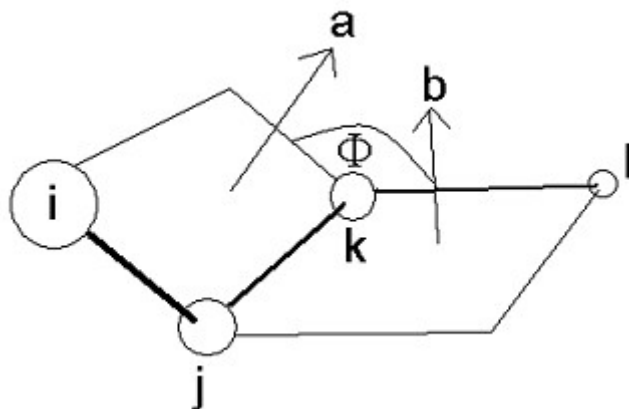


Subject:
Re: [cnsbb] Ask about a concept -- improper dihedral angle
From:
Zeljko Dzakula <zdz@accelrys.com>
Date:
Fri, 06 May 2005 11:10:07 -0700
To:
Wei Heng <weiheng@ust.hk>
CC:
CNS Bulletin Board <cnsbb@yahoogroups.com>

>> Could anyone please explain to me what the term "improper dihedral angle"
>> exactly means, and what the difference between "improper dihedral angle"
>> and "dihedral angle" is?
>>
>> The Xplor manual writes that, "The definition (of improper angle) is
identical
>> to the dihedral angle, but it uses a different set of parameters..."
Well, I
>> still don't quite catch what the words mean, and wherever I met
"IMPRoper" in
>> a .inp script, I got confused. I don't know what the use of improper
>> angle is.

A dihedral or torsion angle Φ corresponding to four non-colinear atoms i , j , k , and l is the angle between the planes defined by the atom triads i, j, k and j, k, l . If the atom pairs $i-j$, $j-k$, and $k-l$ are covalently bound, the dihedral angle $i-j-k-l$ describes the internal rotation of the vicinal neighbors i and l around the central bond $j-k$.



(pic06334.jpg)

The torsion angle Φ can be computed from the coordinates of the atoms i , j , k , and l by noting that the normals on the planes $i-j-k$ and $j-k-l$ are equal to the vector products of the vectors connecting the four atoms.

$$\vec{a} = \vec{r}_{ij} \times \vec{r}_{jk} \quad (\text{pic26500.jpg})$$

$$\vec{b} = \vec{r}_{jk} \times \vec{r}_{kl} \quad (\text{pic19169.jpg})$$

The dihedral angle is simply the angle between the two normals.

$$\cos \Phi = \frac{\vec{a} \cdot \vec{b}}{|\vec{a}| |\vec{b}|} = \frac{(\vec{r}_{ij} \times \vec{r}_{jk}) \cdot (\vec{r}_{jk} \times \vec{r}_{kl})}{\sqrt{(\vec{r}_{ij} \times \vec{r}_{jk})^2} \sqrt{(\vec{r}_{jk} \times \vec{r}_{kl})^2}} \quad (\text{pic15724.jpg})$$

The mixed product $(\vec{u} \times \vec{v}) \cdot (\vec{w} \times \vec{q})$ (pic11478.jpg) can be rewritten in terms of scalar products.

$$\begin{aligned} (\vec{u} \times \vec{v}) \cdot (\vec{w} \times \vec{q}) &= \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix} \cdot \begin{vmatrix} \vec{e}_x & \vec{e}_y & \vec{e}_z \\ w_x & w_y & w_z \\ q_x & q_y & q_z \end{vmatrix} = \begin{pmatrix} u_y v_z - u_z v_y \\ u_x v_z - u_z v_x \\ u_x v_y - u_y v_x \end{pmatrix}^T \begin{pmatrix} w_y q_z - w_z q_y \\ w_x q_z - w_z q_x \\ w_x q_y - w_y q_x \end{pmatrix} \\ &= (\vec{u} \cdot \vec{w})(\vec{v} \cdot \vec{q}) - (\vec{u} \cdot \vec{q})(\vec{v} \cdot \vec{w}) \end{aligned} \quad (\text{pic29358.jpg})$$

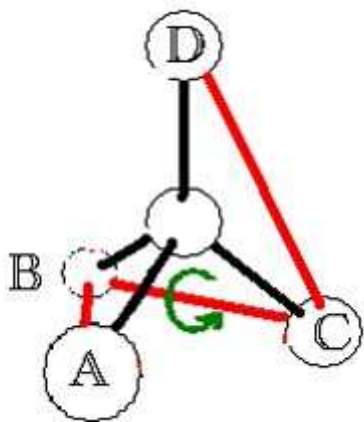
This leads to the following expression for the torsion angle.

$$\Phi = \arccos \frac{(\vec{r}_{ij} \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \vec{r}_{kl}) - (\vec{r}_{ij} \cdot \vec{r}_{kl}) r_{jk}^2}{\sqrt{[(\vec{r}_{ij} \cdot \vec{r}_{jk})^2 - r_{ij}^2 r_{jk}^2] [(\vec{r}_{jk} \cdot \vec{r}_{kl})^2 - r_{jk}^2 r_{kl}^2]}} \quad (\text{pic26962.jpg})$$

By convention, positive dihedral angle values i-j-k-l correspond to clockwise rotations of the bond k-l with respect to the fixed bond i-j when viewed along the axis of rotation j-k with the atom j being closer to the observer.

