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Application of adaptive curvilinear coordinates to the electronic structure of solids

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Adaptive coordinates are shown to be effective in allowing the accurate calculation of structures and interatomic forces for solids containing first-row atoms using relatively small orthonormal sets of basis functions. Several polymorphs of SiO_2 are studied as illustrative test cases.

An enhancement of the widely used plane-wave pseudopotential approach to electronic-structure calculations was recently introduced by Gygi to deal with the highly localized nature of the orbitals of first-row and transition-metal atoms.[1,2] Electron wave functions are expanded in plane waves in a generalized curvilinear coordinate system. Transformed to ordinary Euclidean coordinates, the spatial frequency of such a "plane" wave becomes a varying function, and surfaces of constant phase are no longer planes. When the parameters describing the coordinate transformation are allowed to adapt to minimize the energy of the system, spatial frequencies tend to be peaked where occupied atomic orbitals are localized.

The coefficients of a set of plane waves are mapped by the discrete Fourier transform to values on an evenly distributed mesh of points in coordinate space. The evenly spaced mesh in curvilinear coordinates becomes a variably spaced mesh in Euclidean coordinates, and the points tend to be dense within localized orbitals, and sparse in open regions away from atoms and bonds. The effect of the coordinate transformation may be viewed as concentrating the variational freedom represented by the wave-function expansion coefficients where it can do the most good.

Gygi showed that an implementation of the density-functional formalism within the local-density approximation (LDA) with curvilinear plane waves retains all the most important advantages of ordinary plane waves, including basis orthogonality, absence of Pulay forces, and the ability to use fast Fourier transforms and the Car-Parrinello (CP) approach[3] to efficiently optimize wave functions and atomic geometries.[2]

The examples Gygi used to illustrate his adaptive coordinate method were small molecules (CO and H_2O) in large supercells, for which he obtained large enhancements of the effective plane-wave cutoff energy.[2] The research reported here was undertaken to test this approach in the context of solids, where the atoms with localized orbitals are distributed throughout space. First, it was unclear to what extent cutoff enhancement would survive in the face of competition among many atoms. The second issue is more subtle, although somewhat related: The coordinate transformation is parametrized in a totally unbiased fashion by the coefficients of another set of plane waves.[1,2] While these variables have no explicit coupling to the atoms or electrons, optimizing them in connection with a *finite* set of electron basis functions has the effect of indirectly introducing a coupling. In principle, "coordinate modes" could mediate a spurious interatomic force, and it is crucial to know the magnitude of this effect to assess the accuracy of the method. A feasibility demonstration of the application of adaptive coordinates to solids in an all-electron context including cores has recently been reported, but these questions were not addressed.[4]

SiO_2 was chosen as the primary test case, both because of the author's interest and because it is particularly challenging in terms of the questions discussed above. My independent implementation of the method follows Gygi's formalism in most details, and will be fully described elsewhere.[5] In particular, Gygi's shear elastic energy tending to resist coordinate deformations away from Euclidean was retained, with strength proportional to a modulus μ_{shear}.[2] A fictitious mass was introduced so that the coordinate parameters could be included as additional dynamical variables in the damped CP dynamics used for the wave-function coefficients and the atomic positions, and all these variables were advanced simultaneously at each time step. The Poisson equation is nontrivial in curvilinear coordinates, and the Hartree potential was calculated exactly using the preconditioned conjugate gradient method at each time step. Since Bloch wave vectors in an irreducible wedge were used for Brillouin-zone sampling, forces on the coordinate transformation parameters and on the atoms were symmetrized according to the space group of the solid. Norm-conserving pseudopotentials comparable to those of Bachelet, Hamann, and Schlüter were used,[6] with s nonlocality for O and s and p nonlocality for Si implemented in the fully separable Kleinmann-Bylander form.[7] Ceperley-Alder exchange and correlation as parametrized by Perdew and Zunger were utilized.[8]

