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A Study of Negative Force Constants: A Method to Obtain Force Constants by Electronic Structures

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The potential of negative force constants appearing in the valence-force model is discussed from the viewpoint of electronic structures. Prior to discussing this, a general procedure for obtaining force constants by the first-principles calculations is given, while simpler examples are worked out. For the strongest bond-stretching force, it is almost always calculable without ambiguity by using the breathing type deformation. For noncentral forces, such as angle-bending forces, there is a practical difficulty in estimation. The expansion of the adiabatic potential obtained by the first-principles calculations involves so many force constants other than the bond-stretching and angle-bending forces that the values of angle-bending force constants so obtained usually exhibit large errors. Only for more simple molecules is it possible to evaluate the noncentral forces without ambiguity. In such a case, negative values of the angle-bending force constants appear, depending on the electronic configuration. How the Jahn–Teller effect participates in negative force constants has been investigated. The Jahn–Teller effect can contribute, but not all negative forces are ascribed to this effect.

I. INTRODUCTION

In vibration problems of molecules and nonmetallic crystals, force constants are usually treated as fitting parameters. But the mathematical formulation of force constants has been founded on quantum mechanics, so that it must be, in principle, possible to calculate them by the electronic structures. This paper treats how to obtain force constants by the first-principles calculations and discusses negative force constants. The latter issue has some consequences in the lattice dynamics of boron solids (1).

If we are asked how to calculate force constants in a sense that the force constants are merely the expansion coefficients of an adiabatic potential with respect to atomic displacements, the problem has been already solved. The theoretical foundations, on the basis of the adiabatic and harmonic approximations, are written thoroughly in a classical textbook of Born and Huang (2). The most general definition for force constants is given there. Evaluation of the electronic part in the dynamical matrices has been then developed on various schemes of the band theory (3). A recent development in numerical methods furnishes us with effective calculational methods (4). The problem of obtaining force constants in which we are concerned here is not in this category.

In standard calculations of molecular and lattice vibrations, more specific definitions of the force constant are commonly used. The valence force, Keating, and Born models are examples. These definitions are physically more appealing and hence are useful for interpretation. If we are asked the same question for these specific force constants, the answer is not obvious. Although these specific definitions are not so different from the general definition, slight differences bring a subtle problem. This is the present issue. For definiteness, we take here the valence force model as the representative.

When we use a classical analogy, namely a spring, for a valence force, we may think that the force constant must be positive. A negative force constant implies instability. The displacements from the equilibrium positions in this case do not exert a restoring force, but instead amplification takes place. We are thus liable to believe that all force constants must be positive no matter the type. This would be true if the forces are independent of each other. In the case of a bending molecule XY_2, there are two types of force: one is a stretching force of the bond X–Y and the other is an angle-bending force between Y–X–Y. Normally, these two parameters are enough to calculate the vibrations. In this case, two forces are independent of each other. Thus, these two must be positive. The terminal Y atoms interact with each other only through the angle-bending force.

If the terminal Y atoms interact with each other directly through a bond stretching force, the situation will be changed. Let us consider a regular triangular molecule. We are unable to change a bond angle without changing any bond length. In this sense, the angle-bending force is not independent of the bond stretching force. Fortunately, we will see, later, that it is possible to discriminate between

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these two forces in this particular case. In a general case, however, it is not always clear to say whether these two are independent or not. The first purpose of this paper is, therefore, to discuss a consistent method to determine force constants.

We will see that negative force constants are sometimes found, particularly for angle-bending forces. Nevertheless, this does not imply instability. The mathematical condition for the mechanical stability for a small disturbance is expressed by (2) the following:

THEOREM 1a. *The dynamical matrix is positive definite.*

In terms of the eigenvalue, this condition is rephrased:

THEOREM 1b. *All the eigenvalues of the dynamical matrix are positive.*

A negative value for the angle-bending force is still permissible as long as the angle bending motion is associated with bond-stretching motions and the bond-stretching forces overcome the negative contribution of the angle-bending force. The second purpose of this paper is to show how this situation happens in the three-center bonding and the icosahedral bonding in boron solids. Arguments are given in a rather pedagogic way. To emphasize principles rather than numeric accuracy, more simple molecules are taken up as the substance and the tight-binding scheme is used as the electronic calculation.

II. SIMPLE EXAMPLES

For the sake of simplicity, we assume that all the atoms constituting a molecule are the same species, with the mass being unity. In the language of the valence-force model, the central force α corresponds to the bond stretching force f_r. The noncentral force β means, in general, any type other than the central force, but here is used as the same meaning as the angle-bending force f_a. It is understood that the bond length d is absorbed in β, i.e., $\beta = f_a/d^2$.

