# COMBINING RULES FOR INTERATOMIC POTENTIAL FUNCTIONS OF BUCKINGHAM FORM

K. V. MIRSKAYA

Institute of Elemento-Organic Compounds, Academy of Sciences of the USSR, Vavilova St. 28, Moscow, USSR

**Abstract**—The geometric mean combining rule for the total interaction energy of two non-bonded atoms, the energy being described by the Buckingham type potential, is suggested. Some numerical examples are given to compare this rule with the combining rules for the exp-six potentials proposed by Mason and Rice.

The atom–atom approximation for the energy of interaction of neutral molecules, as has been shown in a number of recent papers,[1-11] is a convenient and efficient model to study intermolecular forces. A sufficiently good representation of the interaction energy of two non-bonded atoms is a central potential (the energy depends only on the interatomic distance), with numerical parameters being determined on the basis of experimental data.[12,13] The most frequently used interatomic potentials are generally written either in the Lennard–Jones

$$\varphi = -Ar^{-6} + Br^{-12} = \epsilon[-2(r_0/r)^6 + (r_0/r)^{12}] \quad (1)$$

or modified Buckingham form

$$\varphi = -Ar^{-6} + B \exp(-\alpha r) = \frac{\epsilon\lambda}{\lambda - 6}[-(r_0/r)^6 + (6/\lambda)\exp\lambda(1 - r/r_0)], \quad (2)$$

where $r$, $\epsilon$, $r_0$, $\lambda$ are the interatomic distance, the depth of the potential well, the value of $r$ for the energy minimum and the steepness of exponential repulsion respectively[14] (Fig 1).

As a rule, a molecule consists of more than one type of atoms. Therefore, to evaluate the inter-
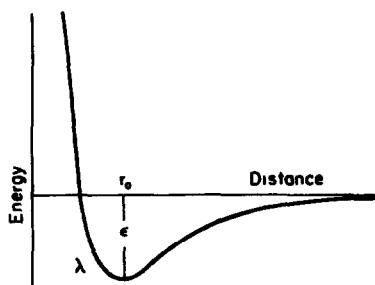
molecular interaction in the atom–atom approximation we must know the potential parameters $A$, $B$, $\alpha$ (or, alternatively, $\epsilon$, $r_0$, $\lambda$) both for the interaction of pairs of like atoms of types XX, YY, ZZ and for mixed interactions of types XY, XZ, YZ. The problem of empirical fitting of the $A$, $B$, $\alpha$ constants usually involves considerable difficulties owing to a limited number of suitable experimental data. In order to decrease the number of constants to be fitted and, consequently, the number of independent theoretical parameters, one tries when possible, to use as standards the compounds consisting of only one type of atoms and to determine the constants for mixed interactions in more complicated molecules by means of the so-called combining rules which connect the parameters for pairs of unlike atoms with those for like atoms.

The combining rules so far used by various authors[2,14-18] are "empirical" and have no rigorous theoretical foundation. The combining rule most often used for an equilibrium interatomic distance is the arithmetic mean

$$(r_0)_{12} = [(r_0)_{11} + (r_0)_{22}]/2 \quad (3)$$

which is rigorously valid for "hard-sphere" particles (recently Good and Hope[19] suggested, for the sake of convenience, to use the geometric mean for $r_0$).

For the two-parameter Lennard–Jones potential function, Eq. (3) is usually supplemented by $\epsilon_{12}$, the geometric mean for the interaction energy of two atoms at a distance of $r = r_0$ apart,

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}. \quad (4)$$

This relation approximately follows from Eq. (1) and the London expression for dispersion energy through the polarizabilities ($\alpha$) and ionization potentials ($I$) of interacting particles provided $I_1$ and $I_2$ and the diameters of the particles do not differ greatly.[16]



Fig 1. Parameters of an interatomic potential function of the Buckingham form.

