

## Molecular Packing Analysis\*

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A general method of molecular packing analysis based on the minimization of the crystal lattice energy is described. The lattice energy was approximated by a pairwise sum over nonbonded atoms in different molecules, using (exp-6-1) potential functions. Increased speed of calculation of the lattice sums was achieved by a convergence acceleration technique. The variables considered were six rigid body rotations and translations for each molecule in the asymmetric unit, and the six lattice constants. Molecular flexibility was allowed in the form of internal rotations about bonds (subrotations). In this event additional subrotation potentials of the  $\cos^2 \psi$  type could be used to allow for conjugation energy, and the subrotation angles were additional variables. An optional thermal correction, based on the mean square thermal amplitudes and the potential anharmonicities, was applied to calculate the anisotropic thermal expansion. Nonbonded potential parameters, including conjugation energies, were found by fitting them to observed crystal structures.

### Introduction

The study of molecular packing in crystals gained increased popularity as the result of the appearance of a book by Kitaigorodsky (1955). References to recent work in this field may be found in review articles by Mason (1970) and by Kitaigorodsky (1970).

In the present work the intermolecular lattice energy of a crystal was approximated by a pairwise sum of (exp-6-1) nonbonded interatomic potential functions:

$$E = \frac{1}{2} \sum_{jkm} [B_{\alpha\beta} \exp(-C_{\alpha\beta} r_{jkm}) - A_{\alpha\beta} r_{jkm}^{-6} + q_{\alpha} q_{\beta} r_{jkm}^{-1}],$$

where  $r_{jkm}$  is a nonbonded interatomic distance,  $A_{\alpha\beta}$  is the coefficient of the London dispersion attraction term between atoms of type  $\alpha$  and  $\beta$ ,  $B_{\alpha\beta}$  and  $C_{\alpha\beta}$  characterize the short-range repulsive energy, and  $q_{\alpha}$  is the electrostatic charge on the atom. Subscript  $j$  runs over the atoms of the asymmetric unit,  $k$  over all atoms in different molecules, and  $m$  over the space group symmetry operations of the unit cell. In practical computation advantage may be taken of the fact that  $r_{jkm} = r_{kjm'}$ , where  $m'$  represents the symmetry operation inverse to  $m$ . Thus the sum may be taken over  $j \geq k$ , with the  $j > k$  terms being given double weight. Additional intramolecular terms may optionally be included if the molecule is not rigid.

The theoretical model assumes that the molecules are rigid except for internal rotations about bonds (subrotations). It may be desirable to shift the hydrogen atom repulsion centers inward along the bond axis (Williams, 1965). Higher order terms in  $r^{-8}$ ,  $r^{-10}$  etc. are neglected, as are nonpairwise additive effects (Margenau & Kestner, 1969; Hirschfelder, 1967) and anisotropic dispersion interactions (Haugh & Hirschfelder, 1955; Sternlicht, 1964; Cheng & Nyburg, 1969).

### Evaluation of derivatives

The following equations have been incorporated into a Fortran computer program, designated *PCK6*. In an early version of this program, the first and second derivatives of the lattice energy were evaluated numerically. In an effort to speed up the calculation, a later version was written in which all derivatives were evaluated analytically. This change resulted in a decrease of about 50% in computer time required for a typical calculation.

An interatomic distance,  $r_{jkm}$ , between atom  $j$  and atom  $k$  transformed by symmetry operation  $m$  is evaluated by the equation (Williams, 1969):

$$r_{jkm} = (C_1^2 + C_2^2 + C_3^2)^{1/2} = |\mathbf{C}|,$$

where

$$\mathbf{C} = \mathbf{X}_j - \mathbf{S}_m \mathbf{X}_k - \mathbf{T}_m.$$

Here  $\mathbf{X}_j$  are the Cartesian atomic coordinates of the asymmetric unit,  $\mathbf{S}_m$  is a  $3 \times 3$  matrix giving the point symmetry, and  $\mathbf{T}_m$  is a vector giving the translation symmetry including cell translations. The first derivative with respect to a parameter,  $p$ , is given by

$$\frac{\partial r}{\partial p} = \frac{1}{r} \left[ C_1 \frac{\partial C_1}{\partial p} + C_2 \frac{\partial C_2}{\partial p} + C_3 \frac{\partial C_3}{\partial p} \right].$$

The second derivatives with respect to parameters  $p_{\mu}$  and  $p_{\nu}$  are given by

$$\begin{aligned} \frac{\partial^2 r}{\partial p_{\mu} \partial p_{\nu}} = & \frac{1}{r} \left[ C_1 \frac{\partial^2 C_1}{\partial p_{\mu} \partial p_{\nu}} + C_2 \frac{\partial^2 C_2}{\partial p_{\mu} \partial p_{\nu}} + C_3 \frac{\partial^2 C_3}{\partial p_{\mu} \partial p_{\nu}} \right. \\ & + \left( \frac{\partial C_1}{\partial p_{\mu}} \right) \left( \frac{\partial C_1}{\partial p_{\nu}} \right) + \left( \frac{\partial C_2}{\partial p_{\mu}} \right) \left( \frac{\partial C_2}{\partial p_{\nu}} \right) \\ & \left. + \left( \frac{\partial C_3}{\partial p_{\mu}} \right) \left( \frac{\partial C_3}{\partial p_{\nu}} \right) - \left( \frac{\partial r}{\partial p_{\mu}} \right) \left( \frac{\partial r}{\partial p_{\nu}} \right) \right]. \end{aligned}$$

