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Fast full-potential calculations with a converged basis of atom-centered linear muffin-tin orbitals: Structural and dynamic properties of silicon

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For fast and accurate density-functional calculations we devise a small basis set consisting of atom-centered linear muffin-tin orbitals (LMTO's). For the test case Si, an absolute total-energy convergence of 0.02 eV/atom is obtained with 22 LMTO's/atom. The calculated lattice constant, elastic constants, phonon frequencies, mode Grüneisen, and strain parameters, as well as the energy-volume curves for various crystalline phases are in accord with experimental data. This includes the 0.43-eV/atom energy difference between the diamond and bcc phases. Compared with pseudopotential plane-wave (PP-PW) calculations, our full-potential LMTO calculations are at least as accurate. In contrast with the PP-PW method, and in common with the linear augmented plane-wave method, the LMTO method can treat materials with atoms of any kind. By virtue of its 5–10 times smaller basis set, it is much faster.

It is the experience of the past ten years that structural and lattice-dynamic properties of solids may be obtained *ab initio* with good accuracy by calculating the electronic energy as a function of the atomic positions using density-functional (DF) theory.[1] Four years ago, Car and Parinello demonstrated the feasibility of molecular-dynamics (MD) DF calculations, and herewith of *ab initio* simulations of the mechanical behavior of materials.[2]

Many interesting applications cannot, however, be treated due to restrictions set by the standard technique for structural DF calculations: namely, norm-conserving pseudopotentials (PP) and plane-wave (PW) basis functions.[3] The reasons are that only about one-quarter of the elements in the Periodic Table have sufficiently weak pseudopotentials to allow expansion of the pseudowave functions in PW's, and that even for such materials the slow convergence of the PW basis imposes severe limits on the number of atoms in the supercell; for Si the number of PW's needed per atom is of order 100, and for SiO_2 it is four times larger.[4] Linear basis functions,[5] on the other hand, are designed to treat the potential from all the electrons and therefore apply to any material. But, since they are augmented by numerical radial Schrödinger-equation solutions (ϕ and $\dot{\phi}$) inside muffin-tin (MT) spheres surrounding the atoms, and they equal analytical functions (e.g., PW's or spherical Hankel functions) only in the interstitial region, they are more difficult to deal with. For conventional structural calculations, the linear augmented plane-wave (LAPW) method[5,6] is often used when the PP-PW method does not apply. However, here again the largeness of the basis (50–100 LAPW's/atom) limits the number of atoms in the supercell. The most economical basis functions are probably linear muffin-tin orbitals[5,7] (LMTO's), but these are generally considered incapable of providing the accuracy needed in structural energy calculations. We reconsider this point in the present paper.

The extreme efficiency of the standard LMTO method for solids[5,8] is partly due to the atomic-spheres approximation (ASA), which uses Hankel functions with vanishing kinetic energy ($\kappa^2=0$), eliminates the interstitial region by substituting the muffin-tin (MT) spheres with "space-filling" Wigner- Seitz (WS) spheres, and ignores the nonspherical parts of the electron density. For open structures, not only the atomic but also the interstitial (E, empty) regions are described by WS spheres and have orbitals associated with them. The standard LMTO basis set uses 9 LMTO's/sphere. Unfortunately, only isotropic deformations are properly dealt with in the ASA; energy changes associated with shears, phonon displacements, and atomic relaxations are not. Moreover, the use of E orbitals in some and not in other structures is a source of inaccuracy and, for MD calculations, E orbitals can hardly be used. One is thus presented with the problems (i) of devising a set of *atom*-centered LMTO's, which is converged to about 0.01 eV/atom for all conceivable structures; and (ii) of finding efficient ways of representing the full charge density in all space, of solving Poissons equation, and of evaluating the matrix elements of the full potential (FP). These problems have been studied extensively in connection with LMTO calculations for molecules,[7,9–11] surfaces,[12] and solids.[13–17]

Concerning the problem (i) of the basis set, in recent FP calculations for Si,[14–16] using a basis of $\kappa=0$ LMTO's centered at the Si and E sites of the diamond structure, it was found that only with nonoverlapping spheres do the shear elastic constants and phonon frequencies agree with experiments and PP-PW calculations. The total energy, however, was 0.5 eV/atom too high when touching spheres (radius of 2.21 a.u.) were used, and this indicates that the $\kappa=0$ set is inadequate. To remedy this by adjusting the κ value to minimize the total energy[7] is not only cumbersome but will also be insufficient when the E-LMTO's are dropped and the interstitial region increases even further. A double-κ basis with fixed κ values may not suffice either, because although it can treat the dependence of the kinetic energy $[\epsilon_k - V(\mathbf{r})]$ on one-electron energy (ϵ_k) in the interstitial region,[13] it may not be able to treat the structural dependence of Rydberg-sized variations of the potential $V(\mathbf{r})$ in this region, unless the κ values are chosen to depend on the application.[9,11]

We shall consider double- and triple-κ sets with fixed κ values (ϕ and $\dot{\phi}$ are the same for all κ values) and we shall use no E orbitals.