Convergence enhancement is illustrated in Fig. 1 for ideal β-cristobalite with a lattice constant of 7.39 Å chosen to give the normal Si-O bond length of 1.6 Å (real β-crystobalite is a distorted form with a smaller lattice constant).[9] The total energy of this system is plotted as a function of the cutoff energy of the wave-function plane-wave basis set for conventional and adaptive-coordinate calculations using identical pseudopotentials. The coordinate transformation plane-wave set is cut off at 5 Ry independent of basis set cutoff for consistency, and $\mu_{\text{shear}} = 2\times10^{-4}$. The total energy converges dramatically faster using adaptive coordinates. It is possible to calculate the effective cutoff as a function of position from the determinant of the Riemannian metric tensor, and the maximum effective cutoff is also shown in Fig. 1. The maximum grows much less rapidly than the average cutoff, with the enhancement factor dropping from 5 to 2 as the average cutoff grows from 8 to 55 Ry. Clearly, when the

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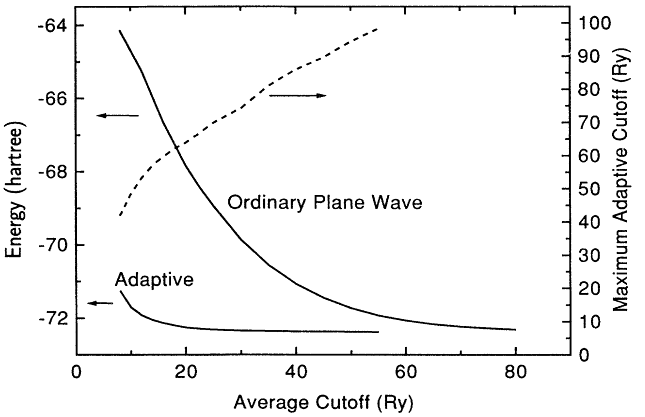

FIG. 1. Total-energy convergence for conventional and adaptive plane-wave calculations, and maximum effective cutoff for Si_2O_4 in the ideal β-cristobalite structure.

calculation is well converged with ordinary plane waves, there is no energy to be gained from deforming the coordinates. Published plane-wave SiO_2 calculations with norm-conserving pseudopotentials employ cutoffs from 40 to 70 Ry.[10–12] An adaptive calculation with an average cutoff of 20 Ry and a maximum cutoff of 64 Ry should be comparably well converged, and requires only $\frac{1}{5}$ as many basis functions. The "ultrasoft" method, which abandons norm-conservation and basis orthogonality in favor of a form of augmentation, also converges comparably well for SiO_2.[13]

A better qualitative understanding of the adaptive behavior of the method may be had by examining the spatial distribution of the enhancement. Figure 2 shows a contour plot of the distribution of effective cutoff in α-cristobalite. α-crystobalite has a tetragonal structure consisting of four vertex-sharing SiO_4 tetrahedra arranged in an alternating spiral structure around the c axis.[9] There is no simple plane intersecting several atoms. The plot in Fig. 2 is in the b-c plane, showing two unit cells in the b direction, and offset from the origin by $0.75a$. This plane passes within 0.06 Å of a pair of O's in each unit cell, and their locations are clearly seen as the four maxima in the cutoff plot. The Si's bonded to these O's are 0.26 Å above and below the plane, and their projected positions are indicated on the plot. In this calculation the average cutoff is 20 Ry, and slightly more aggressive adaptation than described above is obtained by increasing the coordinate cutoff to 8 Ry and decreasing μ_{shear} to 1×10^{-4}. The maximum and minimum effective cutoffs are 70 and 13.6 Ry. The lack of enhancement of the Si's is consistent with the fact that bulk Si with this pseudopotential would already be well converged at the minimum effective cutoff. Bulk Si done with adaptive coordinates in fact shows minimal adaptation, with the effective cutoff ranging from 8.9 to 11.2 Ry for an average cutoff of 10 Ry.

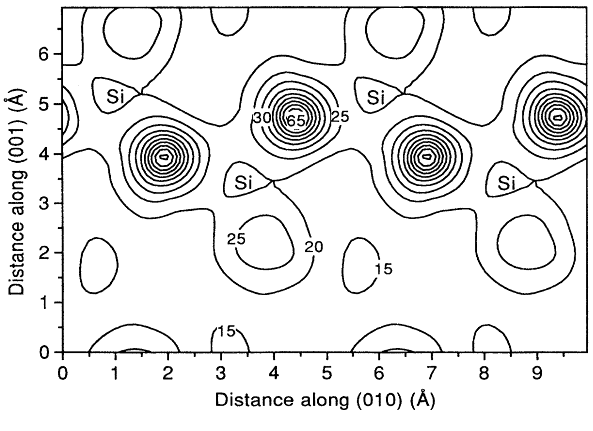

FIG. 2. Spatial dependence of effective cutoff (in Ry) for α-cristobalite. Average cutoff is 20 Ry.

