

# Nonapplicability of the Hellmann-Feynman Theorem to Infinitely Periodic Systems\*

LEONARD KLEINMAN

Department of Physics, University of Texas, Austin, Texas 78712

(Received 2 January 1970)

Wannier, Misner, and Schay have recently applied the Hellmann-Feynman molecular force theorem to metals and found a mutual repulsion of the ions. They conclude that the extra charge along the nearest-neighbor directions provided by computed Bloch wave functions is an order of magnitude too small to provide binding and that *nearly free-electron metals do not exist*. We show that they have misapplied the Hellmann-Feynman theorem and that nearly free-electron metals do exist.

IT has been shown by Hellmann<sup>1</sup> and Feynman<sup>2</sup> that the total force on an atomic nucleus in a molecule is just equal to the electrostatic force originating from the electrons and other nuclei. Wannier, Misner, and Schay<sup>3</sup> (WMS) have applied the Hellmann-Feynman theorem to obtain the generalized force  $\partial U/\partial q$  opposing a lattice distortion in a simple crystal lattice of cubic symmetry. They find<sup>4</sup>

$$\frac{\partial U}{\partial q} = -Ze^2 \int_{\text{cell}} [Z\delta(\mathbf{r}) - \rho(\mathbf{r})] \frac{\partial}{\partial q} \left[ \sum_i' \frac{1}{|\mathbf{R}_i - \mathbf{r}|} \right] d\mathbf{r}, \quad (1)$$

where  $Ze$  is the nuclear charge,  $N$  is the number of atoms in the crystal,  $\rho(\mathbf{r})$  is the electron density,  $q$  is a generalized coordinate, and  $\mathbf{R}_i$ , the nuclear positions, are the only quantities depending on  $q$ . In deriving (1), *periodic boundary conditions* have been assumed in that sums like  $\sum_{i,j}' |\mathbf{R}_i - \mathbf{R}_j|^{-1}$  have been replaced by  $N \sum_i' 1/R_i$ . WMS noted that if the electron charge density is a constant (free-electron model) and  $q$  is taken to represent a dilation, Eq. (1) yields a negative force opposing the dilation, in other words a repulsion between unit cells. They also determined  $\partial U/\partial q$  for lithium from (1) using computed Bloch wave functions. These functions produced a surplus of charge along the (111) nearest-neighbor directions, which led to a force opposing the dilation but which was an order of magnitude too small to cancel the repulsive force. WMS state that either present-day computed Bloch functions are very poor and improved band calculations will yield Bloch functions which when inserted in (1) will give  $\partial U/\partial q = 0$  or that the entire Bloch band picture has a qualitative defect which can be corrected only by considering strong correlation effects such as the Pauling resonant bond<sup>5</sup> or the Wigner electron crystal. In either

event, their conclusion is that nearly free-electron metals do not exist.

It is the purpose of this note to demonstrate that nearly free-electron metals do exist and that this is not in conflict with the Hellmann-Feynman theorem. Note that if  $q$  is taken to be one component of the position vector for a single nucleus in the crystal, Eq. (1) yields  $\partial U/\partial q = 0$  for the free-electron metal, as it must, there being no preferred direction for the force to act on a nucleus within an infinitely periodic crystal. Thus we find the paradox that each nucleus is at equilibrium, but the crystal as a whole is not at equilibrium. This paradox is easily resolved when we recall that the Hermiticity of the Hamiltonian operator is vital to the derivation of the Hellmann-Feynman theorem.<sup>2</sup> The Hermiticity of an operator is defined only within a space of functions all obeying the same boundary conditions. In the present case those boundary conditions are just the periodicity of the crystal.<sup>6</sup> Thus the Hellmann-Feynman theorem may be applied to finite systems for which the boundary conditions involve merely the vanishing of the wave functions at infinity or to infinitely periodic systems to determine the forces aiding or opposing nuclear displacements which do not affect the periodicity of the system,<sup>7</sup> but not to strains which, of course, change the periodicity condition.

For a finite crystal Eq. (1) is replaced by

$$\begin{aligned} \frac{\partial U}{\partial q} = & -\frac{1}{2}Ze^2 \frac{\partial}{\partial q} \sum_{i \neq j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} \\ & + Ze^2 \frac{\partial}{\partial q} \sum_i \int_{\text{crystal}} \frac{\rho(\mathbf{r})}{|\mathbf{R}_i - \mathbf{r}|} d\mathbf{r}. \quad (2) \end{aligned}$$

If  $q$  is taken to be a component of one of the interior  $\mathbf{R}_i$ , Eq. (2) can be reduced to Eq. (1), and  $\partial U/\partial q = 0$ . If  $q$  is taken to be a component of one of the  $\mathbf{R}_i$  near the surface of the metal and  $\rho(\mathbf{r})$  is either taken to be a constant or calculated from Bloch functions, there will

\* Research sponsored by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Grant No. AFOSR 68-1507.

