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Linear-response calculation of electron-phonon coupling parameters

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An *ab initio* method for calculating electron-phonon coupling parameters is presented. The method is an extension of the plane-wave-based linear-response method for the calculation of lattice dynamics. Results for the mass enhancement parameter λ and the electron-phonon spectral function $\alpha^2 F(\omega)$ for Al, Pb, and Li are presented. Comparisons are made to available experimental data.

The electron-phonon interaction in metals plays an important role in a variety of experimentally accessible quantities including the enhancement of the electron mass, the phonon lifetime arising from electron-phonon scattering, electrical and thermal conductivities, and the superconducting transition temperature. The electron-phonon spectral function $\alpha^2 F(\omega)$ measures the effectiveness of phonons with energy ω to scatter electrons from one part of the Fermi surface to another part. Once it and the Coulomb pseudopotential μ^* are determined for a superconducting material, all of the thermodynamic properties of the superconductor, including the superconducting gap as a function of temperature, the transition temperature, and the discontinuity in the specific heat at T_c, can be computed.[1] In addition, transport properties of materials in the normal state can be calculated from the closely related spectral function $\alpha_{tr}^2 F(\omega)$.

The ability to accurately calculate electron-phonon coupling parameters has long been a sought-after goal. It is a formidable task requiring knowledge of the low-energy electronic excitation spectrum, the complete vibrational spectrum, and the self-consistent response of the electronic system to lattice vibrations. *Ab initio* calculations of electron-phonon coupling parameters have proceeded along two distinct lines. In the rigid ion[2] (RI) and rigid muffin tin[3] (RMT) schemes, the screened electron-phonon potential is approximated by neglecting changes in the potential everywhere except within the atomic sphere of the displaced atom. While these non-self-consistent approximations appear to be

adequate for many transition metals,[4] their validity has been questioned in some cases, especially for anisotropic or low-density-of-states materials.[5–7] An alternative to the RI and RMT methods is the frozen-phonon total-energy method.[8] In this approach, the electron-phonon matrix elements are evaluated using the self-consistently screened potentials corresponding to frozen-in phonon displacements. The primary drawback of the frozen-phonon approach is that only phonon wave vectors that are commensurate with the lattice and that correspond to reasonably sized supercells can be considered. This makes it difficult to determine accurately quantities that involve integrations over the phonon wave vector $\mathbf{q}$ throughout the Brillouin zone. These include, for example, the electron-phonon mass enhancement parameter λ, the phonon density of states $F(\omega)$, and the electron-phonon spectral function $\alpha^2 F(\omega)$.

Recently, linear-response theory within the framework of density-functional calculations has been shown to be an efficient and powerful alternative to the frozen-phonon method for calculating lattice dynamical properties of solids.[9] Atomic displacements are treated as perturbations, and the electronic response to the perturbation is calculated self-consistently. Perturbations of arbitrary wave vector $\mathbf{q}$ can be treated without using supercells. The linear-response method has been implemented with a variety of different basis sets for representing the electronic wave functions, and it has been successfully applied to the study of lattice dynamics in

a wide range of systems including semiconductors,[9,10] metals,[11–13] ferroelectrics,[14] and surfaces.[15]

In this paper, we extend the plane-wave-based density-functional linear-response method to the calculation of electron-phonon coupling parameters. A similar method based on linearized muffin-tin orbitals was recently presented in Ref. 16. The use of a plane-wave basis has the advantage of simplicity both in terms of formalism and implementation. We apply our method to the calculation of the electron-phonon spectral function $\alpha^2 F(\omega)$ for several elemental metals: Al, which is a well-studied weak-coupling superconductor; Pb, which is the prototypical strong-coupling superconductor; and Li, which is not observed to have a superconducting phase, but which earlier calculations have found to have a moderate electron-phonon mass enhancement parameter.

