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Hellmann-Feynman theorem, elastic moduli, and the Cauchy relations

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The Hellmann-Feynman theorem is used to derive a formula for the harmonic elastic moduli of crystals in which every atom is at a center of symmetry in terms of the electron density and its distortion due to the crystal deformation. It is shown that these moduli satisfy the Cauchy relations if the electron density distribution deforms according to the same affine transformation which governs the crystal deformation.

Theoretical investigations of the elastic moduli of crystals are generally based on empirical interatomic force laws. These are framed to reflect the expected nature of the electron density distribution for the particular type of crystal being considered. In this paper we use the Hellmann-Feynman theorem[1–3] to express the elastic moduli of centrosymmetric crystals directly in terms of the electron distribution and its change due to crystal deformation. This result is used to derive a new sufficient condition for the satisfaction of the Cauchy relations for elastic moduli.

ADIABATIC APPROXIMATION

The starting point for the quantum-mechanical derivation of interatomic force laws for molecules and crystals is generally the adiabatic approximation. For a system of n electrons with positions denoted by $\vec{r}_k$, $k = 1,\ldots,n$, and N nuclei with positions denoted by $\vec{x}_l$, $l = 1,\ldots,N$, this approximation leads to the electron ground state $\psi(\vec{r}_1,\ldots,\vec{r}_n;\vec{x}_1,\ldots,\vec{x}_N)$ in a form in which the nuclei positions play the role of parameters. The corresponding electron ground-state energy $E(\vec{x}_1,\ldots,\vec{x}_N)$ is the expected value of the sum of the electron kinetic energy, the electron-electron interaction energy, and the electron-nucleus interaction energy when the nuclei are at the positions $\vec{x}_1,\ldots,\vec{x}_N$; it does not, in the convention employed here, include the nucleus-nucleus interaction energy.

HELLMANN-FEYNMAN THEOREM

Once the adiabatic approximation has been adopted, the Hellmann-Feynman theorem[1,2] provides a useful interpretation of the internucleus force law implied by $E(\vec{x}_1,\ldots,\vec{x}_N)$. The electron density of the kth electron is defined as

$$\rho_k(\vec{r};\vec{x}_1,\ldots,\vec{x}_N) = \int_{R_{3(n-1)}} \psi^*\psi\, d\vec{r}_1 \ldots d\vec{r}_{k-1}\, d\vec{r}_{k+1} \ldots d\vec{r}_n \,, \tag{1}$$

where $\psi = \psi(\vec{r}_1,\ldots,\vec{r}_n;\vec{x}_1,\ldots,\vec{x}_N)$, $R_{3(n-1)}$ is the configuration space for the $n-1$ electrons, k omitted, and we have used $\vec{r} = \vec{r}_k$ as the argument of ρ_k. The electron density of all of the electrons is

$$\rho(\vec{r};\vec{x}_1,\ldots,\vec{x}_N) = \sum_{k=1}^{n} \rho_k(\vec{r};\vec{x}_1,\ldots,\vec{x}_N) \,. \tag{2}$$

(Note that the identity of the electrons leads to the equality of the distributions ρ_k, $k = 1,\ldots,n$.) The nucleus-nucleus interaction is

$$V_{N,N}(\vec{x}_1,\ldots,\vec{x}_N) = \sum_{l,l'=1}^{N} q_l q_{l'} s_{ll'}^{-1}\,, \quad l > l' \tag{3}$$

where q_l is the charge on nucleus l and $s_{ll'} = |\vec{x}_l - \vec{x}_{l'}|$. The Hellmann-Feynman theorem then states that the force $\vec{F}_l$ on nucleus l can be written

$$\begin{aligned} F_{l\alpha} &= \frac{-\partial}{\partial x_{l\alpha}}(V_{N,N} + E) \\ &= \frac{-\partial V_{N,N}}{\partial x_{l\alpha}} + e q_l \int_{R_3} \frac{\partial s_{l\vec{r}}^{-1}}{\partial x_{l\alpha}} \rho(\vec{r};\vec{x}_1,\ldots,\vec{x}_N)\, d\vec{r} \,, \end{aligned} \tag{4}$$

with the integration carried out over all of three-dimensional space R_3. Here $x_{l\alpha}$, $\alpha = 1,2,3$ are the Cartesian components of $\vec{x}_l$ (and similarly for other vectors and tensors in what follows), $-e$ is the charge on the electron, and $s_{l\vec{r}} = |\vec{x}_l - \vec{r}|$. We introduce an effective total potential energy function V for the nuclei defined as

$$V(\vec{x}_1,\ldots,\vec{x}_N) = V_{N,N} + \int_{R_3} V_{N,e}\rho\, d\vec{r}\,, \tag{5}$$

where

$$V_{N,e}(\vec{r};\vec{x}_1,\ldots,\vec{x}_N) = -e\sum_{l=1}^{N} q_l s_{l\vec{r}}^{-1}\ . \tag{6}$$