On the adiabatic approximation, the potential Φ, which the nuclei experience is

$$\Phi(\{R_i\}) = E_{en}(\{R_i\}) + U_n(\{R_i\}), \qquad [1]$$

when the positions $\{R_i\}$ of the nuclei are given. The first and the second terms of the right-hand side of Eq. [1] correspond, respectively, to the electron energy of the ground state as a function of $\{R_i\}$ and the ion–ion repulsive potential. In this paper, the part of the electron energy $E_{en}(\{R_i\})$ is calculated by the tight-binding scheme (5). The orthonomalized atomic orbitals $|sn\rangle$, which are called Löwdin functions, are used as the basis set, where s denotes an atomic site and n denotes the atomic orbital at this site. Only the nearest neighbor integrals are taken into account. There are many matrix elements $\langle sn|H|tm\rangle$, but these can be deduced from a few of the prototype elements by symmetry reason. Such prototypes $V_{ll'm}$ are further approximated by a form $V_{ll'm} = \eta_{ll'm}\hbar^2/md^2$ with appropriate coefficients $\eta_{ll'm}$, where m is the mass of electron (6). Only s and p orbitals in the valence level are used in the following. For a square molecule and a triangular molecule, the data of carbon atom tabulated in the solid state table in Ref. (6) are used for the coefficients $\eta_{ll'm}$ and the bond length d, while the data of boron atom are used for an icosahedral molecule.

For the ion–ion repulsive potential $U_n(R)$, we use either a type of inverse power of R,

$$\text{(type I)} \qquad U_n(R) = a/R^n,$$

or Yukawa-type potential,

$$\text{(type II)} \qquad U_n(R) = b\exp(-aR)/R.$$

The repulsive potential of type II is frequently used as the screened Coulomb potential, and thereby the constant b may be interpreted as the square of the effective atomic charge $(Z^*e)^2$. Both forms have two unknown parameters. The equilibrium condition $\partial\Phi/\partial R = 0$ eliminates one of these two.

a. Square Molecule

Our first example is a planar square molecule with symmetry C_{4v}. The molecule has four distinct frequencies. These frequencies are given by $\omega^2(A_1) = 2\alpha$, $\omega^2(B_1) = 8\beta$, $\omega^2(B_2) = 2\alpha$, and $\omega^2(E) = 2\alpha + 4\beta$ in the two-force model, i.e., the nearest bond-stretching force α and angle-bending force β.

The molecular orbitals are presented by $2a_1\ (sp) + a_2\ (p) + 2b_1\ (sp) + b_2\ (p) + 3e(sp^2)$ for the equilibrium position. The constituting atomic orbitals are indicated in parentheses. The energy levels are arranged as $a_1, e, b_2, a_1, b_1, e, \ldots$ in ascending order in energy. In the case where each atom has two valence electrons, the levels up to b_2 are occupied in the ground state. The electron energy $E_{en}(\{R_i\})$ is then given by the sum of these occupied states for small displacements near the equilibrium position.

Among various force constants, the stretching force α is by far the strongest one. Normally, this stretching force can be determined unambiguously by the uniform breathing mode A_1, because only the bond lengths are variants in this case.[1] Since the normal coordinate q_{A_1} is given by $q_{A_1} = \sqrt{2}\Delta d$, where Δd is the change in the length of the

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[1] This is, however, not the case for low-symmetry molecules.

nearest-neighbor bond, α is computed from

$$\Delta\Phi = 2\alpha(\Delta d)^2. \qquad [2]$$

In obtaining α in this way, four nearest-neighbor bonds are enough for the repulsive force. However, the repulsive forces of the next-nearest-neighbour bonds, i.e., the diagonal bonds, have been included to keep consistency with the calculation of β.

The B_1 mode depends on the angle-bending force β solely. Since the change in the angle $\Delta\theta$ is given by $d_0\Delta\theta = \sqrt{2}q_{B_1}$, the $\Delta\Phi$ is given by

$$\Delta\Phi = 4\beta(q_{B_1})^2. \qquad [3]$$

In this case, the repulsive forces of the next-nearest-neighbor bonds are required, otherwise no restoring force would be exerted. We assumed the same parameters for both repulsive forces of the nearest-neighbor and the next-nearest-neighbor bonds. In this way, two force constants α and β have been completely and separately determined.

It is interesting to see how the Jahn–Teller effect influences the angle-bending force. We should note that the Jahn–Teller distortion occurs for the B_1 type deformation (7). The deformed molecule has C_{2v} symmetry. The electronic states are then split as $a_1 \rightarrow a_1$, $e \rightarrow b_1 + b_2$, and $b_2 \rightarrow a_2$. Among those deformed states, the energy of b_1 and b_2 has a linear term in $\Delta\theta$, whereas for the others it depends only in the second order or higher. These two states are thus enough to evaluate the derivative of Φ with respect to θ.

