

Elastic Constants of Crystals from Linear-Response Theory

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(Received 1 September 1987)

We propose a new scheme to calculate the elastic constants of solids which is based on linear-response theory. Elastic constants are given directly by a single self-consistent calculation (i.e., they are *not* obtained by numerical differentiation of total energies or stresses). As an illustration, we apply our procedure to the determination of the equilibrium lattice constant, bulk modulus, and pressure derivative of the bulk modulus of silicon.

PACS numbers: 62.20.Dc, 63.10.+a, 71.10.+x

It is well known that normal frequencies associated with *microscopic* displacements of ions in crystals (i.e., phonon frequencies) are closely related to the electronic linear response (LR) of the undistorted crystals.^{1,2} Elastic constants can be viewed as normal frequencies associated with homogeneous strains, i.e., *macroscopic* distortions of the crystal. In any finite system, there is no conceptual difference between a strain and a microscopic distortion, and LR techniques are straightforwardly applicable in both cases. In an infinite system, in contrast, a homogeneous strain changes the boundary conditions of the Hamiltonian. As the use of perturbation theory requires the existence of a common basis set for the perturbed and unperturbed systems, macroscopic strains have not been treated so far within LR theory.

A few years ago a technique was put forward to calculate stresses in crystals within the local-density approximation (LDA)³; the state of the art in this field is to obtain elastic constants from the stresses calculated at different strains. In a recent Letter,⁴ the present authors have shown that the study of linear response in semiconductors can be conveniently formulated in terms of an

appropriate self-consistent Green's-function technique. However, the above-mentioned difficulties seem to indicate that LR methods are not suitable to the study of homogeneous strains.

The purpose of the present paper is to show that elastic constants can indeed be obtained by LR theory much in the same way as phonon frequencies. To this end, we formulate the strain problem in terms of perturbation theory, introducing a fictitious Hamiltonian which is related to the unperturbed one by a unitary transformation and obeys the same boundary conditions as the strained Hamiltonian. At first order we recover the expression for the stresses derived by Nielsen and Martin³ from the *virial theorem*.⁵ At second order we then obtain the elastic constants; these are calculated in the LDA with use of the LR theory.

For simplicity, in this paper we restrict ourselves to isotropic strains. The anisotropic case follows straightforwardly. As an example, we apply the linear-response Green's-function technique of Ref. 4 to the calculation of the equilibrium lattice parameter, bulk modulus, and pressure derivative of the bulk modulus of silicon.

In the LDA, the total energy of a crystal is given by

$$E_0 = \sum_{\mathbf{k},v} \epsilon_{\mathbf{k},v} + \int n(\mathbf{r}) [\epsilon_{XC}(n(\mathbf{r})) - \mu_{XC}(n(\mathbf{r}))] d^3r - \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' + E_{NN}, \quad (1)$$

where $n(\mathbf{r}) = \sum_{\mathbf{k},v} |\psi_{\mathbf{k},v}(\mathbf{r})|^2$, and $\epsilon_{\mathbf{k},v}$ and $\psi_{\mathbf{k},v}(\mathbf{r})$ are given by

$$\left[-\nabla^2 + \sum_{\mathbf{R}} V_N(\mathbf{r}-\mathbf{R}) + 2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \mu_{XC}(n(\mathbf{r})) \right] \psi_{\mathbf{k},v}(\mathbf{r}) = \epsilon_{\mathbf{k},v} \psi_{\mathbf{k},v}(\mathbf{r}), \quad (2)$$

$V_N(\mathbf{r}-\mathbf{R})$ indicates the interaction potential between electrons and an ion at lattice site \mathbf{R} , ϵ_{XC} and μ_{XC} are the exchange-correlation (XC) energy density and potential of the homogeneous electron gas, and E_{NN} is the ion-ion interaction energy. Atomic (Rydberg) units are used throughout. For clarity in the notation, we shall assume in the following that the electron-ion interaction V_N is local. The actual calculations, however, are performed with use of accu-

rate norm-conserving pseudopotentials.⁶

When the crystal is strained, the electron-ion interaction is modified as

$$V_{eN} \equiv \sum_{\mathbf{R}} V_N(\mathbf{r} - \mathbf{R}) \rightarrow V_{eN}^a \equiv \sum_{\mathbf{R}} V_N(\mathbf{r} - a\mathbf{R}).$$

