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Observations on Generalized Forces in Solids

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The relationship of the Hellmann-Feynman theorem to present-day solid-state physics is reviewed. The empirical evidence for the theorem in its proposed form is not favorable. Suggestions why it might be invalid are therefore examined with particular care. In the course of this examination, a derivation of it is presented which does not make use of the Born-Oppenheimer approximation.

Some time ago, one of us published, with two coauthors, a short article pointing out that the balance of forces in solids poses some difficult questions.[1] In present-day physics, forces are generally considered derived quantities, while energies are considered primary. In this spirit, wave functions are accepted as true as soon as they produce a satisfactory energy. Decades ago, Pauling objected to the electron distributions arrived at by theorists, on the basis that the bonding of the nuclei by the valence electrons was missing.[2] Our present preoccupation with the Hellmann-Feynman theorem is essentially an attempt to give to this intuitive feeling a quantitative form. The theorem makes a direct statement about forces.[3,4] It tells us that the forces are conceptually much simpler than the energies, because the troublesome electron-electron interaction drops out of the computation. In fact, the theorem in its original form reduces the computation of forces to an exercise in classical electrostatics involving only point nuclei and a negative electronic charge cloud having no self-interaction.

The previous communication assumes that the primary term arising from the theorem is the bulk term associated with the interior of the material. If this is the case, the theorem for a crystal takes the form of an indefinite number of constraints on the electron distribution within a primitive cell. Only the simplest of these constraints – the one associated with a change in the lattice parameter – has been applied so far to published wave functions. The result was that the constraint is not obeyed by the published wave function, and that a Pauling type of electron concentration along the bonding directions must be introduced to produce agreement. The concentration would involve about 5% of an electron per atom. At the present time, we can add to this by saying something about empirical electron densities measured by x-ray diffraction. Measured *f* factors for aluminum, which is face-centered cubic, have been published by Raccah and co-workers.[5,6] Again, the constraint on the electron density is seemingly not verified; specifically, one would expect a reduction in the *f* factor for the (2, 2, 0) reflection as compared to atomic aluminum because such a reduction would transfer charge from the corners of the Wigner-Seitz cell to the centers of the faces. To have the constraint verified this *f* factor should be reduced from 7.26 to 6.84. According to Raccah, such a shift is not in agreement with experiment. He informs us, however, that it is possible that the distortion of charge does not occur for the valence electrons, but for the inner shells. In this case, present-day x-ray techniques could not detect it.

Under these circumstances, it is proper to look for reasons why the theorem might not hold in its assumed form, or might not hold at all. One suggestion came from Kleinman, namely, that the electrostatic balance is supplied by distortions of the surface.[7] It will, no doubt, be some time before the possibility will have been fully explored. The only comment we want to make at this time is that the electrostatic imbalance of the interior is equivalent to thousands of atomospheres of internal pressure, and that it is at least unusual to expect surface effects to cancel a quantity which is so large.

Another suggestion was offered by Varma.[8] The simplest derivation of the Hellmann-Feynman theorem starts out from the Born-Oppenheimer approximation. For this approximation to be valid, electronic frequencies should be large in comparison with nuclear frequencies. This is not the case for metals where a continuum of excited electronic states adjoins the ground state. If Varma's view is correct, the theorem should hold in its assumed form for insulators and semiconductors. The absence of forces on the nuclei in metals, on the other hand, would arise because the electronic states rearrange as soon as a nucleus is displaced.

We present in the following a derivation of the theorem, with makes no use of the Born-Oppenheimer approximation. We do not wish to imply by this that Varma's argument is thereby refuted, but only that it contains certain difficulties of its own which are not easily removed.

We consider the entire crystal as a quantum system for which all particle coordinates and momenta are operators. Only their expectation values are numbers. From such a point of view, the Hamiltonian $\mathcal{H}$ of any system of nuclei and electrons retains its simple form: kinetic energy plus potential energy, with potential energy consisting exclusively of bare Coulomb terms. If we now consider a particular nucleus s of mass M whose position vector is $\vec{X}(s)$ and whose momentum is $\vec{P}(s)$, the following equations hold for the time derivatives:

$$\begin{aligned} M\frac{d\vec{X}(s)}{dt} &= \frac{M}{i\hbar}\left[\vec{X}(s)\mathcal{H} - \mathcal{H}\vec{X}(s)\right] = \vec{P}(s) \ , \\ \frac{d\vec{P}(s)}{dt} &= \frac{1}{i\hbar}\left[\vec{P}(s)\mathcal{H} - \mathcal{H}\vec{P}(s)\right] = -\frac{\partial V}{\partial\vec{X}(s)} \ . \end{aligned} \tag{1}$$