These states b_1 and b_2 can be inverted by a C_4 rotation, and accordingly the energy levels are interchanged by the change $\Delta\theta \rightarrow -\Delta\theta$. From this relationship, we can see that both the b_1 and b_2 states have linear dependence on $\Delta\theta$. See the left-hand side of Fig. 1a. The linear dependence implies instability. Nevertheless, the molecule remains stable. This is because, in our example, both b_1 and b_2 states are occupied and the total energy is an even function of $\Delta\theta$. The origin $\Delta\theta = 0$ becomes again the true equilibrium position unless the restoring force is too weak (the right-hand side of Fig. 1a).

The result by using the potential of type II is shown in Table 1. As the constant a is increased, which means that the repulsive force exhibits more short-range character, the stretching force α becomes larger. Conversely, the angle-bending force β becomes smaller. This is reasonable. The β is determined by the repulsive force of the next-nearest-

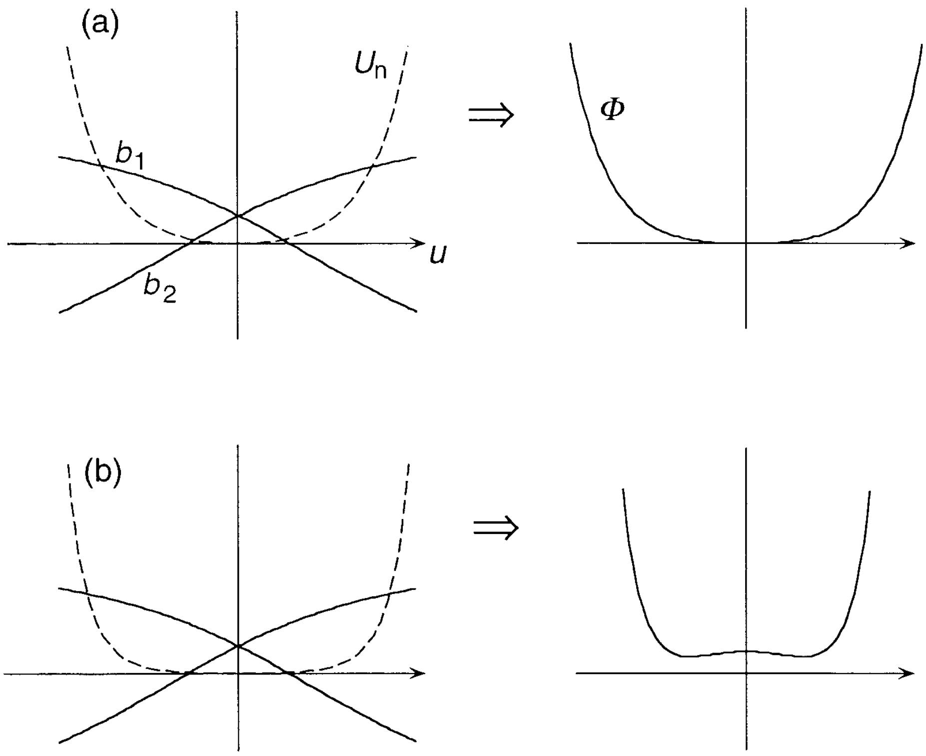

FIG. 1. Schematic drawing of the adiabatic potential of a square molecule; (a) for long-range repulsive force, (b) for short-range repulsive force. The left-hand side shows the individual contributions of the electron energy $E_{en}(r)$ of the level r (solid lines) and the ion–ion potential U_n (dashed lines). The right-hand side shows the total adiabatic potential Φ.

TABLE 1
The Force Constants of a Square Molecule by Using the Yukawa Potential as the Repulsive Force

a $(1/d_0)$	Z^*	α (mdyn/Å)	β (mdyn/Å)	β/α (%)
5.337	12.45	7.298	0.1155	1.58
4.663	9.36	4.663	0.1564	2.68
3.985	7.08	3.985	0.1979	4.52
3.305	5.38	2.920	0.2366	8.11
2.964	4.71	2.190	0.2537	11.6
2.483	3.93	1.168	0.2716	23.3
2.207	3.55	0.584	0.2785	47.7

Note. The shielding parameter a is given in the unit $1/d_0$, where d_0 is the equilibrium distance of the nearest-neighbor bond.

neighbor bonds, and that force is decreased more rapidly than the nearest-neighbor force as the range of the repulsive force becomes shorter. In effect, the restoring force against the angle deviation is decreased, which is equivalent to stating decrease in β.

In the table, the effective atomic charge Z^* is also listed for the purpose of showing to what extent this potential is realistic. The screening length can be measured by the inverse of the coefficient a. The screening length becomes shorter as Z^* increases to eliminate the strong repulsive force.