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*Lattice constants*

The effect of a lattice constant change is to change only  $\mathbf{T}$ ; the  $\mathbf{X}_j$  are invariant. It is convenient to refer the lattice constant changes to the translation vector in unit-cell space,  $\mathbf{t}$ , where  $\mathbf{T} = \mathbf{D}\mathbf{t}$ ,

$$\mathbf{D} = \begin{bmatrix} a \sin \gamma & 0 & c(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma \\ a \cos \gamma & b & c \cos \alpha \\ 0 & 0 & V/ab \sin \gamma \end{bmatrix}$$

and

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2} = abc\delta.$$

Thus, the components of  $\mathbf{T}$  may be expressed in terms of the components of  $\mathbf{t}$ :

$$\begin{aligned} T_1 &= t_1 a \sin \gamma + t_3 c(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma \\ T_2 &= t_1 a \cos \gamma + t_2 b + t_3 c \cos \alpha \\ T_3 &= t_3 c \delta / \sin \gamma. \end{aligned}$$

Of the 81 first and second derivatives, 45 are zero. Derivation of the analytical form of the nonzero derivatives is straightforward, but somewhat tedious. For convenience, the results are displayed in Table 1.

*Molecular rotations*

We wish to rotate the rigid body through angle  $\theta$  about axis  $\mathbf{l}$ , where  $|\mathbf{l}| = 1$ . The  $\mathbf{l}_i$  are thus the direction cosines of the rotation axis with respect to the reference cartesian system defined by matrix  $\mathbf{D}$ . The effect of the rotation is given by the matrix equation (*International Tables for X-ray Crystallography*, 1959),

$$\mathbf{X}_j = \mathbf{R}(\theta, \mathbf{l})\mathbf{X}_j^0,$$

where

$$\mathbf{R} = \begin{bmatrix} \cos \theta + l_1^2(1 - \cos \theta) & l_1 l_2(1 - \cos \theta) + l_3 \sin \theta & l_1 l_3(1 - \cos \theta) - l_2 \sin \theta \\ l_1 l_2(1 - \cos \theta) - l_3 \sin \theta & \cos \theta + l_2^2(1 - \cos \theta) & l_2 l_3(1 - \cos \theta) + l_1 \sin \theta \\ l_1 l_3(1 - \cos \theta) + l_2 \sin \theta & l_2 l_3(1 - \cos \theta) - l_1 \sin \theta & \cos \theta + l_3^2(1 - \cos \theta) \end{bmatrix}.$$

$\mathbf{T}$  is not affected by the rotation. The three rotation axes were taken parallel to the principal axes of inertia. The order of differentiation is significant, since rotations about different axes do not commute. The effect of first applying rotation  $\mathbf{R}_\nu$  and then  $\mathbf{R}_\mu$  is:

$$\mathbf{X}_j = \mathbf{R}_\mu \mathbf{R}_\nu (\mathbf{X}_j^0 - \mathbf{X}_0^0) + \mathbf{R}_\mu (\mathbf{X}_0^0 - \mathbf{X}_0^0) + \mathbf{X}_0^0,$$

where  $\mathbf{X}_j^0$  are the trial atomic coordinates, and  $\mathbf{X}_0^0$  and  $\mathbf{X}_0^0$  are the respective centers of rotation.

Since the rotation variables are separated in  $\mathbf{R}_\nu$  and  $\mathbf{R}_\mu$ , the second derivatives depend only on the first rotation center  $\mathbf{X}_0^0$ , and not on  $\mathbf{X}_0^0$ . The first derivatives (evaluated at the trial coordinates) are given by the matrix equation

$$\frac{\partial \mathbf{C}}{\partial \theta} = \mathbf{L}(\mathbf{X}_j^0 - \mathbf{X}_0^0) - \mathbf{S}\mathbf{L}(\mathbf{X}_k^0 - \mathbf{X}_0^0)$$

where

$$\mathbf{L} = \begin{bmatrix} 0 & l_3 & -l_2 \\ -l_3 & 0 & l_1 \\ l_2 & -l_2 & 0 \end{bmatrix}.$$

It is easily verified that these equations for the first derivatives reduce to those shown by Williams (1969), except for a reversal of rotation direction, if  $\mathbf{l}$  is taken parallel to any of the Cartesian axes. The second derivatives are given by

$$\frac{\partial^2 \mathbf{C}}{\partial \theta_\mu \partial \theta_\nu} = \mathbf{L}_\mu \mathbf{L}_\nu (\mathbf{X}_j^0 - \mathbf{X}_0^0) - \mathbf{S}\mathbf{L}_\mu \mathbf{L}_\nu (\mathbf{X}_k^0 - \mathbf{X}_0^0).$$

*Translations*

The first derivatives are:

$$\frac{\partial \mathbf{C}}{\partial \Delta X_\nu} = \mathbf{l}_\nu - \mathbf{S}\mathbf{l}_\nu.$$

As above, the equations simplify if  $\mathbf{l}_\nu$  is parallel to a Cartesian axis. The second derivatives with respect to translation are all zero.

