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Symmetry-general least-squares extraction of elastic coefficients from *ab initio* total energy calculations

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A symmetry-general scheme for the simultaneous least-squares extraction of the elastic coefficients and of the residual strain components from *ab initio* total energy calculations on crystal structure models of materials is proposed. It is quite efficient and avoids error propagation. An appropriate, but usually singular, set of normal equations is first formulated in a triclinic framework, with 21 stiffness coefficients and 6 residual strain components. Rank reduction of this 27×27 least-squares system of normal equations is then performed through systematic implementation of the constraints corresponding to the known symmetry of the material. A regular $p\times p$ matrix is obtained through this process, where p is the total number of independent coefficients and components. This computationally robust approach to the extraction of elastic coefficients and their standard deviations can be used to analyze any number of adequately selected and weighted values of the total energy that is larger than the number of independent parameters. It also provides values for the minimum energy and for the corresponding cell data, again with standard errors. The present work enables the automated calculation of elastic coefficients from crystals with any symmetry through a single logical flow. Examples are given for a few cubic, hexagonal, rhombohedral, tetragonal, and orthorhombic materials with known experimental stiffness values. It would be difficult to exaggerate the convenience of the automated implementation of this symmetry-general approach based on total energy calculations.

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I. INTRODUCTION

Numerous results of experimental studies of elastic coefficients of elements and compounds with a variety of crystal symmetries have been reported over the years. Independent studies usually report values that are consistent within 1 or 2%. Many such numerical results and hundreds of corresponding references can be found in books or handbooks.[1–4]

Extraction of stiffness coefficients C_{ij} from *ab initio* total energy calculations has been commonly performed since about 1990. A sample of printed reports for such calculations can be found in Refs. 5–12, but many more results have been presented at conferences. Where reported, the methodology is usually as follows. The minimum-energy cell data are first derived. The system is then strained, preserving as much crystal symmetry as possible, in order to extract corresponding stiffness values. Several strain magnitudes are applied for each strain type, giving an energy parabola. The magnitude of stiffness appropriate for the type of strain is then derived from the curvature of the parabola. Some strains are related to a single coefficient of the stiffness matrix, while others lead to a linear combination of coefficients, from which individual coefficients are finally calculated.

In most cases, the materials in *ab initio* literature studies are cubic or hcp elements, and less frequently cubic or hexagonal binary compounds. A few studies report on tetragonal UIr or UIr-type compounds.[5,6,8] For cubic symmetry, the minimum-energy conformation requires about four simulations. The derivation of coefficients requires an additional three or four simulations per independent coefficient. For a cubic compound, 15 energy calculations are required, from which the three independent coefficients C_{11}, C_{12}, C_{44} are derived. For an hcp material, about 20 simulations produce the 5 independent elastic coefficients. The task of reaching the minimum energy in a hexagonal case can also require a comparable number of additional simulations. It is difficult to assess the numerical accuracy of the results both because of the propagation of errors in the combinations of coefficients, and also because the calculations for the strains may involve different conditions. Because the symmetries for each type of strain are different, the numerical grids, etc, common to the *ab initio* programs often differ, leading to e.g., different energies for the unstrained system calculated in that symmetry. Thus it is difficult to relate the energy curves for the various strains to each other.

Another *ab initio* method for the extraction of elastic coefficients uses the radically different stress-strain approach,[18] whereby the stress resulting from an applied strain is directly calculated. This more recent method is also commonly used. See, for example, Ref. 19 and the references it contains. It would be premature to perform any comparisons between the computing efforts and the relative accuracies of the numbers obtained through the total-energy approach and through the stress-strain approach to the extraction of elastic coefficients. We will therefore not be concerned with this other approach in the remainder of the present study.

We know of no example of calculation of the elastic coefficients of a triclinic compound. The fact that there are few both technologically important and computationally feasible compounds with that symmetry may explain this observation. It is, nevertheless, worth examining whether the triclinic case, with its 21 independent elastic coefficients, could be the starting point for a symmetry-general method of extracting elastic coefficients.

II. LEAST-SQUARES EXTRACTION OF ELASTIC COEFFICIENTS IN THE TRICLINIC CASE

Using the matrix notation for elasticity, the well-known relationship

$$2U(\varepsilon)=2U0+\sum_{i}\sum_{j}C_{ij}\varepsilon_i\varepsilon_j \tag{1}$$

describes the energy U of strained states of a crystalline compound *in the harmonic approximation*. In this equation, $U0$ is the minimum energy for the relaxed material, C_{ij} are the elastic coefficients of the material, and ε_i is the ith component ($i=1,6$) of the strain ε. At first glance, Eq. (1) appears to be a linear equation involving the 21 unknowns C_{ij}.