When type I is used as $U_n(R)$, the magnitude of β relative to α varies with the exponent n, as shown in Fig. 2. Since a large n means short-range character of the repulsive potential, we can see again that β becomes weaker as the range of the repulsive force is shorter. Note that β becomes negative when n exceeds 6.8. Beyond this value, the repulsive force is so weak that the total potential Φ has the minimum at points different from the origin (Fig. 1b). The Jahn–Teller distortion explicitly appears for the ground state of electrons of this molecule.

In this way, the Jahn–Teller effect has significant consequence on the angle-bending force, the contribution being negative. It may be worthwhile, however, noting that not all the negative contributions to force constants come in a way that the Jahn–Teller instability occurs. The original statement of the Jahn–Teller theorem is the degenerate electronic states necessarily couple with some distortion Γ_r of the molecule in the first order. The theorem does not say anything about nondegenerate states. Actually, nondegenerate states of electrons Γ_i and Γ_j also do couple with the distortion Γ_r, if the symmetrized product $\Gamma_i \times \Gamma_j$ contains Γ_r. Off-diagonal elements of the deformed electron system could have a linear term in q_r, whereas for the degenerate states such linear terms appear also in the diagonal elements. In fact, in the present problem, the lowest a_1 state has a negative contribution to the Φ for the B_1 type deformation. Merely, the magnitude is small.

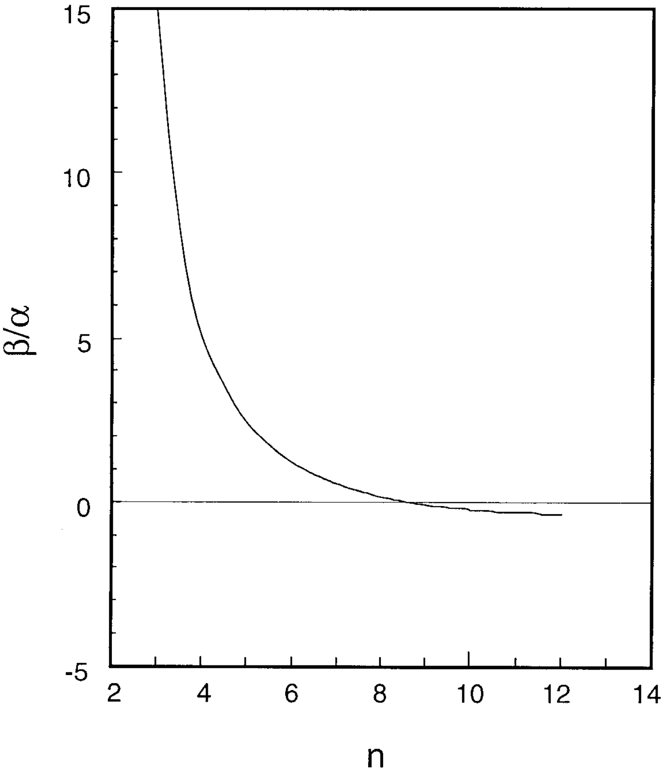

FIG. 2. The ratio of the bond-stretching and angle-bending forces of a square molecule as a function of the exponent in the type I potential.

b. Triangular Molecule

The next example is a triangular molecule with symmetry C_{3v}. The molecule has two distinct frequencies; $\omega^2(A_1) = 3\alpha$ and $\omega^2(E) = 3\alpha/2 + 9\beta/2$. The molecular orbitals are presented by $2a_1$ (sp) + a_2 (p) + $3e$ (sp^2) for the equilibrium position. The energy levels are arranged as a_1, e, a_1, e, a_2, and e in ascending order.

The α can be again obtained unambiguously by the breathing mode A_1 solely. For the other mode E, however, both force constants α and β appear. Even in this case, we can determine both force constants uniquely. First, we determine α by the A_1 mode. Then, $\partial^2\Phi/\partial R^2$ is evaluated for the E mode, where both α and β terms are present. Then, β is obtained by subtracting the α term from this.

This way of obtaining β, of surprising matter, gives the value independent of the repulsive potential, as long as the repulsive forces are central ones. In the following, we will verify this independence.