*Subrotations*

Internal molecular rotations may be handled by analogy with molecular rotations. A difference is that only the atoms in the rotating subgroup are affected by the subrotation, and therefore a given nonbonded contact (perhaps intramolecular) may or may not contribute to derivatives involving subrotations. The subrotation axis, of course, is taken coincident with the bond joining the subgroup to the molecule. The subrotation conjugation potentials were taken as

$$E_c = E_c^0 \cos^2 \psi,$$

where  $E_c^0$  is the (negative) conjugation energy for  $\psi = 0$ . The subrotation angle,  $\psi$ , may be defined by any four nonlinear atoms. If we designate the atom sequence (3,1,2,4),  $\psi$  is the angle between planes defined by

atoms (3,1,2) and (1,2,4). Thus (1,2) is the bond joining the subgroup to the molecule, and 3 and 4 are rotation reference atoms defining  $\psi$ . Atoms 2 and 4 are in the subgroup.

*Evaluation of the lattice sum*

The theory of convergence acceleration of general lattice sums of the type  $\sum q'_\alpha q'_\beta r^{-n}$  has been discussed by Williams (1971). The application of convergence acceleration to the coulombic energy is straightforward, since  $q'$  may be set equal to  $q$  in this case. For the London dispersion energy we set  $q' = \sqrt{A}$ . The application of the convergence acceleration technique requires that the geometric-mean combining law hold, *i.e.* that  $A_{\alpha\beta} = \sqrt{(A_{\alpha\alpha} A_{\beta\beta})}$ .

The geometric-mean combining law seems to be a fairly good approximation for the London dispersion energy. London's (1930) classic formula,

$$E_{\text{disp}} = -\frac{3}{2} \left( \frac{I_\alpha I_\beta}{I_\alpha + I_\beta} \right) \frac{P_\alpha P_\beta}{r_{\alpha\beta}^6},$$

relates the dispersion energy to the ionization energy  $I$  and the polarizability  $p$ . Since the range of variation of the polarizabilities is much greater than that of the ionization energies, the geometric mean laws holds fairly well (Hirschfelder, Curtiss & Bird, 1954). This has been experimentally verified in hydrocarbon crystals (Williams, 1966, 1967).

In contrast, theory does not predict that the geometric-mean combining law holds for short-range repulsion. For hydrocarbon crystals, analysis of experimental data indicates that  $B_{CH}$  is significantly less than would be predicted by this combining law (Williams, 1966, 1967). Fortunately, the repulsive energy decreases so rapidly that all significant terms may be summed directly without the need for convergence acceleration.

In program PCK6 only the direct lattice sum, and the constant terms, are evaluated. Therefore, the maximum summation limit on  $r_{jkm}$  and the values of the convergence constants,  $K_1$  and  $K_6$ , were selected so as to make the reciprocal sum negligible. At a 1% error level, the use of convergence acceleration yielded a factor of about ten in increased speed of calculation, without considering the reciprocal space lattice sum.

With convergence acceleration, the lattice sum is given by:

$$E = \frac{1}{2} \sum_{jkm} [B_{\alpha\beta} \exp(-C_{\alpha\beta} r_{jkm}) - A_{\alpha\beta} r_{jkm}^{-6} (1 + a_6^2 + \frac{1}{2} a_6^4)] \\ \times \exp(-a_6^2) + q_{\alpha} q_{\beta} r_{jkm}^{-1} \operatorname{erfc}(a_1) \\ - \frac{\pi^3 K_6^3}{6V} (\sum_{\alpha} A_{\alpha\alpha}^{1/2})^2 + \frac{\pi^3 K_6^6 Z}{12} (\sum_{\alpha} A_{\alpha\alpha}) \\ - K_1 Z (\sum_{\alpha} q_{\alpha}^2),$$

where  $a_i^2 = \pi K_i^2 r_{jkm}^2$ ,  $\operatorname{erfc}(a_1) = \int_{a_1}^{\infty} \exp(-t^2) dt$ ,  $Z$  is the

number of molecules in the unit cell, and  $A_{\alpha\beta} = (A_{\alpha\alpha})^{1/2} (A_{\beta\beta})^{1/2}$ . The first derivatives with respect to a parameter  $p$  are

$$\frac{\partial E}{\partial p} = \frac{1}{2} \sum_{jkm} \{ -B_{\alpha\beta} C_{\alpha\beta} \exp(-C_{\alpha\beta} r_{jkm}) + A_{\alpha\beta} r_{jkm}^{-7} \\ \times (6 + 6a_6^2 + 3a_6^4 + a_6^6) \exp(-a_6^2) - q_{\alpha} q_{\beta} r_{jkm}^{-2} \\ \times [2K_1 r_{jkm} \exp(-a_1^2) + \operatorname{erfc}(a_1)] \} \frac{\partial r_{jkm}}{\partial p} \\ + \frac{\pi^3 K_6^3}{6V^2} (\sum_{\alpha} A_{\alpha\alpha}^{1/2})^2 \frac{\partial V}{\partial p}.$$

Table 1. Derivatives of  $C_1$ ,  $C_2$ , and  $C_3$  with respect to the lattice constants

