Elastic constants and phonon frequencies of Si calculated by a fast full-potential linear-muffin-tin-orbital method

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A new approach for including full-potential terms in a linear-muffin-tin-orbital calculation is presented. The implementation for crystals leads to a method which is at the same time fast and accurate. Calculated elastic constants and phonon frequencies for Si agree well with experiment.

I. INTRODUCTION

During the last decade, the linear-muffin-tin-orbital (LMTO) method^{1,2} for solving the one-particle Schrödinger equation self-consistently has become very popular for the calculation of the electronic structure of crystalline systems, and modifications of it have been applied successfully to molecules.^{3,4} The LMTO method combines the following advantages: (1) It uses a minimal basis, which leads to high efficiency and makes calculations possible for large unit cells; (2) it treats all elements in the same way, so that d and f metals as well as atoms with a large number of core states can be considered; (3) it is very accurate, due to the augmentation procedure which gives the wave function the correct shape near the nucleii: (4) it uses atom-centered basis functions of welldefined angular momentum, which makes the calculated properties transparent.

Because of its accuracy and efficiency in handling large unit cells, one expects that the LMTO method is well suited for first-principles self-consistent frozen-phonon calculations or for the Car-Parrinello combined localdensity molecular-dynamics approach.⁵ However, the potential approximation which leads to the efficiency of the standard solid-state LMTO method (the atomicsphere approximation or ASA) disregards the symmetrybreaking terms which are crucial for energies of frozen phonons and the forces on the nucleii. On the other hand, it has been shown for molecules and recently for crystals⁶ that good results can be obtained using the LMTO basis set if all potential terms are evaluated correctly. In these calculations, the overlapping atomic spheres were shrunk to nonoverlapping muffin-tin spheres. The potential matrix elements were then split up into contributions from the atomic spheres and from the complicated interstitial region. Whereas the former are straightforward to evaluate by means of expansions in spherical harmonics, the interstitial contributions are quite difficult to calculate and are treated in different ways by the various methods. The techniques used include numerical integration methods 7,3,4 and the expansion of all interstitial quantities in plane waves⁶ or in spherical Hankel functions and time-consuming evaluation of three-center integrals.⁸ In each case, the evaluation of the interstitial potential matrix elements is the dominating factor for the speed of the method and for the number of atoms which can be treated simultaneously, both being reduced by at least an order of magnitude relative to the standard LMTO-ASA method.

In this paper a new and very efficient approach for evaluating the matrix elements of the interstitial potential in a full-potential LMTO method is presented. As in Ref. 8, Hankel functions are used to represent interstitial quantities, but here the three-center integrals are reduced to linear combinations of two-center integrals (which are easy to evaluate analytically) by numerical means. An advantage of the method is that no plane waves are required throughout, so that the applicability of the LMTO basis to both periodic and nonperiodic systems is retained. Below, a specific implementation for crystals is described whose computing speed is close to that of the standard LMTO-ASA method. Calculations for the optical phonon at Γ in Si and diamond reproduce the accurate results obtained by the more time-consuming fullpotential LMTO method (using plane-wave expansions) of Weyrich.⁶ Finally, calculated elastic constants and phonon frequencies at Γ and X for Si agree well with the experimental values.

II. DESCRIPTION OF THE METHOD

The task is to calculate the interstitial-potential matrix elements

$$V_{\nu L\nu'L'}^{I} = \int_{I} \chi_{\nu L}^{*}(\mathbf{x}) V_{I}(\mathbf{x}) \chi_{\nu'L'}(\mathbf{x}) d\mathbf{x} , \qquad (2.1)$$

where I is the interstitial region, V_I is the interstitial potential, and $\chi_{\nu L}$ is a LMTO envelope function centered at site ν with angular momentum L. [Upper-case letters L and K are abbreviations for the angular-momentum quantum numbers (l, m_L) and (k, m_K) .] A related problem is to bring into a tractable form the output charge density in the interstitial region, which is given as a linear combination of the products $\chi_{\nu L}^* \chi_{\nu L'}$. This second problem is frequently solved by fitting a linear combination of atom-centered Hankel functions of negative energy to the charge density.^{4,8} It seems reasonable that the separate contributions can be represented in a similar way, albeit with a higher angular-momentum cutoff because they vary more strongly. Thus, coefficients $A_{\mu K\alpha}^{\nu L\nu' L'}$ are sought with the property that, throughout the interstitial region,