To solve the problem (ii), we shall use a fast FP scheme recently developed for close sphere packings.[15] It treats the spherical-harmonics components with $l \leq 4$ of the charge density and the potential exactly inside the spheres and, for the interstitial region plus the intrasphere components with $l > 4$, it exploits the following facts: (a) The product of two Hankel functions (e.g., LMTO tails) is well fitted in the interstitial region by that linear combination of Hankel functions (with two chosen, negative kinetic energies, λ_1^2 and λ_2^2) which matches values and slopes at all spheres and for all $l \leq 4$; (b) with this fit to the interstitial charge density, Poissons equation can be solved analytically; (c) the integral over the interstitial region of the product of two Hankel functions is given analytically in terms of the structure constants and their energy derivative. This scheme thus interpolates and integrates over the interstitial region using the values and gradients at the spheres. The components with $l > 4$ inside the spheres are included as tails of the fitting Hankel functions, and the charge density and potential therefore have no jumps at the sphere surfaces. For open structures, empty spheres are needed for the fitting but their positions and sizes are uncritical; we shall use them in the diamond and simple-cubic (sc) structures, but not in the β-tin structure. Multiple-κ sets pose no problem for this scheme. For accurate fitting of the interstitial exchange-correlation potential and energy density, we use a constraint based on a procedure described in Ref. 18. The interpolation scheme was tested thoroughly by inspecting the change of the total energy as λ_1^2 and λ_2^2 were varied in the range from -0.5 to -10 Ry.

In this paper, we first seek the smallest, *atom*-centered LMTO basis which gives mRy absolute convergence for the total energy of Si in the diamond structure. Si is chosen as the test case because the convergence of the LMTO method is the worst for open structures, and because we can compare with extensive experimental and theoretical PP-PW results. Having decided upon the basis, we calculate the lattice constant, the cohesive energy, the valence-electron density, the one-electron eigenvalues, the elastic constants, the phonon frequencies at Γ and X, their pressure derivatives, the splitting of the LTO(Γ) (where LTO denotes longitudinal transverse optical) phonon frequency under tetragonal and trigonal shears, and the internal strain parameter. Finally, we use the same basis set to calculate the energy-volume curves for crystalline phases of increasing close packing: diamond, simple cubic, β-tin, bcc, and fcc.

To investigate the convergence of the LMTO basis for Si in the diamond structure, we first generated an accurate potential by performing a self-consistent FP calculation as described in Ref. 15, but using a double-κ basis with $\kappa_1^2 = 0$ and $\kappa_2^2 = -1$ Ry, and with orbitals on both the Si and E sites. This is a very complete basis with 36 LMTO's/atom. The potential was then kept fixed, and the total energy was computed from single-band calculations using various atom-centered LMTO sets with MT radius 2.13 a.u. Starting with a single κ and only s and p orbitals, i.e., with a $1s1p$ basis with 4 LMTO's/atom, orbitals were added until reaching the $3s3p3d2f$ basis with 41 LMTO's/atom. Interestingly, addition of the κ_n orbitals of a given l causes a decrease of the total energy which is essentially independent of how complete the basis already is in the other l channels. This makes it possible to associate well-defined energy decrements with the addition of the first, second, and third orbitals of a given l; these decrements are given in Table I. For the third orbitals we used $\kappa_3^2 = -2.3$ Ry, and other similar choices for the three κ values hardly changed the decrements. It may be seen that addition of the second s and p orbitals, as well as the first d orbitals, are important. For convergence in the mRy/atom range, the third s and p orbitals, as well as the second d orbitals, must be included, but the third d and all f orbitals can be neglected. Finally, by comparing the energy obtained using an excessively complete triple-κ basis with 54 LMTO's/atom and orbitals on both Si and E sites, it was found that the effect of adding the third f orbitals plus the fourth s, p, and d orbitals was less than 1 mRy/atom. We conclude that absolute convergence to within 1.5 mRy/atom is obtained with a $3s3p2d$ basis of 22 LMTO's/atom. This basis is only slightly larger than the set of 18 LMTO's/atom used in standard LMTO-ASA calculations for the diamond structure, and it is an order of magnitude smaller than the PW set of similar precision.[19] Using the 22 LMTO's/atom basis, we have performed a large number of total-energy calculations for Si in various phases to determine whether the basis is adequate in all cases. The MT spheres were always chosen to be slightly smaller than touching, and extreme care was taken to ascertain that the Brillouin-zone summations were always converged.