Parameter	$C_1$					$C_2$					$C_3$							
	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$
First	1	0	2	3	4	5	6	7	8	9	0	10	0	0	11	12	13	14
Second: $a$	0	0	0	0	0	15	0	0	0	0	0	16	0	0	0	0	0	0
$b$		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$c$			0	17	18	19	0	20	0	0	0	0	0	0	0	21	22	23
$\alpha$				24	0	25	0	26	0	0	0	0	0	0	27	28	29	0
$\beta$					30	31			0	0							32	33
$\gamma$						34				35								36
1: $-t_1 \sin \gamma$	9: $t_3 c \sin \alpha$					18: $t_3 \sin \beta / \sin \gamma$												
2: $-t_3 (\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$	10: $t_1 a \sin \gamma$					19: $t_3 (\cos \beta \cos \gamma - \cos \alpha) / \sin^2 \gamma$												
3: $-t_3 c \sin \alpha \cos \gamma / \sin \gamma$	11: $-t_3 \delta / \sin \gamma$					20: $t_3 \sin \alpha$												
4: $t_3 c \sin \beta / \sin \gamma$	12: $t_3 c \sin \alpha (\cos \beta \cos \gamma - \cos \alpha) / (\delta \sin \gamma)$					21: $t_3 \sin \alpha (\cos \beta \cos \gamma - \cos \alpha) / (\delta \sin \gamma)$												
5: $-t_1 a \cos \gamma$	13: $t_3 c \sin \beta (\cos \alpha \cos \gamma - \cos \beta) / (\delta \sin \gamma)$					22: $t_3 \sin \beta (\cos \alpha \cos \gamma - \cos \beta) / (\delta \sin \gamma)$												
$+ t_3 c (\cos \beta \cos \gamma - \cos \alpha) / \sin^2 \gamma$	14: $t_3 c [(\cos \alpha \cos \beta - \cos \gamma) / \delta + \delta \cos \gamma / \sin^2 \gamma]$					23: $t_3 [(\cos \alpha \cos \beta - \cos \gamma) / \delta + \delta \cos \gamma / \sin^2 \gamma]$												
6: $-t_1 \cos \gamma$	15: $-t_1 \cos \gamma$					24: $-t_3 c \cos \alpha \cos \gamma / \sin \gamma$												
7: $-t_2$	16: $t_1 \sin \gamma$					25: $t_3 c \sin \alpha / \sin^2 \gamma$												
8: $-t_3 \cos \alpha$	17: $-t_3 \sin \alpha \cos \gamma / \sin \gamma$					26: $t_3 c \cos \alpha$												
27: $\frac{t_3 c}{\delta \sin \gamma} [(\cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha + \sin^2 \alpha) + \sin^2 \alpha (\cos \beta \cos \gamma - \cos \alpha)^2 / \delta^2]$																		
28: $\frac{t_3 c}{\delta \sin \gamma} [\sin \beta \sin \alpha (\cos \alpha \cos \gamma - \cos \beta) (\cos \beta \cos \gamma - \cos \alpha) / \delta^2 - \sin \alpha \sin \beta \cos \gamma]$																		
29: $t_3 c \sin \alpha [-\cos \beta / \delta - \cos \gamma (\cos \beta \cos \gamma - \cos \alpha) / \delta \sin^2 \gamma + (\cos \beta \cos \gamma - \cos \alpha) (\cos \alpha \cos \beta - \cos \gamma) / \delta^3]$																		
30: $t_3 c \cos \beta / \sin \gamma$																		
31: $-t_3 c \sin \beta \cos \gamma / \sin^2 \gamma$																		
32: $\frac{t_3 c}{\delta \sin \gamma} [\cos \alpha \cos \beta \cos \gamma - \cos^2 \beta + \sin^2 \beta + \sin^2 \beta (\cos \alpha \cos \gamma - \cos \beta)^2 / \delta^2]$																		
33: $\frac{t_3 c}{\delta \sin \gamma} [\sin \beta \sin \gamma (\cos \alpha \cos \beta - \cos \gamma) (\cos \alpha \cos \gamma - \cos \beta) / \delta^2 - \cos \alpha \sin \beta \sin \gamma - \frac{\cos \gamma \sin \beta}{\sin \gamma} (\cos \alpha \cos \gamma - \cos \beta)]$																		
34: $t_1 a \sin \gamma - t_3 c [\cos \beta (1 + \cos^2 \gamma) - 2 \cos \alpha \cos \gamma] / \sin^3 \gamma$																		
35: $t_1 a \cos \gamma$																		
36: $t_3 c [\sin \gamma / \delta - \delta (\cos^2 \gamma + 1) / \sin^3 \gamma - \cos \gamma (\cos \alpha \cos \beta - \cos \gamma) / (\delta \sin \gamma) + \sin \gamma (\cos \alpha \cos \beta - \cos \gamma)^2 / \delta^3]$																		

The second derivatives are given by

$$\begin{aligned} \frac{\partial^2 E}{\partial p_\mu \partial p_\nu} = & \frac{1}{2} \sum_{jkm} \left\{ B_{\alpha\beta} C_{\alpha\beta} \exp(-C_{\alpha\beta} r_{jkm}) \right. \\ & \times \left[ C_{\alpha\beta} \left( \frac{\partial r_{jkm}}{\partial p_\mu} \right) \left( \frac{\partial r_{jkm}}{\partial p_\nu} \right) - \frac{\partial^2 r_{jkm}}{\partial p_\mu \partial p_\nu} \right] \\ & - A_{\alpha\beta} r_{jkm}^{-8} \exp(-a_6^2) \\ & \times \left[ (42 + 42a_6^2 + 21a_6^4 + 7a_6^6 + 2a_6^8) \left( \frac{\partial r_{jkm}}{\partial p_\mu} \right) \left( \frac{\partial r_{jkm}}{\partial p_\nu} \right) \right. \\ & \left. - r_{jkm} (6 + 6a_6^2 + 3a_6^4 + a_6^6) \left( \frac{\partial^2 r_{jkm}}{\partial p_\mu \partial p_\nu} \right) \right] \\ & + q_\alpha q_\beta r_{jkm}^{-3} \left\{ 2 \operatorname{erfc}(a_1) + 4K_1 r_{jkm} \exp(-a_1^2) \right. \\ & \times (1 + a_1^2) \left. \left[ \left( \frac{\partial r_{jkm}}{\partial p_\mu} \right) \left( \frac{\partial r_{jkm}}{\partial p_\nu} \right) \right. \right. \\ & \left. \left. - [r_{jkm} \operatorname{erfc}(a_1) + 2K_1 r_{jkm}^2 \exp(-a_1^2)] \left( \frac{\partial^2 r_{jkm}}{\partial p_\mu \partial p_\nu} \right) \right] \right\} \\ & + \frac{\pi^3 K_\delta^3}{6V^2} \left( \sum_\alpha A_{\alpha\alpha}^{1/2} \right)^2 \\ & \times \left[ \frac{\partial^2 V}{\partial p_\mu \partial p_\nu} - \frac{2}{V} \left( \frac{\partial V}{\partial p_\mu} \right) \left( \frac{\partial V}{\partial p_\nu} \right) \right]. \end{aligned}$$

