A Short Note on the Fast Evaluation of Dihedral Angle Potentials and their Derivatives

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Dihedral angle potentials, which are used in many force fields for molecular dynamics simulations, model the energy of twisting a bond as a function of the angle $\phi_{ijkl}$ between the surfaces spanned by the particles $p_i, p_j$ and $p_k, p_l$ respectively.

The potential function may have several forms. In the AMBER [4], CFF [6], CHARMM [7], DREIDING [8], GROMOS [9] and SHAPES [1] force fields, the potential is defined as

$$v_1(\phi) = K \left[1 + \cos(n\phi - \delta)\right], \quad (1)$$

where $K$ is the energy of the potential, $n$ its multiplicity and $\delta$ its phase shift. The multiplicity $n$ is an integer and $\delta$ is usually an integer multiple of $\pi$.

In the Unified Force Field (UFF) [11], the potential function is generalized as

$$v_2(\phi) = K \sum_{k=0}^{n} c_k \cos(k\phi), \quad (2)$$

or, in Desmond [2], as

$$v_3(\phi) = K \sum_{k=0}^{n} c_k \cos(k\phi - \phi_0), \quad (3)$$

where $\phi_0$ is the equilibrium dihedral angle.

The first (1) and third (3) forms can be converted to the second form (2) when $\delta$ and $\phi_0$ are integer multiples of $\pi$. For all other values of $\delta$ and $\phi_0$, all three forms generalize to the form

$$v_4(\phi) = K \sum_{k=0}^{n} [a_k \cos(k\phi) + b_k \sin(k\phi)], \quad (4)$$

where the coefficients $a_k$ and $b_k$ can be obtained by applying the equivalence

$$\cos(\alpha \pm \beta) = \cos(\alpha) \cos(\beta) \mp \sin(\alpha) \sin(\beta). \quad (5)$$

In practice, the angle $\phi$ is obtained by computing its sine and/or cosine from the vectors $p_i - p_j, p_k - p_j$ and $p_l - p_k$, and computing its inverse sine, cosine or tangent. In NAMD [10] and GROMACS [5], $\phi$ is computed using the
inverse tangent and then inserted into (1). In Desmond, the sine and cosine are computed using vector calculus and (3) is evaluated by repeated application of the equivalence (5), thus requiring no evaluations of any trigonometric functions or their inverses.

The entire computation can, however, be drastically simplified. Assuming that we have computed \( x = \cos(\phi) \) using vector calculus, we can then re-write (1)-(4) in terms of \( x \):

\[
\begin{align*}
  v_1(x) &= K \left[ 1 + T_n(x) \cos(\delta) + U_{n-1}(x)(1 - x^2)^{1/2} \sin(\delta) \right], \\
  v_2(x) &= K \sum_{k=0}^{n} c_k T_k(x), \\
  v_3(x) &= K \sum_{k=0}^{n} c_k \left[ T_k(x) \cos(\phi_0) + U_{k-1}(x)(1 - x^2)^{1/2} \sin(\phi_0) \right], \\
  v_4(x) &= K \sum_{k=0}^{n} \left[ a_k T_k(x) + b_k U_{k-1}(x)(1 - x^2)^{1/2} \right],
\end{align*}
\]

where \( T_k(x) \) and \( U_k(x) \) are the Chebyshev polynomials of the first and second kind which satisfy

\[
T_k(x) = \cos \left( k \cos^{-1}(x) \right), \quad U_{k-1}(x) = \frac{\sin \left( k \cos^{-1}(x) \right)}{(1 - x^2)^{1/2}}.
\]

Using the derivatives of the Chebyshev polynomials

\[
\frac{d}{dx} T_k(x) = kU_{k-1}(x) \quad \text{and} \quad \frac{d}{dx} U_{k-1}(x) = \frac{kT_k(x) - xU_{k-1}(x)}{x^2 - 1},
\]
we can write the corresponding derivatives of the potentials with respect to \( x \) as

\[
\begin{align*}
  \frac{d}{dx} v_1(x) &= K \left[ 1 + nU_{n-1}(x) \cos(\delta) + (2xU_{n-1}(x) - nT_n(x))(1 - x^2)^{-1/2} \sin(\delta) \right], \\
  \frac{d}{dx} v_2(x) &= K \sum_{k=0}^{n} c_k kU_{k-1}(x), \\
  \frac{d}{dx} v_3(x) &= K \sum_{k=0}^{n} c_k \left[ kU_{k-1}(x) \cos(\phi_0) + (2xU_{k-1}(x) - kT_k(x))(1 - x^2)^{-1/2} \sin(\phi_0) \right], \\
  \frac{d}{dx} v_4(x) &= K \sum_{k=0}^{n} \left[ a_k kU_{k-1}(x) + b_k (2xU_{k-1}(x) - kT_k(x))(1 - x^2)^{-1/2} \right].
\end{align*}
\]

Note that when \( \delta \) and \( \phi_0 \) are integer multiples of \( \pi \), the terms in \( \sin(\delta) \) and \( \sin(\phi) \) can be dropped.
The advantage of this formulation is that the Chebyshev polynomials can be evaluated using the three term recurrence relations

\[ T_0(x) = 1 \]
\[ T_1(x) = x, \]
\[ T_k(x) = 2xT_{k-1}(x) - T_{k-2}(x), \]
\[ U_0(x) = 1 \]
\[ U_1(x) = 2x, \]
\[ U_k(x) = 2xU_{k-1}(x) - U_{k-2}(x) \]

i.e. in \(2n - 2\) additions and \(2n - 1\) multiplications to obtain all \(T_k(x), U_k(x)\) for \(k = 0 \ldots n\). Alternatively, the polynomials \(U_k(x)\) for odd/even \(k\) can be computed as twice the sum of \(T_j(x)\), for all odd/even \(0 \leq j \leq k\). Furthermore, \(v_2(x)\) and \(\frac{d}{dx}v_2(x)\) (as well as \(v_3(x)\) and \(\frac{d}{dx}v_3(x)\) when \(\phi_0\) is an integer multiple of \(\pi\)) can be evaluated concurrently using the Clenshaw algorithm [3].

Although the relation of such potentials to polynomials in \(\cos(\phi)\) is not entirely new [12], the connection to Chebyshev polynomials provides an efficient and general recipe for their evaluation.

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References