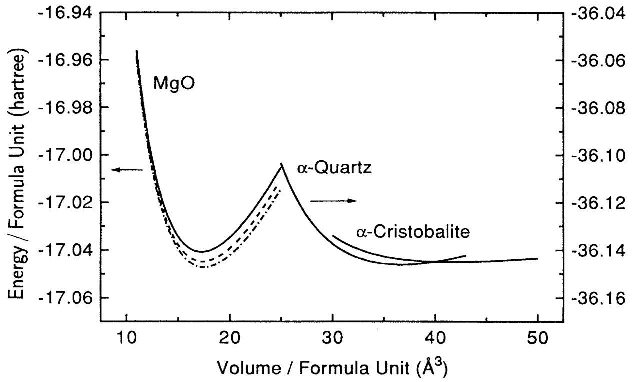

FIG. 3. Volume dependence of total energy for MgO and two SiO_2 polymorphs. Differences among the three MgO plots are explained in the text.

To quantitatively test the adaptive coordinates in the context of solids, structural properties were calculated for several test cases. The simplest is the rocksalt-structure oxide MgO, for which wave function and coordinate cutoffs of 25 and 5 Ry were used, along with two special **k** points.[14] The Murnaghan equation of state[15] gives an excellent fit to the results over a wide range of lattice constants, and energy vs volume fits for three calculations are shown as the leftmost curves in Fig. 3. The solid, dashed, and dash-dotted curves correspond to $\mu_{\text{shear}}=2$, 1, and 0.5×10^{-4}, respectively. The predicted lattice constants of 4.103, 4.111, and 4.121 Å and bulk moduli of 155, 153, and 150 GPa are nearly equivalent compared to the experimental values of 4.21 Å (Ref. 9) and 160 GPa,[16] and the differences from experiment are well within the range one expects for pseudopotential-LDA calculations. The reason for showing all three is to call attention to the elastic energy that Gygi introduced to stabilize the adaptation of the coordinates for his small-molecule calculations.[2] The magnitude of the energy is 7.70, 4.97, and 3.09×10^{-3}, respectively, and accounts for part of the upward shift of the first and second curves. The other part of the shift is increased LDA energy with increasing stiffness. Examining the maximum effective cutoff for the MgO calculations, it is seen to vary significantly with volume for $\mu_{\text{shear}}=5\times10^{-5}$, increasing from 68 to 78 Ry over the range shown in Fig. 1. For $\mu_{\text{shear}}=2\times10^{-4}$, however, it is nearly constant. The volume dependence of the cutoff is clearly a result of competition for wave-function degrees of freedom among the O atoms as discussed earlier. The volume-dependent shift of the energy curves relative to each other

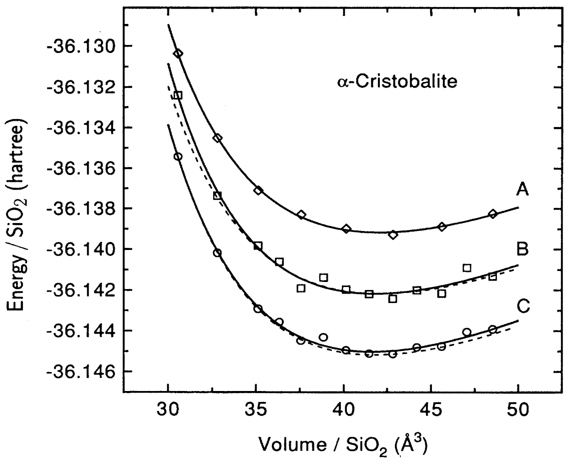

FIG. 4. Reference 80-Ry plane wave (A) and two 25-Ry adaptive coordinate calculations (B,C) for α-cristobalite, offset for clarity. Each dashed curve repeats the above solid curve.

can be interpreted as a spurious repulsive interatomic force. However, μ_{shear} of 2×10^{-4} has the important effect of *limiting the range* of the competition, thus removing the spurious force while still allowing substantial adaptation.

