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## On the Refinement of Atom–Atom Potential Parameters in Molecular Crystals

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The refinement of atom–atom parameters for molecular crystals has been considered. A simple formalism is developed for reducing the time taken for numerical computations and ensures reliable results. This formalism consists in defining independent potential parameters and deriving physically meaningful relations between the parameters which refer to the 'mixed' atom–atom interactions and other parameters. This procedure was applied to four aromatic hydrocarbon crystals; however it can be generalized to any molecular crystal with any molecule with any number of heteroatoms.

In recent years the atom–atom model was certainly the leading model for the intermolecular interactions in molecular crystals. This model was extensively applied to the calculation of several crystal properties (Schnepp & Jacobi, 1972). Among the atom–atom potentials, the Buckingham functions have been used the most successfully. A typical Buckingham potential function is the following

$$V(r) = A \exp(-Br) - Cr^{-6} \quad (1)$$

where  $A$ ,  $B$  and  $C$  are variable parameters and  $r$  is the distance between two atoms belonging to different molecules ('non-bonded atoms'). Nine different parameters are to be defined for the hydrogen–hydrogen ( $H \cdots H$ ), carbon–hydrogen ( $C \cdots H$ ) and carbon–carbon ( $C \cdots C$ ) interactions of a hydrocarbon crystal. Very reliable sets of these parameters were obtained by Williams (1966) on the basis of a refinement procedure which was performed considering the crystal sublimation energy and the lattice equilibrium conditions with respect to the unit-cell parameters, the molecular orientations

and displacements of the molecule's centre of mass.

Williams (1966) refined independently five out of the nine necessary parameters, *i.e.*  $A_{HH}$ ,  $A_{CH}$ ,  $A_{CC}$ ,  $C_{HH}$  and  $C_{CC}$ , whereas  $B_{HH}$ ,  $C_{CH}$ ,  $B_{CC}$  are fixed *a priori* and  $C_{CH}$  is assumed to equal the geometric mean of  $C_{HH}$  and  $C_{CC}$ . The validity of this procedure is debatable for two reasons: (i)  $A$ ,  $B$  and  $C$  are not actually independent of each other, (ii)  $A$ ,  $B$  and  $C$  of the 'mixed'  $C \cdots H$  interactions can be connected with the parameters of the interactions  $H \cdots H$  and  $C \cdots C$  by more suitable relations.

Point (i) is clarified by writing (1) in the form:

$$V(r) = \frac{\varepsilon}{\mu - 1} \left\{ \exp \left[ -6\mu \left( \frac{r}{\varrho} - 1 \right) \right] - \mu \left( \frac{\varrho}{r} \right)^6 \right\} \quad \text{with } \mu > \frac{7}{6} \quad (2)$$

where  $\varrho$  and  $\varepsilon$  are respectively the equilibrium distance and the equilibrium potential depth of the function and  $\mu$  is its 'steepness' (Hirschfelder, Curtiss & Bird, 1954). The condition  $\mu > \frac{7}{6}$  arises because the function  $V(r)$

admits a minimum.  $\mu$  can be related to the distance,  $\sigma$ , at which the potential function becomes zero, by the logarithmic equation (3) obtained from (2) by straightforward algebra:

$$\frac{\sigma}{\varrho} - \frac{1}{\mu} \ln \left( \frac{\sigma}{\varrho} \right) = 1 - \frac{1}{6\mu} \ln \mu. \quad (3)$$

It is evident from (2) that  $\varrho$ ,  $\varepsilon$ , and  $\mu$  have a physical meaning and are truly independent of each other, so that it is more convenient to refine the potential functions with respect to  $\varrho$ ,  $\varepsilon$ ,  $\mu$  rather than to  $A$ ,  $B$ ,  $C$ .\*

The relations between  $A$ ,  $B$ ,  $C$  and  $\varrho$ ,  $\varepsilon$ ,  $\mu$  were obtained from (1) and (2)

$$A = \frac{\varepsilon}{\mu - 1} \exp(6\mu); \quad B = \frac{6\mu}{\varrho}; \quad C = \frac{\mu\varepsilon\varrho^5}{\mu - 1}. \quad (4)$$

Point (ii) raises the possibility of introducing suitable relations between the parameters of the 'mixed' interactions  $A_{CH}$ ,  $B_{CH}$ ,  $C_{CH}$  and  $A_{HH}$ ,  $B_{HH}$ ,  $C_{HH}$ ,  $A_{CC}$ ,  $B_{CC}$  and  $C_{CC}$ . The possibility is more evident if we consider (2). In this case we look for relations of the type  $\varrho_{CH} = f(\varrho_{HH}, \varrho_{CC})$ ,  $\varepsilon_{CH} = f(\varepsilon_{HH}, \varepsilon_{CC})$  and  $\mu_{CH} = f(\mu_{HH}, \mu_{CC})$ .

We first assume that

$$\varrho_{CH} = \frac{1}{2}(\varrho_{HH} + \varrho_{CC}) \quad (5)$$

which corresponds to considering the atoms as spheres of diameter  $\varrho$ . This assumption is consistent with the atom-atom model.

