

## A new rotation sum rule for the atomic force constants

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 386233

(<http://iopscience.iop.org/0953-8984/19/38/386233>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 05:17

Please note that [terms and conditions apply](#).

# A new rotation sum rule for the atomic force constants

Shao-Feng Wang, Hui-Li Zhang and Xiao-Zhi Wu

Institute for Structure and Function, Chongqing University, Chongqing, 400044,  
People's Republic of China

E-mail: [sfwang@cqu.edu.cn](mailto:sfwang@cqu.edu.cn)

Received 5 April 2007, in final form 14 August 2007

Published 4 September 2007

Online at [stacks.iop.org/JPhysCM/19/386233](http://stacks.iop.org/JPhysCM/19/386233)

## Abstract

A new sum rule has been derived for the atomic force constants from the invariance of the potential energy under the rigid body rotation of a crystal. For instance, it is found that there are actually two force constants in the nearest-neighbour approximation of a face-centred cubic (FCC) lattice, rather than three force constants, as usually supposed.

## 1. Introduction

In lattice dynamics, it is generally assumed that the interaction between atoms can be described by a set of atomic force constants [1, 2]. The atomic force constants must satisfy certain relations resulting from the symmetry of the lattice. Furthermore, they also must satisfy the sum rule resulting from invariance under the rigid body translation and rotation of a crystal. The sum rule from the rigid body translation can be obtained easily. However, the sum rule from the rigid body rotation seems not to have been established satisfactorily. A rotation sum rule was given first by Born and Huang, and repeated by Leibfried [3] and Maradudin *et al* [2]. Their sum rule was derived by requiring that no extra force will be produced under a small rigid body rotation. As pointed out by Gazis and Wallis [4], the Born–Huang sum rule is a necessary condition, but not a sufficient condition, for rotation invariance. In fact, for the simple Bravais lattice, the Born–Huang sum rule is a trivial identity. A few years later, Gazis and Wallis derived a sum rule by acquiring that no potential energy be produced under a small rigid body rotation [4]. However, in analogy to the Born–Huang sum rule, the sum rule given by Gazis and Wallis is also a trivial identity in the case of the simple Bravais lattice. It is not a complete set of necessary and sufficient conditions as they claimed.

In this paper, a new rotation sum rule has been derived by requiring that the potential energy be invariant under a small rigid body rotation of a crystal. It is no longer a trivial identity for the simple Bravais lattice. It can be applied generally and it yields new constraint relations.

## 2. The rotation sum rule

In this section, the new rotation sum rule is presented first and then proved in detail. Let us consider a crystal specified by a set of lattice vectors  $\mathbf{R}$  that locate each cell of the crystal. Each cell contains  $r$  atoms, whose equilibrium positions are specified by vectors  $\mathbf{R} + \mathbf{d}^\alpha$  ( $\alpha = 1, 2, \dots, r$ ), where  $\mathbf{d}^\alpha$  is the position vector of the  $\alpha$ th atom relative to lattice point  $\mathbf{R}$ . For the atom  $\alpha$  in cell  $\mathbf{R}$ , the displacement relative to the equilibrium position will be denoted by  $\mathbf{u}^\alpha(\mathbf{R})$ , and the force by  $\mathbf{f}^\alpha(\mathbf{R})$ . The components in Cartesian coordinates will be labelled by subscript Latin characters, for example, force components  $f_i^\alpha(\mathbf{R})$  ( $i = 1, 2, 3$ ), displacement components  $u_i^\alpha(\mathbf{R})$  ( $i = 1, 2, 3$ ), etc. In the harmonic approximation, the force acting on an atom is a linear function of the displacements relative to the equilibrium configuration

$$f_i^\alpha(\mathbf{R}) = - \sum_{\mathbf{R}'} C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}') u_j^\beta(\mathbf{R}'), \quad (1)$$

where the coefficients  $C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}')$  are the atomic force constants. The atomic force constants can be obtained from the potential energy  $\Phi$  of a crystal,

$$C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}') = \frac{\partial^2 \Phi}{\partial u_i^\alpha(\mathbf{R}) \partial u_j^\beta(\mathbf{R}')}, \quad (2)$$

where the derivatives are evaluated with all the atoms at the equilibrium positions. Let us decompose the atomic force constants  $C_{ij}^{\alpha\beta}(\mathbf{R})$  into the symmetric and antisymmetric parts