The other curves in Fig. 3 show energy vs volume for two SiO$_2$ polymorphs, α-quartz and α-cristobalite. The three plots were combined to emphasize the extreme range of compressibility spanned by these three materials, and to allow the reader to appreciate that α-cristobalite poses an extremely sensitive test of interatomic forces. In MgO, both Mg-O and O-O contacts are essentially at their ionic radii, and volume change involves only stretching and compressing these distances. α-cristobalite, on the other hand, has less than 0.01 Å change in bond length over the entire range of volumes in Fig. 3. The volume change is entirely accommodated by rotations of the SiO$_4$ tetrahedra, with the Si-O-Si bond angle changing from 120° to 170°, and hence involves weak bond-bending forces and distant second-neighbor Si-Si interactions, leaving α-cristobalite extremely soft. α-quartz is an intermediate case. Both SiO$_2$ calculations were done at the experimental c/a ratio.

Figure 4 compares several calculations for α-cristobalite on an expanded scale. To provide the most consistent possible reference, a conventional plane-wave calculation with the same pseudopotential and an 80-Ry cutoff was carried out, using one special **k** point[14] and fully relaxing all internal coordinates. These calculated points are shown with curve A in the plot, and lie extremely close to the Murnaghan fit. This fit is shifted and repeated as the dashed line of curves B, where it is compared to the adaptive coordinate points and fit (solid) calculated with $\mu_{\text{shear}}=2\times10^{-4}$ and cutoffs as for MgO. The considerable scatter of the points is due to the passage of discrete wave-vector stars through the cutoff sphere as the volume is changed, and is much greater for the small basis of the adaptive calculation than for the 80-Ry cutoff, where the outermost stars have very little weight in the wave functions. In fact, what is plotted is not the LDA energy alone, but the sum of it and the elastic energy of the coordinates. While at first glance this seems like an arbitrary and unphysical procedure, note that the function which is minimized by the damped CP dynamics is this entire function, so that only this sum is in fact variational. While the elastic energy changes little on the average over the volume range, the "truncation noise" in it, or the LDA energies taken separately, is considerably greater than that of the sum. The magnitude of the elastic energy, incidentally, is 0.016 hartrees per SiO$_2$, exceedingly small compared to the total energy. The dashed curve of the set C is the solid B fit (shifted), which is compared to the energies and fit (solid) computed with three special **k** points. The truncation noise is considerably reduced, and the curvature is slightly increased.

A few adaptive calculations at different c/a ratios indicated that the energy minimum was very close to the experimental value, but a complete two-parameter energy surface was not explored since this was not the main purpose of the present research. Within the fixed c/a constraint, lattice constants a of 4.94, 4.93, and 4.92 Å were found for calculations A, B, and C, compared to the experimental value of 4.96 Å.[17] The curvature of $E(V)$ at fixed c/a corresponds to the Voigt (polycrystalline average) bulk modulus, which can be calculated from the elastic constants and is actually quite close to the conventional modulus for the materials considered here. Calculated values of 10.6, 11.6, and 12.9 GPa for A through C are all small compared to the experimental value of 16.8 GPa.[18] While other calculations have been reported showing closer agreement,[10,11,13] we find the fitted value to be sensitive to the fitting range, and note that the absolute error is still very small by LDA standards because the material is so soft. Average Si-O bond lengths of 1.601, 1.604, and 1.605 Å were calculated compared to 1.609 for experiment.[17] Si-O-Si bond angles were 145°, 144°, and 144° compared to 145° for experiment. All O-Si-O bond angles are tetrahedral within 1°.

For α-quartz, the calculation in Fig. 3 was carried out with two special **k** points, and parameters otherwise the same. Much less truncation noise was evident in the $E(V)$ points (not shown) than in Fig. 4. The brief summary of calculated/experimental quantities is 4.87/4.91 Å for a, 41.3/34.9 GPa for the Voigt modulus, 1.61/1.61 Å for the average Si-O bond length, and 143°/144° for the Si-O-Si bond angle.[16,19] Quartz is lower in energy than cristobalite by 0.03 eV per SiO$_2$ (taking cristobalite calculation C as the best-converged result), which appears to be identical to the experimental value.[20] Subtracting spin-polarized atomic energies, the cohesive energy found here for α-quartz is 21.86 eV.