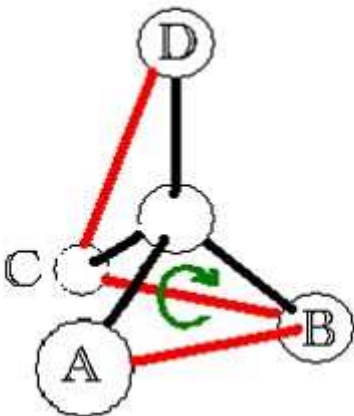
Mathematically, improper angles are defined in the same way as dihedral angles. The main difference between dihedral and improper angles is that, traditionally, the order of atoms making up a dihedral angle follows the lineup of covalent bonds, whereas the sequence of atoms in a definition of an improper angle often permutes the succession of chemical bonds, so that the axis of an improper "rotation" does not necessarily coincide with a chemical bond. The following figure illustrates this point on a molecular fragment that does not have any rotatable bonds at all. The central, sp³-hybridized atom is covalently bound to four different substituents (black lines pointing toward the vertices of the imaginary tetrahedron); the spatial arrangement of the substituents is expressed by the improper angle (green circular arrow), depicted in the figure. by red-colored bars. None of the red lines match any of the chemical bonds. Moreover, the entire structure is rigid and there is no (or very little)

rotation around the axis B-C.



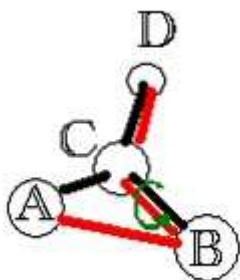
(pic24464.jpg)

Another difference between the two classes of angles arises from the way how they are employed: dihedral angles describe torsional motions around rotatable bonds; improvers, on the contrary, enforce static spatial relationships among atom quartets, such as planarity of molecular fragments or chirality of asymmetric centers. To understand how an improper angle determines the chirality of an asymmetric center, compare the previous figures with the following figure: the angle between planes ABC and BCD is positive (clockwise) in the previous figure and negative (counterclockwise) in the following figure. Accordingly, structures of opposite chiralities present improper angles of the same magnitude but opposite signs.



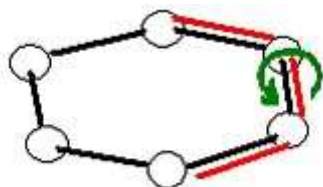
(pic05705.jpg)

An improper angle reflecting planar configuration of an sp^2 -hybridized atom is illustrated in the following figure. In this case, the axis of the improper angle overlaps with one of the chemical bonds. Nevertheless, very little rotational motion around the axis B-C takes place and no significant deviations are expected from the improper angle value of 180.



(pic28145.jpg)

Improper angles describing planar structures can also take the value of 0 in aromatic rings.



(pic23281.jpg)

The current value of an improper angle can be checked using the command `pick improper`, as in the following example.

```
pick improper
  (name N and residue 3)
  (name C and residue 3)
  (name CB and residue 3)
  (name HA and residue 3)
  geometry
```

The improper potential is similar to the empirical potential assigned to dihedrals.

$$E_{\text{improper}} = k_{\Phi} \begin{cases} 1 + \cos(n\Phi - \delta), & n > 0 \\ (\Phi - \delta)^2, & n = 0 \end{cases} \quad (\text{pic16827.jpg})$$

The parameterization also follows a similar pattern and affects improper angles declared within the topology statement.

```
topology
  residue XYZ
    atom X type=A1 end
    atom Y type=A2 end
    atom Z type=A3 end
    atom W type=A4 end
    improper X Y Z W
  end
end
parameter
  improper A1 A2 A3 A4 kF n d
end
```

Multiple terms are allowed in the Fourier expansion of the improper potential. Just as with the dihedral potentials, the topology statement declaring an improper angle with composite potential must use the keyword multiple.

$$E_{\text{improper}} = \sum_{i=1}^m k_{\Phi i} \begin{cases} 1 + \cos(n_i \Phi - \delta_i), & n_i > 0 \\ (\Phi - \delta_i)^2, & n_i = 0 \end{cases} \quad (\text{pic09961.jpg})$$

```

topology
  residue XYZ
    atom XX type=B1 end
    atom YY type=B2 end
    atom ZZ type=B3 end
    atom WW type=B4 end
    improper      X Y Z W      multiple m
  end
end
parameter
  improper      B1 B2 B3 B4      multiple m  kF1 n1 d1
                                          kF2 n2 d2
                                          kF3 n3 d3
                                          ...
                                          kFm nm dm
end

```

The order of atoms is essential in the definition of an improper angle, as illustrated by the previous four figures. Great care thus must be paid to the correct ordering of atom selections within the topology and parameter statements.