38 1537

$$\chi^*_{\nu L}(\mathbf{x})\chi_{\nu' L'}(\mathbf{x}) \approx \sum_{\mu,K,\alpha} A^{\nu L' L' L'}_{\mu K \alpha} H_{\mu K \alpha}(\mathbf{x}) , \qquad (2.2)$$

with

$$H_{\mu K \alpha}(\mathbf{x}) = h_k(i\lambda_\alpha | \mathbf{x} - \mathbf{R}_\mu |) Y_K((\mathbf{x} - \mathbf{R}_\mu) / | \mathbf{x} - \mathbf{R}_\mu |) ,$$
(2.3)

i.e., the $H_{\mu K\alpha}$ are of the same general form as the LMTO envelope functions themselves. For crystals, the latter are k-dependent Bloch sums of Hankel functions whose kinetic energy is usually chosen to be zero and the $H_{\mu K\alpha}$ are replaced by periodic Bloch sums. In general, functions of at least two different decays, λ_{α} , must be included in the fit so that the localization can vary.

Equation (2.2) is the central relation of the present approach. Since no analytical theorem of this form is known, the expansion must be obtained by some numerical means. Leaving this point for later, we consider the result when (2.2) is substituted in (2.1). The matrix element then reduces to a linear combination of integrals of the functions $H_{\mu K \alpha}$ times the interstitial potential. Next, it is assumed that the interstitial potential itself is expanded in functions of the type (2.3). This is often done for self-consistent molecular calculations^{4,8} and is connected with the fact that the Poisson equation can be solved analytically in the Hankel-function basis. The desired interstitial integral has now been expressed as a linear combination of integrals of products of pairs of Hankel functions; i.e., the three-center integral has been reduced to a sum of two-center integrals. Using Gauss's theorem and the fact that the $H_{\mu K \alpha}$ are eigenfunctions of the Laplace operator, it is straightforward to express the two-center integrals as surface integrals over the spheres. These are easy to evaluate by means of standard structure-constant expansions. From the preceding, it is concluded that once an accurate enough expansion of the form (2.2) is available, the interstitial potential matrix elements can be evaluated in a straightforward manner. As an additional bonus, (2.2) can be used to represent the output charge density as a linear combination of $H_{\mu Ka}$, thereby solving the second problem stated above.

The crucial step in this procedure is to determine the coefficients in the expansion (2.2). Various approaches could be pursued, but the following leads to a very fast method for the case that the interstitial region is not too large. This is the case for crystals if extra empty spheres are introduced for loosely-packed systems in the usual way.⁹ Then every point in the interstitial region lies close to one or more atomic spheres. This, together with the fact that the products are smooth functions, suggests that a suitable representation can be obtained by interpolating between the surfaces of the spheres. This can be done by adjusting the coefficients in (2.2) until the best fit of the values and slopes of the right-hand side to the values and

slopes of the product is obtained on all spheres simultaneously. In effect, the approach described here assumes that for any smooth function $f(\mathbf{x})$, its values inside the interstitial region are defined by its values $f_{\mu K}$ and slopes $f'_{\mu K}$ on the sphere surfaces. Once this is postulated, the integral of $f(\mathbf{x})$ times the interstitial potential must be a linear functional of the $f_{\mu K}$ and $f'_{\mu K}$. To determine the functional in practice, it is useful to construct special linear combinations $U_{\mu K}$ and $S_{\mu K}$ of the $H_{\mu K \alpha}$ which can be denoted as functions of "pure value" and "pure slope," respectively. $U_{\mu K}$ is defined as that linear combination which has all values and slopes zero, except for the Kth value on the μ th atomic sphere, which is equal to one. Similarly, $S_{\mu K}$ has only the (μ, K) th slope equal to one. It is useful to make the number of conditions in the fit equal to the number of unknowns by choosing the angular-momentum cutoffs for the expansion and for the conditions equal and by including functions for exactly two different λ_{α} -values in the set of $H_{\mu K\alpha}$; then the number of $U_{\mu K}, S_{\mu K}$ is equal to the number of all $H_{\mu K\alpha}$ and the two sets span the same space. Then the fit to $f(\mathbf{x})$ can be written down immediately as

$$\widetilde{f}(\mathbf{x}) = \sum_{\mu,K} \left\{ f_{\mu K} U_{\mu K}(\mathbf{x}) + f'_{\mu K} S_{\mu K}(\mathbf{x}) \right\} , \qquad (2.4)$$