$$C_{ij}^{\alpha\beta}(\mathbf{R}) = S_{ij}^{\alpha\beta}(\mathbf{R}) + T_{ij}^{\alpha\beta}(\mathbf{R})$$

with

$$\begin{aligned} S_{ij}^{\alpha\beta}(\mathbf{R}) &= S_{ji}^{\alpha\beta}(\mathbf{R}) = \frac{1}{2}[C_{ij}^{\alpha\beta}(\mathbf{R}) + C_{ji}^{\alpha\beta}(\mathbf{R})], \\ T_{ij}^{\alpha\beta}(\mathbf{R}) &= -T_{ji}^{\alpha\beta}(\mathbf{R}) = \frac{1}{2}[C_{ij}^{\alpha\beta}(\mathbf{R}) - C_{ji}^{\alpha\beta}(\mathbf{R})], \end{aligned}$$

and introduce

$$\begin{aligned} \Psi_{mn} &= -\frac{1}{4} \sum_{\mathbf{R}} S_{ij}^{\alpha\beta}(\mathbf{R}) \epsilon_{mik} \epsilon_{njl} (R_k + d_k^\alpha - d_k^\beta) (R_l + d_l^\alpha - d_l^\beta) \\ &\quad + \frac{1}{2} \sum_{\mathbf{R}} T_{ij}^{\alpha\beta}(\mathbf{R}) \epsilon_{mik} \epsilon_{njl} (R_k + d_k^\alpha) d_l^\beta, \end{aligned} \quad (3)$$

where  $\epsilon_{mik}$  is the completely antisymmetric three-order tensor with  $\epsilon_{123} = 1$ ,  $\epsilon_{mik} = -\epsilon_{imk} = -\epsilon_{mki}$ ;  $d_k^\alpha$  is the position vector of the  $\alpha$ th atom relative to the lattice point  $\mathbf{R}$ , and the convention that repeated indices are summed is used for brevity. The new rotation sum rule asserts that

$$\Psi_{mn} = -\Psi_{nm}, \quad (4)$$

i.e.  $\Psi_{mn}$  is antisymmetric. In general, six constraint relations will be obtained from the sum rule.

In the following, the sum rule is derived in detail. Obviously, if the higher-order terms are neglected, the potential energy  $\Phi$  can be expressed as

$$\Phi = \Phi_0 + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}') u_i^\alpha(\mathbf{R}) u_j^\beta(\mathbf{R}'), \quad (5)$$

where  $\Phi_0$  is a constant corresponding to the cohesive energy. Because of the translation symmetry of the crystal,  $C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}')$  depends on  $\mathbf{R}$  and  $\mathbf{R}'$  only through their difference  $\mathbf{R} - \mathbf{R}'$ ,

$$C_{ij}^{\alpha\beta}(\mathbf{R}, \mathbf{R}') = C_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}'). \quad (6)$$

Because the mix-partial derivative is independent of the order in which the differential are carried out, it follows from equation (2) that

$$C_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') = C_{ji}^{\beta\alpha}(\mathbf{R}' - \mathbf{R}).$$

If the atoms in a crystal move uniformly,

$$u_i^\alpha(\mathbf{R}) = u_i,$$

i.e. the crystal has a rigid body displacement, there must be no force acting on the atoms. As a consequence, the atomic force constants must satisfy the following translation sum rule:

$$\sum_{\mathbf{R}',\beta} C_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') = \sum_{\mathbf{R},\beta} C_{ij}^{\alpha\beta}(\mathbf{R}) = 0. \quad (7)$$

Apparently,  $S_{ij}^{\alpha\beta}(\mathbf{R})$  and  $T_{ij}^{\alpha\beta}(\mathbf{R})$  satisfy the same translation sum rule,

$$\begin{aligned} \sum_{\mathbf{R}} \sum_{\beta} S_{ij}^{\alpha\beta}(\mathbf{R}) &= \sum_{\mathbf{R}} \sum_{\alpha} S_{ij}^{\alpha\beta}(\mathbf{R}) = 0, \\ \sum_{\mathbf{R}} \sum_{\beta} T_{ij}^{\alpha\beta}(\mathbf{R}) &= \sum_{\mathbf{R}} \sum_{\alpha} T_{ij}^{\alpha\beta}(\mathbf{R}) = 0. \end{aligned}$$