In Table II we compare the experimental static and dynamical properties of diamond Si with the results of our calculations (FP-LMTO) and with those of PP-PW calculations.[19–22] As for the static properties, we obtain the correct lattice constant, but our cohesive energy is too large. This is a well-known failure of the local-density approximation (LDA), rather than of our method, and the size of the discrepancy depends somewhat on the parametrization used.[1] Figure 1 shows our calculated valence charge density which is very similar to the ones obtained

TABLE I. Decrease of the diamond-Si total energy with increasing basis size in mRy/atom. The two values for each orbital are the minimal and maximal energy changes found depending on the completeness in the other l channels. The MT radius was 2.13 a.u.

Orbital	First	Second	Third
s	· · ·	24.5	12.0
			13.1
p	· · ·	83.8	4.4
		88.6	5.4
d	25.7	3.0	0.1
	28.8	5.1	0.2
f	0.8	0.4	· · ·
	1.4		

TABLE II. Static and dynamic properties of diamond Si.

	Expt.	FP-LMTO	PP-PW
Lattice constant (Å)	5.43[a]	5.41	5.45[b]/5.40[c]
Cohesive energy (eV/atom)	4.63[a]	5.23	4.84[d]/5.28[e]
Elastic constants			
Bulk modulus (Mbar)	0.98[f]	0.99	0.98[b]/0.93[c]
$C_{11}-C_{12}$ (Mbar)	1.02[f]	1.02	1.07[g]/0.98[c]
C_{44} (Mbar)	0.80[f]	0.83	0.85[c]
Phonon frequencies			
LTO(Γ) (THz)	15.53[a]	15.47	15.16[g]
k_{xyz} (eV/Å^3)	−35.1[f]	−38.7	−32.8[g]
TO(X) (THz)	13.90[a]	13.75	13.48[g]
LOA(X) (THz)	12.32[a]	11.82	12.16[g]
TA(X) (THz)	4.49[a]	4.50	4.45[g]
Grüneisen parameters			
LTO(Γ) (THz)	0.98[h]	0.99	0.92[g]
TO(X) (THz)	1.5[h]	1.51	1.34[g]
LOA(X) (THz)	0.9[h]	1.03	0.92[g]
TA(X) (THz)	−1.4[h]	−1.42	−1.50[g]
Strain parameters			
ζ	0.54[i]	0.51	0.53[c]
s_{100}	0.24[j]	0.23	0.13[c]
s_{111}	−0.93[j]	−1.45	−0.90[c]

[a] *Landolt-Börnstein: Numerical Data and Functional Relationships Science,* edited by O. Madelung, New Series, Vol. 22a (Springer, New York, 1987), p. 19.

[b] Reference 19 using 90 PW's/atom and Wigner LDA.

[c] Reference 22 using 90 (+180 downfolded) PW's/atom and Wigner LDA.

[d] Reference 19 using 200 PW's/atom and Wigner LDA.

[e] Reference 21 using 200 PW's/atom and Ceperley-Alder LDA.

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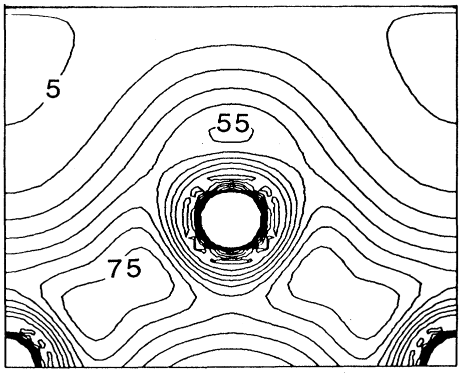

FIG. 1. Calculated valence-electron density of Si in the $(1\bar{1}0)$ plane. The contour unit is 0.001 electrons/(a.u.)^3.

with the LAPW method[23] and from experiment.[24] Our one-electron eigenvalues agree to within a few hundredths of an eV with pseudopotential results obtained using 200 PW's/atom.[19] Returning to Table II we now discuss the results obtained for deformations of the crystal. Our bulk modulus and shear elastic constants are in as good, or even better, agreement with experiments than the PP-PW results. The same is true for our phonon frequencies, except for the LAO(X) mode (where LAO denotes longitudinal acoustic optical). We note that both calculations correctly describe the difficult, soft transverse acoustical TA(X) mode. The anharmonicity constant k_{xyz} for the LTO(Γ) phonon is numerically a bit too large in our calculation and too small in the PP-PW calculation. Our Grüneisen mode parameters (logarithmic volume derivatives of the phonon frequencies) seem to be more accurate than the PP-PW results, especially in view of the inherent uncertainty in measurements involving the LAO(X) mode. Next, we discuss the internal strain parameter ζ and the tetragonal and trigonal shear-splitting constants s_{100} and s_{111}, which describe the splitting of the LTO(Γ) phonon frequency under shear. Our value for ζ agrees with the new experimental result as well as with the prediction of Nielsen and Martin.[22] As regards s_{100}, we are in better agreement with experiment than they are, but for s_{111} the situation is reversed. It order to provide some feeling for the importance of the latter discrepancy, we note that within a classical model using anharmonic valence-field force constants,[25] the trigonal shear-splitting parameter and the internal strain parameter are related by $s_{111} = \frac{1}{2} + (1-\zeta)\times\text{const}$, where the constant is proportional to k_{xyz}. This shows that there is a large cancellation, and that small relative errors in ζ and k_{xyz} could have considerable effects on s_{111} (this is not the case for s_{100}). Therefore, the discrepancy that we find is hardly dramatic, and is consistent with our overestimation of k_{xyz}.