In order to avoid the high computational cost of fully relaxing the cell data under the exact conditions used for the energy simulations, we usually perform this optimization much faster, using less stringent execution parameters. As a result, the *applied* strain $\mathbf{e}$ is only an approximation of the *total* strain ε that is used in the description of the tensor behavior of the material in Eq. (1). We accordingly need to introduce a small unknown residual strain $\mathbf{S}=\varepsilon-\mathbf{e}$, that we will also need to evaluate. Taking into account that residual strain, Eq. (1) can then be rewritten in matrix form as

$$2U(\mathbf{e})=2U0+(\mathbf{e}+\mathbf{S})^T\mathbf{C}(\mathbf{e}+\mathbf{S}). \tag{2}$$

When written in this form, it is obvious that there is not a linear relationship between the unknowns because Eq. (2) contains products of the unknown quantities C_{ij}, S_i, and S_j.

We wish to produce a tractable set of equations that will approximate a linear system for values of the variables that are close to the correct solutions. We accordingly consider that the values of elastic coefficients are approximated by the current value c_{ij}, with $C_{ij}=c_{ij}+\delta(c_{ij})$, i.e., $\mathbf{C}=\mathbf{c}+\delta\mathbf{c}$. We also consider that the initial strain $\mathbf{S}$ is approximated by the value $\mathbf{s}$ with an error $\delta\mathbf{s}$, i.e., $\mathbf{S}=\mathbf{s}+\delta\mathbf{s}$. Equation (2) can then be rewritten as

$$2U(\mathbf{e})=2U0+(\mathbf{e}+\mathbf{s}+\delta\mathbf{s})^T(\mathbf{c}+\delta\mathbf{c})(\mathbf{e}+\mathbf{s}+\delta\mathbf{s}). \tag{3}$$

Strictly speaking, Eq. (3) is not linear because it still contains products of its variables $\delta\mathbf{c}$ and $\delta\mathbf{s}$. However, for values of $\mathbf{c}$ and $\mathbf{s}$ which approximate very well the correct values $\mathbf{C}$ and $\mathbf{S}$, the corresponding values of variables $\delta\mathbf{c}$ and $\delta\mathbf{s}$ become very small. Under this condition, the products of the variables $\delta\mathbf{c}$ and $\delta\mathbf{s}$ then become infinitesimal and will be neglected. In order to implement this approximation, Eq. (3) can be rewritten as follows:

$$\begin{aligned}2U(\mathbf{e})={}&2U0+(\mathbf{e}+\mathbf{s})^T\mathbf{c}(\mathbf{e}+\mathbf{s})+(\mathbf{e}+\mathbf{s})^T\delta\mathbf{c}(\mathbf{e}+\mathbf{s})\\&+\delta\mathbf{s}^T\mathbf{c}(\mathbf{e}+\mathbf{s})+(\mathbf{e}+\mathbf{s})^T\mathbf{c}\delta\mathbf{s}+\text{higher-order terms.}\end{aligned} \tag{4}$$

Equation (4) decomposes $2U(\mathbf{e})$ into the sum of six terms. The first two terms are constant. The third term is a linear function of $\delta\mathbf{c}$, while the fourth and the fifth terms are linear functions of $\delta\mathbf{s}$. The last term regroups higher-order terms of variables $\delta\mathbf{c}$ and $\delta\mathbf{s}$ that are not spelled out here because they will not be used in the successive approximations $\mathbf{c}$ and $\mathbf{s}$ of the true values $\mathbf{C}$ and $\mathbf{S}$ through the following full-matrix linear least-squares procedure.

An adequate number of samples of U values is calculated by *ab initio* simulation of strained states $\mathbf{e}_k$ $(k=0,n)$ of the material. Instead of giving the exact value $U(\mathbf{e}_k)$, those simulations give the ''experimental'' values $u(k)$, where the quantity $\delta u(k)=2U(\mathbf{e}_k)-2u(k)$ is a random quantity with expected average value zero and known estimated standard deviation $\sigma(k)$. Under those conditions, for each observation k, Eq. (3) can then be rewritten as

$$\delta u(k)=2U0-2u(k)+(\mathbf{e}_k+\mathbf{s}+\delta\mathbf{s})^T(\mathbf{c}+\delta\mathbf{c})(\mathbf{e}_k+\mathbf{s}+\delta\mathbf{s}), \tag{5}$$

where

$$\begin{aligned}2U0={}&1/(n+1)\\&\times\sum_{h=0,n}[2u(h)+\delta u(h)-(\mathbf{e}_h+\mathbf{s}+\delta\mathbf{s})^T\\&\times(\mathbf{c}+\delta\mathbf{c})(\mathbf{e}_h+\mathbf{s}+\delta\mathbf{s})].\end{aligned} \tag{6}$$