The derivative of V with respect to $x_{l\alpha}$ will give the correct force on nucleus l providing, as shown in Eq. (4), ρ is not the differentiated in this calculation. More simply, since the force interpretation is not necessary for our purpose, we may say that the first partials with respect to $x_{l\alpha}$ of V and of $V_{N,N}+E$ are equal, providing ρ is not differentiated in the computation of $\partial V/\partial x_{l\alpha}$.

ELASTIC MODULI

We next apply this general discussion to the case of a crystal, one which corresponds to a simple Bravais lattice or one with two or more types of atoms in which each atom is at a center of symmetry, as in the NaCl structure, for example. Consider the crystal in its reference stress-free state and in its deformed state. In both cases we assume that the atoms are at rest at the appropriate lattice sites. That is, we are neglecting thermal and zero-point motion and the elastic moduli are therefore those of the classical harmonic theory.[4]

In order to avoid lattice distortions near the surface, we confine attention to an interior region of the crystal whose volume is $\mathscr{V}$ in the reference state. Let $\vec{X}_l$, $l = 1,\ldots,N$ be the positions in the reference state of the nuclei in $\mathscr{V}$, as well as those nuclei outside of $\mathscr{V}$ with which there is significant interaction.[5] In the deformed crystal these nuclei are at the positions

$$x_{l\alpha} = a_{\alpha\beta}X_{l\beta} = (\delta_{\alpha\beta} + e_{\alpha\beta})X_{l\beta}\,, \tag{7}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta, and $e_{\alpha\beta}$ is the small strain tensor characterizing the deformation, with $e_{\alpha\beta} = e_{\beta\alpha}$ and $|e_{\alpha\beta}| << 1$. The summation convention on repeated Greek subscripts is employed throughout. Given an arbitrary function $f(\vec{x}_1,\ldots,\vec{x}_N)$, it follows from Eq. (7)

$$\frac{\partial f}{\partial e_{\alpha\beta}} = \sum_{l=1}^{N} \frac{\partial f}{\partial x_{l\alpha}} X_{l\beta}\,. \tag{8}$$

Therefore, the stress tensor $t_{\alpha\beta}$ required to maintain the deformation $e_{\alpha\beta}$ is

$$t_{\alpha\beta} = \frac{1}{\mathscr{V}}\frac{\partial V}{\partial e_{\alpha\beta}}$$

$$= \frac{1}{\mathscr{V}}\sum_{l=1}^{N}\left[\frac{\partial V_{N,N}}{\partial x_{l\alpha}} + \int_{R_3}\frac{\partial V_{N,e}}{\partial x_{l\alpha}}\rho\, d\vec{r}\right]X_{l\beta}\,, \tag{9}$$

where we have used Eq. (5) and the understanding that ρ is not differentiated in computing the first derivative of V. By use of Eq. (8) we can also write

$$t_{\alpha\beta} = \frac{1}{\mathscr{V}}\left[\frac{\partial V_{N,N}}{\partial e_{\alpha\beta}} + \int_{R_3}\frac{\partial V_{N,e}}{\partial e_{\alpha\beta}}\rho\, d\vec{r}\right]. \tag{10}$$

Equation (10) can be simplified by use of the translational symmetry of the crystal to involve a sum over interacting primitive cells each of which is electrically neutral,[5] but we shall not pursue this here. We next introduce a new variable $\vec{R}$ for the integration over R_3 through the relation

$$r_\alpha = a_{\alpha\beta}R_\beta = (\delta_{\alpha\beta} + e_{\alpha\beta})R_\beta\,, \tag{11}$$

and describe the electron density in the deformed crystal in terms of $\vec{R}$ through the relation

$$\rho(\vec{r};\vec{x}_1,\ldots,\vec{x}_N)\,|a_{\alpha\beta}| = \tilde{\rho}(\vec{R};\vec{x}_1,\ldots,\vec{x}_N)\,, \tag{12}$$

where $\vec{r}$ and $\vec{R}$ are related by Eq. (11) and $|a_{\alpha\beta}|$ is the determinant of $a_{\alpha\beta}$. Since $|a_{\alpha\beta}|$ is the ratio of corresponding volumes in the deformed and in the reference states, $\tilde{\rho}$ is the electron density per unit of original volume. With this new variable of integration, Eq. (10) takes the form

$$t_{\alpha\beta} = \frac{1}{\mathscr{V}}\left[\frac{\partial V_{N,N}}{\partial e_{\alpha\beta}} + \int_{R_3}\frac{\partial V_{N,e}}{\partial e_{\alpha\beta}}\tilde{\rho}(\vec{R};\vec{x}_1,\ldots,\vec{x}_N)\,d\vec{R}\right]. \tag{13}$$