For the 3-parameter potential of form (2) a combining rule is to be used which would take into account not only the coordinates of the minimum point of the potential well but also the shape of the $\varphi(r)$ potential curve, that is the third numerical parameter $\lambda$ (or $\alpha$). Among several others, the following combining rules for the exp-six potential, Eq. (2), between two unlike molecules that have been suggested by Mason and Rice,[15] are often used:

$$A_{12} = (A_{11}A_{22})^{1/2}, \quad B_{12} = (B_{11}B_{22})^{1/2},$$
$$\alpha_{12} = (\alpha_{11} + \alpha_{22})/2. \tag{5}$$

These expressions can be obtained by separately employing the geometric mean rule for the attractive and repulsive terms in Eq. (2). In this case rules (3) and (4) do not hold.

However, a number of experimental data and theoretical results imply that the geometric mean rule is valid for the total interaction energy of atoms and not for its separate terms. Amdur et al.[20] in their study of scattering of high velocity neutral particles showed that the potential energy between the helium atom and the argon atom at small distances derived from the measured cross sections may be represented by a function of the form $\varphi = Kr^s$, which is the geometric mean of the potentials between two helium and two argon atoms. The range of distances for the He-A system is described by the arithmetic mean of the individual interaction distances.

In the detailed numerical study by Abrahamson[21] it was found that the rule $\varphi_{12} = (\varphi_{11}\varphi_{22})^{1/2}$ is accurate to within 0·01–1 per cent (rising but rarely to a few per cent) for the energy of interaction of atoms with $Z = 2$ to $Z = 105$, which is derived quantum mechanically in the small distances approximation. From theoretical papers by Tang[22] and Weinhold[23] it follows that the upper bound for interaction energy of unlike particles, derived from quantum mechanics in the large distances approximation, is also determined by this rule.

Taking into consideration the results of these papers we shall try to apply the geometric mean rule for the total interaction energy of atoms within the framework of a semi-empirical approach, when the energy is described by Eq. (2) assumed valid in the whole possible range of interatomic distances (large, small and intermediate).

Let $z$ be the reduced distance $(r/r_0)$. Assume that for every value of $z$ the interaction energy of two unlike atoms is the geometric mean of the interaction energies of two like atoms

$$\varphi_{12}(z) = [\varphi_{11}(z)\varphi_{22}(z)]^{1/2}. \tag{6}$$

If $z = 1$, that is if $r = r_0$, we have relation (4) as a particular case of (6). By calculating $\epsilon_{12}$, and $\varphi_{12}$

from (6) for some value of $z \neq 1$ ($z = z_k$), the value of $\lambda_{12}$ may be found from the equation

$$\varphi'_{12}(\lambda) = (\varphi_{12}/\epsilon_{12})$$
$$= [\lambda/(\lambda - 6)][z_k^{-6} - (6/\lambda) \exp \lambda (1 - z_k)].$$

The $\varphi'(\lambda)$ function at a fixed $z$ can be tabulated or represented by a curve. Fig 2 shows the $\varphi'(\lambda)$ curve corresponding to $z_k = 2/3$. The calculations show that for $\lambda_{12}$ the relation $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$ is approximately valid.

In order to obtain the third constant of potential (2) we have to supplement combining rule (6) by some rule for the equilibrium distance $r_0$. In our calculations of structure and properties of molecular crystals we take arithmetic mean rule (3). Using $(r_0)_{12}$, $\epsilon_{12}$ and $\lambda_{12}$, we find the constants $A$, $B$ and $\alpha$ of the Buckingham potential for mixed interactions from the formulas $A = -\epsilon r_0^6 \lambda/(\lambda - 6)$, $B = -6e^\lambda/(\lambda - 6), \alpha = \lambda/r_0$.

Below we give some numerical examples to compare rules (5) and (6). In these examples the $C-C$ and $H-H$ potential curves that have been employed in[11] for calculating the elastic constants of the naphthalene crystal are used (Table 1). In Table 2 the parameters of the two $C-H$ curves calculated by means of rules (5) and (6) are given. Fig 3 represents the difference between the two curves.

