PHYSICAL REVIEW B VOLUME 8, NUMBER 8 15 OCTOBER 1973

Valence-Force-Field Potentials for Diamondlike Crystals[*]

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(Received 27 April 1973)

Analytical vibrational potential energy functions similar to ones accurate to fourth order in linear triatomic molecules are shown to have encouraging accuracy to second order for solid carbon and silicon. The theoretical basis for the potential functions is discussed.

I. INTRODUCTION

Analytical functions for valence-force-field potentials allow for the possibility of extrapolation to outside the quadratic region of the multidimensional surface in valence coordinates. The simplicity of the valence coordinates, which are bond lengths and angles, allows one to visualize the contributions to the force field in terms of physical interpretations given to terms in the force-field potential function. Such features are of established importance in the chemical literature concerning molecules. It is expected that they will be helpful in the understanding of solids, the topic of this paper.

Keating's proof[1] that, within the Born-Oppenheimer approximation, the $(3N-6)$-dimensional vibrational potential energy field in a solid of N atoms is central for nearest-neighbor quadratic force constants provides the reason for the success of valence force fields for covalent solids. To date, the work of Tubino *et al.*[2] on diamond-structure carbon, silicon, germanium, and tin appears to represent the extent of the direct determination, through the lattice dynamics and vibrational spectra, of valence force fields in solids. Keating fits his own force field to elastic constants.[1] At the quadratic level both methods should be equivalent, and Keating's field is capable of predicting valence force constants. In this paper such predictions will be compared to the valence force constants determined from experimental spectra by Tubino *et al.*[2]

The main theme of this paper is the introduction of a simple-potential energy function for diamondlike crystals. One experimental bending valence-force-field constant will be used in the parametrization. An additional variable parameter is an integer that is about 4. All other parameters come from the crystal structure and lattice constant and from ground-electronic-state diatomic-molecular vibrational potential energy data, and they are used according to a theory for pure-stretching vibrations, and correction terms, which will be presented. The valence-force-field force constants will be predicted and compared with constants calculated using Keating's force field and with constants from experiment as determined by Tubino *et al.*

II. KEATING'S FORCE FIELD

It is worthwhile to examine Keating's force field and to show valence-force-field force constants may be evaluated from it. Keating writes the potential energy W for diamondlike crystals,[1]

$$W=\frac{1}{2}\sum_{l}\left(\frac{\alpha}{4a^2}\sum_{i=1}^{4}[R_i^2(l)-3a^2]^2+\frac{\beta}{2a^2}\sum_{j>i}^{4}[\vec{R}_i(l)\cdot\vec{R}_j(l)+a^2]^2\right), \qquad (1)$$

where α is the central first-neighbor force constant, β is the noncentral second-neighbor force constant, a is the lattice constant, and $R_i(l)$ is the distance from nucleus i in cell l to the central nucleus. The four nuclei are coordinated tetrahedrally about the central nucleus in the undeformed (equilibrium) solid.

With the central nucleus as origin of coordinates there are four bond lengths $\{R\}$ and six angles $\{\theta\}$ which are the valence-force-field coordinates. The quadratic valence-force-field force constants are written

$$\begin{aligned}
k_{RR}&=\frac{\partial^2 W}{\partial R^2} && \text{(pure stretch)},\\
k_{RR'}&=\frac{\partial^2 W}{\partial R\partial R'} && \text{(stretch-stretch)},\\
k_{\theta\theta}&=\frac{\partial^2 W}{\partial\theta^2} && \text{(pure bend)}, \qquad (2)\\
k_{R\theta}&=\frac{\partial^2 W}{\partial R\partial\theta} && \text{(stretch-bend)},\\
k_{\theta\theta'}&=\frac{\partial^2 W}{\partial\theta\partial\theta'} && \text{(bend-bend)},
\end{aligned}$$

where the derivatives are evaluated at the equilibrium structure and as many coordinates as possible are held constant when taking a derivative. For the diamond structure the equilibrium angle

θ_e has the value 109.471°.

The force constants in Eq. (2) were determined by Tubino *et al.*[2] by fitting lattice-dynamics equations to reproduce phonon dispersion curves based on inelastic neutron-diffraction experiments. In making these fits, they included an additional force constant corresponding to a bend-bend interaction for a chain of four bonded atoms. They considered these six force constants to be the minimal number of pertinent variable parameters needed to produce a satisfactory fit to the experimental spectra.

