirms, for this function, the quartic dependence of the total energy on σ. In the following the HG1 function has been used with a linewidth ranging between 0.3 and 0.7 eV, always checking the **k**-point convergence of the results, which may be different for different quantities.

The equilibrium properties of the materials considered are shown in Table I. The results are very insensitive to the value of σ, as can be expected from the previous analysis, and are of the typical accuracy of local-density-approximation pseudopotential calculations. Lead turns out to be the worst case as compared with experiment (lattice parameter 4% too small and bulk modulus substantially too large). After several checks, I attribute these discrepancies to the shallow $5d$ Pb core electrons that should not be completely neglected in the calculation, as they are using BHS pseudopotentials.

In Fig. 2 the phonon dispersions for Al, Pb, and Nb are displayed, along with available experimental data.[20–22] Results for two different smearing linewidths are shown (0.3 and 0.7 eV, solid and dashed lines, respectively). In order to establish the genuine effect of the smearing linewidth on the calculated frequencies a very large number of sampling points have been used (280 and 112 points for the smaller linewidth in the irreducible wedge of fcc and bcc BZ, respectively). With this choice the calculated frequencies are converged within a fraction of a percent with respect to BZ sampling.

TABLE I. Calculated lattice parameter (a.u.) and bulk modulus (kbar) for the metals considered in this work. Experimental data (in parentheses) are given for comparison.

	Structure	a_0 (a.u.)		B (kbar)	
Al	(fcc)	7.50	(7.63)	783	(783)
Pb	(fcc)	9.01	(9.35)	516	(432)
Nb	(bcc)	6.16	(6.22)	1780	(1714)

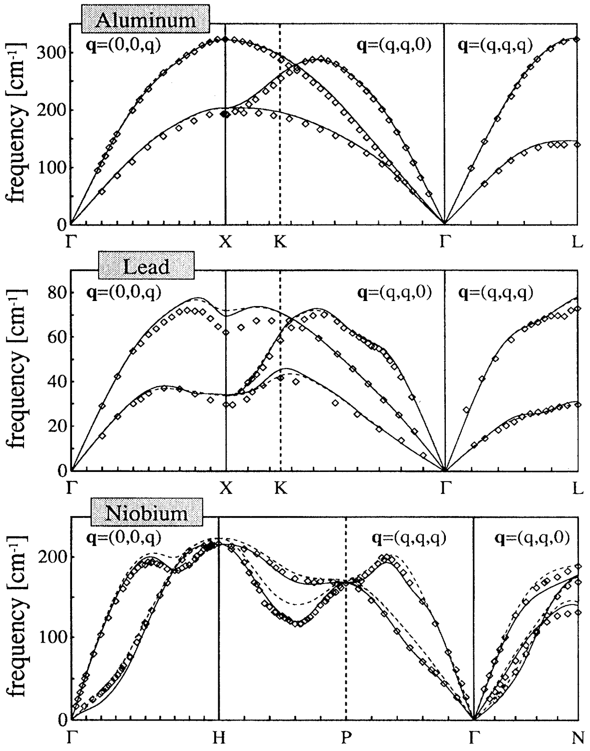

FIG. 2. Calculated phonon dispersions for fcc simple metals Al and Pb and for the bcc transition metal Nb. Solid and dashed lines refer to different smearing widths (0.3 and 0.7 eV, respectively). Experimental data are denoted by diamonds (from Refs. 20–22).

Theoretical phonon dispersions for aluminum agree perfectly with experimental data, for both values of the smearing width, confirming this to be a somewhat *easy* case. Good agreement and little (although somewhere noticeable) linewidth dependence is also found for lead. The overestimate of the phonon frequencies near zone boundaries in this case may probably be attributed, as the analogous overestimate of bulk modulus, to the neglected $5d$ Pb core electrons. Note, however, that the pronounced dip of the longitudinal branch near X, as well as the wiggle in the $[qq0]$ direction are well reproduced by the calculation (the better, the smaller the linewidth used).

The most interesting case is niobium where an important linewidth dependence of the calculated phonon dispersions is found. Again, closer agreement with experiment is obtained with the smaller smearing width. I stress that in this case the expected finite-linewidth error is very small being, from the generalization of Eq. (6) to total-energy derivatives, an order of magnitude smaller than the difference of the two dispersions displayed. All major anomalies found experimentally are reproduced: there is a crossover of the longitudinal and transverse branches in the Γ-H direction near $q=0.7$ and an additional maximum and minimum appears; the transverse branches cross near $q=0.3$ in the Γ-N direction; the $[00q]$

transverse branch is clearly below the sound velocity around $q=0.2$ and rises above for larger q values.

The dependence on smearing found in niobium is consistent with the semiempirical tight-binding calculation of Ref. 23, where a good fit to lattice vibrations in Nb was obtained but it was shown that by neglecting virtual transitions near the Fermi level very poor phonon dispersions are instead obtained. This can be explained considering that the Fermi energy in this material coincides with a large peak in the density of states and that more than 60% of points in the BZ have states within 0.5 eV from the Fermi level. Our results demonstrate that, even in the delicate case of transition metals, accurate phonon dispersions can be obtained in a simple way using density-functional perturbation theory.

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