Using the potentials from Tables 1 and 2 we have calculated some characteristic features of the naphthalene crystal potential energy surface $U$ as a function of the geometrical lattice parameters. The method of atom–atom potentials, in the form described in our previous papers,[12,24] has been used for these calculations. The dependence of the results on the combining rules is illustrated by Table 3.
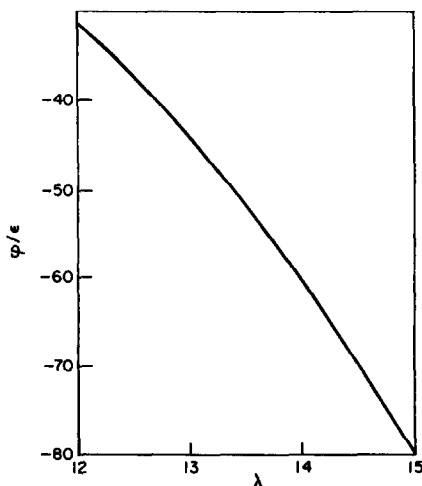


Fig 2. Reduced interatomic potential energy $\varphi' = \varphi/\epsilon$ as a function of $\lambda$ for $z_k = 2/3$.

Table 1. C−C and H−H pair potentials parameters

| | $A, \frac{kcal}{mole} Å^6$ | $B, \frac{kcal}{mole}$ | $\alpha, Å^{-1}$ | $\epsilon, \frac{kcal}{mole}$ | $r_0, Å$ | $\lambda$ |
|---|---|---|---|---|---|---|
| C−C | 353 | $6\cdot0 . 10^4$ | 3·68 | −0·067 | 3·8 | 14 |
| H−H | 46·6 | $7\cdot8 . 10^3$ | 4·29 | −0·048 | 2·8 | 12 |

Table 2. C−H pair potential parameters

| Combining rules | $A, \frac{kcal}{mole} Å^6$ | $B, \frac{kcal}{mole}$ | $\alpha, Å^{-1}$ | $\epsilon, \frac{kcal}{mole}$ | $r_0, Å$ | $\lambda$ |
|---|---|---|---|---|---|---|
| (5) | 128 | $2\cdot16 . 10^4$ | 3·98 | −0·0575 | 3·26 | 12·99 |
| (6) | 137 | $2\cdot07 . 10^4$ | 3·93 | −0·0578 | 3·30 | 12·98 |

Table 3. Some characteristic features of the potential energy surface of the naphthalene crystal calculated on the basis of the two combining rules

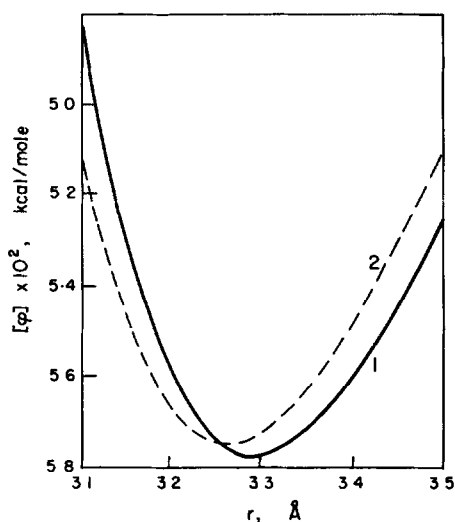| Combining rule | $\theta$ | $\varphi$ | $\psi$ | $U_{min}$ $(\theta, \varphi, \psi)$ | $\frac{\partial^2 U}{\partial a^2}$ | $\frac{\partial^2 U}{\partial b^2}$ | $\frac{\partial^2 U}{\partial (c \sin \beta)^2}$ | $a$ | $U_{min}(a)$ |
|---|---|---|---|---|---|---|---|---|---|
| (5) | 30°19′ | 47°17′ | 292°18′ | −16·42 | 2·29 | 5·47 | 5·23 | 7·71 | −16·73 |
| (6) | 30°17′ | 47°19′ | 292°20′ | −16·56 | 2·55 | 6·22 | 5·70 | 7·75 | −16·80 |
| $\frac{(6)}{(5)}$ % | 0 | 0 | 0 | 0·8 | 11·2 | 13·7 | 9·0 | 0·5 | 0·4 |



Fig 3. Comparison of the two C−H potential functions obtained by means of combining rules (6)−curve 1, and (5)−curve 2.

In the first three columns of Table 3 the equilibrium values of the Eulerian angles $\theta$, $\varphi$, $\psi$ are given, that correspond to the minimum of the $U(\theta, \varphi, \psi)$ energy surface when the unit cell parameters $a$, $b$, $c$, $\beta$ are fixed (the Eulerian angles describe the orientation of a molecule in the unit cell). The fourth column contains lattice energy calculated at the minimum point of the $U(\theta, \varphi, \psi)$ surface. In the three following columns we give the values of the second derivatives of the energy with respect to lattice parameters. Finally, the two last columns contain the position and the depth of the minimum of the $U(a)$ curve when the Eulerian angles are fixed.