After decomposing Eq. (6) similar to Eq. (3), Eq. (4) finally becomes

$$\begin{aligned}\delta u(k)={}&-2u(k)+(\mathbf{e}_k+\mathbf{s})^T\mathbf{c}(\mathbf{e}_k+\mathbf{s})\\&+1/(n+1)\sum_{h=0,n}[2u(h)-(\mathbf{e}_h+\mathbf{s})^T\mathbf{c}(\mathbf{e}_h+\mathbf{s})]\\&+(\mathbf{e}_k+\mathbf{s})^T\delta\mathbf{c}(\mathbf{e}_k+s)-1/(n+1)\\&\times\sum_{h=0,n}[(\mathbf{e}_h+\mathbf{s})^T\delta\mathbf{c}(\mathbf{e}_h+\mathbf{s})]+2\,\delta\mathbf{s}^T\mathbf{c}(\mathbf{e}_k+\mathbf{s})\\&-2/(n+1)\sum_{h=0,n}[\delta\mathbf{s}^T\mathbf{c}(\mathbf{e}_h+\mathbf{s})]+1/(n+1)\\&\times\sum_{h=0,n}\delta u(h)+\text{higher-order terms.}\end{aligned} \tag{7}$$

Equation (7) decomposes $\delta u(k)$ into the sum of nine terms. The first three terms are constant. The fourth and fifth terms are linear combinations of the change $\delta\mathbf{c}$ in the coefficients C_{ij}. The sixth and seventh terms are linear combinations of the change $\delta\mathbf{s}$ in the initial strain $\mathbf{s}$. The eighth term has zero expected value and the last term is made of higher-order products of $\delta\mathbf{c}$ and $\delta\mathbf{s}$ that will be vanishingly small for values of $\mathbf{c}$ and $\mathbf{s}$ that approach their true values $\mathbf{C}$ and $\mathbf{S}$. This will be achieved iteratively, adding the predicted change to the previous approximation, giving a better approximation for the next cycle.

The least-squares solution for the redundant quasilinear system of Eqs. (7) is extracted through the well-known 27×27 system of normal equations. The resulting values of $\mathbf{c}$ and $\mathbf{s}$ minimize the sum $\Sigma_{k=0,n}W(k)\,\delta u(k)^2$, where $W(k)=1/\boldsymbol{\sigma}^2(k)$ is called the weight of the observation. The process can also give the standard errors $\boldsymbol{\sigma}(\mathbf{c})$ and $\boldsymbol{\sigma}(\mathbf{s})$ on all refined parameters through the standard assumption that χ^2 is equal to 1 at convergence.

III. EXTENSION TO NONTRICLINIC CRYSTALS

There are two obvious ways for adapting the above considerations to symmetrical crystals. We implemented both in order to ensure the soundness of the concepts and the correctness of the algorithms and calculations. The first way is to operate with crystal symmetry on the applied strain, creating symmetry-related energy data points, and then process the problem as a triclinic problem. The second way is to constrain the matrix of normal equations for the well-known constraints on stiffness coefficients and initial strain imposed by the crystal symmetry.

A. ''Triclinic'' formulation through symmetry-related strains

In this paragraph, we use the tensor notation for strains e_{ij}, $i,j=1,3$ rather than the single-index matrix notation of the previous and following paragraphs. Strains are rank-2 symmetrical tensors, meaning that a point-group symmetry operation which transforms the Cartesian unit vectors into new vectors with direction cosines a_{ij}, will transform a given strain e_{ij} into a strain e_{kl} according to the expression $e_{kl}=a_{ki}a_{lj}e_{ij}$ (with implicit summation on i and j). Direct-space and reciprocal-space grids used commonly by *ab initio* methods for symmetry-related strained states are usually selected to be symmetry related. As a result, the total energies that are calculated for such symmetry-related deformation states are numerically equal down to the last digit. It is then not necessary to actually perform the duplicate simulations. Instead, we can create several triclinic energy data points from the result of a single simulation for a symmetrical crystal, laying out the problem and analyzing it as if it were a triclinic problem. This provided a check that the least-squares formulation for the triclinic case is correct. However, we preferred the next method, using constraints, because it provides a cleaner interpretation of the standard deviations.

B. Constraint of the matrix of normal equations

We assume that we have a selection of energy data that is sufficient to solve for the independent elastic coefficients by any given method, say by the standard method explained in the introduction. We build the matrix of normal equations with this scant data as explained above, but without considering the symmetry-related strains. Unless the crystal is actually triclinic, that matrix will usually be singular, implying that it cannot be solved by plain inversion of the 27×27 matrix. This is because the data is aimed at the extraction of just the independent coefficients, and not of the coefficients that are related to them by symmetry. A frequent reason for singularity will be that the number of data points is less than the number of variables (27) in the normal equations.