The term in $\mathcal{H}$ made up of the electron-electron interaction commutes with $\vec{P}(s)$ and therefore

$$V = \frac{1}{2}\sum_{s_1\neq s_2}\frac{e^2Z^2}{|\vec{X}(s_1)-\vec{X}(s_2)|} - \sum_s\int d\vec{x}\,\rho(\vec{x})\frac{e^2Z}{|\vec{x}-\vec{X}(s)|} \ , \tag{2}$$

where Ze is the nuclear charge and $\rho(\vec{x})$ is the electron-density operator. For simplicity, we have confined ourselves to monatomic solids for which the atoms form a simple Bravais lattice. Taking expectation values, we obtain the mean force on the nucleus s in a system of nuclei and electrons

$$\langle\vec{F}(s)\rangle = -\left\langle\frac{\partial V}{\partial\vec{X}(s)}\right\rangle . \tag{3}$$

This looks exactly as before [Eq. (4) of Ref. 4], except that expectation values must be taken over the nuclear as well as the electronic part of the total wave function.

The one assumption we have to make here is that crystal deformations can be specified in terms of nuclear coordinates only. We then can, from (3), determine the stresses opposing the strains which result from a homogeneous deformation of the lattice. To this end we introduce a three-by-three matrix $\underline{\mathfrak{A}}^0$ which measures the size and the shape of the unit cell of the lattice.[9] Each lattice vector $\vec{X}^0(s)$ is then given by

$$\vec{X}^0(s) = \underline{\mathfrak{A}}^0\,\vec{s} \ , \tag{4}$$

where $\vec{s}$ is a set of three integers numbering the unit cells. Identifying $\vec{X}^0(s)$ with the expectation value of $\vec{X}(s)$ is equivalent to the assumption that the equilibrium positions of the nuclei form a regular array.

In the following, we shall restrict ourselves to homogeneous deformations. They can be put in the form

$$\langle\vec{X}(s)\rangle = \underline{\mathfrak{A}}\,\vec{s} \ , \tag{5}$$

where $\underline{\mathfrak{A}}$ is a numerical matrix differing somewhat from $\underline{\mathfrak{A}}^0$. The strain tensor $\underline{\Sigma}$ is defined through the relation

$$\langle\vec{X}(s)\rangle = \underline{\Sigma}\ \vec{X}^0(s) + \vec{X}^0(s) \tag{6}$$

and therefore, from (4)–(6), $\underline{\Sigma}$ can be expressed as

$$\underline{\Sigma} = \underline{\mathfrak{A}}\ \ (\underline{\mathfrak{A}}^0)^{-1} - \underline{\mathfrak{E}} \tag{7}$$

with $\underline{\mathfrak{E}}$ the unit tensor. The components σ_{ij} of $\underline{\Sigma}$ or equivalently the components of $\underline{\mathfrak{A}}$ are the required deformation variables.

The stress tensor $\underline{\Pi}$ conjugate to the strain tensor $\underline{\Sigma}$ is obtained by scalar multiplication of (3) with $(Nv)^{-1}\partial\langle\vec{X}(s)\rangle/\partial\sigma_{ij}$ and summation over s,

$$\Pi_{ij} = -\frac{1}{Nv}\sum_{s,k}\left\langle\frac{\partial V}{\partial X_k(s)}\ \frac{\partial\langle X_k(s)\rangle}{\partial\sigma_{ij}}\right\rangle \ , \tag{8}$$

where $v = \det(\underline{\mathfrak{A}})$ denotes the volume of the unit cell and (Nv) the volume of the crystal. Equation (8) is a generalization of the Hellmann-Feynman theorem. Using (6) we may rewrite Eq. (8) as a sum of tensor products of vectors as follows:

$$\underline{\Pi} = -\frac{1}{Nv}\sum_s\left\langle\frac{\partial V}{\partial\vec{X}(s)}\right\rangle\vec{X}^0(s) \ . \tag{9}$$

In particular, the isotropic pressure P is given by a sum of scalar products, namely,

$$P = -\frac{1}{3}\sum_i\Pi_{ii} = \frac{1}{3Nv}\sum_s\left\langle\frac{\partial V}{\partial\vec{X}(s)}\right\rangle\cdot\vec{X}^0(s) \ . \tag{10}$$

The essence of the results (8)–(10) is that only the nuclear coordinates enter as intermediates in the definition of the stresses. This is plausible in a crystalline solid, but can be interpreted as a hidden use of the Born-Oppenheimer approximation. This type of use does seem, however, justified by the facts of experience even for metals.

The final results differ from previous forms of the Hellmann-Feynman theorem in so far as we now have to average over the nuclei as well as the electrons; whether this is effectively a departure from previous results in a problem of zero-point motions. The corrections could be significant for extreme quantum crystals or near the melting temperature and phase transitions.[10] At nonzero temperatures $\langle\cdots\rangle$ denotes an equilibrium ensemble average with respect to $\mathcal{H}$. The important result, namely, that only nuclear coordinates appear on the right, is preserved in the generalized version of the theorem.

We wish to express our thanks to Dr. Paul Raccah for putting his x-ray results for aluminum at our disposal, and for taking a sustained interest in our theoretical efforts.

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