In terms of  $S_{ij}^{\alpha\beta}(\mathbf{R})$  and  $T_{ij}^{\alpha\beta}(\mathbf{R})$ , the potential energy can be divided into three parts:

$$\Phi = \Phi_0 + \Phi_S + \Phi_T,$$

with

$$\begin{aligned} \Phi_S &= \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_i^\alpha(\mathbf{R}) u_j^\beta(\mathbf{R}'), \\ \Phi_T &= \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} T_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_i^\alpha(\mathbf{R}) u_j^\beta(\mathbf{R}'). \end{aligned}$$

It is crucial to observe that  $\Phi_S$  can be changed into

$$\Phi_S = \frac{1}{4} \sum_{\mathbf{R},\mathbf{R}'} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') [u_i^\alpha(\mathbf{R}) - u_i^\beta(\mathbf{R}')][u_j^\beta(\mathbf{R}') - u_j^\alpha(\mathbf{R})], \quad (8)$$

which depends on the atomic position through relative displacement between two atoms. The proof is simple: expanding the right-hand side of equation (8), we have

$$\begin{aligned} &\frac{1}{4} \sum_{\mathbf{R},\mathbf{R}'} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') [u_i^\alpha(\mathbf{R}) u_j^\beta(\mathbf{R}') + u_i^\beta(\mathbf{R}') u_j^\alpha(\mathbf{R}) - u_i^\alpha(\mathbf{R}) u_j^\alpha(\mathbf{R}) - u_i^\beta(\mathbf{R}') u_j^\beta(\mathbf{R}')] \\ &= \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') u_i^\alpha(\mathbf{R}) u_j^\beta(\mathbf{R}') - \frac{1}{4} \sum_{\mathbf{R}} u_i^\alpha(\mathbf{R}) u_j^\alpha(\mathbf{R}) \sum_{\mathbf{R}',\beta} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') \\ &\quad - \frac{1}{4} \sum_{\mathbf{R}'} u_i^\beta(\mathbf{R}') u_j^\beta(\mathbf{R}') \sum_{\mathbf{R},\alpha} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}'), \end{aligned}$$

where the symmetric property  $S_{ij}^{\alpha\beta} = S_{ji}^{\alpha\beta}$  has been used and the order of the summation has been rearranged. By virtue of the translation sum rule, we see that the last two terms have vanished and the first term is just the symmetric part  $\Phi_S$ .

Next, let us investigate the change of  $\Phi_S$  and  $\Phi_T$  caused by an infinitesimal rigid body rotation of a crystal. Consider the displacement resulting from an infinitesimal rigid body rotation of the crystal,

$$u_i^\alpha(\mathbf{R}) = \omega_{ij}(R_j + d_j^\alpha), \quad (9)$$

where the parameters  $\omega_{ij}$  are the elements of an infinitesimal antisymmetric matrix

$$\omega_{ij} = -\omega_{ji}.$$

Substituting the expression of the displacement, equation (9), resulting from an infinitesimal rigid body rotation into  $\Phi_S$ , we have

$$\Phi_S = \frac{1}{4} \sum_{\mathbf{R}, \mathbf{R}'} S_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') \omega_{ik}(R_k + d_k^\alpha - R'_k - d_k^\beta) \omega_{jl}(R'_l + d_l^\beta - R_l - d_l^\alpha).$$

Because the term in the sum only depends on the relative lattice vector, the summation over lattice vectors  $\mathbf{R}$  and  $\mathbf{R}'$  can be carried out by summing the lattice vectors and the relative lattice vector, and  $\Phi_S$  is given by

$$\Phi_S = -\frac{N}{4} \sum_{\mathbf{R}} S_{ij}^{\alpha\beta}(\mathbf{R}) \omega_{ik}(R_k + d_k^\alpha - d_k^\beta) \omega_{jl}(R_l + d_l^\alpha - d_l^\beta), \quad (10)$$

where  $N$  is the total number of primitive cells of the crystal. Equation (10) can be obtained in a more transparent way. It is apparent that the uniformity is kept after a rigid body rotation, i.e. all the cells are still equivalent. Thus,  $\Phi_S$  can be obtained by considering the contribution of a typical cell and then multiplying by the number of cells; that is just the result of equation (10).