In order to raise this singularity, we then implement the well-known constraints on stiffness coefficients[13,14] for the various crystal symmetries, producing in this way an equivalent system of normal equations with lower rank. In the case of a parameter which is dependent on one other parameter (e.g., equal, opposite, half etc.), a column with zero values is first created at the dependent parameter through factorization of the coefficient attached to the dependent parameter into the column corresponding to the independent parameter. The ordering of the parameters in the equations is then altered, in order to move that zero column to the last position each time such a condition is processed. In parallel with this operation, the row with same rank also gets moved to the last position. Processing of a linear combination of parameters (e.g., $2C_{66}=C_{11}-C_{12}$, etc.) is a simple adaptation of the above process, while processing a parameter constrained to be zero is obvious.

All constraints, including those on initial residual strain, are handled one at a time through the same simple above process. This approach has no symmetry-specific details or cases, and so is symmetry general. If it works for one symmetry, it will work for all symmetries. At the end of the elimination of constrained variables, an equivalent system of p equations with p unknowns involving only the p-independent parameters is stored in the top-left corner of the 27×27 matrix. That $p\times p$ system is solved by matrix inversion for the independent parameters and their standard errors. A check is then performed that this is indeed the correct solution of the full set of equations by ensuring that all components of the normal vector become zero within numerical accuracy (not just within experimental error) at convergence.

This straightforward algorithm, which processes all crystal symmetries through the same logical path is therefore symmetry general. It also includes a built-in safeguard against a deficient application of the scheme of constraints.

IV. SELECTION OF SIMULATIONS

Assuming exact knowledge of the cell data corresponding to minimum energy $U0$, the diagonal elastic coefficients C_{ii} can be determined from just the energy $U(\varepsilon)$ of the state deformed with the single-component strain ε_i using the relationship $C_{ii}=2[U(\varepsilon)-U0]/\varepsilon_i^2$. The nondiagonal coefficients C_{ij} can then be determined using the expression $2U=C_{ii}\varepsilon_i^2+C_{jj}\varepsilon_j^2+2C_{ij}\varepsilon_i\varepsilon_j$ for the energy of the state deformed with the two-component strain $\varepsilon=\varepsilon_i+\varepsilon_j$. It follows that a number of observations *chosen in this way*, and equal to the number of independent nonconstrained coefficients, plus one observation properly chosen to fix the minimum energy, is then sufficient to determine the elastic coefficients. It is obvious that, as that selection of data would be adequate to perform the calculation of independent stiffness coefficients by hand, it will also be adequate for solving a 21×21 least-squares system not involving residual strain, after rank reduction to boil down the problem to its independent parameters.

The ith component of the residual strain corresponding to the point of zero *applied* deformation can be extracted by considering the opposite of the strain used to determine the C_{ii} terms. For example, a cubic cell has only one variable parameter, namely the length of its edge. This is modeled in Eq. (2) through the S_1 component of the residual strain $\mathbf{S}$.

The invariance of the cubic symmetry of the model implies the existence of the constraints $S_1=S_2=S_3$, $S_4=S_5=S_6=0$. The C_{11} term was obtained by considering the energy of a state deformed by just a positive *applied* e_1 strain component, i.e., an extension along *a*. If the original cell were completely relaxed, a strain $-e_1$, i.e., a compressive strain by the same amount along **a**, should have the same energy *for suitably small strain moduli, like a percent or so. In the harmonic approximation*, if those two energies are observed to be different, then the point of zero *applied* deformations was not in fact the point of minimum energy. The offset can then be calculated from the energy data because the three data points $U(0)$, $U(e_1)$, and $U(-e_1)$ allow one to calculate the coefficients *A*, *B*, and *C* of the parabola describing the total energy $U=Ae^2+Be+C$ through them, hence the location $-s_1$ and value $U0$ of its minimum.

If we proceed in the above way, it then follows that the three independent elastic coefficients of a cubic material, as well as the cell data offset between minimum energy and zero applied strain can be extracted by the above least-squares process with calculation of just five energies for properly chosen strain states. Our goal is not to save on calculation time, but to calculate better values of elastic coefficients with the same computing effort. With the 15 or so simulations performed using other methods, the problem is therefore overdetermined by a factor 3 in the cubic case, an acceptable situation for the least-squares extraction of the variables and their standard deviations. This least-squares assessment of the precision of the extracted stiffness coefficients and the concomitant extraction of the residual on the processed energy differences constitute valuable improvements over the straight arithmetic extraction of the elastic numbers.