For the A_1 mode, the second derivative of Φ with respect to the bond length R gives the eigenvalue 3α,

$$3\alpha = \frac{\partial^2 E_{\mathrm{en}}}{\partial R^2} + \frac{\partial^2 U_n}{\partial R^2} = \frac{\partial^2 E_{\mathrm{en}}}{\partial R^2} + 3\frac{\partial^2 \varphi}{\partial R^2}, \qquad [4]$$

where φ is a repulsive pair potential between any two atoms. For the E mode, the normal vector is given by $\{\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3\} = \{1/2, 1/2\sqrt{3}; -1/2, 1/2\sqrt{3}; 0, -1/\sqrt{3}\}$. The change in the bond length R_{ij} is given by $\Delta R_{ij} = (\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{e}_{ij}$, where $\mathbf{e}_{ij}$ is a unit vector connecting atoms i and j. With the help of $\partial\varphi_{ij}/\partial q_E = (\mathbf{u}_i - \mathbf{u}_j) \cdot \mathbf{e}_{ij}\, \partial\varphi/\partial R$, we have $(\partial^2/\partial q_E^2) \sum_{ij} \varphi_{ij} = (3/2)(\partial^2\varphi/\partial R^2)$. On the other hand, $\partial^2\Phi/\partial q_E^2$ gives the restoring force for the E mode, which is given by $3\alpha/2 + 9\beta/2$. Hence, we have

$$\frac{3}{2}\alpha + \frac{9}{2}\beta = \frac{\partial^2 E_{\text{en}}}{\partial q_{\text{E}}^2} + \frac{3}{2}\frac{\partial^2\varphi}{\partial R^2}, \qquad [5]$$

for the E mode. From Eqs. [4] and [5], we can see that the angle-bending force β is completely determined by the part of the electron energy alone,

$$9\beta = 2\frac{\partial^2 E_{\text{en}}}{\partial q_E^2} - \frac{\partial^2 E_{\text{en}}}{\partial R^2}. \qquad [6]$$

This is a consequence that all bonds associated with the repulsive forces are symmetry equivalent. It is not enough to say that simply because it has the central-force character.

The value of the angle-bending force β is, instead, critically affected by the electronic configuration. For a system which has two electrons, only the lowest a_1 level is occupied. This configuration somehow simulates the situation of the three-center bonding, which is a characteristic bonding in the chemistry of boranes. The angle-bending force β is evaluated to be 0.048 (mdyn/Å), and the ratio β/α is smaller than any value of the square molecule listed in Table 1. When a system has six electrons, a degenerate e level is also occupied. The e state couples with the E type distortion, that is, the Jahn–Teller distortion takes place. In this case, the β is greatly reduced and even becomes negative, -0.43 (mdyn/Å). What happens is that one state of the degenerate e level extends its orbital along the direction of the E type distortion. This type distortion enhances the s–p coupling appreciably. The stronger this coupling is, the more the electron energy E_{en} is reduced for the E deformation. This contributes the β negatively via the first term of Eq. [6].

III. CONSISTENCY

Going back to the square molecule problem, we should examine the consistency of obtaining force constants. In the case of square molecule, use of A_1 and B_1 modes is absolutely a wise choice for obtaining the force constants, because of well separability between α and β for those modes. There are, however, other nonzero-frequency modes. A problem then arises as to whether or not the values obtained by different modes are consistent with each other. The answer is generally no. Remember that our solutions of the eigenfrequencies depend on how many forces are assumed, even though a two-force model is adequate for practical use.

The adiabatic potential Φ is expressed by a set of all the displacements $\mathbf{u}_i$ of atoms, as $\Phi(\{\mathbf{u}_i\})$. The force constants are the second-order coefficients of the expansion of Φ with respect to the displacements,

$$\Phi = \Phi_0 + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2\Phi}{\partial u_i \partial u_j}\right)_0 u_i u_i. \qquad [7]$$

To obtain the correct form for force constants of valence forces, Cartesian-coordinate displacements u_i must be converted to the internal coordinates s_i. The conversion of these two is a right place of the standard technique of molecular vibrations (8). The internal coordinates s_i include changes in the bond length Δr_{ij}, in the bond angle $\Delta\theta_{ijk}$, and in the dihedral angle $\Delta\varphi_{ijkl}$. The corresponding force constants f_i are, respectively, the bond stretching force, the angle-bending force, and the torsion force. A torsion term appears when a molecule has more than three atoms. In addition, there are cross terms, such as $\Delta r\Delta\theta$, in the expansion of Φ. Classical interpretation of the valence force becomes rather difficult for those cross term.

By converting the internal coordinates $\{s_i\}$ to the normal modes $\{q_i\}$, we have two expressions for a change in the adiabatic potential $\Delta\Phi$. The one is expressed by the eigenfrequencies ω_r, which are obtained by the valence forces $\{f_i\}$. The other is the expression of $\Delta\Phi$ obtained by the first-principles calculations, which is now expanded with respect to the normal coordinates. These two expression must be coincident.

$$\sum_r \omega_r^2(\{f_i\})q_r^2 = \sum_{ij} D_{ij} s_i s_j = \sum_r F_r(\{D_{ij}\})q_r^2, \qquad [8]$$

where F_r is a function of the expansion coefficients $D_{ij} \equiv \{\partial^2\Phi/\partial s_i \partial s_j\}_0$. The left-hand side of the equation usually contains only restricted number of parameters, while the right-hand side contains many terms of expansion.