The antisymmetric matrix  $\omega_{ij}$  can be expressed in terms of the completely antisymmetric three-order tensor  $\epsilon_{kij}$

$$\omega_{ij} = \theta_k \epsilon_{kij}, \quad (11)$$

where  $\theta_k$ ,  $k = 1, 2, 3$  are rotational parameters. Substituting  $\omega_{ij}$  into equation (10), we have

$$\Phi_S = -\frac{N}{4} \sum_{\mathbf{R}} S_{ij}^{\alpha\beta}(\mathbf{R}) \theta_m \epsilon_{mik}(R_k + d_k^\alpha - d_k^\beta) \theta_n \epsilon_{njl}(R_l + d_l^\alpha - d_l^\beta). \quad (12)$$

$\Phi_T$  can be handled in the same way. Substituting equation (9) into the expression for  $\Phi_T$ , we have

$$\begin{aligned} \Phi_T &= \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} T_{ij}^{\alpha\beta}(\mathbf{R} - \mathbf{R}') \omega_{ik}(R_k + d_k^\alpha) \omega_{jl}(R'_l + d_l^\beta) \\ &= \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} T_{ij}^{\alpha\beta}(\mathbf{R}) \omega_{ik}(R_k + R'_k + d_k^\alpha) \omega_{jl}(R'_l + d_l^\beta). \end{aligned} \quad (13)$$

Paying attention to the fact that

$$\sum_{\mathbf{R}'} \mathbf{R}' = 0,$$

and using the translation sum rule, it is easy to obtain

$$\begin{aligned} \Phi_T &= \frac{N}{2} \sum_{\mathbf{R}} T_{ij}^{\alpha\beta}(\mathbf{R}) \omega_{ik}(R_k + d_k^\alpha) \omega_{jl} d_l^\beta \\ &= \frac{N}{2} \sum_{\mathbf{R}} T_{ij}^{\alpha\beta}(\mathbf{R}) \theta_m \epsilon_{mik}(R_k + d_k^\alpha) \theta_n \epsilon_{njl} d_l^\beta. \end{aligned} \quad (14)$$

The potential energy should be invariant under a rigid body rotation of a crystal. From equations (12) and (14), we finally arrive at

$$\begin{aligned} & -\frac{1}{4} \sum_{\mathbf{R}} S_{ij}^{\alpha\beta}(\mathbf{R}) \theta_m \epsilon_{mik}(R_k + d_k^\alpha - d_k^\beta) \theta_n \epsilon_{njl}(R_l + d_l^\alpha - d_l^\beta) \\ & + \frac{1}{2} \sum_{\mathbf{R}} T_{ij}^{\alpha\beta}(\mathbf{R}) \theta_m \epsilon_{mik}(R_k + d_k^\alpha) \theta_n \epsilon_{njl} d_l^\beta = 0. \end{aligned} \quad (15)$$

In terms of  $\Psi_{mn}$  defined by equation (3), equation (15) can be written as

$$\Psi_{mn} \theta_m \theta_n = 0. \quad (16)$$

Because  $\theta_m$  ( $m = 1, 2, 3$ ) is an arbitrary parameter, equation (16) implies that  $\Psi_{mn}$  is antisymmetric:

$$\Psi_{mn} = -\Psi_{nm}.$$

This is the new rotational sum rule equation (4) derived from requiring that the potential energy of a crystal should be invariant under a small rigid body rotation.

Sometimes, the atomic force constants are given in wavevector space. The atomic force constants in real space and in wavevector space are related through the Fourier transformation

$$\begin{aligned} C_{ij}^{\alpha\beta}(\mathbf{R}) &= \frac{1}{\Omega^*} \int_{\text{BZ}} \tilde{C}_{ij}^{\alpha\beta}(\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{R}} d\mathbf{q}, \\ \tilde{C}_{ij}^{\alpha\beta}(\mathbf{q}) &= \sum_{\mathbf{R}} C_{ij}^{\alpha\beta}(\mathbf{R}) e^{i\mathbf{q}\cdot\mathbf{R}}, \end{aligned}$$

where  $\Omega^*$  is the volume of the Brillouin zone. It is easy to see that

$$\begin{aligned} \sum_{\mathbf{R}} C_{ij}^{\alpha\beta}(\mathbf{R}) &= \tilde{C}_{ij}^{\alpha\beta}(0), \\ \sum_{\mathbf{R}} C_{ij}^{\alpha\beta}(\mathbf{R}) R_l &= \left. \frac{1}{i} \frac{\partial \tilde{C}_{ij}^{\alpha\beta}}{\partial q_l} \right|_{\mathbf{q}=0}, \end{aligned}$$