The pressure and the bulk modulus are given by $P = -(1/3V)(dE/d\alpha)_{\alpha=1}$, and $B = (1/9V)(d^2E/d\alpha^2)_{\alpha=1} + \frac{2}{3}P$. The self-consistent Hamiltonian H_{SCF} defined by Eq. (2) depends upon α not only via V_{eN}^a but also implicitly through the self-consistent electron density $n^a(\mathbf{r})$. The difficulty of applying perturbation theory to Eqs. (1) and (2) stems from the fact that the unperturbed and strained Hamiltonians— $H_{\text{SCF}}^{\text{unstr}}$ and H_{SCF}^a —obey different boundary conditions. To cope with this difficulty, we introduce a *fictitious* strained Hamiltonian obtained from the unperturbed one through a scale transformation: $\tilde{H}_{\text{SCF}}^a(\mathbf{r}, \nabla) = H_{\text{SCF}}(\mathbf{r}/a, a\nabla)$. The advantage of our

introducing \tilde{H}_{SCF}^a is that it obeys the same boundary conditions as the physical strained Hamiltonian, and hence perturbation theory can be used to calculate the relative energy difference. At the same time, \tilde{H}_{SCF}^a and $H_{\text{SCF}}^{\text{unstr}}$ differ by a unitary transformation and their spectra are trivially related: $\tilde{\epsilon}_{\mathbf{k},v}^a = \epsilon_{\mathbf{k},v}$; $\tilde{\psi}_{\mathbf{k},v}^a(\mathbf{r}) = \alpha^{-3/2} \times \psi_{\mathbf{k},v}(\mathbf{r}/a)$; $\tilde{n}^a(\mathbf{r}) = \alpha^{-3}n(\mathbf{r}/a)$. As a consequence of these relations, the energy difference between the fictitious strained system and the unperturbed one is trivial to obtain, as expounded below.

Our procedure to calculate the energy change due to a strain thus consists of two steps: We first calculate the energy difference between the unperturbed crystal and the fictitious strained one described by \tilde{H}_{SCF}^a ; we then compute the energy difference between the latter and the physical strained system using perturbation theory. The first step is trivial: From Eq. (1), the total energy of the fictitious strained system, \tilde{E}^a , is related to the energy E_0 of the unstrained system in the following way:

$$\tilde{E}^a = E_0 + \int n(\mathbf{r}) [\epsilon_{\text{XC}}(\alpha^{-3}n(\mathbf{r})) - \epsilon_{\text{XC}}(n(\mathbf{r})) - \mu_{\text{XC}}(\alpha^{-3}n(\mathbf{r})) + \mu_{\text{XC}}(n(\mathbf{r}))] d^3r - \left[\frac{1}{\alpha} - 1 \right] \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'. \quad (3)$$

As for the second step, we first note that the Hartree and XC terms in \tilde{H}_{SCF}^a are *not* the Hartree and XC potentials generated by \tilde{n}^a . Hence, if we wish to interpret \tilde{H}_{SCF}^a as a genuine Kohn-Sham Hamiltonian, we must modify the definition of the external potential:

$$\tilde{H}_{\text{SCF}}^a = -\alpha^2 \nabla^2 + \tilde{V}_{\text{ext}}^a(\mathbf{r}) + 2 \int \frac{\tilde{n}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \mu_{\text{XC}}(\tilde{n}^a(\mathbf{r})), \quad (4)$$

where

$$\tilde{V}_{\text{ext}}^a(\mathbf{r}) = \sum_{\mathbf{R}} V_N(\mathbf{r}/a - \mathbf{R}) + 2(1 - 1/\alpha) \int \frac{n(\mathbf{r}')}{|\mathbf{r}/a - \mathbf{r}'|} d^3r' - \mu_{\text{XC}}(\alpha^{-3}n(\mathbf{r}/a)) + \mu_{\text{XC}}(n(\mathbf{r}/a)). \quad (5)$$

The key point of our argument is that the energy difference between the fictitious and the real strained systems, $E^a - \tilde{E}^a$, can be calculated by perturbation theory since H_{SCF}^a and \tilde{H}_{SCF}^a obey the same boundary conditions.