so that the corresponding integral is given as

$$\int_{I} \tilde{f}(\mathbf{x}) V_{I}(\mathbf{x}) d\mathbf{x} = \sum_{\mu K} \left\{ f_{\mu K} \alpha_{\mu K} + f'_{\mu K} \beta_{\mu K} \right\} , \qquad (2.5)$$

with

$$\alpha_{\mu K} = \int_{I} U_{\mu K}(\mathbf{x}) V_{I}(\mathbf{x}) d\mathbf{x}, \quad \beta_{\mu K} = \int_{I} S_{\mu K}(\mathbf{x}) V_{I}(\mathbf{x}) d\mathbf{x} .$$
(2.6)

Equation (2.5) can be considered as a special, problemadapted quadrature formula; the functions $H_{\mu K\alpha}$ then play the role of test functions for which the formula has been constructed to give the exact result.

To apply (2.5) for $f = \chi_{\nu L}^* \chi_{\nu L'}$, Clebsch-Gordan coefficients are used to multiply out the values and slopes of f from those of $\chi_{\nu L}, \chi_{\nu' L'}$ on each sphere. Substitution in (2.5) then gives the interstitial integral (2.1) as a quadratic form in the values and slopes of the two envelope functions. A final linear transformation can be done to express the integral as a quadratic form in the coefficients $a_{\mu K}^{\nu L}, b_{\mu K}^{\nu L}$ in the one-center expansions of $\chi_{\nu L}$ around the different sites. That is, the one-center expansion near site μ is

$$\chi_{\nu L}(\mathbf{x}) = \sum_{K} \left\{ a_{\mu K}^{\nu L} H_{\mu K}(\mathbf{x}) + b_{\mu K}^{\nu L} J_{\mu K}(\mathbf{x}) \right\} , \qquad (2.7)$$

where $H_{\mu K}$ is given as in (2.3) and $J_{\mu K}$ is defined similarly for the spherical Bessel function, both at the same kinetic energy as $\chi_{\nu L}$. The final result for the interstitial matrix element then is

$$\int_{I} \chi_{\nu L}^{*}(\mathbf{x}) V_{I}(\mathbf{x}) \chi_{\nu' L'}(\mathbf{x}) d\mathbf{x} = \sum_{\mu, K, K'} \left\{ a_{\mu K}^{\nu L} D_{\mu K K'}^{HH} a_{\mu K'}^{\nu L'} + a_{\mu K}^{\nu L} D_{\mu K K'}^{HJ} b_{\mu K'}^{\nu' L'} + b_{\mu K}^{\nu L} D_{\mu K K'}^{H} a_{\mu K'}^{\nu' L'} + b_{\mu K}^{\nu L} D_{\mu K K'}^{H} b_{\mu K'}^{\nu' L'} \right\}.$$
(2.8)

The matrices $D_{\mu KK'}$ are all independent of **k** and are obtained by straightforward but somewhat tedious linear algebra from the coefficients in (2.5). This expression for the integrals has the advantage that the k-dependent quantities $a_{\mu K}^{\nu L}, b_{\mu K}^{\nu L}$ are already available in conventional LMTO calculations as Kronecker deltas or structure constants. If the recently developed LMTO tight-binding representation is used,¹⁰ the quantities may be given as Bloch sums of simple expressions involving the tightbinding structure constants.

Note that the evaluation of the nonspherical potential terms inside the atomic spheres leads to an expression of the same form as (2.7), with the $D_{\mu KK'}$ replaced by integrals which give the coupling between the augmented "heads" and "tails" on the μ th sphere. Thus, once the matrices in (2.7) have been calculated, the corrections to the muffin-tin potential from inside the spheres and from the interstitial can be treated together. The effort for the full-potential calculation has in this way been reduced to its minimum, namely that of evaluating the effect of the nonspherical potential in the spheres. The effort in calculating the matrices in (2.7) is mainly that of constructing $U_{\mu K}$ and $S_{\mu K}$. This involves the inversion of a matrix with dimension equal to the number of functions $H_{\mu K\alpha}$ included. If the angular momentum cutoff for the interstitial fits is taken as 4, and if two decays are included, the dimension is the number of atomic spheres per unit cell multiplied by 50. While this step can be time consuming, it should be emphasized that it depends only on the positions and radii of the spheres, and does not depend on the k vector or the potential. Thus it can be done once and for all in the beginning of a calculation. Therefore, this method for finding the coefficients in the expansion (2.2) is suitable for self-consistent computations for fixed atomic positions. In this case, the setup time is no more than 10% of the total time used. However, for the Car-Parrinello method a different strategy will be needed based on the arguments following Eqs. (2.1) - (2.3).