Calculations with $\mu_{\text{shear}}=1\times10^{-4}$ for α-quartz gave results that were comparable to those quoted above. The resultant slight increase of the adaptive coordinate competition apparently did not introduce significant systematic errors. For α-cristobalite with one **k** point, however, the truncation noise was amplified by the increased coordinate adaptation to the point where meaningful fits could not be made. Calculations attempted for both materials with an average basis function cutoff of 20 also suffered from this problem. Nonetheless, these calculations gave good bond lengths and angles, and these parameters may be entirely satisfactory for calculations at constant volume where internal structure is the principal desired result.

We note for completeness that the average cutoff energy for the expansion of the electron charge density was generally kept at four times that of the wave functions. This procedure is guaranteed to avoid aliasing errors in its discrete Fourier transform, as in conventional calculations. However, several geometric quantities entering the calculation of the kinetic energy in curvilinear coordinates in principle contain arbitrarily high multiples of the maximum spatial frequency of the transformation itself. The same is true of the Laplacian that enters the Poisson equation. In addition, the pseudopotentials can contain high spatial frequencies, and were applied directly on the adaptive coordinate mesh. The magnitude of possible aliasing errors connected with these terms was tested by doubling the cutoff for the charge, which decreases the discrete Fourier transform mesh spacing by $1/\sqrt{2}$ for the entire calculation, and found to be less than 10^{-4} hartrees per SiO_2.

In summary, the adaptive coordinate method has been shown to allow the treatment of solids containing first-row atoms with small orthonormal basis sets. A potential source of systematic errors has been identified, but these errors have been shown to be controllable so that even the effects of very weak interatomic forces can be correctly described. The reader should note that the systematic errors inherent in the pseudopotentials themselves are rarely examined so critically. One can conclude that Gygi's approach should prove useful for a wide variety of interesting solid-state calculations.

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[1] F. Gygi, Europhys. Lett. **19**, 617 (1992).

[2] F. Gygi, Phys. Rev. B **48**, 11 692 (1993).

[3] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[4] A. K. Devenyi, K. Cho, T. A. Arias, and J. D. Joannopoulos, Phys. Rev. B **49**, 13 373 (1994).

[5] D. R. Hamann, Phys. Rev. B (to be published).

[6] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[7] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[8] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[9] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Krieger, Malabar, FL, 1982), Vol. 1, pp. 88 and 318.

[10] D. C. Allan and M. P. Teter, Phys. Rev. Lett. **59**, 1136 (1987).

[11] J. R. Chelikowsky, H. E. King, N. Troullier, J. L. Martins, and J. Glinnemann, Phys. Rev. Lett. **65**, 3309 (1990).

[12] R. M. Wentzcovitch, J. L. Martins, and B. D. Price, Phys. Rev. Lett. **70**, 3947 (1993).

[13] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); F. Liu, S. H. Garofalini, D. King-Smith, and D. Vanderbilt, *ibid.* **49**, 12 528 (1994).

[14] A. Baldereschi, Phys. Rev. B **7**, 5212 (1973); D. J. Chadi and M. L. Cohen, *ibid.* **8**, 5747 (1973); H. J. Monkhorst and J. D. Pack, *ibid.* **13**, 5188 (1976).

[15] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[16] A. G. Every and A. K. McCurdy, in *Numerical Data and Functional Relationships in Science and Technology*, edited by D. F. Nelson, Landolt-Börnstein, New Series, Group III, Vol. 29, Pt. a (Springer-Verlag, Berlin, 1992), pp. 73 and 148.

[17] J. J. Pluth and J. V. Smith, J. Appl. Phys. **56**, 1045 (1985).

[18] A. Yeganeh-Haeri, D. J. Weidner, and J. B. Parise, Science **257**, 650 (1992).

[19] Y. Le Page and B. Donnay, Acta Crystallogr. Sec. B **32**, 2456 (1976).

[20] P. Richet, Y. Bottinga, L. Denielou, J. P. Petitet, and C. Tequi, Geochim. Cosmochim. Acta **46**, 2639 (1982); J. L. Holm, O. J. Kleppa, and E. F. Westrum, Jr., *ibid.* **31**, 2289 (1967).