Let us denote $H_{\text{SCF}}^a - \tilde{H}_{\text{SCF}}^a$ by ΔH_{SCF}^a and the bare contribution to ΔH_{SCF}^a (i.e., the difference between the two Hamiltonians ignoring any charge redistribution) by ΔH_0^a :

$$\Delta H_0^a = (\alpha^2 - 1)\nabla^2 + \sum_{\mathbf{R}} V_N(\mathbf{r} - a\mathbf{R}) - \tilde{V}_{\text{ext}}^a(\mathbf{r}), \quad (6)$$

$$\Delta H_{\text{SCF}}^a = \Delta H_0^a + \int \frac{n^a(\mathbf{r}') - \tilde{n}^a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \mu_{\text{XC}}(n^a(\mathbf{r})) - \mu_{\text{XC}}(\tilde{n}^a(\mathbf{r})).$$

Standard linear-response theory gives the energy difference $E^a - \tilde{E}^a$ up to second order in ΔH_0^a :

$$E^a = \tilde{E}^a + \tilde{E}^{a(1)} + \tilde{E}^{a(2)} + \Delta E_{\text{NN}} + O((\Delta H_0^a)^3), \quad (7)$$

where

$$\tilde{E}^{a(1)} = \sum_{\mathbf{k},v} \langle \tilde{\psi}_{\mathbf{k},v}^a | \Delta H_0^a | \tilde{\psi}_{\mathbf{k},v}^a \rangle, \quad (8)$$

$$\tilde{E}^{a(2)} = \text{Re} \sum_{\mathbf{k},v} \langle \Delta \tilde{\psi}_{\mathbf{k},v}^a | \Delta H_0^a | \tilde{\psi}_{\mathbf{k},v}^a \rangle, \quad (9)$$

and $\Delta \tilde{\psi}^a$ is the correction to $\tilde{\psi}^a$ calculated to first order in ΔH_{SCF}^a . Each term $\tilde{E}^{a(n)}$ in Eq. (7) is a complicated function of α whose leading order in $\alpha - 1$ is $(\alpha - 1)^n$.

The knowledge of terms up to $\tilde{E}^{a(n)}$ is thus sufficient to evaluate the n th-order derivative of the energy with respect to α . Note that the *dressed* perturbation enters the definition of $\Delta \tilde{\psi}^a$: As a consequence, a self-consistent calculation is necessary to obtain it. Note also that the perturbation defined by Eq. (6) is intrinsically nonlocal not only because of the possible nonlocality of the electron-ion interaction potential, but also because of the kinetic-energy operator which enters its very definition. It results that dielectric-matrix techniques are not suitable to treat macroscopic strains within the present for-

malism, and one has necessarily to resort to the Green's-function linear-response technique expounded in Ref. 4.

In order to calculate the pressure, we expand Eq. (7) to first order in $\alpha - 1$. As remarked above, only \tilde{E}^a , $\tilde{E}^{a(1)}$, and ΔE_{NN} contribute to this order. Combining Eq. (7) with Eqs. (3) and (8), we finally obtain

$$\left(\frac{dE_a}{d\alpha} \right)_{\alpha=1} = 2 \sum_{\mathbf{k},r} \int \psi_{\mathbf{k},r}^*(\mathbf{r}) \nabla^2 \psi_{\mathbf{k},r}(\mathbf{r}) d^3r + \sum_{\mathbf{R}} \int n(\mathbf{r}) \nabla V_N(\mathbf{r}-\mathbf{R}) \cdot (\mathbf{r}-\mathbf{R}) d^3r - \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' + 3 \int n(\mathbf{r}) [\epsilon_{XC}(n(\mathbf{r})) - \mu_{XC}(n(\mathbf{r}))] d^3r + \frac{dE_{NN}}{d\alpha}. \quad (10)$$

Equation (10) is equivalent to the expression of the stress by Nielsen and Martin,³ specialized to the case of isotropic strain.

Elastic constants are then obtained by the expansion of Eq. (7) to second order in $\alpha - 1$. Contributions from \tilde{E}^a and $E^{a(1)}$ are trivial; some care must be taken when we evaluate Eq. (9) to second order in $\alpha - 1$. One has

$$\Delta \tilde{\psi}_{\mathbf{k},c}^a(\mathbf{r}) = \sum_c \tilde{\psi}_{\mathbf{k},c}^a(\mathbf{r}) \langle \tilde{\psi}_{\mathbf{k},c}^a | \Delta H_{\text{SCF}}^a | \tilde{\psi}_{\mathbf{k},c}^a \rangle / (\epsilon_{\mathbf{k},r} - \epsilon_{\mathbf{k},c}), \quad (11)$$

$$\tilde{E}^{a(2)} = \text{Re} \sum_{\mathbf{k},r,c} \langle \tilde{\psi}_{\mathbf{k},r}^a | \Delta H_{\text{SCF}}^a | \tilde{\psi}_{\mathbf{k},c}^a \rangle \langle \tilde{\psi}_{\mathbf{k},c}^a | \Delta H_0^a | \tilde{\psi}_{\mathbf{k},r}^a \rangle / (\epsilon_{\mathbf{k},r} - \epsilon_{\mathbf{k},c}). \quad (12)$$

