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## A note on mathematical relationships among bond-torsion force fields

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A set of mathematical relationship between torsion potential functions such as trigonometric and Fourier series is presented herein. A harmonic approximation form is also introduced, and its stiffness constant is related to the parameters of trigonometric and Fourier series. Mathematical relationships between various force field parameters are presented in the form of conversion matrices.

**KEY WORDS:** bond torsion, conversion matrices, force field

**AMS subject classification:** 70C20, 74B15, 74E40

### 1. Introduction

Molecular modeling can be broadly categorized into two major groups: quantum mechanics approach and molecular mechanics approach. Quantum mechanics explicitly represents the electrons in a calculation, thereby enabling it to derive behaviors that depend upon the electronic distribution and, in particular, in studying chemical reactions in which bonds are broken and formed. Molecular mechanics (also known as the force field method) neglect electronic motions and calculates the energy of a system as a function of nuclear positions only. Some problems that are considered too large for quantum mechanics can be dealt with by force field approach. Though unable to provide properties that depend upon the electronic distribution in a molecule (such as bond breaking and formation in chemical reaction), the force field method can provide solutions (such as material modulus) that are reasonably good and in a fraction of computation time in comparison to the quantum mechanical method. Force fields include bonded interactions (such as bond stretching, bending and torsion) as well as non-bonded interaction (such as van der Waals and Coulombic forces). As the name suggests, bond stretching force field refers to the potential energy stored when two covalently bonded atoms are stretched further from or compressed nearer to one another such that  $r - r_0 \neq 0$  (see figure 1). Similarly, bond bending corresponds to the stored potential when three atoms linked by two covalent bonds are relatively displaced such that the bond angle changes, i.e.,  $\theta - \theta_0 \neq 0$ . Likewise, torsion force field is associated to the stored potential when

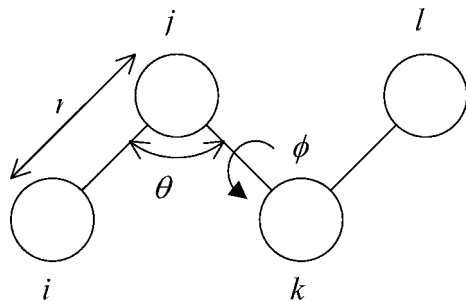


Figure 1. Schematic for bonded interactions.

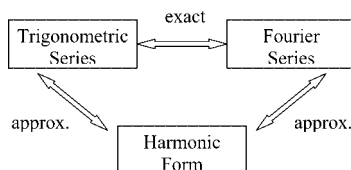


Figure 2. Inter-relationships between molecular mechanics torsional parameters developed herein.

a bond is twisted by an angle  $\phi$ , as determined by four atoms linked in series by covalent bonds. With reference to figure 1, torsion of the bond linking atoms  $j$  and  $k$  is said to have taken place when the plane formed by atoms  $ijk$  bends with respect to the plane formed by atoms  $jkl$ , about the axis  $jk$ .

Two of the most highly utilized molecular mechanics models for torsional potential energy of a covalent bond are the trigonometric series [1–16]

$$U_{\phi} = \frac{1}{2} \sum_{n=1}^m k_{\phi n} (1 - \cos n\phi) \quad (1)$$

and the Fourier series [17–26]

$$U_T = \sum_{n=0}^m k_{Tn} \cos^n \phi. \quad (2)$$

To a much lesser extent, a harmonic approximation of the form

$$U_H = \frac{1}{2} k_H \phi^2 \quad (3)$$

is valid only when the amount of dihedral twisting is infinitesimal. Relationships between the three types of molecular mechanics models for torsion of single covalent bonds are developed herein using trigonometry and Maclaurin's series for cosine. In the foregoing analysis, both trigonometric and Fourier series are expanded up to  $m = 5$ , which is the maximum value considered in the literature. A summary of relationships made herein amongst the trigonometric series function, Fourier series function and harmonic approximation form is shown in figure 2.