and  $\Psi_{mn}$  can be expressed as

$$\begin{aligned} \Psi_{mn} &= -\frac{1}{4} \epsilon_{mik} \epsilon_{njl} \left( \frac{1}{i} \frac{\partial}{\partial q_k} + d_k^\alpha - d_k^\beta \right) \left( \frac{1}{i} \frac{\partial}{\partial q_l} + d_l^\alpha - d_l^\beta \right) \tilde{S}_{ij}^{\alpha\beta} \Big|_{\mathbf{q}=0} \\ &\quad + \frac{1}{2} \epsilon_{mik} \epsilon_{njl} \left( \frac{1}{i} \frac{\partial}{\partial q_k} + d_k^\alpha \right) d_l^\beta \tilde{T}_{ij}^{\alpha\beta} \Big|_{\mathbf{q}=0}, \end{aligned} \quad (17)$$

where  $\tilde{S}_{ij}^{\alpha\beta}$  and  $\tilde{T}_{ij}^{\alpha\beta}$  are the symmetric and antisymmetric parts of  $\tilde{C}_{ij}^{\alpha\beta}$ . In particular, for a simple Bravais lattice,  $\Psi_{mn}$  is simplified as

$$\begin{aligned} \Psi_{mn} &= -\frac{1}{4} \sum_{\mathbf{R}} C_{ij}(\mathbf{R}) \epsilon_{mik} \epsilon_{njl} R_k R_l \\ &= \frac{1}{4} \epsilon_{mik} \epsilon_{njl} \left. \frac{\partial^2 \tilde{C}_{ij}}{\partial q_k \partial q_l} \right|_{\mathbf{q}=0}, \end{aligned} \quad (18)$$

where the atomic indices  $\alpha, \beta$  have been removed since every primitive cell contains only one atom.

### 3. Discussion and summary

In order to clearly compare the results given by the different sum rules, the simple Bravais lattice is considered in this section. For the simple Bravais lattice, the sum rule given by Born and Huang can be written as [1, 2]

$$\sum_{\mathbf{R}} [C_{ij}(\mathbf{R}) R_l - C_{il}(\mathbf{R}) R_j] = 0, \quad (19)$$

where  $C_{ij}(\mathbf{R})$  is the atomic force constant; the Greek indices  $\alpha, \beta$  have been removed. Because there always exists inverse symmetry for a simple Bravais lattice, the atomic force constant is an even function of the lattice vector,

$$C_{ij}(-\mathbf{R}) = C_{ij}(\mathbf{R}), \quad (20)$$

and

$$\sum_{\mathbf{R}} C_{ij}(\mathbf{R})R_l = \sum_{\mathbf{R}} C_{ij}(-\mathbf{R})(-R_l) = -\sum_{\mathbf{R}} C_{ij}(\mathbf{R})R_l = 0,$$

the summation over  $\mathbf{R}$  in equation (19) vanishes. Therefore, the constraint relation equation (19) is automatically satisfied by the atomic force constants of a simple Bravais lattice.

The work by Gazis and Wallis is extremely relevant to ours. Their sum rule was also derived on the basis of invariance of the potential energy. However, the main results are different. For the simple Bravais lattice, the sum rule derived by Gazis and Wallis can be expressed as

$$\sum_{\mathbf{R}, \mathbf{R}'} \{ [C_{ik}(\mathbf{R} - \mathbf{R}')(R_j - R_j^0) - C_{jk}(\mathbf{R} - \mathbf{R}')(R_i - R_i^0)](R_l' - R_l^0) + [C_{jl}(\mathbf{R} - \mathbf{R}')(R_i - R_i^0) - C_{il}(\mathbf{R} - \mathbf{R}')(R_j - R_j^0)](R_k' - R_k^0) \} = 0. \quad (21)$$

Introducing relative lattice vector  $\mathbf{r} = \mathbf{R} - \mathbf{R}'$ , and changing the sum over  $\mathbf{R}'$  into the sum over  $\mathbf{r}$ , the left-hand side of equation (21) becomes