The above reasoning for the triclinic and the cubic cases can be extended to all symmetries, giving the minimum number of adequately selected simulations in the various cases shown in Table I. This minimum number of simulations is sufficient to extract numerical values for the independent parameters from the data provided they are selected as indicated above. Any desired number of observations can then be added, but in most cases about three times that minimum number of simulations should adequately balance the conflicting requirements of obtaining reliable least-squares results by overdetermining the problem without unduly straining the computing resources. That number is also roughly the minimum number of simulations required by other current methods.

We do not claim that the above way of selecting the simulations is necessarily optimal for all symmetries, but that it is symmetry general and fairly efficient. Marginally better schemes can be devised for specific symmetries, for example through a rhombohedral distortion of cubic symmetry,[12] while the above scheme generates an orthorhombic distortion in the same case. However, whatever the adopted distortion scheme, if its total energies can be analyzed for the elastic coefficients by any method, then the symmetry-general least-squares approach developed here could also analyze the total energies of the same distortions *calculated as detailed in Sec. V C below*. This is because feasibility boils down to a matter of singularity or not of the constrained least-squares matrix, not to a matter of difficulty to process given distortion symmetries.

TABLE I. Minimum number of energy data points required by the present method for the various point groups. It should be noted that under the IRE (1949) rules (Ref. 15), two orientations are allowed for the monoclinic point groups and the hexagonal point groups 32, $3m$, and $-32/m$, but not for the equivalent rhombohedral ones. They correspond to the same number of coefficients, but to different constraints. This leads to a total of 11 distinguishable sets of constraints for elastic coefficients rather than the 9 cases listed here. It should be noted that, although there is no unique way for choosing the strained systems, they must appropriately span the strain space. See the first paragraph of Sec. IV in the text. The column ''Total+1'' is then the minimum number of *ab initio* energy calculations required to extract the elastic coefficients for the corresponding point-group symmetry.

	Independent		
Crystal system + point group	Elastic coefficients	Residual strains	Total + 1
Triclinic	21	6	28
Monoclinic	13	4	18
Orthorhombic	9	3	13
Tetragonal 4, -4, and $4/m$	7	2	10
422, $4mm$, $-42/m$, $4/mmm$	6	2	9
Hexagonal & rhombohedral 3, -3	7	2	10
32, $3m$, and $-32/m$	6	2	9
Hexagonal 6, -6, $6/m$, 622, $6mm$, $-62m$, and $6/mmm$	5	2	8
Cubic	3	1	5

V. EXPERIMENT

A. Exact artificial data, triclinic processing

We programmed the least-squares methods and experimented first with exact artificial data generated with Eq. (2) for a perfectly harmonic cubic system. The energy data were used to find the elastic coefficients and initial strain assuming triclinic symmetry. Convergence is fast, and the calculation takes less than a second on a 233-MHZ PC. We started with zero as the initial guess for the elastic constants and residual strains and used three phases in the refinement. First, we refined the elastic constants while holding the residual strains fixed. Then we refined the residual strains while fixing the elastic constants to their previously refined values. Finally, we refined all 27 parameters simultaneously. The first two steps converged in one iteration each; the last step, in a few more cycles. Parameters that would have been constrained in an analysis assuming cubic symmetry were indeed consistent with the (nonimplemented) constraints down to numerical accuracy. This test shows the soundness of the approach and the correctness of the set of normal equations before implementing constraints.

TABLE II. Example of elastic coefficients for Si, $Fd\text{-}3m$. The simulation for calculation of C_{44} has *Imma* space-group symmetry, with Si in Wyckoff position $4e$: 0, $\frac{1}{4}$, z, requiring relaxation of the z coordinate of Si. If no relaxation is performed, a C_{44} value of 103 GPa is obtained. A $5\times5\times5$ reciprocal-space mesh was used. S_1 is the predicted residual strain relative to the experimental structure.

	C_{11}	C_{12}	C_{44} (GPa)	S_1 (no units)	
Strain					
0.5%	162	66	69	-0.00149	5 energy diffs
1.0%	161	65	74	-0.00152	5 energy diffs
1.5%	160	64	74	-0.00156	5 energy diffs
All 16 data $R=1.0\%$	161	64	76	-0.00154	15 energy diffs
Expt. (Ref. 3) (77 K)	168	65	80		

B. Exact artificial data, cubic processing

Five symmetry-unrelated artificial energy data $u(k)$ calculated using Eq. (2) above were created. The corresponding sparse system of normal equations was produced. Rank reduction of the normal matrix from 27 to 4 unique variables was then performed assuming cubic symmetry. Using the same refinement strategy as above (1 cycle of C_{ij} refinement only starting from zero values for all parameters, 1 cycle of s_1 refinement, retaining the previous C_{ij} values, and then a refinement on all four variables S_1, C_{11}, C_{12}, and C_{44}) converged for all practical purposes in three cycles. At the end of the refinement, the magnitude of the ratio of the constant term divided by C_{11} was less than 10^{-13} for all 27 normal equations. This indicates that the 23 additional triclinic equations that were not included in the above matrix inversion had indeed the same solution as the 4×4 system from which the independent parameters were derived. Those 23 additional equations were then consistent with zero shifts at convergence for all 27 change variables.