<sup>1</sup> H. Hellmann, *Einführung in die Quantenchemie* (Franz Deuticke, Leipzig, 1937), p. 285.

<sup>2</sup> R. P. Feynman, Phys. Rev. **56**, 340 (1939).

<sup>3</sup> G. H. Wannier, C. Misner, and G. Schay, Jr., Phys. Rev. **185**, 983 (1969).

<sup>4</sup> We have corrected a misprint in Eq. (1) of Ref. 3. They have omitted the factor of  $-Z$ . They have also included a factor of  $\frac{1}{2}$ , which is correct when  $q = a = |\mathbf{R}_i - \mathbf{R}_j|/|i - j|$  but not when  $q = (R_i)_x$ .

<sup>5</sup> L. Pauling, Proc. Roy. Soc. (London) **A196**, 343 (1949).

<sup>6</sup> The periodicity we refer to is not the cellular periodicity of the crystal but rather the artificial cyclic boundary conditions  $\mathbf{R}_{l+n_1a_1} = \mathbf{R}_{l+n_2a_2} = \mathbf{R}_{l+n_3a_3} = \mathbf{R}_l$ , which were applied in order to be able to neglect the actual crystal boundaries as was done in the derivation of Eq. (1).

<sup>7</sup> The displacement  $\eta_l$  of a single nucleus does not affect the periodicity condition since one can take  $\eta_{l+n_1a_1} = \eta_{l+n_2a_2} = \eta_{l+n_3a_3} = \eta_l$ .

exist an outward force on the  $i$ th nucleus due to the multipole fields from all the inner unit cells. If, however, the nucleus is allowed to relax outward very slightly from the center of its cell, it will feel an equal force inward from the charge distribution in its own cell and neighboring cells. Thus every nucleus in the crystal will be in electrostatic equilibrium and the entire crystal will also be in electrostatic equilibrium with respect to a dilational strain.

Just because an equilibrium distribution of nuclei within a particular electronic charge density distribution can always be found, does not imply the crystal is at equilibrium. The Hellmann-Feynman theorem also requires that the charge density be calculated from electronic eigenstates of the nuclear distribution. This coupled with the fact that interior nuclei in a periodic array always feel no force makes the theorem completely impractical for determining the lattice constant of metals. One could start with a periodic array with lattice constant  $a_0$ . If one could calculate eigenfunctions for a finite crystal, one could then apply the theorem to determine the forces on the nuclei near the surface. Using these forces, one might estimate new positions for the surface nuclei. If one could calculate eigenfunctions for this new nuclear distribution one could apply the theorem again to get new values for the forces. If  $a_0$  were the correct bulk lattice constant, after several iterations one would locate the true equilibrium positions for the surface nuclei. On the other hand, if  $a_0$  were

not the correct bulk lattice constant, this surface dilation would propagate further into the bulk of the crystal with each iteration, and convergence to the correct lattice constant would be interminable. Therefore the equilibrium lattice constant of metals can only be determined by maximizing the binding energy. Such a calculation has been performed for aluminum.<sup>8</sup> The conduction-electron wave functions were taken to be a single plane wave orthogonalized to the core wave functions. These core functions were calculated self-consistently in the crystal using the complete Hartree-Fock Hamiltonian. Except for the neglected band contributions (i.e., the added binding energy obtained from using exact Bloch eigenfunctions instead of plane waves), the calculation is believed accurate to within 0.002 Ry. The total binding energy was found to be 4.06 Ry per ion at an equilibrium lattice constant  $0.99a_0$  where  $a_0$  is the experimental lattice constant and the experimental binding energy is 4.16 Ry per ion. Less accurate calculations<sup>9</sup> using Bloch eigenfunctions indicate that the band contribution to the binding is about 0.10 Ry per ion. Thus we see that aluminum is a nearly free-electron metal, differing from a completely free-electron metal by less than 3% in the binding energy. The Hellmann-Feynman theorem in no way contradicts this.

---

<sup>8</sup> P. C. Chow and L. Kleinman, Phys. Rev. **178**, 1111 (1969).

<sup>9</sup> L. Kleinman, Phys. Rev. **146**, 472 (1966).