$$\begin{aligned} & \sum_{\mathbf{R}, \mathbf{r}} \{ [C_{ik}(\mathbf{r})(R_j - R_j^0) - C_{jk}(\mathbf{r})(R_i - R_i^0)](R_l - R_l^0 - r_l) \\ & \quad + [C_{jl}(\mathbf{r})(R_i - R_i^0) - C_{il}(\mathbf{r})(R_j - R_j^0)](R_k - R_k^0 - r_k) \} \\ & = \sum_{\mathbf{R}, \mathbf{r}} \left\{ [C_{ik}(\mathbf{r})(R_j - R_j^0)(R_l - R_l^0) - C_{jk}(\mathbf{r})(R_i - R_i^0)(R_l - R_l^0)] \right. \\ & \quad + C_{jl}(\mathbf{r})(R_i - R_i^0)(R_k - R_k^0) - C_{il}(\mathbf{r})(R_j - R_j^0)(R_k - R_k^0) \\ & \quad - \sum_{\mathbf{R}, \mathbf{r}} [C_{ik}(\mathbf{r})r_l(R_j - R_j^0) - C_{jk}(\mathbf{r})r_l(R_i - R_i^0) \\ & \quad \left. + C_{jl}(\mathbf{r})r_k(R_i - R_i^0) - C_{il}(\mathbf{r})r_k(R_j - R_j^0)] \right\}. \quad (22) \end{aligned}$$

By using the translation sum rule, equation (7), we see that the first sum in the last expression of equation (22) vanishes. By using the inverse symmetry of the simple Bravais lattice, the second sum vanishes, too. Therefore, in analogy to the Born–Huang sum rule, Gazis–Wallis sum rule is also a trivial identity for the simple Bravais lattice.

In contrast, the new sum rule can provide substantial relationships for the atomic force constants. For example, substituting the atomic force constants of the face-centred cubic (FCC) lattice given in [5] into equation (4), we obtain the following constraint relation:

$$\alpha_1 + \beta_1 - \gamma_1 + 2\beta_2 + 2\alpha_3 + 10\beta_3 - 2\gamma_3 - 8\epsilon_3 = 0, \quad (23)$$

where  $\alpha_1, \alpha_2, \alpha_3 \dots$  are the first, second and third atomic force constants, respectively. This constraint relation has not been mentioned before. If only the nearest-neighbour atoms are considered, the constraint relation becomes

$$\alpha_1 + \beta_1 - \gamma_1 = 0. \quad (24)$$

Therefore, the three force constants  $\alpha_1, \beta_1$  and  $\gamma_1$  are not independent. There are only two free force constants in the nearest-neighbour approximation of an FCC lattice. In the FCC example,  $\alpha_1$  and  $\beta_1 - \gamma_1$  are the transverse force constants ( $\beta_1 + \gamma_1$  is the longitudinal force constant). This indicates that the constraint is mainly imposed on the transverse force constants. In fact, if all the transverse force constants vanish, the potential energy will be invariant under rotation, and so the sum rule will be automatically satisfied by the force constants. For a simple cubic (SC) lattice, there is only one force constant in the first-neighbour approximation. The transverse force constant is fixed to be zero by the sum rule. As a consequence, the shear modulus become

zero in the first-neighbour approximation. However, it can be shown that the shear modulus is free if the second-neighbour interaction is introduced. When the distant-neighbour force are considered, the number of force constants increases rapidly and the meaning of force constants becomes obscure. A crucial question is: what relationships should be satisfied by the force constant introduced? The sum rule presented here gives us a new necessary condition that must be satisfied.

In Gazis and Wallis's paper, they presented another sum rule for the symmetric atomic force constants<sup>1</sup>. This sum rule cannot be obtained from their first sum rule which has been claimed to be the complete set of necessary and sufficient conditions. This sum rule is consistent with our result. Obviously, for the symmetric atomic force constants, our sum rule degenerates into the second sum rule given by Gazis and Wallis.

In summary, a general rotation sum rule has been presented for the atomic force constants. The sum rule can be applied easily and can yield new constraint relations that should be satisfied by the atomic force constants.

### Acknowledgments

The authors wish to thank Guo Ping-Bo, Ye Jin-Qin, Liu Rui-Ping, Zhang Fu-Zhou and Wang Rui for their helpful discussions and suggestions. The work is supported by the National Natural Science Foundation Project of CQ CSTC (Grant No. 2006BB4156).

### References

- [1] Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (London: Oxford University Press)
- [2] Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 Theory of lattice dynamics in the harmonic approximation *Solid State Physics, Supplement 3* (New York: Academic)
- [3] Leibfried G and Ludwig W 1960 *Z. Phys.* **160** 80
- [4] Gazis and Wallis 1966 *Phys. Rev.* **151** 578
- [5] Born M and Begbie G H 1946 *Proc. Soc. (London)* **188** 179  
Begbie G H 1946 *Proc. Soc. (London)* **188** 189  
Harrison C W 1958 *Phys. Rev.* **112** 1092

<sup>1</sup> See equation (15) in [4]