#### Cell volume derivatives

The cell volume derivatives are obtained in a straightforward manner and are listed in Table 2 for convenient reference. Three of the possible 27 first and second derivatives are zero.

#### Lattice sum derivatives

The first and second derivatives of the lattice sum may now be evaluated at the trial model coordinates

by substitution of the cell volume derivatives and the nonbonded distance derivatives back into the above equations. Since no simplification of the equations occurs, in practice the cell volume and distance derivatives are evaluated numerically before substitution.

#### Lattice energy minimization

Program *PCK6* prepares a table of nonbonded contacts for use in several refinement cycles. Since the second derivatives change relatively slowly, and are time-consuming to evaluate, they are evaluated only once for the table. The first derivatives are re-evaluated for each cycle of refinement.

The matrix of the second derivatives is not in general symmetric, but it may be separated into symmetric and antisymmetric parts. The eigenvalues of the symmetric part were found. If all eigenvalues were nonzero and positive, a Gauss-Newton refinement cycle was performed. This would normally be the case if the trial model were close to an energy minimum. The Gauss-Newton cycle requires the solution,  $\Delta \mathbf{p}$ , to the matrix equation

$$\mathbf{F} \Delta \mathbf{p} = \mathbf{g},$$

where

$$F_{\mu\nu} = \sum_i \left( \frac{\partial^2 E}{\partial p_\mu \partial p_i} \right) \left( \frac{\partial^2 E}{\partial p_\nu \partial p_i} \right)$$

and

$$g_\mu = \sum_i \left( \frac{\partial E}{\partial p_i} \right) \left( \frac{\partial^2 E}{\partial p_\mu \partial p_i} \right).$$

If any eigenvalue was zero or negative, a steepest descent refinement cycle was performed. That is, the parameters were shifted according to the equation

$$\Delta \mathbf{p} = -\lambda \frac{\partial E}{\partial \mathbf{p}},$$

where  $\lambda$  is initially chosen large. If the energy failed to decrease after the shifts were made,  $\lambda$  was halved and

Table 2. Derivatives of the unit cell volume

First	a	b	c	$\alpha$	$\beta$	$\gamma$
	1	2	3	4	5	6
Second: a	0	7	8	9	10	11
b		0	12	13	14	15
c			0	16	17	18
$\alpha$				19	20	21
$\beta$				22	23	
$\gamma$					24	
1: $bc\delta$				7: $c\delta$		
2: $ac\delta$				8: $b\delta$		
3: $abd$				9: $bc \sin \alpha (\cos \alpha - \cos \beta \cos \gamma) / \delta$		13: $ac \sin \alpha (\cos \alpha - \cos \beta \cos \gamma) / \delta$
4: $abc \sin \alpha (\cos \alpha - \cos \beta \cos \gamma) / \delta$				10: $bc \sin \beta (\cos \beta - \cos \alpha \cos \gamma) / \delta$		14: $ac \sin \beta (\cos \beta - \cos \alpha \cos \gamma) / \delta$
5: $abc \sin \beta (\cos \beta - \cos \alpha \cos \gamma) / \delta$				11: $bc \sin \gamma (\cos \gamma - \cos \alpha \cos \beta) / \delta$		15: $ac \sin \gamma (\cos \gamma - \cos \alpha \cos \beta) / \delta$
6: $abc \sin \gamma (\cos \gamma - \cos \alpha \cos \beta) / \delta$				12: $a\delta$		16: $ab \sin \alpha (\cos \alpha - \cos \beta \cos \gamma) / \delta$
						17: $ab \sin \beta (\cos \beta - \cos \alpha \cos \gamma) / \delta$
						18: $ab \sin \gamma (\cos \gamma - \cos \alpha \cos \beta) / \delta$
19: $abc [(\cos^2 \alpha - \sin^2 \alpha - \cos \alpha \cos \beta \cos \gamma) / \delta - \sin^2 \alpha (\cos \alpha - \cos \beta \cos \gamma) / \delta^3]$						
20: $abc [\sin \alpha \sin \beta \cos \gamma / \delta - \sin \alpha \sin \beta (\cos \beta - \cos \alpha \cos \gamma) (\cos \alpha - \cos \beta \cos \gamma) / \delta^3]$						
21: $abc [\sin \alpha \cos \beta \sin \gamma / \delta - \sin \alpha \sin \gamma (\cos \alpha - \cos \beta \cos \gamma) (\cos \gamma - \cos \alpha \cos \beta) / \delta^3]$						
22: $abc [(\cos^2 \beta - \sin^2 \beta - \cos \alpha \cos \beta \cos \gamma) / \delta - \sin^2 \beta (\cos \beta - \cos \alpha \cos \gamma) / \delta^3]$						
23: $abc [\cos \alpha \sin \beta \sin \gamma / \delta - \sin \beta \sin \gamma (\cos \beta - \cos \alpha \cos \gamma) (\cos \gamma - \cos \alpha \cos \beta) / \delta^3]$						
24: $abc [(\cos^2 \gamma - \sin^2 \gamma - \cos \alpha \cos \beta \cos \gamma) / \delta - \sin^2 \gamma (\cos \gamma - \cos \alpha \cos \beta) / \delta^3]$						