C. Real ''experimental'' data

We then proceeded with real *ab initio* energy data through automated generation of conventional crystallographic data for unstrained and then strained models as explained above, within SciCo's *MedeA* data preparation and submission environment, using the full-potential linear muffin-tin orbital LMTO code ORESTES.[16] All calculations reported employed the local-density approximation (LDA) in the Kohn-Sham approximation, except for the calculations on Al_2O_3, where because of the cost of the calculation we used the non-self-consistent Harris functional. We used a single modified Hankel function per angular momentum to represent the atomic orbitals outside the LMTO spheres. In this minimal basis, we allowed s and p functions for Be and C, and s, p, and d functions for all other elements. Testing showed that the results were surprisingly insensitive to details of the basis used, with nothing being gained using e.g., a double-κ basis. The same held for the real-space mesh used for the smooth part of the density between the atoms. We therefore used a grid spacing of 0.2 Å for all calculations. The muffin-tin radius for the atoms was chosen to be about 5–10% less than the contact radius to allow for the changes of the cell during both optimization and also the subsequent distortions. The atom positions were optimized in all distortions where they had any degrees of freedom, except in Al_2O_3 because of the cost of the calculation.

The results can be quite sensitive to the reciprocal-space mesh used to integrate over the Brillouin zone. As expected, a coarse mesh was sufficient for insulators, where we typically used a mesh spacing of 0.5 $Å^{-1}$. However, for metals a considerably finer mesh was required. We ran a series of calculations with finer spacings until the calculated elastic constants converged to within a few percent. This was achieved for all systems except Mg, where due to limitations in the program, we were unable to ensure convergence to perhaps about 10%. It is important to note that the meshes were held constant for all the strained structures. The size of the reciprocal-space mesh used for the primitive cell is noted in the following tables. The stiffness calculations rely on a consistent set of energies for all the structures, and the variation of the energy due to the distortions is on the order of 1 meV. Thus it was crucial to converge the calculations to at least 10^{-6} eV, to keep the real- and reciprocal-space meshes identical; to hold the muffin-tin radii fixed; and to ensure that distorted cells were as similar as possible to the undistorted cell. For the last condition, we were careful to automatically retain the origin and selection of the primitive lattice vectors and grids of the undistorted structure throughout the various distortions. We retained in this way the starting primitive fractional coordinates of the atoms and their placement with respect to grid points, *thus ensuring a same value of UO for all simulations*.

We first performed an analysis of 16 Si data points obtained by implementing five strain types ($+/-\boldsymbol{\varepsilon}_1$, $\boldsymbol{\varepsilon}_1+/-\boldsymbol{\varepsilon}_2$, and $\boldsymbol{\varepsilon}_4$) at each of three strain magnitudes for $\boldsymbol{\varepsilon}$ (0.5, 1.0, and 1.5%), plus the unstrained model. Least-squares analysis of each strain magnitude separately, and then of all magnitudes together, produced essentially the same elastic numbers four times (Table II), *indicating that anharmonic effects are negligible*. The residual on the 16 observations was about 1% and the standard errors on final values of variables were of about 2% of their refined values. The results for Si closely match the experimental numbers, but one should nevertheless not confuse the standard errors, i.e., the fit of the energy numbers to the predicted parabolic and tensor behavior, with the accuracy of the calculated elastic data relative to the experimental results.

In order to ensure the soundness of the approach and the reliability of the calculations, we then performed additional *ab initio* simulations starting from the refined cell read off the least-squares analysis. The simulations corresponding to the application of opposite strains gave virtually equal energies, as predicted by Eq. (1), confirming that the cell was indeed accurately relaxed. Simple-minded finite differences for the elastic coefficients based on Eq. (1), and implemented with a pocket calculator, gave elastic coefficients that were equivalent to the previously refined ones, usually within one *esd*. We accordingly conclude that the discrepancies between the observed and the experimental numbers are attributable to imperfections in either the simulation or the experiment, but not to the present analysis of the energy numbers.