Keating expressed α and β in Eq. (1) in terms of elastic constants.[1] It is noted that Eq. (1) is a functional of distances between nonbonded nuclei since

$$\vec{R}_i \cdot \vec{R}_j = R_i R_j \cos\theta_{ij} = \tfrac{1}{2}(R_i^2 + R_j^2 - R_{ij}^2), \tag{3}$$

where $R_{ij}^2 = |\vec{R}_i - \vec{R}_j|^2$. Thus, the second summation could be viewed as containing, in part, central second-neighbor components, central first-neighbor components, and products of them. Keating's noncentral second-neighbor interactions are functionals of central pairwise interactions. The valence force constants of Eq. (2) are obtained by taking derivatives of Eq. (1). In addition to Eq. (3), some useful formulas are

$$R_{ij} = [R_i^2 + R_j^2 - 2R_i R_j \cos(\tfrac{1}{2}\theta_{ik}) \cos(\pi - \tfrac{1}{2}\theta_e)]^{1/2},$$

$$R_{ij} = \{R_i^2 + R_j^2 - 2R_i R_j [\sin(\theta_{ik} - \tfrac{1}{2}\pi) \sin(\theta_{jk} - \tfrac{1}{2}\pi) - \tfrac{1}{2}\cos(\theta_{ik} - \tfrac{1}{2}\pi)\cos(\theta_{jk} - \tfrac{1}{2}\pi)]\}^{1/2}. \tag{4}$$

TABLE I. Comparison of force constants evaluated using Keating's potential, the results of this paper, and experiment.[a]

	Diamond			Silicon		
	Keating[b]	Eq. (15) of text[c]	Expt.[d]	Keating[b]	Eq. (15) of text[c]	Expt.[d]
k_{RR}	4.295	3.802	3.831	1.524	1.540	1.469
$k_{\theta\theta}$	3.366	(0.872)	0.872	1.267	(0.164)	0.164
$k_{RR'}$	0.142	0.759	0.164	0.023	0.053	0.052
$k_{R\theta}$	1.153	0.260	0.392	0.284	0.030	0.073
$k_{\theta\theta'}$	0.898	0.345	−0.015	0.338	0.075	−0.025

[a] These force constants are second derivatives of the energy at the equilibrium geometry of the diamondlike structure. As many valence coordinates as possible are held constant when evaluating derivatives.

[b] Equation (1) of the text. From Ref. 1 of the text, for diamond, $\alpha = 1.29$, $\beta = 0.85$; for silicon, $\alpha = 0.485$, $\beta = 0.29$, all in mdyn/Å.

[c] Using Eqs. (11)–(14) in Eq. (15) with $N = 5$ for diamond and $N = 3$ for silicon. Using Ref. 11 of the text. for ground $(X\,^3\pi_u)$ state C_2, $R_e = 1.3117$, $k_e = 9.523$, $l_e = -59.4$; for ground $(X\,^3\Sigma_g^-)Si_2$, $R_e = 2.252$, $k_e = 2.12$, $l_e = -8.55$ (Å, mdyn/Å, mdyn/Å^2). In diamond R_e becomes 1.54452 and in solid silicon it becomes 2.352. For diamond, $A = 13.2467$, $B = -28.3642$ and for silicon, $A = 3.0015$, $B = -3.8983$.

[d] From Ref. 2 of the text. Units are, from top to bottom, mdyn/Å, mdyn·Å, mdyn/Å, mdyn, mdyn·Å.

Experimental valence force constants and force constants determined from Keating's function are in Table I.

III. POISSON EQUATION FOR NUCLEAR VIBRATIONAL STRETCHING POTENTIALS IN MOLECULES AND SOLIDS

Here a theory is presented for stretching force constants k_{RR}. The usefulness of this theory for quadratic, cubic, and quartic stretching force constants in diatomic and triatomic molecules has been demonstrated elsewhere.[3–10] The higher-order force constants will not be considered here since Tubino *et al.*[2] did not determine them. However, they may be easily evaluated.

According to classical electrostatics, a Poisson equation for the interaction of nucleus a of charge Z_a at positions $\vec{R}_a$ in a rigid molecular electronic charge density $\rho(\vec{r})$, where $\vec{R}_a$ and $\vec{r}$ are from an arbitrary origin, can be written

$$\nabla^2_{\vec{R}_a} W_{cl}(\vec{R}_a) = 4\pi Z_a \rho(\vec{R}_a), \tag{5}$$

where W_{cl} is the classical electrostatic energy. According to an assumption that the density is made up of a superposition of rigid densities centered on each nucleus, $\rho(\vec{r})$ takes the form

$$\rho(\vec{r}) = \sum_j \rho_j(|\vec{R}_j - \vec{r}|). \tag{6}$$

Because of translational invariance, ρ_a will not contribute to Eq. (5). Equation (5), in the density approximation of Eq. (6), may be given a quantum-mechanical basis through the Hellmann-Feynman force theorem; W_{cl} is then an approximation to the total molecular energy via the Poisson equation.

