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VIBRATIONAL FREQUENCIES VIA FROZEN PHONONS *

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Abstract.- We have used a first principles linear combination of atomic orbitals (LCAO) method to calculate the total ground state energy for crystals of Si, Nb and Mo involving lattice distortions. From these calculations the equilibrium lattice constant, cohesive energy, and bulk modulus as well as the vibrational frequencies for selected phonons were determined.

1. Introduction.- Band theoretical methods are finding increased use in the study of electronic response to lattice distortion (caused by compression, stress, phonons, etc.). These techniques provide a tool for accurately calculating from first principles the frequency and charge density response for phonons at selected wavevectors. These techniques have already been applied to Si with considerable success using the pseudopotential [1,2] and LCAO [3] methods. Here we briefly present our LCAO method and our results for Si and then discuss the application of the method to metals giving preliminary results for Nb and Mo.

2. Method.- We have used the local density approximation for exchange and correlation[4] combined with a first principles tight binding method, the details of which have been described elsewhere.[3,5,6] The method employs an atomic basis composed of Gaussian functions which allow easy analytic evaluation of all three center integrals. The potential is expanded in a second Gaussian basis set and is general (i.e., no muffin-tin approximation is made). The calculations are iterated until the total energy is stable to seven significant digits. Absolute errors, for example those associated with the approximate treatment of exchange and correlation, are of course larger, but they are expected to cancel since we consider only energy differences.

3. Application to Si.- Si was used as a test case to first avoid complications caused by a Fermi surface. Using the frozen core approximation the total energy was evaluated at eight values of the lattice constant and least squares fit with

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a fourth order polynomial. The corresponding equilibrium lattice constant, bulk modulus and cohesive energy are listed in Table 1. The total energy was also calculated as a function of displacement for lattice distortions corresponding to particular normal vibrational modes. These yield essentially classical potential wells whose curvature gives the phonon force constant or frequency. The frequencies for the transverse optic phonon at Γ [TO(Γ)] and the transverse accoustic phonon at X [TA(X)] are also listed in Table 1. There is good agreement with experiment, and the detailed analysis of the contributions to the total energy agree with previous studies.[1,2] The charge density for the TO(Γ) phonon is shown in Figure 1.

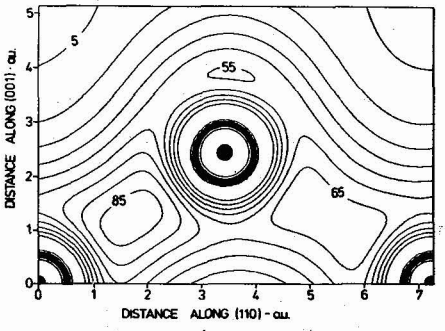

Fig. 1 : The charge density in the (1$\bar{1}$0) plane for the lattice distortion corresponding to the TO(Γ) phonon with a displacement of -0.137Å along the (111) direction. (atomic units x 10^3).

4. Application To Metals.- For metals small distortions of the lattice cause changes in the band occupation near the Fermi level which must be accounted for in calculating changes in total energy. Indeed such effects frequently give rise to phonon anomalies in transition metals.[7] One approach for metals is to simply keep increasing the number of $\vec{k}$ points sampled until convergence is reached, however, this is costly and not necessary. Our approach has been to divide the irreducible Brillouin zone into a number of large tetrahedrons (32 for the H point phonon in Nb and Mo) and take the center of mass $\vec{k}$ vectors as a sample grid. At each iteration a tight binding (TB) fit (see Ref. 7) is made to the eigenvalues on this grid and is used to determine an accurate Fermi energy and surface. The occupied volume as determined by the TB fit using 64 smaller tetrahedrons inside eacn large one is used to weight the $\vec{k}$ points. Calculations using a mixed basis pseudopotential technique for phonons in Nb and Mo also confirm the importance of carefully weighting the $\vec{k}$ points.[8]

The equilibrium lattice constant, bulk modulus and cohesive energy are listed in the table and again indicate the method is functioning well for the evaluation of bulk properties. To date we have only tested the method for the H-point phonon in Nb and Mo with the results listed in the table. This phonon in Mo is particularly anomalous as a result of a nesting feature in the Fermi surface.[7] The accurate modeling of changes in the Fermi surface as provided by the TB fit was required before the theoretical frequency was reduced from ∿9Thz to 5.7 THz. The frequency was determined by fitting (rms error = 10^{-6} Ry/atom)

a parabola to the energy calculated for displacements of 0.064Å, 0.078Å, and 0.092Å, which are comparable to the displacement caused by the real phonon. Very small displacements led to numerical problems because of the linear interpolation used inside the small tetrahedrons, and much larger displacements caused previously unoccupied portions of bands to dip below the Fermi level, giving rise to anharmonic or non-parabolic behavior in the total energy vs displacement curve.

5. Conclusion.- Our encouraging results suggest that modern band theory techniques are capable of becoming a useful tool in studying the details of electronic response to certain high symmetry lattice distortions.

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Table 1. Calculated and experimental properties

		a Lattice Constant (a. u.)	B Bulk Modulus (Mbar)	Cohesive Energy (eV/atom)	Phonon Frequency (THz)
Si	calc.	10.40	0.89	4.92	4.9 TA(X), 15.0 TO(Γ)
	exp.	10.26	0.99	4.84	4.5 TA(X), 15.4. TO(Γ)
Nb	calc.	6.32	1.62	6.63	6.6* H point
	exp.	6.23	1.74	7.57	6.4
Mo	calc.	5.99	2.57	6.28	5.7 H point
	exp.	5.95	2.63	6.82	5.5

*This is a preliminary value based on a fewer number of small tetrahedrons and both large and zero displacements so that it is less precise than the value for Mo (see text).

7. References.-

1. H. Wendel and R. M. Martin Phys. Rev. B19, 5251 (1979).
2. M. T. Yin and M. L. Cohen Phys. Rev. Lett. 45, 1004 (1980).
3. B. N. Harmon, W. Weber, and D. R. Hamann Phys. Rev. B (in press).
4. The approximate correlation functional was obtained from E. Wigner, Phys. Rev. 46, 1002 (1934).
5. H. Sambe and R. H. Felton, J. Chem. Phys. 62, 1122 (1975).
6. J. A. Appelbaum and D. R. Hamann, p. 111, Transition Metals, Eds. M. J. G. Lee, J. M. Perz and E. Fawcett (Inst. of Physics, Bristol, 1978), and P. J. Feibelmann, J. A. Appelbaum and D. R. Hamann, Phys. Rev. B20, 1433 (1979).
7. C. M. Varma and W. Weber, Phys. Rev. B19, 6142 (1979).
8. K.-M. Ho, private communication.