The required relation for the energy depth  $\varepsilon_{CH}$  is more questionable. We assume that for two spheres of diameter  $\varrho_{HH}$  and  $\varrho_{CC}$  attracted to each other by London dispersion forces (Sutherland model), the relation is given by

$$\varepsilon_{CH} = \frac{128E_{CH}\alpha_H\alpha_C\varepsilon_{HH}\varepsilon_{CC}}{[(E_H\alpha_H^2\varepsilon_{CC})^{1/6} + (E_C\alpha_C^2\varepsilon_{HH})^{1/6}]^6} \quad (6)$$

where  $\alpha_H, \alpha_C$  are the atomic polarizabilities,  $E_H, E_C$  the ionization potentials and  $E_{CH} = E_H E_C / (E_H + E_C)$ . (6) was easily obtained from the London equation assuming the additivity law (5).

Alternatives to (6) will be discussed later. For the second 'radial' parameter,  $\sigma_{CH}$ , which determines  $\mu_{CH}$  via (3), we propose an additivity law equivalent to (5). In short we are able to evaluate  $\varrho_{CH}$ ,  $\varepsilon_{CH}$ ,  $\mu_{CH}$  from  $\varrho_{HH}$ ,  $\varepsilon_{HH}$ ,  $\mu_{HH}$ ,  $\varrho_{CC}$ ,  $\varepsilon_{CC}$ ,  $\mu_{CC}$  by (5), (6) and (3). This fact allows us to reduce the independent parameters to be refined from nine to six. This advantage becomes more evident when the number  $N$  of different atomic species is greater than two, as in molecular crystals containing heteroatoms. In fact, the total number of parameters

including the 'mixed' ones is  $3N(N+1)/2$ , whereas the number of parameters to be refined is  $3N$  only.

For the refinement of  $\varrho$ ,  $\varepsilon$ , and  $\mu$  of  $H \cdots H$  and  $C \cdots C$  interactions we considered four molecular crystals of the aromatic series, *i.e.* benzene, naphthalene, anthracene and phenanthrene, in particular crystals containing molecules with one, two and three condensed benzene rings of which the necessary structural and thermodynamic data are well known (Williams, 1966).

The refinement procedure considers the same conditions introduced by Williams (1966) and discussed before. In particular cases some of these conditions are dropped because of the symmetry of the crystal. The lattice sublimation energy (at absolute zero and for rigid molecules) is assumed to be  $E = \frac{1}{2} \sum_{ij} V(r_{ij})$  where

$V(r_{ij})$  is the contribution of one pair of non-bonded atoms and the sum is extended over the whole crystal. We have actually considered in the sum only the atom-atom interactions within a radius of 6 Å, since we have ascertained that the contributions to  $E$  of further interactions is less than 20%, as found by Williams (1966).

We have adopted the well-known least-squares method in the refinement procedure. The parameters to be refined for  $H \cdots H$  and  $C \cdots C$  interactions belong to set IV of Williams's (1966) paper. This set gives very reliable results for many hydrocarbon aromatic crystals and was applied successfully in calculations of several crystal properties (Schnepf & Jacobi, 1972). We have obtained the final parameters [set (a)] in only five refinement cycles. The fast convergence is assured because  $\varrho$ ,  $\varepsilon$ ,  $\mu$  are independent of each other. On the other hand, the refinement calculations performed on the parameters  $A$ ,  $B$ ,  $C$  are very difficult and time consuming since in this case the Jacobian matrix of the least-squares method has a vanishing determinant. We have also obtained a second set [set (b)] starting from a different initial set of parameters (see later).

The refined parameters are tested with the crystal structures of minimum energy of benzene, naphthalene, anthracene and phenanthrene by using the Williams *PXCK3* program which utilizes a steepest-descent method starting from the observed structures.† Table 1 reports the results of this test for sets (a) and (b) in terms of the deviations of the calculated lattice constants and molecular positions with respect to the observed values. These deviations are satisfactory results since they are not much larger than the corresponding experimental errors. The last column of Table 1 collects the differences between the calculated and the observed lattice energies.

The refined  $\varrho$ ,  $\varepsilon$ ,  $\mu$  [set (a)] for the interactions  $H \cdots H$ ,  $C \cdots H$  and  $C \cdots C$  are listed in Table 2. Direct comparison (see Table 2) between set (a) and the corresponding Williams (1966) set IV shows that the largest difference occurs where the 'mixed' interactions

\* An additional advantage in using  $\varrho$ ,  $\varepsilon$ ,  $\mu$ , rather than  $A$ ,  $B$ ,  $C$  follows from the well-known peculiarity of the Buckingham functions that when  $r \rightarrow 0$ ,  $V(r) \rightarrow -\infty$ . This fact introduces some difficulties in the refinement procedure with respect to  $A$ ,  $B$ ,  $C$ . During these computations, the exponential term of a Buckingham function may become so small that the function comes out negative for every value of  $r$ . Obviously such a function is meaningless. The use of (1) and (3), where  $\sigma$  is defined, guarantees instead that this singularity never occurs in refining  $\varrho$ ,  $\varepsilon$ , and  $\mu$ .