As a final demonstration of the capability of our 22 LMTO's/atom basis, we show in the left-hand side of Fig. 2 the energy-volume curves calculated for various crystalline phases of Si. The right-hand side gives the PP-PW results of Yin and Cohen,[19] who used the *same* PW cutoff of 11.5 Ry for *all* volumes; this corresponds to using $(V/V_0)\times 90$ PW's/atom. The structures considered are, in order of increased packing: diamond, β-tin, sc, bcc, and fcc with, respectively, 4, 4+2, 6, 8, and 12 nearest neighbors and interstitial regions taking up more than, respectively, 66, 48, 48, 32, and 26% of the cell volume. For a given volume, we expect an atom-centered LMTO basis to be least complete for the most open structure (provided that l convergence is no issue) and, for this, our set is mRy converged at the normal volume. What may go wrong in an energy-volume calculation is that the convergence of the basis deteriorates with compression. However, the LMTO method is particularly suited for pressure studies because it uses numerical volume-dependent radial functions inside the MT spheres; only, as outer core states broaden into bands, may it be necessary to include more than one ϵ panel in the calculation.[26] The present calculations employed one panel. Both FP-LMTO and PP-PW calculations correctly reproduce the pressure-induced

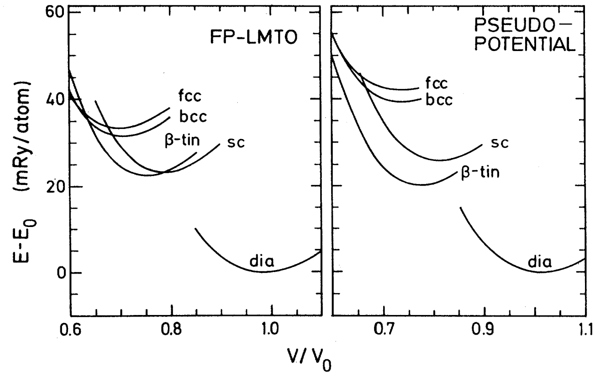

FIG. 2. Energy-volume curves for crystalline phases of Si calculated by Yin and Cohen using the pseudopotential method (Ref. 19) and by us using the FP-LMTO method. V_0 is the experimental equilibrium volume and E_0 is the calculated minimum energy in the diamond structure.

phase transition from the diamond to the β-tin structure, whereby our pressure for the onset of the transition of 115 kbar is closer to the experimental value of 113 kbar (Ref. 27) than the 99 kbar (Ref. 19) [93 kbar (Ref. 28)] obtained from PP-PW calculations. For the β-tin phase we used the experimental c/a ratio. We calculate the energy difference between the bcc and the diamond phases to be 0.43 eV/atom. This is in good agreement with a thermodynamic estimate of 0.46,[29] but in less satisfactory agreement with the PP-PW result of 0.53 eV/atom. This discrepancy is the most pronounced difference between the results of the two calculations. Only 0.02 eV/atom of this is caused by the use of different LDA parametrizations. Our own PP-PW calculations for the diamond and bcc structures with 11.5-Ry PW cutoff confirm the result of Yin and Cohen.[19] However, increasing the cutoff to 24 Ry and using the same LDA parametrization, we reproduce the FP-LMTO result to within 0.01 eV/atom.

In conclusion, we have presented an atom-centered $3s3p2d$ LMTO basis with 22 orbitals per atom, which gives absolute total-energy convergence within 0.02 eV/atom for Si in the diamond structure at normal volume, and which can be expected to yield equally (or more) precise results for other structures of similar (or closer) packings. By extensive calculations of static and dynamic properties of diamond Si, as well as of the energy-volume curves for several crystalline phases, we have found that our method is at least as accurate as, and much faster than, the PP-PW method. Since the LMTO method applies to materials containing atoms from any part of the Periodic Table, new applications of structural DF calculations are made possible.

Useful discussions with M. Cardona about pressure and strain dependencies of phonon frequencies, with J. Tersoff about the phase stability, and with K. Kunc about PP-PW calculations are gratefully acknowledged.

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