For notational simplicity, we consider the case of a single atom of mass M per unit cell. The electron-phonon matrix element for scattering of an electron from a Bloch state $n\mathbf{k}$ to another Bloch state $n'\mathbf{k}'$ by a phonon of frequency $\omega_{\mathbf{k}-\mathbf{k}'\nu}$ is

$$g(n\mathbf{k},n'\mathbf{k}',\nu) = \left(\frac{\hbar}{2M\omega_{\mathbf{k}-\mathbf{k}'\nu}}\right)^{1/2} \langle \psi_{n\mathbf{k}} | \hat{\epsilon}_{\mathbf{k}-\mathbf{k}'\nu} \cdot \nabla_{\mathbf{R}} V_{\text{sc}} | \psi_{n'\mathbf{k}'} \rangle, \tag{1}$$

where $\hat{\epsilon}_{\mathbf{k}-\mathbf{k}'\nu}$ is the phonon polarization vector, and $\nabla_{\mathbf{R}} V_{\text{sc}}$ is the gradient of the self-consistent potential with respect to atomic displacements. The linewidth of phonon $\mathbf{q}\nu$ arising from electron-phonon scattering is given by

$$\gamma_{\mathbf{q}\nu} = 2\pi\omega_{\mathbf{q}\nu} \sum_{n,n',\mathbf{k},\mathbf{k}'} \delta(E_{n\mathbf{k}}-E_F)\delta(E_{n'\mathbf{k}'}-E_F)$$
$$\times \delta_{\mathbf{k}-\mathbf{k}'-\mathbf{q}} |g(n\mathbf{k},n'\mathbf{k}',\nu)|^2, \tag{2}$$

where E_F is the Fermi energy.

For many applications, the quantity of interest involves a sum or average of the electron-phonon coupling strength over wave vectors throughout the Brillouin zone. For example, the spectral function $\alpha^2 F(\omega)$, which plays an important role in the strong-coupling theory of superconductivity, is given by

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{\mathbf{q}\nu} \delta(\omega-\omega_{\mathbf{q}\nu}) \frac{\gamma_{\mathbf{q}\nu}}{\hbar\omega_{\mathbf{q}\nu}}. \tag{3}$$

Here $N(E_F)$ is the electronic density of states at the Fermi level. The dimensionless electron-phonon mass enhancement parameter also involves a sum over modes and can be expressed as the first inverse frequency moment of the spectral function: $\lambda = 2\int d\omega \alpha^2 F(\omega)/\omega$.

In this work, the electronic wave functions $\psi_{n\mathbf{k}}$ and eigenvalues $E_{n\mathbf{k}}$ are calculated using the *ab initio* pseudopotential local-density formalism. The electron-ion interaction is represented by soft separable pseudopotentials,[17] and the single-particle wave functions are expanded in a plane-wave basis set. The Wigner form of the exchange and correlation functional is employed,[18] and in the case of Pb and Li, the partial core correction is used to handle the nonlinearity of the exchange and correlation interaction between the core and valence charge densities.[19] Unless otherwise indicated, the calculations are performed at lattice constants that are

determined within the local-density approximation (LDA) and that are in good agreement with the experimental values.

The phonon frequencies and polarization vectors are calculated using linear-response theory. The second-order change in the total energy, and hence the dynamical matrix, depends only on the first-order change in the electronic charge density. The linear response of the electronic density to atomic displacements is determined self-consistently by solving a Bethe-Salpeter equation as discussed in Ref. 11. We have generalized the method to include corrections for the overlap between core and valence charge densities.[12] The electron-phonon matrix elements, $g(n\mathbf{k},n'\mathbf{k}',\nu)$, are easily computed from the first-order change in the self-consistent potential.

The doubly constrained Fermi surface sums in Eq. (2) are performed using dense meshes of 1300 and 728 $\mathbf{k}$ points in the irreducible Brillouin zones (IBZ) of the fcc and bcc structures, respectively. The δ functions in energy are replaced by Gaussians of width 0.02 Ry. Because of the large number of $\mathbf{k}$ points sampled, the results are not very sensitive to the Gaussian width. Phonon wave vectors are sampled on coarser meshes of 89 and 140 points in the fcc and bcc IBZ's, respectively.

To test the accuracy of the method, we consider first the simple metal Al. The LDA gives very good structural properties for fcc Al, and the linear-response method yields phonon dispersion curves in excellent agreement with experiments throughout the Brillouin zone.[11] The $\alpha^2 F(\omega)$ for Al calculated in this work is shown in Fig. 1 (solid line), along with results from two experiments (long- and short-dashed lines).[20] Extraction of $\alpha^2 F$ from conventional McMillan-Rowell tunneling spectroscopy is not possible for Al since it is too close to an ideal BCS superconductor. Instead the experimental spectral functions shown in Fig. 1 were extracted from proximity electron tunneling data.[20] Unfortunately, the inversion of this type of tunneling data involves the introduction of additional fitting parameters characterizing the proximity layer. This introduces uncertainties in the extracted spectral functions, as evidenced by the differences between the two experimentally determined $\alpha^2 F$ functions shown in Fig. 1. The calculated spectral function agrees reasonably well with the experimental curves.