another attempt was made (binary chopping). Binary chopping of the shifts was also performed for the Gauss-Newton shifts, if necessary. Steepest-descent cycles of refinement were generally selected when the trial model was not close to an energy minimum.

The relative merits of steepest descent and Gauss-Newton refinement have been discussed, for example, by Marquardt (1963). The steepest-descent method has the widest convergence range but suffers from a slow convergence rate near the minimum. The Gauss-Newton method has a smaller range of convergence but a faster convergence rate near the minimum.

### Results of calculations

We have made several types of calculations with *PCK6* for hydrocarbon crystals. For these crystals electrostatic and multipole effects are small and may be neglected (Kitaigorodsky & Mirskaya, 1964; Mason, 1970).

#### Derivation of nonbonded potential parameters

If reasonable values for  $C_{\alpha\beta}$  can be assumed, the lattice energy is linear in the nonbonded potential parameters  $A_{\alpha\beta}$  and  $B_{\alpha\beta}$ . These parameters may be derived from observed crystal structures by a least-squares fitting process. The number of observational equations is equal to the geometrical degrees of freedom for each structure, with a maximum of 12 equations for the rotation and translation of one molecule in a triclinic unit cell. The scale of  $A_{\alpha\beta}$  and  $B_{\alpha\beta}$  may be set by fitting the calculated lattice energy to the observed heat of sublimation at absolute zero. The second derivatives of the lattice energy may also be related to the elastic constants, yielding more observational equations (Kitaigorodsky & Mirskaya, 1964).

For hydrocarbons, assuming the geometric-mean combining law for the dispersion attraction, values of  $A_{CC}$ ,  $A_{HH}$ ,  $B_{CC}$ ,  $B_{CH}$  and  $B_{HH}$  are sought. It is expected that the most universally applicable values would be obtained by fitting a large number and variety of hydrocarbon crystal structures simultaneously. The most exhaustive calculation reported so far is that of Williams (1970) where 130 observational equations from 18 hydrocarbon crystal structures were fitted. It was found that the same  $C \cdots C$  parameters could be used for both aromatic and saturated carbon atoms, at this accuracy level. Also, no evidence was found for bond-centered, rather than atom-centered, dispersion attractions.

#### Derivation of phenyl-phenyl conjugation energy

We selected the structure of *p,p'*-bitolyl (Casalone, Mariani, Magnoli & Simonetta, 1969) for derivation of the phenyl-phenyl conjugation energy. In this structure there are two molecules in the asymmetric unit, with twist angles of 36 and 40°. Thus, the geometrical structure is specified by 6 rotations, 6 translations, 2 subrotations, and the lattice constants.

In our calculations we held the lattice constants

fixed, because allowing them to vary might lead to poorer values for the conjugation energy. This could happen because of a combination of untreated effects such as those mentioned in the introduction: nonpairwise additivity, anisotropic dispersion forces, higher order terms in  $r^{-n}$ , deviations from the geometric-mean combining law, etc.

The molecular geometry was taken as two regular hexagonal arrays joined together, with attached tetrahedral methyl groups. In the rings, the C-C and C-H distances were set as 0.1397 and 0.1027 nm, with a central bond length of 0.1473 nm. The methyl C-C and C-H distances were set as 0.1520 and 0.1040 nm, and the observed rotational orientation was approximated. The C-H distances were assumed to be foreshortened by 0.0070 nm (Williams, 1965). The nonbonded parameters used were set (*C*) of Williams (1970).

Successive calculations were made, minimizing the lattice energy each time as a function of the 14 variables. As  $E_c^0$  was made larger in magnitude, the molecules became more planar. Table 3 shows the results obtained for the twist angles as a function of  $E_c^0$ . It is seen that the observed conjugation energy is about  $-9.0 \cos^2 \psi$  kcal/mole for each molecule. The calculations confirm that the difference of 4° in the twist angles is indeed an intermolecular packing effect.

Table 3. Conjugation energy of *p,p'*-bitolyl (kcal/mole and °)

$E_c^0$	$\psi_1$ (calc.)	$\psi_2$ (calc.)
-7.0	39.6	44.7
-8.0	37.5	42.6
-9.0	35.7	40.8
-10.0	33.0	38.8

For comparison, Fischer-Hjalmar (1963) calculated  $E_c^0 = -6.2$  kcal/mole for gaseous biphenyl by the Parriser-Parr-Pople method. Dashevsky & Kitaigorodsky (1967) used  $E_c^0 = -9$  kcal/mole to obtain the gas phase twist angle of biphenyl. They used a different set of hydrocarbon nonbonded potential functions, and also set  $E_c = E_c^0 \cos \psi$ . Casalone *et al.* (1968) calculated  $E_c^0 = -7.6$  kcal/mole by the Hückel method. Dewar & Harget (1970) calculated  $E_c^0 = -8.87$  kcal/mole by a semi-empirical self-consistent-field molecular-orbital treatment. While our excellent agreement with Dewar & Harget's value may be fortuitous (the methyl groups, for example, may have some effect on  $E_c^0$ ), the present results indicate some utility for this method of obtaining conjugation energies.