Comparison of the results obtained with the two C−H curves is given in the last row of Table 3. It may be noticed that for the equilibrium orientation of molecules in a crystal the two combining rules lead to the same results. There is but a slight difference in the lattice energy values. It can be seen also that utilization of Eqs. (5) results in a decrease of the equilibrium unit cell parameters. However, there is a rather significant difference (10–15%) between the values of the second derivatives of the energy with respect to lattice parameters and, consequently, the elastic moduli.[11] It is to be noted that the results obtained by means of Eq. (6) are in better agreement with experiment than those obtained with Eqs. (5).

The above examples and Fig 3 show that, in principle, the shape of the curve for mixed interactions and the values obtained by calculation depend on the choice of the combining rules though for some problems the effect may not be significant. However, even in this case Eq. (6), introduced here as a combining rule, seems to be preferable, since it relates to the total interaction energy and, besides, since it makes it possible to preserve the validity of Eqs. (3) and (4), which has been confirmed by many authors.[14, 16−18]

## REFERENCES

[1] A. I. Kitaigorodsky, *Tetrahedron* **14**, 230 (1961).

[2] A. I. Kitaigorodsky, *Advances in Structure Research by Diffraction Methods* **3**, 173 (1970).

[3] D. E. Williams, *J. Chem. Phys.* **45**, 3770 (1966); **47**, 4680 (1967).

[4] G. S. Pawley, *Phys. Stat. Sol.* **20**, 347 (1967).

[5] E. Giglio and A. M. Liquori, *Nuovo Cimento* **56B**, 57 (1968).

[6] R. F. McGuire, G. Vanderkooi, F. A. Momany, R. T. Ingwall, G. M. Crippen, N. Lotan, R. W. Tuttle, K. L. Kashuba and H. A. Scheraga, *Macromolecules* **4**, 112 (1971).

[7] A. Warshel and S. Lifson, *J. Chem Phys.* **53**, 582 (1970).

[8] D. P. Poshkus and A. Ya. Afreimovich, *Zh. Fiz. Chim.* **42**, 1201 (1968).

[9] A. I. Kitaigorodsky and N. A. Ahmed, *Acta Cryst.* **A28**, 207 (1972).

[10] A. I. Kitaigorodsky and K. V. Mirskaya, *Molec. Cryst. and Liquid Crystals* **6**, 339 (1970).

[11] K. V. Mirskaya, *Kristallografia* **17**, 67 (1972).

[12] A. I. Kitaigorodsky and K. V. Mirskaya, *Ibid.* **9**, 174 (1964).

[13] K. V. Mirskaya and V. V. Nauchitel, *Ibid.* **17**, 73 (1972).

[14] J. O. Hirschfelder, Ch. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, N.Y.; Chapman and Hall., Lim., London (1954).

[15] E. A. Mason and W. E. Rice, *J Chem. Phys.* **22**, 522 (1954).

[16] G. H. Hudson and J. C. McCoubrey, *Trans. Far. Soc.* **56**, 761 (1960).

[17] J. R. Sams, *Ibid.* **60**, 149 (1964).

[18] E. A. Mason, R. J. Munn and F. J. Smith, *Disc. Far. Soc.* **40**, 27 (1965).

[19] R. J. Good and C. J. Hope, *J. Chem. Phys.* **53**, 540 (1970).

[20] I. Amdur, E. A. Mason and A. L. Harkness, *Ibid.* **22**, 1071 (1954).

[21] A. A. Abrahamson, *Phys. Rev.* **133**, A990 (1964); **178**, 76 (1969).

[22] K. T. Tang, *J. Chem. Phys.* **49**, 4727 (1968).

[23] F. Weinhold, *J. Phys. (Proc. Phys. Soc.)* **B2**, 517 (1969).

[24] A. I. Kitaigorodsky, K. V. Mirskaya and A. B. Tovbis, *Kristallografia* **13**, 225 (1968).