The value of the electron-phonon mass enhancement parameter determined from the first inverse-frequency moment of the calculated spectral function is $\lambda = 0.438$, which is in good agreement with other linear-response[16] and frozen-phonon calculations,[21] and with heat capacity data.[22] Within Eliashberg theory, T_c is a functional of the spectral function $\alpha^2 F(\omega)$ and the Coulomb parameter μ^*. Using the calculated $\alpha^2 F$ as input into the Eliashberg equations, we find that a μ^* of 0.162 is needed to obtain the measured transition temperature of $T_c = 1.18$ K. The same value of μ^* yields a gap equal to the experimental value of 0.180 meV. This consistency between independent fits to the gap and to T_c is a measure of the accuracy of our results for $\alpha^2 F$.

We consider next the case of the strong-coupling superconductor Pb, for which high-quality conventional tunneling data are available. From the theoretical standpoint, the importance of relativistic effects in Pb make it a more difficult system to treat than Al. The present calculations for Pb are performed in the scalar relativistic approximation. The pho-
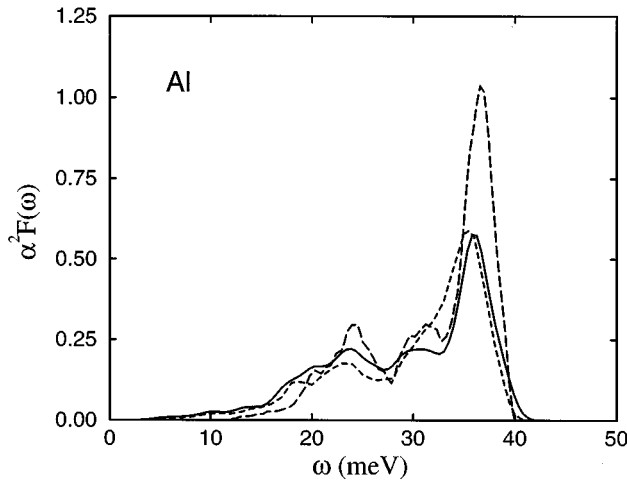
FIG. 1. Electron-phonon spectral function for Al. Results from the present calculation are represented by the solid line. Results from proximity electron tunneling spectroscopy experiments are indicated by the long- and short-dashed lines.

FIG. 3. Electron-phonon spectral function for Pb. The results based on the calculated frequencies are shown as a solid line, those based on the frequencies obtained from the force-constant fit are given by the dashed line, and the results from the inversion of tunneling data are plotted as circles.