In general, for a molecular system without any symmetry, there are N different eigenfrequencies, where N is the total degree of freedom minus 6. There are, on the other hand, $N(N+1)/2$ independent matrix elements, because of the Hermitian property of the dynamical matrix. To solve consistently Eq. [8], we should prepare a set of force constants as many as the number of independent matrix elements, i.e., $N(N+1)/2$. This is a hopeless task for large molecules or crystals.

Another problem is that, since the number of independent force constants N_{c} is much larger than the number of the eigenfrequencies, we cannot determine uniquely all the force constants by knowing the eigenfrequencies solely. In many cases, due to symmetry of the molecule, the number N_c becomes less than $N(N+1)/2$. This number N_c is obtained by counting the number of the invariants involved in the symmetrized product of the subspace which is spanned by the internal coordinates (9). This method gives the formula

$$N_c = \frac{1}{2} \sum_r n_r (n_r + b_r). \qquad [9]$$

In this expression, n_r is the number of the normal modes which belong to the rth irreducible representation. A constant b_r can take either $+1$ or 0 for molecular systems. This number N_c is less than $N(N+1)/2$, but is still greater than N. Only for molecules of small size, sometimes, it accidentally happens that $N_c = N$. Our previous examples are this case. For a triangular molecule, $N_c = 2$. Accordingly, two force constants, f_r and f_a, are sufficient to retain consistency. For a square molecule, $N_c = 4$. We have already met the nearest neighbor stretching force f_r and the angle-bending force f_a. The next nearest neighbor stretching force $f_{r'}$ can be treated as an independent force. As the remaining one, we can take either cross terms f_{ra}, or $f_{rr'}$.

IV. APPLICATION TO AN ICOSAHEDRAL MOLECULE

Our last example is an icosahedral molecule, which has an application to the boron crystals consisted of icosahedral units. The molecule has eight nonzero frequencies: $A_g + T_{1u} + T_{2u} + U_g + U_u + 2V_g + V_u$. The explicit form of the eigenfrequencies in terms of the bond-stretching and angle-bending forces are given in Ref. (1).

TABLE 2
The Matrix Elements for the Electronic Structure of B_{12} Molecule, According to the Symmetry Block Γ

Γ	l	Matrix elements
A_g	2 $(1s + 1p)$	$\varepsilon_s + 5V_{ss\sigma},\ \varepsilon_p + \frac{5-\sqrt{5}}{2} V_{pp\sigma} + \frac{5+\sqrt{5}}{2} V_{pp\pi};\ \sqrt{\frac{5(5-\sqrt{5})}{10}}\, V_{sp\sigma}$
T_{1g}	1 $(1s)$	$\varepsilon_p + \frac{5+\sqrt{5}}{4} V_{pp\sigma} - \frac{5-3\sqrt{5}}{4} V_{pp\pi}$
T_{1u}	3 $(1s + 2p)$	$\varepsilon_s + \sqrt{5}\, V_{ss\sigma},\ \varepsilon_p + \frac{5}{3}(V_{pp\sigma} + 2V_{pp\pi}),\ \varepsilon_p - \frac{11+3\sqrt{5}}{12} V_{pp\sigma} - \frac{1-3\sqrt{5}}{12} V_{pp\pi};$ $-\sqrt{\frac{5(5-\sqrt{5})}{6}}\, V_{sp\sigma},\ -\sqrt{\frac{2(5+2\sqrt{5})}{3}}\, V_{sp\sigma};\ \frac{5-3\sqrt{5}}{6\sqrt{2}}(V_{pp\pi} - V_{pp\sigma})$
T_{2u}	2 $(1s + 1p)$	$\varepsilon_s - \sqrt{5}\, V_{ss\sigma},\ \varepsilon_p - \frac{1-\sqrt{5}}{2} V_{pp\sigma} - \frac{1+\sqrt{5}}{2} V_{pp\sigma};\ -\sqrt{\frac{5-\sqrt{5})}{2}}\, V_{sp\sigma}$
U_g	1 $(1p)$	$\varepsilon_p - \sqrt{5}\, V_{pp\pi}$
U_u	1 $(1p)$	$\varepsilon_p - \frac{1+\sqrt{5}}{2} V_{pp\sigma} - \frac{1-\sqrt{5}}{2} V_{pp\pi}$
V_g	3 $(1s + 2p)$	$\varepsilon_s - V_{ss\sigma},\ \varepsilon_p - \frac{1}{\sqrt{5}}(3V_{pp\sigma} + 2V_{pp\pi}),\ \varepsilon_p + \frac{7-\sqrt{5}}{4\sqrt{5}} V_{pp\sigma} + \frac{13-\sqrt{5}}{4\sqrt{5}} V_{pp\pi};$ $-\sqrt{\frac{3(5-\sqrt{5})}{10}}\, V_{sp\sigma},\ -\sqrt{\frac{2(5+2\sqrt{5})}{5}}\, V_{sp\sigma};\ \frac{1}{10}\sqrt{\frac{3(5+\sqrt{5})}{2}}(V_{pp\pi} - V_{pp\sigma})$
V_u	1 $(1p)$	$\varepsilon_p + \frac{1+\sqrt{5}}{4} V_{pp\sigma} - \frac{5+\sqrt{5}}{4} V_{pp\pi}$

