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Ab initio phonon quantities of simple metals from Hartree-Fock cluster techniques

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It is shown that traditional Hartree-Fock total-energy cluster calculations applied near or outside of what is believed to be the limit of their applicability can provide unexpectedly good agreement with some measured phonon quantities. A conceptually and computationally simple framework is presented for *ab initio* lattice-dynamical calculations of simple metals. Representative results for Li, Be, and Na demonstrate the applicability and the limitations of the present scheme.

In contrast to electronic-band-structure calculations, truly *ab initio* phonon-spectrum calculations for simple metals have appeared only during the last few years and in a rather limited number.[1] The situation for transition metals,[2] which will not be considered here, is even worse. One of the main computational difficulties is that the relatively small phonon frequencies are usually calculated as differences between two very large total-energy values, with uncertainties of the same order as (or sometimes larger than) the phonon frequencies themselves. The very large uncertainties in the phonon calculations stem from complicated matrix elements and sums which must be done in reciprocal space for both a periodically strained crystal (frozen-in phonon) and the original crystal. Alternative approaches use perturbation theory for the energy difference, with equally complicated matrix elements and inclusion of several (third and even fourth) orders of perturbation terms.[1,2] On the other hand, in several very important situations (for instance, in calculating the superconducting transition temperature or the Debye temperature, or even a few high-symmetry phonon frequencies), only a limited but very compact amount of information is required to predict very important characteristics of the material truly *ab initio*. The present approach, invoked, in particular, for this type of situation, attempts to circumvent most of the problems mentioned above by working in real space with a drastically limited number of crystal cells and by narrowing its predictions by concentrating on a restricted but judiciously chosen amount of information. In this approach, a small atomic cluster comprised of a reference atom and its nearest and, at least, next-nearest, neighbors is used to simulate the infinite crystal. Then, traditional *ab initio* Hartree-Fock cluster-computational techniques can provide total-energy differences as a function of atomic displacements from equilibrium. The total-energy differences (not the total energies), in this unusual and rather unorthodox method yield either average phonon quantities (such as the Debye temperature) or even particular high-symmetry phonon frequencies in the "frozen-phonon" approximation.[1,2] Although completely outside the scope of the present paper, other low-symmetry phonon frequencies could, in principle, be calculated by fitting the parameters of a particular force-constant model to the *ab initio*—calculated high-symmetry phonon frequencies.[1–3] This apparently oversimplified approach turns out, as will be illustrated below, to be able to produce good quantitative results at relatively minimal computational cost and with the added advantage of simplicity and transparency in the calculations.

Several obviously legitimate and fundamental questions concerning the suitability of small-cluster techniques for such types of calculations should be addressed before the results of the calculation, which can justify the choice *a posteriori,* are presented. There is apparently a contradiction between the nature of the infinitely extended phonons in simple crystalline metals and small-cluster techniques, which are designed by definition for small systems or local properties of infinite systems,[4] since neither the phonons nor the metallic bond are local in nature. There is no obvious answer to this fundamental conceptual contradiction. Some answer could perhaps be visualized within the spirit of the tight-binding (TB) formalism (whose validity is also questionable for metals, but at a completely different level of objection). In the TB formalism a few parameters determined with a limited number of atomic neighbors (first and second, or even third nearest neighbors), and mere use of the existence of long-range order can determine the complete electronic band structure. The concept of the phonon is only used with reference to the infinite system, whereas in the model a frozen displacement pattern enters the total-energy differences. Since only differences of total energies and not absolute values (for which an enormous discrepancy with experiment may exist[5]) enter the calculation, it seems reasonable to assume that the more-distant-neighbor effects tend to cancel out. This looks like a very plausible conjecture, especially for the force constants and average phonon frequencies which are determined from the second derivatives of the total-energy curve. These derivatives evaluated at the equilibrium distance are dominated by the direct orbital overlap and the repulsive interaction.

Generally speaking, for elemental crystals, the zeroth- and first-order perturbation contributions of the single-particle energies to the dynamical matrix, D_0+D_1 (in standard notation[2]), give rise to essentially short-range forces which do not much extend beyond the range of *direct orbital* overlap.[2] The remaining (second-order) term, D_2, apparently not accounted for here, includes the long-range forces which are responsible for the finer structure of the dispersion curves and the phonon

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anomalies.

Much of the success of the present calculations, as will be illustrated below, should be recognized as being due to the choice of the unrestricted-hartree-Fock (UHF) method for the description of the metallic-cluster Hamiltonian. The UHF method has been judged earlier as the most accurate available simple Hartree-Fock—type method for metal clusters.[5,6] The lack of correlation, however, presents another open problem which was addressed implicitly above and which can, in principle, be solved by configuration-interaction (CI) or perturbation techniques. The use of these techniques, however, besides their controversial effectiveness,[4–6] would destroy the simplicity, the transparency, and the low computational cost of the calculations. More details about using the UHF method in cluster calculations can be found elsewhere.[4,5] The present clusters, simulating the bcc crystal structure for Li and Na and the hcp for Be, include first- and second-nearest neighbors. The basis functions used in the calculation are listed in Table I. Some of the results of the present calculation are summarized in Table II in obvious notation. These results are obtained by elementary methods from the total-energy—difference curves of Fig. 1 for the three representative simple metals Li, Be, and Na.