non dispersion curves are shown in Fig. 2. Overall, there is good agreement between calculated (solid lines) and measured[23] (circles) phonon frequencies, and the calculation is able to reproduce some subtle features in the dispersion curves such as the Kohn anomaly in the longitudinal mode along the Γ to K direction. Note, however, that there are significant quantitative discrepancies between the calculated and measured frequencies for the low-energy transverse mode, especially in the regions near X and K. The minima in both the longitudinal and transverse modes at X are not observed in other fcc metals, and they suggest the presence of very-long-range forces. Indeed, as shown by the dashed curves in Fig. 2, an eighth-neighbor Born–von Karman fit[24] to the measured frequencies is unable to reproduce the dispersion near X, especially in the case of the longitudinal mode. Over the years, a number of exotic mechanisms have been proposed to explain the unusual shape of the dispersion
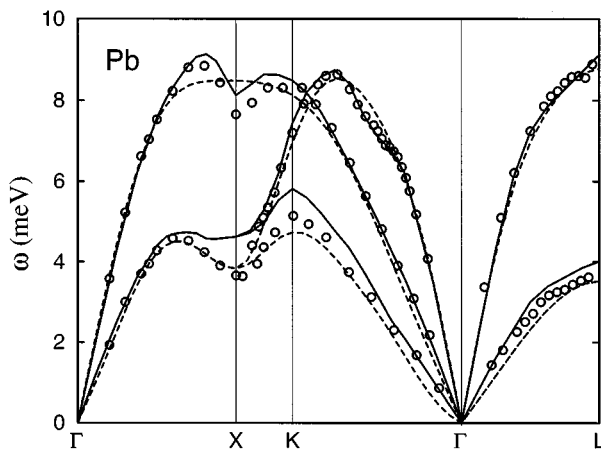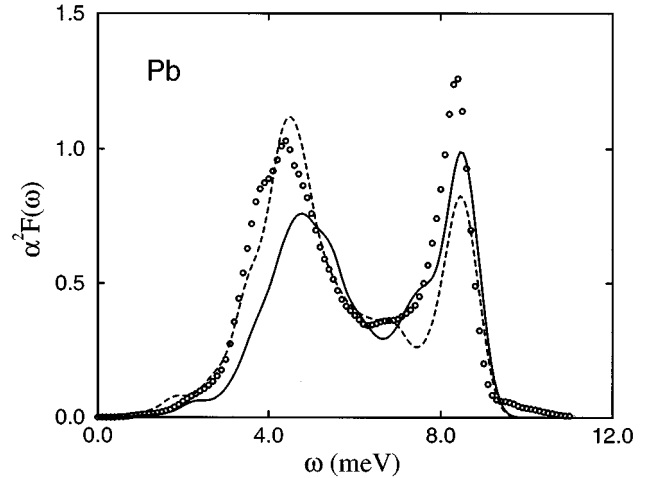

FIG. 2. Phonon dispersion curves for Pb. The solid lines connect frequencies calculated at the sampled wave vectors, and the circles indicate the experimentally measured frequencies. The dashed line is an eighth-neighbor Born–von Karman fit to the measured frequencies.

curves in Pb.[25] Our preliminary results obtained using the frozen-phonon approach indicate that differences between the calculated and measured frequencies are significantly reduced if the spin-orbit interaction is taken into account.

The Eliashberg function for Pb is plotted in Fig. 3. The calculations (solid line) yield the two-peak structure seen in the data (circles),[26] but there are differences in the peak locations and heights, especially in the case of the lower-frequency peak. The mass enhancement parameter is calculated to be $\lambda = 1.20$, which is significantly lower than the tunneling result of 1.55. These discrepancies are due in part to the errors in the calculated transverse-mode phonon frequencies. Note that the location of peaks in the spectral function is determined to a large extent by the location of peaks in the phonon density of states $F(\omega)$ [i.e., by the δ functions in frequency in Eq. (3)]. The overestimation of the transverse-mode frequencies in our calculation results in an upward shift of the lower-frequency peak in both $F(\omega)$ and $\alpha^2 F(\omega)$. We have also computed the spectral function using the phonon frequencies generated from the Born–von Karman fit to the data along with the calculated phonon linewidths.[27] The resulting $\alpha^2 F(\omega)$ is plotted as a dashed line in Fig. 3. Using the empirical force constants, which accurately describe the dispersion of the transverse modes, we obtain good agreement with the experimental results in the low-frequency regime. On the other hand, since the Born–von Karman fit does not yield accurate frequencies for the longitudinal mode, the resulting spectral function is less accurate than the first-principles result in the high-frequency regime. It appears that in order to improve our description of the electron-phonon coupling in Pb, it will be necessary to modify the computational method to take into account the relativistic spin-orbit coupling interaction.