In the Hellmann-Feynman force approximation, the force on a, $\vec{F}_a$, is given by, using Eq. (6),

$$\vec{F} = \nabla_{\vec{R}_a} W = \sum_{i\neq a} \int \rho_i(|\vec{R}_i - \vec{r}|)\, \nabla_{\vec{R}_a}\left(\frac{-Z_a}{|\vec{R}_a - \vec{r}|}\right) d\vec{r} + \sum_{i\neq a} \nabla_{\vec{R}_a} \frac{Z_i Z_a}{|\vec{R}_i - \vec{R}_a|}, \tag{7}$$

where W is the total molecular energy in the Born-Oppenheimer approximation. Clearly, ρ_a does not contribute to the force on nucleus a. The divergence of Eq. (7) yields[3,4]

$$\nabla^2_{\vec{R}_a} W = 4\pi Z_a \sum_{i\neq a} \rho_i(\vec{R}_a). \tag{8}$$

For a diatomic molecule a-b, for the origin on nucleus b, Eq. (8) becomes

$$\nabla^2_a W_D = 4\pi Z_a \rho_b(R_a). \tag{9}$$

The accuracy of Eqs. (8) and (9) depends on the accuracy of the density approximation of Eq. (6) as used in Eq. (7), since Eq. (7) is exact for eigendensities in the Born-Oppenheimer approximation.

Remarkably, for such a simple model, Eq. (9) and its derivatives can contain quadratic, cubic, and quartic force constants k_e, l_e, and m_e to good accuracy when R_a is set equal to the equilibrium distance R_e and atomic electronic charge densities are employed.[3,4] Alternative formulations using the total molecular density[5] lead, with reasonable assumptions and approximations, to an equation of the form of Eq. (9). This means Eq. (8) can be interpreted as a classical equation of the form of Eq. (5). The force constants appear to be governed by a classical electrostatic Poisson equation for a nucleus embedded in the electronic charge density tail due to orbitals centered on the neighboring nucleus. Other energy changes, which affect R_e and correspond to density redistributions, must be nearly Coulombic.[6] The success of Eq. (9) does not necessarily imply that density tails exist at a nucleus since the formula gives an approximation to the interaction of a nucleus with a spherically averaged distorted atom due to the rotational invariance of this component of the energy.

The nuclei a and b may be interchanged in Eq. (9), and for most heteronuclear diatomic molecules the smaller Z is to be used.[3,4] The very ionic LiH molecule is an exception.[4] Furthermore, invoking a generalized model density for diatomic molecules,

$$\rho(R)=C' e^{-\zeta R} \tag{10}$$

leads, on integration of Eq. (9), to a formula for diatomic potentials,[7]

$$W_D(R)=C[e^{-\zeta R}(2/\zeta^3 R+1/\zeta^2)-F_D/R], \tag{11}$$

where

$$F_D=e^{-\zeta R_e}(R_e^2/\zeta+2R_e/\zeta^2+2/\zeta^3) \tag{12}$$

and

$$\zeta=-l_e/k_e-2/R_e, \tag{13}$$

$$C=k_e e^{\zeta R_e} . \tag{14}$$

Equation (11) gives very good predictions of the quartic force constants.[7] Any components of the energy Coulombic near R_e will not effect force constants when F_D is adjusted to give the minimum in $W(R)$ at R_e. Though R^{-1} components may exist for covalent diatomic molecules,[6] Eq. (11) becomes less and less accurate beyond the quartic level in these cases.[7] Although dissociation energies can be fairly well predicted for ionic diatomic molecules[7] by Eq. (11), in general the equation is to be thought of as a source of equilibrium force constants through quartic order and perhaps somewhat beyond. At displacements greater than a few tenths of an angstrom from equilibrium, the rigid-density Poisson equation model should not be expected to hold as charge redistributions may become significant in determining the potential function, especially in covalent cases.

Empirical relationships[8] for quadratic force constants of molecules made of atoms from pairs of columns from the periodic table of the elements collaborate the Poisson equation model and provide another means[9] of determining C and ζ for use in Eqs. (10)–(12). The implication is that effective densities for use in the Poisson equation are rigid and transferable "core" densities.[8,9]

When C and ζ are determined by means of Eqs. (13) and (14) for ground-state C_2 and Si_2,[11] then the effective density of Eq. (10) yields k_{RR} values according to the equation,[9] $k_{RR}=k_e \exp[-\zeta(R_{es}-R_e)]$, where R_{es} is the equilibrium distance in the solid: diamond, 3.179 (3.831); solid silicon, 1.553 (1.469) in units of mdyn/Å, where experimental values in parentheses are from Ref. 2. These are good predictions, encouraging the use of the Poisson equation in solids.