## 2. Analysis

Substituting

$$\cos 2\phi = 2 \cos^2 \phi - 1, \quad (4a)$$

$$\cos 3\phi = 4 \cos^3 \phi - 3 \cos \phi, \quad (4b)$$

$$\cos 4\phi = 8 \cos^4 \phi - 8 \cos^2 \phi + 1, \quad (4c)$$

$$\cos 5\phi = 16 \cos^5 \phi - 20 \cos^3 \phi + 5 \quad (4d)$$

into equation (1), we have

$$U_\phi = \frac{1}{2}(k_{\phi 1} + 2k_{\phi 2} + k_{\phi 3} + k_{\phi 5}) - \frac{1}{2}(k_{\phi 1} - 3k_{\phi 3} + 5k_{\phi 5}) \cos \phi - (k_{\phi 2} - k_{\phi 4}) \cos^2 \phi - 2(k_{\phi 3} - 5k_{\phi 5}) \cos^3 \phi - 4k_{\phi 4} \cos^4 \phi - 8k_{\phi 5} \cos^5 \phi. \quad (5)$$

Comparing equation (5) with equation (2), the stiffness parameters associated with the Fourier series can be obtained from those in trigonometric series:

$$k_{T0} = \frac{1}{2}(k_{\phi 1} + 2k_{\phi 2} + k_{\phi 3} + k_{\phi 5}), \quad (6a)$$

$$k_{T1} = -\frac{1}{2}(k_{\phi 1} - 3k_{\phi 3} + 5k_{\phi 5}), \quad (6b)$$

$$k_{T2} = -(k_{\phi 2} - k_{\phi 4}), \quad (6c)$$

$$k_{T3} = -2(k_{\phi 3} - 5k_{\phi 5}), \quad (6d)$$

$$k_{T4} = -4k_{\phi 4}, \quad (6e)$$

$$k_{T5} = -8k_{\phi 5}. \quad (6f)$$

Solving equations (6a)–(6f) simultaneously gives the stiffness parameters of trigonometric series in terms of those from Fourier series:

$$k_{\phi 1} = -\frac{1}{8}(16k_{T1} + 12k_{T3} + 10k_{T5}), \quad (7a)$$

$$k_{\phi 2} = -(k_{T2} + k_{T4}), \quad (7b)$$

$$k_{\phi 3} = -\frac{1}{8}(4k_{T3} + 5k_{T5}), \quad (7c)$$

$$k_{\phi 4} = -\frac{1}{4}k_{T4}, \quad (7d)$$

$$k_{\phi 5} = -\frac{1}{8}k_{T5}. \quad (7e)$$

Both trigonometric and Fourier series can be approximated into the harmonic form using the Maclaurin series expansion for the cosine function,

$$\cos x = \sum_{n=0}^{+\infty} \frac{(-1)^n x^{2n}}{(2n)!} \approx 1 - \frac{x^2}{2}, \quad (8)$$

which is convergent when  $|x| < 1$ . Neglecting orders higher than  $x^2$  is thus valid when  $x \rightarrow 0$ . Hence for infinitesimal torsion,

$$\cos(n\phi) = 1 - \frac{n^2\phi^2}{2} \quad (9)$$

and

$$\cos^n \phi = 1 - \binom{n}{2} \phi^2. \quad (10)$$

Substituting equations (9) and (10) into equations (1) and (2), respectively, leads to

$$U_\phi = \frac{1}{2} \left( \sum_{n=1}^5 \frac{k_{\phi n} n^2}{2} \right) \phi^2 \quad (11)$$

and

$$U_T = \sum_{n=0}^5 k_{Tn} - \frac{1}{2} \left( \sum_{n=1}^5 k_{Tn} n \right) \phi^2. \quad (12)$$