In order to obtain expressions for the elastic moduli which appear in the macroscopic equation $t_{\alpha\beta} = c_{\alpha\beta\gamma\delta}e_{\gamma\delta}$, it is necessary to expand the terms in Eq. (13) to first order in $e_{\gamma\delta}$. Since the variables $\vec{r}$ and $\vec{R}$ are related by the same affine transformation as are $\vec{x}_l$ and $\vec{X}_l$, it follows from the properties of the small strain tensor $e_{\alpha\beta}$ that

$$s_{l\vec{r}} = S_{l\vec{R}}(1 + e_{\alpha\beta}n_{l\vec{R}\alpha}n_{l\vec{R}\beta})\,, \tag{14}$$

$$s_{ll'} = S_{ll'}(1 + e_{\alpha\beta}n_{ll'\alpha}n_{ll'\beta})\,, \tag{15}$$

where $S_{l\vec{R}} = |\vec{X}_l - \vec{R}|$, $S_{ll'} = |\vec{X}_l - X_{l'}|$, and $\vec{n}_{l\vec{R}}, \vec{n}_{ll'}$ are unit vectors in the directions $\vec{X}_l - \vec{R}$ and $\vec{X}_l - X_{l'}$, respectively. Therefore, to second order in the strains

$$V_{N,N}(\vec{x}_1,\ldots,\vec{x}_N)$$

$$= \sum_{l,l'=1}^{N} q_l q_{l'} S_{ll'}^{-1}(1 - e_{\alpha\beta}n_\alpha n_\beta$$

$$+ e_{\alpha\beta}e_{\gamma\delta}n_\alpha n_\beta n_\gamma n_\delta)\,, \tag{16}$$

$$V_{N,e}(\vec{r};\vec{x}_1,\ldots,\vec{x}_N) = -e\sum_{l=1}^{N} q_l S_{l\vec{R}}^{-1}(1 - e_{\alpha\beta}n_\alpha n_\beta + e_{\alpha\beta}e_{\gamma\delta}n_\alpha n_\beta n_\gamma n_\delta)\ , \qquad (17)$$

and, to first order in the strains,

$$\frac{\partial V_{N,N}}{\partial e_{\alpha\beta}} = \sum_{l,l'=1}^{N} q_l q_{l'} S_{ll'}^{-1}(-n_\alpha n_\beta + 2e_{\gamma\delta}n_\alpha n_\beta n_\gamma n_\delta)\ , \qquad (18)$$

$$\frac{\partial V_{N,e}}{\partial e_{\alpha\beta}} = -e\sum_{l=1}^{N} q_l S_{l\vec{R}}^{-1}(-n_\alpha n_\beta + 2e_{\gamma\delta}n_\alpha n_\beta n_\gamma n_\delta)\ , \qquad (19)$$

with the missing subscripts for $n\,(ll'$ or $l\vec{R})$ the same as those for S in the equations in which they appear. It is also necessary to expand $\tilde{\rho}$ to first order in $e_{\alpha\beta}$

$$\tilde{\rho}(\vec{R};\vec{x}_1,\ldots,\vec{x}_N) = \tilde{\rho}(\vec{R};\vec{X}_1,\ldots,\vec{X}_N) + \frac{\partial\tilde{\rho}}{\partial e_{\gamma\delta}}e_{\gamma\delta}\ , \qquad (20)$$

with $\partial\tilde{\rho}/\partial e_{\gamma\delta}$ computed on the basis of Eq. (8) and evaluated at $e_{\alpha\beta} = 0$. Equations (18)–(20) are substituted into Eq. (13) and the various powers of $e_{\alpha\beta}$ collected. The terms free of $e_{\alpha\beta}$ cancel since the crystal is stress free in the reference state. The terms linear in $e_{\gamma\delta}$ lead to the following expressions for the elastic moduli $c_{\alpha\beta\gamma\delta}$:

$$\mathcal{V}c_{\alpha\beta\gamma\delta} = 2\sum_{l,l'=1}^{N} q_l q_{l'} S_{ll'}^{-1} n_\alpha n_\beta n_\gamma n_\delta - 2e\sum_{l=1}^{N} q_l \int_{R_3} S_{l\vec{R}}^{-1} n_\alpha n_\beta n_\gamma n_\delta \tilde{\rho}\, d\vec{R} + e\sum_{l=1}^{N} q_l \int_{R_3} S_{l\vec{R}}^{-1} n_\alpha n_\beta \frac{\partial\tilde{\rho}}{\partial e_{\gamma\delta}} d\vec{R}\ , \qquad (21)$$

where the missing subscripts for $n\,(ll'$ or $l\vec{R})$ are the same as those for S in the expression in which they appear, and the arguments of $\tilde{\rho}$ and $\partial\tilde{\rho}/\partial e_{\gamma\delta}$ are $(\vec{R};\vec{X}_1,\ldots,\vec{X}_N)$.

CAUCHY RELATIONS

The equalities $c_{\alpha\beta\gamma\delta} = c_{\alpha\gamma\beta\delta}$ are referred to as the Cauchy relations. For the case treated here, in which every atom is at a center of symmetry, the usually derived sufficient condition[6] for the satisfaction of the Cauchy relations is that the resultant interaction (including electron effects) between crystal atoms be two-body in character. That this condition is sufficient and not necessary is sometimes overlooked and the presence of many-body forces, covalent or metallic bonding is regarded as incompatible with the Cauchy relations. The present formulation provides another sufficient condition for the satisfaction of the Cauchy relations, one which does not *a priori* require two-body interactions and includes the possibility of covalent or metallic bonding. As seen from Eq. (21) the Cauchy relations will be satisfied for centrosymmetric crystals if $\partial\tilde{\rho}/\partial e_{\gamma\delta} = 0$ or, from Eq. (20), if

$$\tilde{\rho}(\vec{R};\vec{x}_1,\ldots,\vec{x}_N) = \tilde{\rho}(\vec{R};\vec{X}_1,\ldots,\vec{X}_N)\ , \qquad (22)$$

i.e., if contours of constant electron density undergo the same affine deformation as does the lattice of nuclei as shown schematically in Fig. 1. Since it is

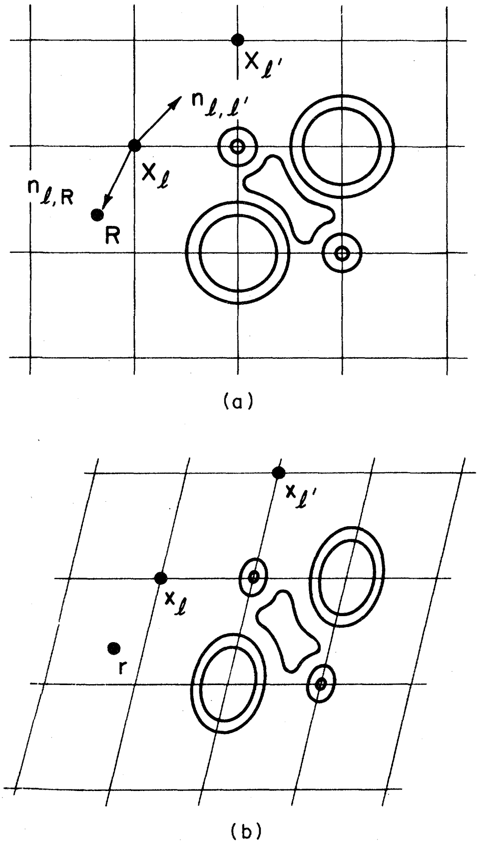

FIG. 1. Schematic representation of crystal in (a) reference and (b) deformed configurations. Curves are contours of constant electron density and they are shown undergoing the same affine deformation as the lattice.

to be expected that the electron density distribution due to the outer shell electrons will suffer greater distortion upon crystal deformation than that due to the inner shell electrons, it is unlikely that this condition will be satisfied exactly in real crystals, although it may be met approximately in some cases. Nevertheless, the existence of a new sufficient condition for the Cauchy relations may serve to put the customary one in better perspective.

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[5] The range of effective interaction can be decreased by use of the method of H. M. Evjen, Phys. Rev. 39, 675 (1932), in which ion assignment to the unit cell is made so as to assure charge neutrality.

[6] cf. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954), p. 136; G. Leibfried and N. Breuer, *Point Defects in Metals I: Introduction to the Theory* (Springer, New York, 1978), pp. 119 and 178.