Note. The second column shows the order l of the submatrices. The matrix elements are listed in the order $H_{11}, \ldots, H_{ll}; H_{12}, \ldots, H_{1l}; \cdots H_{(l-1)l}$.

TABLE 3
The Force Constants of the Icosahedral Molecule

(I)	(II)	(III)	(IV) (mdyn/Å)	(V) (mdyn/Å)
T_{1u}	$\frac{\partial^2\Phi}{\partial q^2} - 3\alpha$	$3(3-\sqrt{5})\beta$	− 1.484	− 0.652
T_{2u}	$\frac{\partial^2\Phi}{\partial q^2} - (3-\sqrt{5})\alpha$	4β	2.45	− 0.007
U_g	$\frac{\partial^2\Phi}{\partial q^2} - \frac{5+\sqrt{5}}{4}\alpha$	$\frac{5}{4}(5+\sqrt{5})\beta$	− 0.884	− 1.212
U_u	$\frac{\partial^2\Phi}{\partial q^2} - \frac{7+3\sqrt{5}}{4}\alpha$	$\frac{3}{4}(7+3\sqrt{5})\beta$	− 1.962	− 1.365
V_u	$\frac{\partial^2\Phi}{\partial q^2} - \alpha$	6β	− 0.296	− 0.213

Note. The first column shows the deformation type that is used for evaluating $\partial^2\Phi/\partial q^2$, and the second column shows the form of the second derivative of the Φ subtracted by the component of the stretching force, which would turn to the form given in the third column if the two-force model is used. The forth and fifth columns show numerical values of (II) when the intraicosahedral bonding orbitals are taken into account and when the outward orbitals are added, respectively.

The molecular orbitals are presented by $2a_g$ (sp) + t_{1g} (s) + $3t_{1u}$ (sp^2) + $2t_{2u}$ (sp) + u_g (p) + u_u (p) + $3v_g$ (sp^2) + v_u (p) for the equilibrium position. The bonding natures of those molecular orbitals are well studied (10). The lowest four orbitals, $a_g + t_{1u} + v_g + u_u$, form the intraicosahedral bonding. A set of other four orbitals, $a_g + t_{1u} + t_{2u} + v_g$, form the outward orbitals, which turn to covalent bonds. The remaining six are antibonding states. All the matrix elements $\langle sn|H|tm\rangle$ for each symmetry block are recorded in Table 2. This form of the matrix enables us to obtain an analytic solution, which is convenient for many purposes. An example of the numeric evaluation of these eigenvalues is shown in Ref. (11), although a more sophisticated method has been used there.

In the present problem, there is no such low-frequency mode that the frequency involves only β force nor that it is given by a linear combination of α and β. The lowest frequency mode V_g has the eigenfrequency for which α and β are not nicely separated. We can seek β by using relatively high-frequency modes. For such modes, α is the dominant term, so that β so obtained involves much error, even disregarded the preceding problem of consistency. When the intraicosahedral bonding states, $a_g + t_{1u} + v_g + u_u$, are used for the ground state, the calculated values for β are listed in column (IV) of Table 3. Again in this case, β is independent of the form of the repulsive force. The β so obtained is scattered both positively and negatively, depending on the mode which is used for calculating $\partial^2\Phi/\partial q^2$. This evidently shows that these modes must include contributions from other than α and β. Uncertainty is so appreciable that we cannot determine the β consistently.

Although obtaining β by the two-force model is a meaningless task, the formula in column (II) may be useful in that it gives a measure of all the contributions other than the central force. By adding the outward orbitals, $a_g + t_{1u}$, which is the situation of the icosahedral boron molecule, let us check all the noncentral contributions, as shown in column (V). In all cases, the contributions of the noncentral forces are totally negative. It is reasonable because the outward orbitals have essentially a nonbonding character, and accordingly any deformation is most likely to cause the overlap between them more appreciably, which makes the electron energy decreased more or less.