We have also calculated the twist angle of the isolated gaseous *p,p'*-bitolyl molecule, using  $E_c^0 = -9.0$  kcal/mole, and including all nonbonded interactions between the two halves of the molecule. We obtained  $\psi = 33.2^\circ$ , which is less than the twist angle of either molecule in the asymmetric unit of the crystal. This result is in contrast to biphenyl, where the twist angle is less (zero, in fact) in the crystal than in the gas phase.

Thus the intermolecular energy tends to flatten bi-phenyl molecules, but twists *p,p'*-bitolyl molecules in the crystal.

#### Thermal expansion

An approximate method of calculating anisotropic thermal expansion has been detailed elsewhere (Williams, 1972). This method is based on increasing the  $B_{\alpha\beta}$  by an amount sufficient to shift the minimum of the nonbonded potential by  $\Delta r$ , where  $\Delta r$  is obtained from the mean-square thermal amplitude and the nonbonded potential anharmonicity.

#### Convergence to the geometrical structure

The range of convergence as used in this section refers to the maximum range of the trial coordinates which leads to the success of either a steepest descent or Gauss-Newton refinement. This attribute of molecular packing analysis is most important when dealing with unknown geometrical parameters and known potential parameters.

We investigated the range of convergence using the observed crystal structures of benzene (Bacon, Curry & Wilson, 1964), naphthalene (Cruickshank, 1957), and phenanthrene (Trotter, 1963). The first two structures are centric, with no molecular translation allowed, since the molecules have crystallographic  $\bar{1}$  symmetry. The phenanthrene structure is acentric, with no molecular symmetry. Only two molecular translations are allowed, since the space group is polar in one direction.

We were particularly interested in comparing the presently described program, *PCK6*, with our earlier program, *PCK5*. Program *PCK5* may be regarded as a simplified version of *PCK6*, in which the nonbonded repulsion is approximated by a quadratic curve. Since no attractions are considered, there are relatively few terms in the lattice sum, and *PCK5* is quite fast in execution even without convergence acceleration. Further, since the repulsion energy is represented by a sum of squared terms, the very powerful full-matrix least-squares technique may be used in *PCK5*. It is apparent that the lattice constants must be known when using *PCK5*, but not necessarily known when using *PCK6*.

For benzene, we duplicated the convergence test made with *PCK5* (Williams, 1969). The results with *PCK6* were not quite as good, with one starting orientation (out of 12) failing to converge to the correct structure. We tested the false minimum from *PCK6* with *PCK5*. The false minimum persisted, and *PCK5* also failed to converge to the correct structure. Thus *PCK5* had somehow skipped over this false minimum structure in the earlier calculation.

For naphthalene and phenanthrene we made similar convergence tests. Our conclusion from these tests was that *PCK5*, the quadratic-repulsion-only program, converged over a larger range of trial models than *PCK6*, the complete (exp-6) program. A part of the

difference probably lies in the fact that the (exp-6) potentials have a physically unrealistic minimum at  $r=0$  (Kitaigorodsky & Dashevsky, 1967). Even if this feature is removed from the potential, another problem remains. Two molecules can interpenetrate in the trial structure, thus locking together and effectively stopping refinement. A visual examination of the model will quickly reveal such cases; a cathode-ray tube display attached online to the computer would be most helpful. We have attempted to avoid this problem in our computer program by keeping the centers of the molecules always sufficiently far apart. But since the molecules are not spherical in shape, this approach is not always successful. An incorrect mode of molecular interlocking may also lead to a false minimum, *e.g.* in naphthalene (Williams, 1969).

In any case, since *PCK5* runs much faster on the computer, its use seems preferable in the early stages of a packing analysis calculation, if the lattice constants are known. An early example of the use of this type of calculation for an unknown structure with the molecule in a general position is dibenzoylmethane (Williams, 1966a). If greater accuracy is required, the model obtained from *PCK5* can be further refined with *PCK6*.

The degree of convergence to the correct structure, using *PCK5*, has already been discussed (Williams, 1969). The models obtained from *PCK5* are usually good enough to begin a structure factor refinement, based on observed X-ray or neutron diffraction data. The degree of convergence of *PCK6* is illustrated by Williams (1966b) for hydrocarbon structures. Typically, the atomic positions may be calculated to 0.005 nm accuracy and the lattice constants to 1% accuracy. Either or both of the above Fortran computer programs are available from the author.

#### References

- BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. Roy. Soc. A* **279**, 98.  
 CASALONE, G., MARIANI, C., MAGNOLI, A., & SIMONETTA, M. (1968). *Mol. Phys.* **15**, 339.  
 CASALONE, G., MARIANI, C., MAGNOLI, A., SIMONETTA, M. (1969). *Acta Cryst.* **B25**, 1741.  
 CHENG, P. & NYBURG, S. C. (1969). 8th International Congress of Crystallography, Abstract X-12.  
 CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504.  
 DASHEVSKY, V. G., & KITAIGORODSKY, A. I. (1967). *Theor. Exp. Chem.* **3**, 22. [*Teor. Eksp. Khim.* (1967). **3**, 43].  
 DEWAR, M. J. S., & HARGET, A. J. (1970). *Proc. Roy. Soc. A* **315**, 443.  
 FISCHER-HJALMARS, I. (1963). *Tetrahedron*, **19**, 1805.  
 HAUGH, E. F., & HIRSCHFELDER, J. O. (1955). *J. Chem. Phys.* **23**, 1778.  
 HIRSCHFELDER, J. O. (1967). *Intermolecular Forces. Advances in Chemical Physics*, Vol. 12. New York: Wiley-Interscience.  
 HIRSCHFELDER, J. O., CURTISS, C. F., & BIRD, R. B. (1954). *Molecular Theory of Gases and Liquids*, p. 963. New York: Wiley.  
*International Tables for X-ray Crystallography* (1959). Vol. 2, p. 63. Birmingham: Kynoch Press.