III. RESULTS

After a setup program is written to do the fitting to the values and slopes on the sphere surfaces and to construct the functions $U_{\mu K}$ and $S_{\mu K}$, it is a relatively minor modification to introduce the full-potential terms into an existing LMTO program as described above. For a self-consistent calculation, it is necessary to compute the local-density potential for the output charge density. In the Hankel-function charge-density representation, the electrostatic potential can be evaluated analytically. The

exchange-correlation terms are treated by interpolating between the spheres in the same way as the envelope products. Since all interstitial quantities are now given as multicenter expansions in Hankel functions, the integrals for the total energy are straightforward to calculate. As a test for the accuracy of the numerically derived expansion (2.2), the interstitial potential was set equal to one. The integrals (2.1) then should be equal to the interstitial overlap matrix, which is known exactly. The result was that the errors in the integrals at a general **k** point were of the order of 1-2% for products of s and p functions and no larger than 3% for d functions.

Table I presents calculated and experimental data for Si. In all calculations, the basis used to expand the products of the LMTO envelopes included functions with $k \leq 4$ and with decays given by $-\lambda_a^2 = -1$ and -3 Ry. This set therefore included 50 functions per atomic sphere. As is standard practice when using the LMTO method, an equal number of empty spheres was included along with the Si atomic spheres.⁹ The LMTO basis included s, p, and d functions on all spheres. The localdensity potential of Hedin and Lundqvist was used.¹¹ For each phonon, total energies were computed for at least four amplitudes and a polynomial fit was made to the energies to extract the quadratic term. The positions of the empty spheres were kept fixed and the core states were frozen to increase precision. The elastic constants were calculated analogously. For C_{44} , the total energy was minimized as function of the internal strain parameter for each trigonal distortion. The calculations were done at the experimental lattice constant of 10.26 a.u. and all sphere radii were taken as 2.13 a.u. The spheres were not permitted to overlap. For a simple metal with one atom per unit cell, the computing time per K point was 0.03 sec on a Cray X-MP. These times increase to 0.45 sec and 2.21 sec for Si (four spheres per cell) and Si distorted by a phonon at X (eight spheres), respectively. The corresponding times for the setup were 0.3, 4.7, and 28 sec, respectively.

An additional calculation for the optical phonon at Γ for diamond gave the frequency 39.2 THz, which is close to the experimental value of 39.9 THz.¹² The optical phonons at Γ for Si and diamond have also been computed by Weyrich with a full-potential LMTO method⁶ which uses plane-wave expansions in the interstitial region, giving values of 15.57 and 42.25 THz, respectively. Thus, the comparison to the results of the more elaborate method indicates that the present method is of equal or better precision. The agreement to experiment for the other quantities in Table I is good, although similar calculations using norm-conserving first-principles pseudo-

TABLE I. Comparison of calculated and measured properties derived from distortions at constant volume for Si. k_{xyz} is the third-order force constant for the LTO(Γ) phonon (Ref. 13). Experimental data are from Ref. 12 except for k_{xyz} from Ref. 14.

states and successive distances where the second states							
	C ₁₁ -C ₂₂ (mbar)	C ₄₄ (mbar)	LTO(Γ) (THz)	k_{xyz} (eV/Å ³)	LOA(X) (THz)	TO(X) (THz)	TA(X) (THz)
Calc.	1.01	0.79	15.73	-41.3	11.74	13.20	4.89
Expt.	1.02	0.80	15.53	- 35.1	12.32	13.90	4.49

potentials lead to slightly better results¹³ for the phonons at X. The cause of the larger deviations here may be that the basis functions used have a kinetic energy of zero in the interstitial region, i.e., in 40% of the volume.

In conclusion, a relatively minor modification of the LMTO method has been presented which makes possible fast and accurate calculations for elastic constants and frozen-phonon frequencies. Plane waves are not used in any step, so that the approach can be generalized to molecules. Good agreement was found with the results of a previous, more elaborate full-potential LMTO method and with the experimental data.

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