IV. VALENCE-FORCE-FIELD POTENTIALS FOR DIAMOND-STRUCTURE CARBON AND SILICON

The goal is to predict the force constants defined in Eq. (2) and to compare with the results of Tubino *et al.* A reasonable approach is to write down analytical functions analogous to those which worked well for free carbon dioxide and other linear triatomic molecules.[10] Thus, the potential function has the form

$$W=\sum_{i=1}^{4} W_D(R_i)+\sum_{i<j}^{4}\left(\frac{A}{R_{ij}^N}-\frac{B}{(R_i+R_j)^N}\right) , \tag{15}$$

where the W_D are ground-state diatomic potential functions of the form of Eq. (11), A is a constant determined by fitting Eq. (15) exactly to $k_{\theta\theta}$, and B is a constant determined by the condition $(\partial W/\partial R_i)\{R_{es}\}=0$. The integer N is expected to be around 4 as it was for the triatomic molecules.[9]

Equation (15) is indeed reasonably successful, as seen in Table I, and the interpretation of the terms in it would appear to be much the same as for the triatomic potentials: The diatomic potentials W_D come from the theory behind the Poisson equation for nuclear motions in rigid-density tails, as discussed in Sec. III, and the additional terms represent valence orbital contributions to mixed force constants.

Whereas according to the theory there is a connection between force constants evaluated using the $W_D(R)$ of Eq. (11) and atomic "core" electronic charge densities, the terms in the second summation of Eq. (15) are not at present associated with particular electronic charge densities or changes in charge densities during deformations in the crystal. These latter terms in Eq. (15) are simply working corrections to the diatomic potentials and their accuracy in predicting mixed force constants is their main justification. They appear to represent contributions to the vibrational energy from the "valence" electrons.[10] For the purposes of this work it is convenient to speak of "core" and "valence" orbitals and electronic charge densities when referring to rigid and deformable densities which may exist during vibrations. There is some evidence for a correspondence such that a rigid core exists for different spectroscopic valence states in a diatomic molecule.[9]

V. RESULTS AND DISCUSSION

Predictions using Keating's two-parameter potential function [Eq. (1)] and our two-parameter function [Eq. (15)] for carbon and silicon are in Table I. Except for one or two cases Eq. (15) gives much better predictions. The angular dependence of Eq. (1) seems poor. The small experimental values of $k_{\theta\theta'}$, which are in fact negative, are surprising. Since a part of $k_{\theta\theta'}$, is proportional to $k_{\theta\theta}$ which is large and positive and fit exactly by Eq. (15), it is expected, if the pairwise interaction model is valid for bends, that the predictions would be accurate. The effect of the choice of the particular six quadratic force constants on the value of any particular force constant in the method of Tubino *et al.*[2] is unknown.

It is perhaps surprising that the model valence force field potential function for these solids contains the same terms as those which worked well for gaseous CO_2 and CS_2.[10] However, the generality of the Poisson equation model leads one to suspect bonded interactions should be describable in terms of ground-state diatomic potentials even in covalent solids. The additional terms, representing valence electron energies, are reasonable in covalent solids due to Keating's proof that the bonded interactions are central at the harmonic level. This is not to say that variations on Eq. (15) could not produce better results even without increasing the number of parameters. In Ref. 10 it is shown that variations are necessary for bent molecules due to the lone-pair electrons. Before modifying Eq. (15) it would be best to compare the cubic force constants, which are easily evaluated by taking further derivatives, with experiment. Further tests on other solids would be worthwhile. Although force constants are available for solid germanium and tin,[2] Eq. (15) could not be parametrized because the diatomic molecules are unknown.

It is nothing new to suggest that valence energies are important to force fields in covalent solids. Localized hybridization effects have been mentioned as important in solids already by Keating[12] and Tubino *et al.*[2] The well-known "shell model"[13] may be viewed as containing valence effects and "core" interactions. In the present work the core interactions with a neighboring atom are handled with the Poisson equation. Equation (15) suggests there is simplicity and generality to potentials for molecules and covalent solids. The inverse R_{ij} terms are like steric interactions and the inverse $(R_i + R_j)$ are like an angle-independent orbital energy on the central atom. Energies of hybridization, which are almost certainly important for triatomic molecules with lone-pair electrons on the central atom,[10] may be contained partially in these terms. Perhaps introducing a purely hybrid term could improve predictions of $k_{\theta\theta'}$. Greater understanding will come with further work on potentials in solids.

There is reason to be optimistic about using formulas similar to Eq. (15) for metals and ionic solids. For detailed discussions of the past work on the microscopic theory of force constants in solids the reader is referred to the work of Pick *et al.*,[14] Phillips,[15] Smith *et al.*,[16] and references in these papers, and finally to Pauling's stimulating book.[17]

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*Aided by research grants to Cornell University from the National Science Foundation.

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