The constancy of elastic numbers vs strain magnitude and the low global residual indicate that the maximum strain used of 1.5% was within the linear elastic region, *or in other words, in the harmonic approximation*. On other elements, we made the same observation at 3% strain levels, which is quite sufficient to get substantial energy differences from the minimum.

We then processed other cubic elements (C, Al, and Cu) and a cubic compound (GaAs) with results reported in Table III. We then tackled two hcp elements (Mg and Be) and one rhombohedral compound (Al_2O_3), with results in Table IV. We then produced numbers for tetragonal In, with results in Table V. We fully report elsewhere[17] on an orthorhombic element calculated by the above method (Ga). All these cases gave residuals comparable with Si, but some of the refined elasticity numbers do not compare quite as well with the experiment. Using the x-ray cell volume in place of the *ab initio* cell volume would have improved the fit in the most discrepant cases. We could find no element or simple binary compound with symmetry lower than orthorhombic for which experimental elastic data is known, and for which the calculation would have been tractable with PC-type computing.

TABLE III. Cubic system: three elements and a binary compound (experimental data from Ref. 3) The residuals were 1, 4, 4, and 3%, using reciprocal-space meshes of 7×7×7, 29×29×29, 25×25×25, and 5×5×5, respectively.

	C_{11}	C_{12}	C_{44} (GPa)	a (Å)	
C	1013	174	603	3.51331	Calc.
	1079	124	578	3.56691	Expt.
Al	120	61	34	3.9912	Calc.
	114	62	32	4.0494	Expt.
Cu	214	155	99	3.55947	Calc.
	168	121	75	3.61465	Expt.
GaAs	112	55	51		Calc.
	119	53	60	5.6533	Expt.

VI. SUMMARY AND CONCLUSIONS

The present paper details a different symmetry-general *least-squares* approach to the calculation of elastic coefficients for known crystal structure models of materials. It demonstrates the soundness of the approach and it presents results showing that elastic coefficients calculated in this way can quite convincingly match experimental results for a number of elements and compounds spanning a range of crystal symmetries. Compounds with lower symmetry and known experimental elastic coefficients would have been

TABLE IV. Hexagonal system. Two hcp elements and a rhombohedral compound.

Mg, (hcp, $P6_3/mmc$)
Nine energy differences at each of three strain magnitudes: 1, 2, and 3%. Residual 1% using a reciprocal-space mesh of 25×25×25.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44} (GPa)	a	c (Å)
27 diffs	70	31	24	74	22	3.1354	5.0909
Expt. (Ref. 3)	59	26	21	61	17	3.2089	5.2101

Be, hcp
Nine energy differences at each of two strain magnitudes: 2 and 4%. Residual 2% using a reciprocal-space mesh of 17×17×11.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44} (GPa)	a	c (Å)
18 diffs	336	81	21	443	181	2.1851	3.4710
Expt. (Ref. 16) (OK extrapolation)	299	27	11	342	166	2.2826	3.5836

Al_2O_3, R-$3c$
11 energy differences at 3% magnitude. Residual 0.2% using a reciprocal space mesh of 5×5×5, the Harris functional, and not optimizing the atomic positions.

	C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44} (GPa)	a	c (Å)
11 diffs	518	131	92	17	475	128	4.7040	12.7055
Expt. (Ref. 3)	500	162	111	−23	502	151	4.754	12.982

TABLE V. Tetragonal element, In, $I4/mmm$. Eight energy differences at each of 0.5, 1, and 2% magnitude. Residual 3%, using a reciprocal-space mesh of $11\times11\times11$.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66} (GPa)	a	c (Å)
24 diffs	71	36	46	58	11	17	3.0971	5.1905
Expt. (Ref. 4)	45	40	41	45	7	12	3.2523	4.9461

computationally too expensive for the purpose of the present contribution, which is to detail the method and demonstrate its general applicability.

The observed numerical precision (as distinguished from accuracy) of the energies for strained states is such that the resulting precision of the minimum-energy cell data that is produced as a by-product of the least-squares refinement process is quite high *as expected from the statistical considerations at the basis of the least-squares method*.[20] Table II shows an example where the minimum-energy cell data for three strain levels is constant to better than one part in 10 000. This was not among the reasons for implementing the present procedure, but it works so well that the present least-squares process might become an efficient way to accurately locate the minimum-energy cell.

The least-squares refinement outlined in this paper has been implemented within the MEDEA environment, where it can drive any of a number of total-energy quantum engines, such as ORESTES, which was used in this work. Since the environment includes structural databases such as CRYSTMET® and ICSD®, it is then a simple matter to pull one or more structures from the databases and submit the calculation of the elastic constants. The code automatically prepares the set of strained structures, runs each of the calculations and gathers the resulting energies from which it sets up and solves the least-squares problem. If desired, the cell parameters and atom positions can be optimized using the same quantum engine before starting the calculation of elastic constants. This may be necessary in cases where the calculated structure is somewhat different from the experimental one. Such differences arise both because the quantum methods have systematic errors and because structure-determination experiments are conducted at finite temperatures, etc.