Equation (12) is a well-defined function of α . However, when calculating matrix elements, we must distinguish between the *implicit* dependence of operators and wave functions upon α —which comes from the fact that they are expressed in terms of the scaled variable \mathbf{r}/α —and any other *explicit* dependences. The former dependence does not give any contribution since it only affects dummy integration variables. In order to keep the second order in $\alpha - 1$, one has then to keep consistently the first order in the matrix elements appearing in Eq. (12). To first order in $\alpha - 1$, the matrix elements of ΔH_0^a are

$$\langle \tilde{\psi}_{\mathbf{k},c}^a | \Delta H_0^a | \tilde{\psi}_{\mathbf{k},r}^a \rangle = (\alpha - 1) \left\{ 2 \int \psi_{\mathbf{k},c}^*(\mathbf{r}) \nabla^2 \psi_{\mathbf{k},r}(\mathbf{r}) d^3r + \sum_{\mathbf{R}} \int \psi_{\mathbf{k},c}^*(\mathbf{r}) \psi_{\mathbf{k},r}(\mathbf{r}) [\nabla V_N(\mathbf{r}-\mathbf{R}) \cdot (\mathbf{r}-\mathbf{R})] d^3r - 2 \int [n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|] \psi_{\mathbf{k},c}^*(\mathbf{r}) \psi_{\mathbf{k},r}(\mathbf{r}) d^3r d^3r' - 3 \int \psi_{\mathbf{k},c}^*(\mathbf{r}) \psi_{\mathbf{k},r}(\mathbf{r}) \mu'_{XC}(n(\mathbf{r})) n(\mathbf{r}) d^3r \right\} + O((\alpha - 1)^2). \quad (13)$$

Besides Eq. (13), the matrix elements of ΔH_{SCF}^a depend upon the charge redistribution,

$$\Delta n^a(\mathbf{r}) = 2 \text{Re} \sum_{\mathbf{k},r} \Delta \tilde{\psi}_{\mathbf{k},r}^{a*}(\mathbf{r}) \tilde{\psi}_{\mathbf{k},r}^a(\mathbf{r}),$$

through the Hartree and XC potentials. $\Delta n^a(\mathbf{r})$ must thus be calculated self-consistently. The dependence of $\Delta n^a(\mathbf{r})$ upon α is of the form $\Delta n^a(\mathbf{r}) \sim (\alpha - 1)f(\mathbf{r}/\alpha)$. According to the previous considerations, the overall scale factor $1/\alpha$ does not contribute to the matrix elements of the Hartree and XC potentials, and they depend upon α only through the $\alpha - 1$ prefactor. We have now all the ingredients to apply the self-consistent techniques of Ref. 4 to the calculation of the elastic constants of crystals.

Actual calculations have been performed for silicon with the use of a plane-wave (PW) basis set and ten special points for Brillouin-zone integrations⁷; norm-conserving pseudopotentials, as well as other technical details, are the same as in Ref. 4. We have performed several calculations at different lattice spacings a and different kinetic-energy cutoffs E_{cut} used to define the PW basis set. Within our technique, a single calculation is enough to provide the energy per cell, the pressure P , and the bulk modulus B . With the use of these data, the equilibrium lattice constant a_0 is also trivially predicted

by a single calculation. The pressure derivative of the bulk modulus, B' , is instead obtained by finite-difference differentiation. Our results are summarized in Table I.