† We are indebted to Professor D. E. Williams for *PXCK3* and other programs which he kindly sent us.

Table 1. Deviations of the calculated lattice constants and molecular positions of carbon atoms with respect to the observed values by using sets (a) and (b)

In the last column are listed the differences between the calculated and observed lattice energies. Energy in kcal mol<sup>-1</sup>, lengths in Å, angles in degrees.

Crystal	Set	$\Delta a$	$\Delta b$	$\Delta c$	$\Delta\beta$	Mean deviation	$\Delta E$
Benzene	(a)	0.02	-0.01	0.02	—	0.047	-0.85
	(b)	-0.05	-0.08	0.00	—	0.072	-0.33
Naphthalene	(a)	-0.04	-0.04	-0.02	0.1	0.034	-0.40
	(b)	-0.03	-0.02	-0.02	1.4	0.044	0.14
Anthracene	(a)	0.00	0.01	0.00	-1.8	0.049	1.23
	(b)	0.00	0.01	0.00	-1.2	0.038	1.30
Phenanthrene	(a)	-0.05	-0.05	-0.03	-2.2	0.034	-1.51
	(b)	0.08	0.08	0.06	-1.1	0.032	-1.00

C...H are involved. Williams found that  $q_{CH}$  is not intermediate between  $q_{HH}$  and  $q_{CC}$ , and it seems very difficult to justify this result. In addition we observe that our  $q_{HH}$  is smaller than the corresponding value of Williams. This difference can be attributed in part to the fact that Williams displaced the centre of the H atom 0.07 Å toward the C atom. To preserve the simplicity of our model we have not introduced this shift in the calculations.

As to the combination law for  $\epsilon_{CH}$ , we observe that in the literature various different equations have been proposed (Hirschfelder, Curtiss & Bird, 1954; Stwalley, 1971 and references quoted therein). Essentially, the more frequently used relations are the following

$$\epsilon_{CH} = (\epsilon_{HH}\epsilon_{CC})^{1/2} \quad (7a); \quad \epsilon_{CH} = \frac{2\epsilon_{HH}\epsilon_{CC}}{\epsilon_{HH} + \epsilon_{CC}} \quad (7b)$$

Table 2. Potential parameters of set (a) and Williams's (1966) set IV for H...H, C...H and C...C non-bonded interactions

Energy in kcal mol <sup>-1</sup> , lengths in Å.						
	Williams set IV			Set (a)		
	H...H	C...H	C...C	H...H	C...H	C...C
$q$	3.452	3.281	3.851	2.842	3.347	3.851
$\epsilon \times 10^2$	1.139	5.594	9.306	3.496	5.484	9.183
$\mu$	2.151 <sub>8</sub>	2.006 <sub>6</sub>	2.310 <sub>5</sub>	2.239 <sub>6</sub>	2.278 <sub>7</sub>	2.308 <sub>6</sub>

Table 3. Potential parameters of set (b) and Williams's (1966) set I for H...H, C...H and C...C non-bonded interactions

Energy in kcal mol <sup>-1</sup> , lengths in Å.						
	Williams set I			Set (b)		
	H...H	C...H	C...C	H...H	C...H	C...C
$q$	3.020	3.376	3.886	2.774	3.332	3.890
$\epsilon \times 10^2$	4.384	2.994	9.979	2.029	4.397	9.739
$\mu$	1.882 <sub>8</sub>	2.065 <sub>2</sub>	2.331 <sub>8</sub>	2.160 <sub>1</sub>	2.254 <sub>4</sub>	2.327 <sub>5</sub>

These relations appear to be simpler than (6), however, they are not properly related either to the London forces, as (6) is, or to the repulsive exponential forces. In fact, (7a) is obtained from the assumption  $\epsilon \propto \exp(-q)$  and from (5); in a similar manner (7b) is obtained from the assumption  $\epsilon \propto 1/q$  and from (5). However in both cases the assumed dependence  $\epsilon = f(q)$  does not contain any constant 'weighting' the strength of the repulsive or Coulombic forces acting between the atoms. On the other hand, (6) properly contains constants weighting the London forces. We have performed calculations considering (7a) and (7b) in place of (6). The differences in the calculated lattice energies for the two cases are negligible (~2% for crystalline benzene).

Finally, we have tried to reproduce set (a) starting from a different initial set. We started from Williams's (1966) set I (for H...H and C...C interactions) which is rather different from set IV. Unfortunately we were unable to reproduce set (a), although several refinement cycles were run. We obtained instead set (b) listed in Table 3. It is interesting to note that the differences between sets (a) and (b) are lower than the differences between Williams's sets IV and I, the larger deviations occurring for H...H and C...C interactions. It may be possible that the refinement procedure performed on a larger number of molecular crystals gives a unique set of potential parameters.

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