The average phonon frequency (or, more precisely, the average force constant) $M\langle\omega^2\rangle$ was calculated directly as the second derivative of the binding-energy curve at the equilibrium spacing. The bulk modulus B was calculated through the relation

$$B=\frac{1}{V}\left[\frac{\partial^2 U}{\partial V^2}\right]_0 \tag{1}$$

from the equilibrium nearest-neighbor distance R_0 and the second derivative of the binding energy curve, $U=U(R)$.

This last step[7] involves an elementary substitution of the atomic volume V in terms of the nearest-neighbor distance R. Finally, the Debye temperature Θ_D was simply obtained by equating, as usual,[8] the average phonon frequency $\langle\omega^2\rangle$ with $\frac{1}{2}\Theta_D^2$.

The agreement with experiment in Table II, as has been already explained, is considerably good in view of the approximations and even oversimplifications of the model discussed earlier. The exceptionally good agreement for Be could be mainly attributed, as was illustrated earlier,[9] to its largest departure from free-electron behavior. This departure renders Be more amenable to a Hartree-Fock cluster description than the others.

To get more information out of the present scheme, we must move to more uncertain grounds, pushing the limits of the method too far. However, even if only to satisfy our curiosity, it is worth finding out if the results we can get do make any sense. Thus, in addition to the average phonon quantities displayed in Table II, single-phonon frequencies can be calculated, as mentioned earlier, for high-symmetry phonons. Within the frozen-phonon approximation,[1,2] the frozen atomic displacements corresponding to the phonon under consideration are established by group theory and the total energies for these displaced configurations are calculated as a function of the displacement u. The fitting of these total energies, $E(u)$, by a polynomial in u of the form

$$E(u)-E(0)=\tfrac{1}{2}Au^2+\tfrac{1}{3}Bu^3+\tfrac{1}{4}Cu^4+\cdots\ , \tag{2}$$

yields the coefficients $A,B,\ldots,$ providing not only the harmonic frequencies but also higher anharmonic contributions. The constants B and C (A is the $M\langle\omega^2\rangle$ of Table II) for Li, Be, and Na for a uniform displacement u, obtained from the total-energy curves of Fig. 1, are listed in Table III. Although large uncertainties exist (the quoted uncertainties reflect only uncertainties due to the fitting process), especially for the quartic term, the numbers do make some sense. The reduced anharmonicity of Li, compared with Na and taking into account its much smaller mass, is a real characteristic confirmed by more

TABLE I. Gaussian-type orbital basis set used in the calculations. Exponents (Expon.) and coefficients (Coeff.) of contracted Gaussians.

Orbital	Li		Be		Na	
type	Expon.	Coeff.	Expon.	Coeff.	Expon.	Coeff.
s	266.274 690	0.125 59	547.083 000	0.013 16	12 262.838 000	0.005 75
	40.048 140	0.924 98	81.602 300	0.992 69	1 836.780 200	0.044 36
	9.028 710	1.000 000	18.237 800	0.299 53	414.620 000	0.223 23
	2.433 000	1.000 000	4.940 190	0.757 55	115.111 780	0.801 30
	0.710 630	1.000 000	1.474 380	1.000 000	36.166 133	1.000 000
	0.047 790	1.000 000	0.177 800	1.000 000	12.162 366	1.000 000
			0.059 380	1.000 000	2.281 458	1.000 000
					0.721 455	1.000 000
					0.044 188	1.000 000
p	0.080 000	0.589 69	0.509 000	0.173 56	80.830 968	0.013 84
	0.020 000	0.531 18	0.118 000	0.895 50	18.510 942	0.091 27
			0.065 000	1.000 00	5.536 469	0.298 26
					1.761 295	0.494 60
					0.536 547	0.344 95
					0.085 000	1.000 000

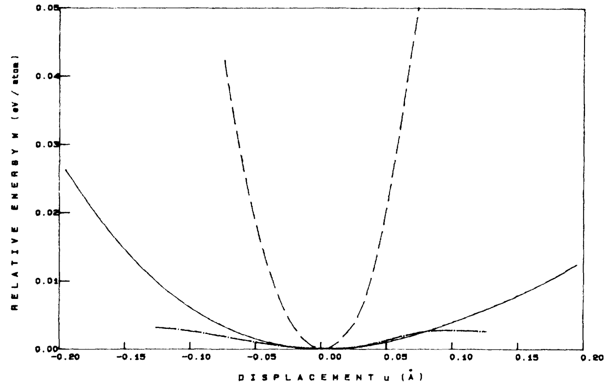

FIG. 1. Relative energy $W = E(u) - E(0)$ vs displacement from equilibrium, u. Solid line represents the results for Li, long-dashed line gives the results for Be, and the dotted-dashed line represents the results for Na.