It may be interesting to examine the Jahn–Teller effect for an icosahedral molecule. The Jahn–Teller effect on the icosahedral symmetry has been recently received considerably attention from theorists (12). Regarding negative force constants, however, the Jahn–Teller effect is not clear in this study. The degenerate electronic states of an icosahedral molecule couple with the U_g or V_g type deformations. By examining $\partial^2\Phi/\partial q^2$ for the individual orbitals for each type of deformation, we failed to extract purely the Jahn–Teller effect on the negative β. As mentioned before, not only the same symmetry orbitals but different symmetry orbitals are able to couple with a particular type of deformation. In the square molecule case, the latter contribution happened to be small. But, in an icosahedral case, that contribution is so appreciable that the Jahn–Teller effect is buried in all.

V. IMPLICATIONS

Our two-force model was not enough to consistently determine the two force constants of an icosahedral molecule by the electronic energy. However, from the present examples, we can mention general trends about noncentral forces. Tetrahedrally coordinate covalent bonds have almost always strong angle-bending forces (13). This is because highly oriented bonding is formed in the direction connecting two atoms (Fig. 3a). Any angle deviation from this orientation will cause an energy increase, so that a large angle-restoring force must be exerted. On the other hand, the bonding states e in the square molecule and triangular molecule are not like this (Figs. 3b and 3c). For both cases, the orientations of bonding are not in the direction of connecting atoms. Hence, either of the degenerate states can get negative energy by deforming the molecule. Negative angle-bending forces would be deduced if the repulsive force is weak. The icosahedral bondings are far from the covalent bonding, so that negative angle-bending forces are reasonably expected. Recent study on the lattice vibrations of boron carbide suggests a negative angle-bending force for the intraicosahedral bonding (14).

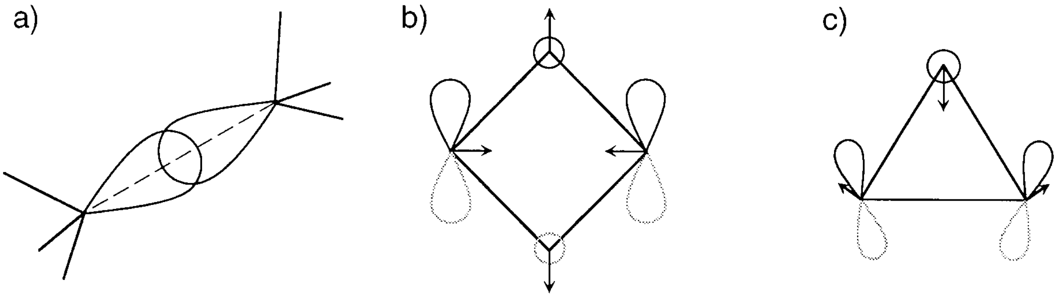

FIG. 3. Bonding orbitals which dominate angle-bending forces; (a) tetrahedrally coordinate covalent bond, (b) the *e* orbital in a square molecule, and (c) the *e* orbital in a triangular molecule. The arrows indicate the deformation which couples with the degenerate states; (b) B_1 type and (c) E type deformations.

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REFERENCES

1. K. Shirai, *J. Solid State Chem.* **133,** 322 (1997).
2. M. Born and K. Huang, "Dynamical Theory of Crystal Lattices." Oxford Univ. Press, Oxford, 1954.
3. S. K. Joshi and A. K. Rajagopal, *Solid State Phys.* **22,** 159 (1968).
4. O. H. Nielsen and R. M. Martin, *Phys. Rev. B* **32,** 3780 (1985); J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12,** 4409 (1979).
5. J. C. Slater and G. F. Koster, *Phys. Rev.* **94,** 1498 (1954); P. O. Löwdin, *J. Chem. Phys.* **18,** 365 (1950).
6. W. A. Harrison, "Electronic Structure and the Properties of Solids." Freeman, San Francisco, 1980.
7. H. A. Jahn and E. Teller, *Proc. R. Soc. London A* **161,** 220 (1937).
8. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations." McGraw-Hill, New York, 1955.
9. M. Lax, "Symmetry Principles in Solid State and Molecular Physics." Wiley, New York, 1974.
10. H. C. Longuet-Higgins and M. de V. Roberts, *Proc. R. Soc. London A* **230,** 110 (1955).
11. K. Shirai and H. Nakamatsu, "Proc. 11th Int. Symp. Boron, Borides and Related Compounds, Tsukuba 1993," JJAP Series 10, pp. 70–71, 1994.
12. D. R. Pooler, *J. Phys. C* **13,** 1029 (1980); A. Ceulemans and P. W. Fowler, *Phys. Rev. A* **39,** 481 (1989).
13. J. C. Phillips, "Bonds and Bands in Semiconductors," Chap. 3. Academic Press, New York, 1973.
14. K. Shirai and S. Emura, *J. Phys.: Condens. Matter* **50,** 10,919 (1996).