Comparing equations (11) and (12) with equation (3) gives

$$k_H = \frac{1}{2} \sum_{n=1}^5 k_{\phi n} n^2, \quad (13)$$

$$k_H = - \sum_{n=1}^5 k_{Tn} n \quad (14)$$

and

$$\sum_{n=0}^5 k_{Tn} = 0. \quad (15)$$

From equations (6) and (7), relationship between trigonometric series and Fourier series form of chemical bond torsion can be summarized as

$$\{k_{Ti}\} = -\frac{1}{2} [\phi^T \mathbf{C}_{ij}] \{k_{\phi j}\}; \quad i = 0, 1, \dots, 5, \quad j = 1, 2, \dots, 5 \quad (16)$$

and

$$\{k_{\phi i}\} = -\frac{1}{8} [T^\phi \mathbf{C}_{ij}] \{k_{Tj}\}; \quad i, j = 1, 2, \dots, 5, \quad (17)$$

where the trigonometric-to-Fourier conversion matrix,  ${}^{\phi T}\mathbf{C}$ , and the Fourier-to-trigonometric conversion matrix,  ${}^{T\phi}\mathbf{C}$ , are

$$[{}^{\phi T}\mathbf{C}] = \begin{bmatrix} -1 & -2 & -1 & 0 & -1 \\ \mathbf{1} & 0 & -3 & 0 & 5 \\ 0 & \mathbf{2} & 0 & -8 & 0 \\ 0 & 0 & \mathbf{4} & 0 & -20 \\ 0 & 0 & 0 & \mathbf{8} & 0 \\ 0 & 0 & 0 & 0 & \mathbf{16} \end{bmatrix} \quad (18)$$

and

$$[{}^{T\phi}\mathbf{C}] = \begin{bmatrix} \mathbf{16} & 0 & 12 & 0 & 10 \\ 0 & \mathbf{8} & 0 & 8 & 0 \\ 0 & 0 & \mathbf{4} & 0 & 5 \\ 0 & 0 & 0 & \mathbf{2} & 0 \\ 0 & 0 & 0 & 0 & \mathbf{1} \end{bmatrix}, \quad (19)$$

respectively. From equations (13) and (14), relationship between the harmonic form and trigonometric and Fourier forms can be summarized as

$$k_H = \frac{1}{2}[{}^H\mathbf{C}_{ij}]^2\{k_{\phi_j}\} = -[{}^H\mathbf{C}_{ij}]\{k_{T_j}\}, \quad (20)$$

where the conversion matrix into harmonic form,  ${}^H\mathbf{C}$ , is

$$[{}^H\mathbf{C}] = \begin{bmatrix} \mathbf{1} & 0 & 0 & 0 & 0 \\ 0 & \mathbf{2} & 0 & 0 & 0 \\ 0 & 0 & \mathbf{3} & 0 & 0 \\ 0 & 0 & 0 & \mathbf{4} & 0 \\ 0 & 0 & 0 & 0 & \mathbf{5} \end{bmatrix}. \quad (21)$$

In all three conversion matrices, there exists some form of integer pattern which gives interesting insight into the mathematical relationship among the bond-torsion force field equations.

### 3. Results and discussion

To verify the validity of these inter-relationships, “barrier” heights ( $k_{T_n}$ ) from Boyd et al. [6,15] are substituted into equation (6), and compared with the coefficients of Fourier series from Sumpter et al. [21,22,24,26]. As shown in table 1, good agreement between the two sets of parameters ascertains the validity of the exact connection between  $k_{\phi_n}$  and  $k_{T_n}$ . The good agreement between both sets of coefficients may well be attributed to the exact relationships up to  $m = 5$  as described in equations (6) and (7). Verification on the limited validity of the harmonic form is shown in figure 3 based on data from Boyd et al. [6,15] whereby  $k_{\phi_1} = 3.35$  kJ/mol and  $k_{\phi_3} = 13.4$  kJ/mol. It can be seen that the harmonic approximation is valid within  $\pm 20$  radians of twisted angle  $\phi$ .

Table 1  
Validation of relationship between trigonometric and Fourier series parameters.