The computational effort involved in preparing the strained structures and solving the least-squares problem amounts to only a few seconds. The quantum calculation on each of the strained structures takes the vast majority of the time. The required time for this step depends strongly on the code used, the nature of the compound, and the accuracy of the calculation. On the other hand, the amount of time it takes a user to prepare and run the calculation using the current scheme is negligible compared to the traditional approach of working out by hand the necessary strained structures and their symmetries. We are currently working, in collaboration, to perform through tests of the present method with the purpose of validating various widespread *ab initio* software packages, based on their ability to reproduce experimental elastic data for a variety of reference materials. Results of those extensive tests will be reported in future studies. The automation and robustness of the current method could open the way to the practical and credible calculation of stiffness data for phases where experimental data is difficult to obtain.

The present method seems to be currently quite convenient for elements and for binary compounds with up to a few atoms per asymmetric unit. Due to the n^3 dependence of the time needed for *ab initio* simulations, and also to the need to relax most atom positions for complex compounds, the computing time quickly becomes prohibitive with the number n of independent atoms. With PC-cluster-type computing, elastic coefficients for compounds with up to about ten atoms per primitive cell can currently be tackled, bringing materials like α-Al_2O_3 and low quartz within the range of currently tractable compounds. Steady progress in speed and accuracy of *ab initio* algorithms, and expectable progress in the speed of inexpensive PC-type CPU's at the rate predicted by Moore's law, will increase the tractable number of atoms by a factor of about 2 every five years. This is expected to gradually transform the current startup efforts into a very effective tool for the useful and inexpensive prediction of elastic coefficients of technologically important materials from crystal structure databases.

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[1] *Smithells' Metals Reference Book*, 7th ed., edited by E. A. Brandes and G. Brook (Butterworths, Oxford, 1992).

[2] *The Elastic Constants of Crystals*, edited by H. B. Huntington (Academic, New York, 1958).

[3] *Single Crystal Elastic Constants and Calculated Elastic Properties: A Handbook*, edited by Gene Simmons and Herbert Wang (M.I.T., Cambridge, MA, 1971).

[4] *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börnstein, New Series, Group III, Vol. 11, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1979).

[5] M. J. Mehl, J. E. Osburn, D. A. Papaconstantopoulos, and B. M. Klein, Phys. Rev. B **41**, 10 311 (1990).

[6] M. J. Mehl, J. E. Osburn, D. A. Papaconstantopoulos, and B. M.

Klein, in *Alloy Phase Stability and Design*, edited by G. M. Stocks, D. P. Pope, and A. F. Giamei, MRS Symposia Proceedings No. 186 (Materials Research Society, Pittsburgh, 1991), pp. 277–282.

[7] M. J. Mehl, Phys. Rev. B **47**, 2493 (1993).

[8] M. J. Mehl, J. E. Osburn, D. A. Papaconstantopoulos, and B. M. Klein, Phys. Rev. B **41**, 10 311 (1995).

[9] M. J. Mehl and D. A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996).

[10] H. Anton and P. C. Schmidt, Intermetallics **5**, 449 (1997).

[11] Suklyun Hong and C. L. Fu, Intermetallics **7**, 5 (1999).

[12] R. Stadler, W. Wolf, R. Podloucky, G. Kresse, J. Furthmüller, and J. Hafner, Phys. Rev. B **54**, 1729 (1996).

[13] W. A. Wooster, *Tensors and Group Theory for the Physical Properties of Crystals* (Clarendon, Oxford, 1973).

[14] J. F. Nye, *Physical Properties of Crystals* (Clarendon, Oxford, 1957).

[15] IRE standard, 49 IRE 14. S1. Reprinted as J. G. Brainerd *et al.*, Proc. IRE **37**, 1378 (1949).

[16] M. Methfessel and M. van Schilfgaarde, Phys. Rev. B **48**, 4937 (1993).

[17] J. Harris *et al.* (unpublished).

[18] R. M. Wentzcovitch, N. L. Ross, and G. D. Price, Phys. Earth Planet. Inter. **90**, 101 (1995).

[19] B. Kiefer, L. Stixrude, and R. M. Wentzcovitch, Geophys. Res. Lett. **24**, 2841 (1997).

[20] C. F. Gauss, *Theory of the Combination of Observations Least Subject to Errors*; *Part 1, Part 2, and Supplement* (SIAM, Philadelphia, 1995). Translated from the Latin by G. W. Stewart.