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THEOREM OF DIFFERENTIATION OF THE ENERGY OF A MULTIATOMIC SYSTEM WITH RESPECT TO ATOMIC COORDINATES (PART I)

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The theorem asserting that the arbitrary-order derivative of the average energy of a solid with respect to atomic coordinates equals the average value of the corresponding derivative of the potential energy operator with respect to atomic coordinates has been proved. This theorem is a generalization of the well-known Gell-Mann–Feynman theorem, which was proved only for the first derivative of the average energy with respect to atomic coordinates. A necessity in such a generalization is associated with the calculation of force constants in solids, which are the derivatives of the average energy with respect to atomic coordinates, and, maybe, other physical quantities.

K e y w o r d s: energy of multiatomic system, Gell-Mann–Feynman theorem.

1. Introduction

In work [1], the expression for the second-order force constants of a multiatomic system, in particular, a crystal, was found in the framework of Hartree–Fock–Roothaan method [2]. However, the calculations by this formula faced principle difficulties associated with the differentiation of the matrix elements of the Hamilton operator with respect to atomic coordinates. It turns out that the differentiation of the wave functions used to calculate the matrix element results in the appearance of functions with the quantum numbers $l < 0$, which have neither physical nor mathematical sense.

While calculating the first derivative of the energy with respect to atomic coordinates, the differentiation of wave functions can be avoided due to the Gell-Mann–Feynman theorem [3]. However, in the case of derivatives of higher orders, such a possibility was not evident.

If the operators of the potential energy derivatives with respect to atomic coordinates are regarded as operators of certain physical quantities, the observed values of which are calculated by the ordinary quantum-mechanical averaging, the problem of differentiation does not arise at all. However, these are only speculations, although rather sound.

In this work, we managed to prove the theorem on the differentiation of the energy of multiatomic systems with respect to atomic coordinates. According to it, the arbitrary-order derivative of the average energy with respect to atomic coordinates equals the average value of the operator of the derivative of the same order of the potential energy of the system with respect to atomic coordinates. This theorem allows one to avoid the differentiation of wave functions in matrix elements and, therefore, makes the calculations of force constants in solids and, probably, other quantities executable.

It should be noted that the potential energy of nuclei is always a value of nucleus potential energy operator averaged over the quantum state of the electron subsystem, which is a direct consequence of the adiabatic approximation.

2. Proof of the Theorem

The mathematical expression of the theorem concerned looks like

$$\frac{\partial^n E}{\partial \mathbf{R}_k^n} = \int \psi^* (R, r) \frac{\partial^n U (R, r)}{\partial \mathbf{R}_k^n} \psi (R, r) \, d\mathbf{R} d\mathbf{r}, \qquad (1)$$

where E is the average energy of the system, n the derivative order, $\psi (R, r)$ the wave function of the system, $U(R, r)$ the operator of the potential energy of the system, and R and r are the coordinate sets for electrons and atoms, respectively.

The start point is the Gell-Mann–Feynman theorem, which has the mathematical expression

$$\frac{\partial E}{\partial \mathbf{R}_k} = \int \psi * (R,r) \frac{\partial U(R,r)}{\partial \mathbf{R}_k} \psi(R,r) d\mathbf{r} d\mathbf{R} \qquad (2)$$

or, since that the potential energy operator commutes with the wave function,

$$\frac{\partial E}{\partial \mathbf{R}_k} = \int \rho\,(R,r) \frac{\partial U(R,r)}{\partial \mathbf{R}_k} d\mathbf{R} d\mathbf{r}, \qquad (3)$$

where

$$\rho\,(R,r) = \psi^*\,(R,r)\,\psi\,(R,r)\,. \qquad (4)$$

The second derivative of the energy equals

$$\frac{\partial^2 E}{\partial \mathbf{R}_k^2} = \int \rho\,(R,r) \frac{\partial^2 U\,(R,r)}{\partial \mathbf{R}_k^2} d\mathbf{R} dr +$$

$$+ \int \frac{\partial}{\partial \mathbf{R}_k} \rho\,(R,r) \frac{\partial U\,(R,r)}{\partial \mathbf{R}_k} d\mathbf{R} d\mathbf{r}. \qquad (5)$$

It is necessary to prove that the second term on the right-hand side of this equality turns to zero. For this purpose, let us integrate it over $\mathbf{r}$ by parts,

$$\int \frac{\partial}{\partial \mathbf{R}_k} \rho\,(R,r) \frac{\partial U\,(R,r)}{\partial \mathbf{R}_k} d\mathbf{R} d\mathbf{r} =$$

$$= \int d\mathbf{R} \frac{\partial U\,(R,r)}{\partial \mathbf{R}_k} \int \frac{\partial}{\partial \mathbf{R}_k} \rho\,(R,r')\,d\mathbf{r}' -$$

$$- \int d\mathbf{R} \frac{\partial^2 U\,(R,r)}{\partial \mathbf{R}_k^2} d\mathbf{r} \int \frac{\partial}{\partial \mathbf{R}_k} \rho\,(R,r')\,d\mathbf{r}'. \qquad (6)$$

The both terms on the right-hand side of Eq. (6) contain, as a multiplier, the expression $\int \frac{\partial}{\partial \mathbf{R}_k} \rho(R,r)\,d\mathbf{r}$, which, according to the condition $\int \rho\,(R,r)\,d\mathbf{r} = 1$ equals zero, so that the whole expression (6) vanishes. Then Eq. (5) reads

$$\frac{\partial^2 E}{\partial \mathbf{R}_k^2} = \int \rho\,(R,r) \frac{\partial^2 U\,(R,r)}{\partial \mathbf{R}_k^2} d\mathbf{R} d\mathbf{r}. \qquad (7)$$

The subsequent differentiations result in the appearance of expressions of the type

$$\frac{\partial^n E}{\partial \mathbf{R}_k^n} = \int \rho\,(R,r) \frac{\partial^n U\,(R,r)}{\partial \mathbf{R}_k^n} d\mathbf{R} d\mathbf{r} +$$

$$+ \int \frac{\partial}{\partial \mathbf{R}_k} \rho\,(R,r) \frac{\partial^{n-1} U\,(R,r)}{\partial \mathbf{R}_k^{n-1}} d\mathbf{R} d\mathbf{r}, \qquad (8)$$

where n is the derivative order, and the equality of the second term on the right-hand side of this expression to zero is proved, as was done above.

Finally, we may write down

$$\frac{\partial^n E}{\partial \mathbf{R}_k^n} = \int \rho\,(R,r) \frac{\partial^n U\,(R,r)}{\partial \mathbf{R}_k^n} d\mathbf{R} d\mathbf{r}. \qquad (9)$$

The theorem is proved.

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ТЕОРЕМА ПРО ДИФЕРЕНЦІЮВАННЯ ЕНЕРГІЇ БАГАТОАТОМНОЇ СИСТЕМИ ПО КООРДИНАТАХ АТОМІВ (ЧАСТИНА I)

Р е з ю м е

Доведено теорему про диференціювання енергії твердого тіла по координатах атомів, яка стверджує, що похідна довільного порядку середньої енергії твердого тіла по координатах ядер дорівнює середньому значенню відповідної похідної оператора потенціальної енергії по координатах ядер. Ця теорема є узагальненням відомої теореми Гелл-Мана–Фейнмана, доведеної лише для першої похідної середньої енергії по координатах ядер. Необхідність такої теореми пов'язана з обчисленням силових сталих твердого тіла, що являються похідними середньої енергії по координатах ядер і, можливо, інших фізичних величин.