- KESTNER, N. R. (1970). *Trans. ACA*, **6**, 1.  
 KITAIGORODSKY, A. I. (1955). *Organic Chemical Crystallography*. New York: Consultants Bureau.  
 KITAIGORODSKY, A. I. (1970). *Advanc. Struc. Res. Diff. Methods*, **3**, 173.  
 KITAIGORODSKY, A. I. & DASHEVSKY, V. G. (1967). *Theor. Exp. Chem.* **3**, 18. [*Teor. Eksp. Khim.* (1967). **3**, 35].  
 KITAIGORODSKY, A. I. & MIRSKAYA, K. V. (1964). *Sov. Phys. Crystallogr.* **9**, 137. [*Kristallografiya*, (1964). **9**, 174].  
 LONDON, F. (1930). *Z. phys. Chem.* **B11**, 222.  
 MARGANAU, H. & KESTNER, N. R., (1969). *Theory of Intermolecular Forces*, London: Pergamon.  
 MARQUARDT, D. W. (1963). *J. Soc. Ind. Appl. Math.* **11**, 431.  
 MASON, R. (1970). *Perspectives in Structural Chemistry*, Vol. III, p. 59 Edited by J. DUNITZ and J. IBERS. New York: Wiley.  
 NEUMAN, M. A. (1970). *Trans. ACA*, **6**, 111.  
 STERNLICHT, H. (1964). *J. Chem. Phys.* **40**, 1175.  
 TROTTER, J. (1963). *Acta Cryst.* **16**, 605.  
 WILLIAMS, D. E. (1965). *J. Chem. Phys.* **43**, 4424.  
 WILLIAMS, D. E. (1966a). *Acta Cryst.* **21**, 340.  
 WILLIAMS, D. E. (1966b). *J. Chem. Phys.* **43**, 4424.  
 WILLIAMS, D. E. (1967). *J. Chem. Phys.* **45**, 3770.  
 WILLIAMS, D. E. (1969). *Acta Cryst.* **A25**, 464.  
 WILLIAMS, D. E. (1970). *Trans. ACA*, **6**, 21.  
 WILLIAMS, D. E. (1971). *Acta Cryst.* **A27**, 452.  
 WILLIAMS, D. E. (1972). *Acta Cryst.* **A28**, 84.

*Acta Cryst.* (1972). **A28**, 635

## Electron Population Analysis of Accurate Diffraction Data. IV. Evaluation of Two-Center Formalisms in Least-Squares Refinement

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Least-squares formalisms which explicitly include scattering by both one and two-center orbital products are applied to a set of theoretical scattering factors for diborane and to the experimental data on cyanuric acid. The diborane calculations confirm the accuracy of the formalisms employed and indicate the importance of selecting an appropriate basis set of atomic orbitals. They further indicate that (1) net electron populations in bonds and on atoms can be determined more precisely than individual population parameters; (2) the set of parameters should be limited by molecular symmetry and assumptions about the symmetry of the bonds; (3) only one of a set of highly correlated parameters on an atom or in a bond should be allowed to vary; (4) the most reasonable basis set is the one giving the best agreement factor. This experience is applied to the refinement of cyanuric acid. It is found that the isolated atom HF functions give the best description of the experimental density. A Mulliken population analysis of the results reproduces the chemical symmetry of the molecule. In general the conclusions reached on diborane are compatible with the analysis of the experimental data. Electron-density maps on cyanuric acid, based on the least-squares population parameters, show that a good description of the density is obtained with a number of parameter sets. These electron-density maps show significant disagreement with thermally-smearred theoretical maps, indicating that the INDO and *ab initio* minimal basis set (STO-3G) calculations do not properly predict the density in the bonding and lone-pair regions of the cyanuric acid molecule. A transformation to uncorrelated combinations of population parameters is proposed to facilitate analysis of the numerical results and comparison with theoretical population parameters.

### Introduction

In the first two articles of this series we have described formalisms and inherent limitations in the charge refinement of accurate diffraction data (Coppens, Willoughby & Csonka, 1971) and the application of a number of *one-center* formalisms to some organic and inorganic molecules (Coppens, Pautler & Griffin, 1971).

The present manuscript describes an evaluation of X-ray scattering formalisms which explicitly include

two-center terms, *i.e.* products between atomic orbitals centered on different atoms. The formalisms are first applied to a theoretical set of structure factors for diborane ( $B_2H_6$ ), obtained through a numerical Fourier transform of the results of a minimal basis set calculation (Jones & Lipscomb, 1970). Experience obtained in this treatment is then applied to the low temperature X-ray diffraction data on cyanuric acid (Verschoor & Keulen, 1971), utilizing positional and thermal parameters from a parallel neutron diffraction study (Coppens & Vos, 1971). In both calculations a variety of different parameter and atomic orbital basis sets are tested. To provide a further evaluation of the formalisms, results are compared in electron-density space

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