accurate pseudopotential calculations.[10] This is due to the strong ion-ion interaction in Li, which has a relatively soft repulsive core. The choice of the finite values of u for which $E(u)$ is calculated is determined mainly by two requirements: First, they have to be sufficiently large to produce an energy numerically distinguishable from the undisplaced energy $E(0)$. At the same time, the displacements should cover a range which includes typical amplitudes of the real vibrations in the crystal. These can be obtained by the Debye formula[1,11]

$$\langle u^2 \rangle = \frac{9\hbar^2 T}{M k_B \Theta_D^2} ,$$

where T is the temperature, M the mass, and $\hbar$ and k_B are Planck's and Boltzmann's constants, respectively. This frozen-phonon procedure has been applied as the most stringent test of the present scheme for the (111) zone-boundary LA mode of Li (for which displacements in neighboring cells are out of phase by 180°) with the results

$$A = 2.2 \pm 0.1 \text{ eV/Å}^2$$

and

$$B = -8.6 \pm 1 \text{ eV/Å}^2 ,$$

and with harmonic frequency

TABLE III. Cubic (B) and quartic (C) constants in the total-energy expansion of Eq. (2) (see text). The constant a_0 in the third column is the equilibrium nearest-neighbor distance.

	B (eV/Å^3)	C (eV/Å^4)	$\frac{Ba_0}{M\langle\omega^2\rangle}$
Li	$-1.02 \pm 10\%$	$-0.32 \pm 30\%$	3.7
Be	$11.80 \pm 10\%$	$280.0 \pm 45\%$	1.6
Na	$-0.32 \pm 15\%$	$-9.0 \pm 35\%$	3.5

$$\omega = 36.5 \pm 2 \text{ meV} ,$$

in excellent agreement with the experimental value,

$$\omega_{\text{expt}} = 37.5 \pm 1 \text{ meV} ,$$

of Beg and Nielsen,[12] for $T = 110$ K. No doubt this excellent agreement, in view of the drastic approximations involved, must be due, in part, to fortuitous cancellations and, in part, perhaps to the fact that the dispersion curves of Li, which are almost featureless without much finer structure, are dominated by the direct ion-ion interactions. To extend this method to heavier elements, atomic pseudopotentials[13] should be used to eliminate the inner-core electrons. However, preliminary work for Al using Topiol's pseudopotential[13] could not reproduce the quality of the results for Li above, or the results in Table II. It is an as-yet-unsettled question if this reflects a deficiency of the pseudopotential or of the method of calculation itself. The problem of the proper choice of the atomic pseudopotential and its implications for the type of calculations presented here is currently under investigation.

Although the very good agreement with experiment for the results already presented is very impressive and is perhaps indicative of the maximum possible precision that could be achieved in some "simple cases," it is not the main objective of this work. The proposed scheme aims at relatively gross features of the phonon and electronic spectrum obtained at minimal computational cost and maximum possible transparency of the calculations. In this respect, standard corrections[4] which are straightforward but not computationally economical have not been considered here. Likewise, applications to heavier elements and compounds will be considered in future work. These applications, especially for materials with high technological importance, will test the practical significance of the proposed simple method.

TABLE II. Comparison of calculated (calc.) and experimental (expt.) phonon quantities.

Physical quantity	Bulk modulus (B) (10^{12} dyn/cm^2)		$M\langle\omega^2\rangle$ (eV/Å^2)		Debye temperature (Θ_D) (K)	
Material	This calc.	Expt.[a]	This calc.	Expt.[b]	This calc.	Expt.[a]
Li	0.099	0.116	0.81	0.73	359	344
Be	0.966	1.003	16.80	16.47	1441	1440
Na	0.056	0.068	0.61	0.52	172	158

[a] Values quoted in Ref. 7.
[b] Values from Ref. 8.

[1] For a recent review and earlier references on first-principles lattice dynamics of simple metals, see, for instance, G. Grimvall, in *Ab Initio Calculation of Phonon Spectra,* edited by J. T. Devreese, V. E. Van Doren, and P. E. Van Camp (Plenum, New York, 1983); see also K. Kunc and R. M. Martin, *ibid*., and J. Ashkenazi and M. Dacorogua, *ibid*.

[2] For a review and further references on *ab initio* lattice dynamics of transition metals, see W. Weber, in *Electronic Structure of Complex Systems,* edited by P. Phariseau and W. M. Temmerman, NATO Advanced Study Institute Series B (Plenum, New York, 1984), Vol. 113.

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