We stress that—contrary to common practice—neither the pressure nor the bulk modulus is obtained by numerical differentiation. As these are delivered directly by our procedure and not as differences between nearly equal numbers, the numerical accuracy is greater than that usually obtained so far, as can be seen by a comparison of the calculated value of B' with experiments. This is a distinct advantage shared by this technique with the direct determination of phonon frequencies expounded in Ref. 4. Contrary to the case of phonons, but analogous to the calculation of stresses performed so far, the present results are rather sensitive to the size of the plane-wave basis set. As a consequence, even though sensible results can be obtained with moderate kinetic-energy cutoffs, rather large ones are necessary to obtain fully converged results. This is so because our formulas provide the *exact* value of the derivatives of the total energy, with the number of plane waves kept fixed. By now it is well known that the errors introduced by the use of a moderate number of PW's (≈ 100 – 200 per atom) do not affect *on the average* the energy differences relevant to

TABLE I. Pressure P , bulk modulus B , predicted equilibrium lattice parameter a_0 , and pressure derivative of the bulk modulus B' , as functions of the lattice spacing a and kinetic-energy cutoff E_{cut} .

| E_{cut} (Ry) | a (a.u.) | P (kbar) | B (kbar) | a_0 (a.u.) | B' |
|--------------------------|-----------------------------------|---------------|---------------|-----------------|------|
| 14 | 10.20 | -37.32 | 1044 | 10.08 | |
| 18 | 10.10 | 19.87 | 1119 | 10.16 | |
| | 10.20 | -10.01 | 996 | 10.17 | 4.03 |
| | 10.30 | -36.18 | 883 | 10.16 | |
| 22 | 10.10 | 28.21 | 1087 | 10.19 | |
| | 10.20 | -1.70 | 965 | 10.19 | 4.14 |
| | 10.30 | -27.86 | 852 | 10.19 | |
| 26 | 10.10 | 29.72 | 1077 | 10.19 | |
| | 10.20 | -0.26 | 955 | 10.20 | 4.18 |
| | 10.30 | -26.52 | 842 | 10.19 | |
| 30 | 10.20 | -0.36 | 955 | 10.20 | |
| | Experiment ^a | | 992 | 10.26 | 4.15 |
| | Present calculation ^b | | 955 | 10.20 | 4.2 |
| | Previous calculation ^c | | 930 | 10.20 | 3.8 |

^aSame experimental data as in Ref. 3b.

^bBest results from the present calculations.

^cPrevious calculations from Ref. 3b.

structural properties, if one keeps fixed the kinetic-energy cutoff (and *not* the number of PW's). The common practice followed so far is to calculate the energy at different volumes (or, more generally, at different strain states) keeping the kinetic-energy cutoff fixed.⁸ As the number of plane waves varies with the volume, the resulting energy-versus-volume curve is ragged and it is usually fitted by a smooth equation of state. The resulting values of a_0 , B , and B' depend somewhat on the explicit form of the equation of state and on the cutoff. A reliable value of the lattice constant can be obtained with rather low cutoffs (≈ 12 – 14 Ry for Si), independently of the detailed form of the equation of state.⁸ The bulk modulus and its pressure derivative are ticklish quantities which depend more sensitively on the chosen equation of state and cutoff. The technique presented here is the most accurate for their determination.

We conclude by summarizing the main goals achieved in this work. As a matter of principle, we have shown that—contrary to common belief—macroscopic distortions of crystals can be dealt with along similar lines as for any other perturbation. To this aim, the use of a previously developed Green's-function technique for treating the linear response has been essential. From a more practical point of view, the numerical efficiency of our method should be compared with the “brute force” calculation of total energies at different strains and/or with the direct calculation of the corresponding stresses.³ In the first approach, the numerical effort of a single calcu-

lation can be kept at a moderate level (≈ 250 PW's), provided several such calculations (typically ≈ 5) are done in order to fit the results by some equation of state. In the second approach (as well as in our own), a larger basis set (≈ 500 PW's) is necessary to obtain sensible results; a couple of calculations near equilibrium are necessary in this case to obtain the equilibrium lattice constants and, by numerical differentiation, the bulk modulus. As the numerical labor of a single calculation scales as the square of the size of the basis set,⁴ we conclude that the cost of the two schemes is comparable. Within the present scheme, the same numerical output can be obtained by a single total-energy calculation near equilibrium followed by a linear-response calculation along the lines exposed above. Since the cost of the latter is analogous to that of the former (both scale essentially as the square of the size of the basis set), we conclude that determining structural properties by our technique costs roughly as much as by the “strain technique.” We stress, however, that our technique is expected to be more accurate, as it requires less numerical differentiation (none at all in the case of elastic constants, first derivatives for nonlinear elastic constants, and so on).

We are grateful to R. Resta for a critical reading of the manuscript. This work has been partially supported by the Italian Ministry of Education through Centro Interuniversitario di Struttura della Materia, and by the Swiss National Science Foundation under Grant No. 2.683-085, and is part of the collaborative project between Scuola Internazionale Superiore di Studi Avanzati and Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Italy.

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