Coefficients of Fourier series	Data from Sumpter et al. [21,22,24,26]	Calculated from Boyd et al. [6,15] where $k_{\phi 1} = 3.35$ kJ/mol and $k_{\phi 3} = 13.4$ kJ/mol
$k_{T0}$	8.37 kJ/mol	8.375 kJ/mol
$k_{T1}$	18.4 kJ/mol	18.425 kJ/mol
$k_{T2}$	0	0
$k_{T3}$	-26.78 kJ/mol	-26.8 kJ/mol
$k_{T4}$	0	0
$k_{T5}$	0	0

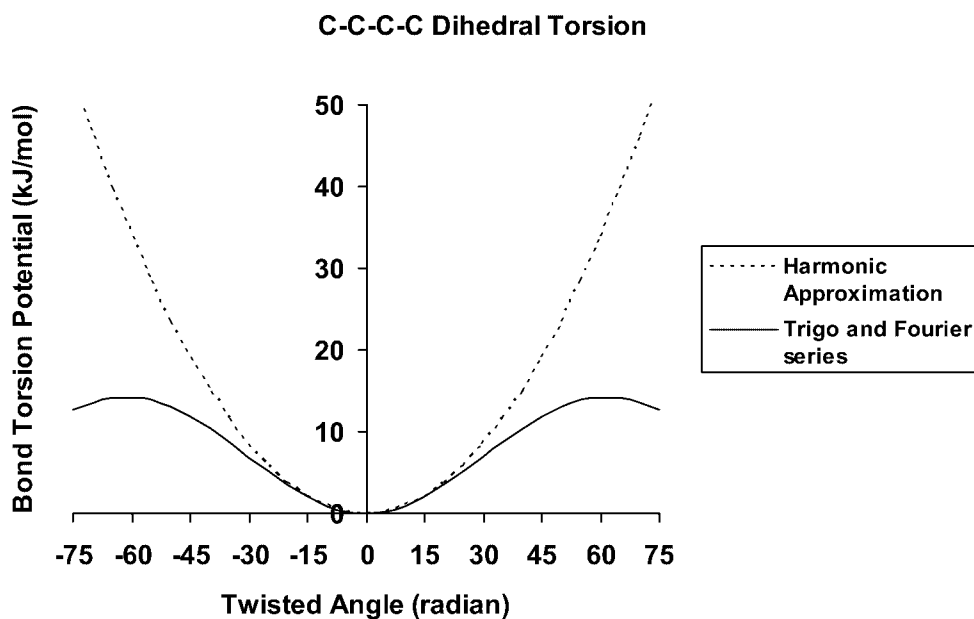


Figure 3. Comparison between series solution and harmonic approximation to torsional potential.

The harmonic form diverges thereafter from the actual result for larger twisted angle, as shown in equation (8). The harmonic approximations described in equations (13) and (14) are nonetheless valid for infinitesimal deformation, and is analogous to the harmonic approximations for bond stretching and bending [5,7,8,16,26], as listed in table 2.

#### 4. Conclusions

A set of mathematical relationships connecting parameters of torsional force field potential has been demonstrated in this note. Notwithstanding the empirical nature of the molecular mechanics models, i.e., the parameters are obtained by curve fitting of experimental results, both “exact” and approximate relationships exist nonetheless between

Table 2  
Molecular mechanics models for stretching and bending, and their relations.

Interactions	Functions	Parameters	Relationships
Bond stretching: $r$ = bond length, $r_0$ = equilibrium bond length	(i) Morse potential $U = D\{1 - \exp[-\alpha(r - r_0)]\}^2$ (ii) Harmonic approximation $U = \frac{1}{2}k_S(r - r_0)^2$	$D, \alpha$ $k_S$	$k_S = 2D\alpha^2$ [5,7,8,16,27]
Bond bending: $\theta$ = bond angle, $\theta_0$ = equilibrium bond angle	(i) Cosine harmonic angle $U = \frac{1}{2}k_{C\theta}(\cos \theta - \cos \theta_0)^2$ (ii) Harmonic approximation $U = \frac{1}{2}k_\theta(\theta - \theta_0)^2$	$k_{C\theta}$ $k_\theta$	$k_\theta = k_{C\theta} \sin^2 \theta_0$ [5,7,16,27]

the three torsional potential functions considered herein. From the applied research and industrial application viewpoint, data from trigonometric series function can now be converted for use in softwares which require those of Fourier series function, and vice versa. From the mathematical view point, relationship between the various bond-torsional force fields can be expressed via conversion matrices.

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