Finally, we examine the electron-phonon coupling in bcc Li. The lack of a superconducting transition in Li has been a longstanding puzzle. Both frozen-phonon[28] and RMT (Ref. 29) calculations have suggested that the electron-phonon coupling strength in Li is similar to that in Al. This would
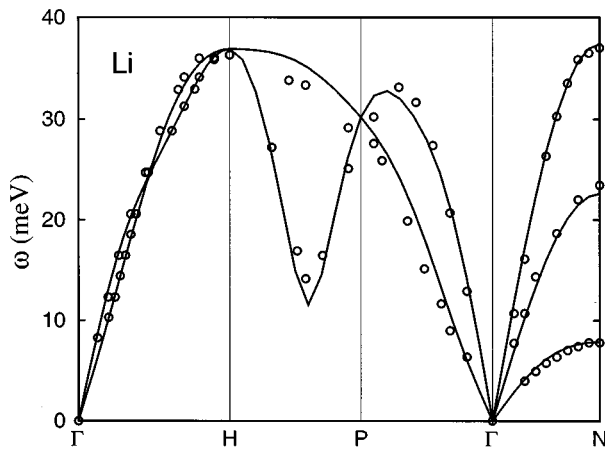
FIG. 4. Phonon dispersion curves for Li. The solid lines connect frequencies calculated at the sampled wave vectors, and the circles denote the experimentally measured frequencies.
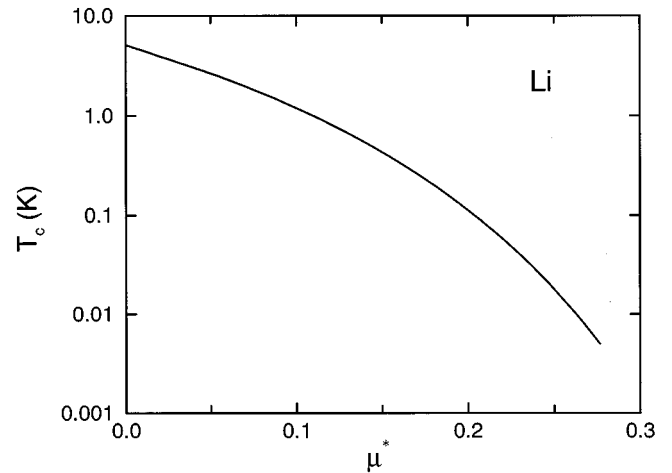

FIG. 5. Transition temperature vs Coulomb pseudopotential for Li. The transition temperature, which is plotted on a log scale, is computed as a function of μ^* using the calculated α^2F as input to the Eliashberg equations.

suggest a transition temperature on the order of 1 K if a value of $\mu^* \approx 0.15$ is assumed. Experimentally, however, no transition is observed, at least down to 6 mK.[30]

The LDA tends to underestimate the lattice constant of alkali metals. For Li, the calculated lattice constant of 3.41 Å is about 2.3% smaller than the measured value of 3.49 Å. We have performed calculations at both values of the lattice constant. The phonon frequencies calculated at the experimental lattice constant are plotted in Fig. 4. Overall, the frequencies agree well with the neutron diffraction data,[31] and subtle features such as the crossing of the longitudinal and transverse modes along the Γ to H direction are reproduced by our calculations. At the LDA lattice constant, the calculated phonon frequencies increase by up to 8%. This is consistent with recent supercell calculations carried out at the LDA lattice constant determined without including core corrections (3.35 Å).[32] In that case, a constant scale factor of about 0.86 was needed to bring the theoretical results in line with the experimental frequencies.

The mass enhancement parameters in Li are calculated to be $\lambda = 0.45$ and 0.51 at the experimental and (core-corrected) LDA lattice constants, respectively. These values are similar to results obtained earlier within the RMT approximation or using the frozen-phonon method. Using our result for $\alpha^2F(\omega)$ as input into the Eliashberg equations, we have calculated the superconducting transition temperature as a function of the Coulomb pseudopotential. As shown in Fig. 5, an unphysically large value of $\mu^* \approx 0.28$ is required in order to suppress T_c below the experimental limit. The observed absence of superconductivity in Li therefore remains an open problem. The resolution of this puzzle may

require consideration of the low-temperature crystal structure of Li, in which the electron-phonon interaction may be weaker,[28] as well as the role of many-body interactions such as electronic correlations and spin fluctuations.[33]

In summary, we have presented an accurate and efficient method for calculating electron-phonon coupling parameters from first principles. The electronic response to the atomic displacements is determined self-consistently and phonons of arbitrary wave vector can be treated. This method, which is an extension of the plane-wave-based linear-response method for calculating lattice dynamics, is applicable to a wide range of materials. Results for the mass enhancement parameter λ and the electron-phonon spectral function $\alpha^2F(\omega)$ for Al are in excellent agreement with available experimental data. In the case of Pb, there are larger discrepancies between our results and the tunneling data, but we attribute this to the neglect of the spin-orbit interaction in our calculations. The present results for the mass enhancement factor in bcc Li are in accord with earlier calculations, indicating that further theoretical investigations are needed to resolve the question of the absence of a superconducting transition in this material.

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