The following figure will help us evaluate the target value for an improper angle describing a tetrahedral chiral center. Let us assume that the vertices of the tetrahedron in the figure, are the substituents attached to the chiral atom and that the improper angle F is defined as in the first figure. Note that the improper angle between planes ABC and BCD is equal to the angle AED , where E splits AD in half. Assuming that all the edges of the tetrahedron have the same length a , the length DE is easily found using Pythagorean theorem.

$$h = \frac{a\sqrt{3}}{2} \quad (\text{pic00491.jpg})$$

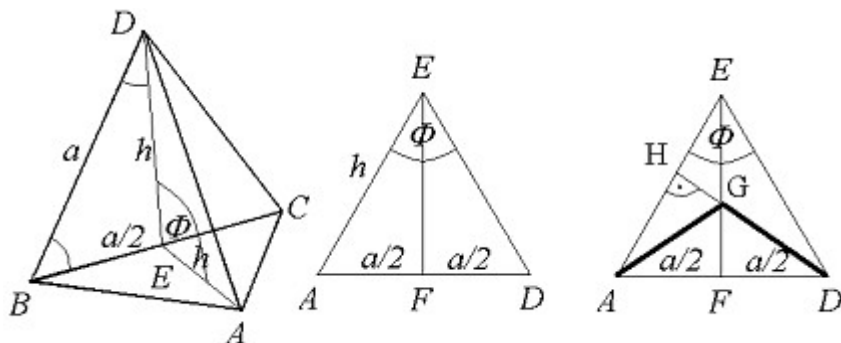
By noting that

$$\sin(\Phi/2) = \frac{\overline{AF}}{\overline{AE}} = \frac{a/2}{h} = \frac{\sqrt{3}}{3} \quad (\text{pic02995.jpg})$$

we arrive at the value for the improper angle A-B-C-D corresponding to an ideal tetrahedron.

$$\Phi = 2 \arcsin\left(\frac{\sqrt{3}}{3}\right) \approx 70.5^\circ \quad (\text{pic11942.jpg})$$

The improper angle in an ideal tetrahedron A-B-C-D has the value -70.5° (counterclockwise), while the angle A-C-B-D is equal to 70.5° (clockwise).



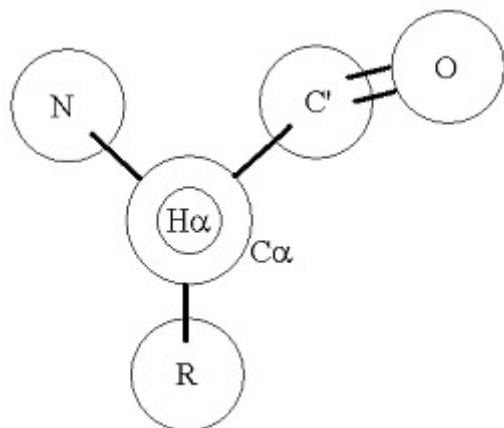
(pic04827.jpg)

The tetrahedra formed by substituents bound to chiral centers are rarely perfect because of the variations in the lengths of chemical bonds. For that reason, target values for improvers describing chirality are usually different from the ideal value of $\pm 70.5^\circ$.

Since we are already at it, let's quickly demystify the value of 109.5° assigned to tetrahedral bond angles in sp^3 hybridized atoms. Since the angle HEG is equal to $\Phi/2$ and GHE is 90° , the remaining angle HGE in the triangle HGE is $180^\circ - 90^\circ - \Phi/2 = 90^\circ - \Phi/2$. The angles FGD and HGE are equal, and the desired tetrahedral angle DGA between the covalent bonds DG and GA, which is twice as large as FGD, is obtained as $180^\circ - \Phi - 180^\circ - 70.5^\circ = 109.5^\circ$, QED.

Ca atoms in amino acids present an illustrative example of the use of improper angles to define the handedness of chiral centers. All standard amino acids, except the achiral glycine, have in common a chiral carbon atom C_α bound to a hydrogen atom H_α , carbonyl group $C'=O$, a side chain R, and an amide nitrogen N. Normally, the chiral center C_α adopts the L-configuration. You can mentally reconstruct this configuration with the help of the so-called CORN mnemonic rule (Richardson, 1981). If you view the C_α atom along the H_α - C_α bond so that H_α is closer to you, and read the remaining substituents in the clockwise direction starting from the carbonyl atom, the groups attached to C_α ($C'=O$, R, and N) form the word CORN.

CORN mnemonic rule.



(pic05436.jpg)

Consider how the CORN rule is implemented within the context of an all-hydrogen force field, normally used for NMR computations. Unlike most

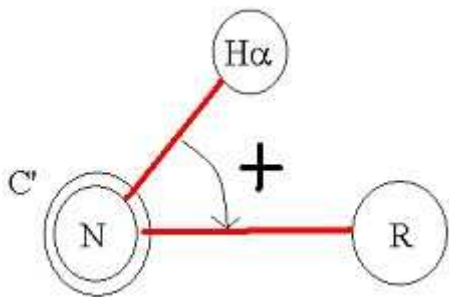
CNS force fields, an all-hydrogen topology library contains the Ha. This enables the amino-acid residue templates to use the substituents Ha, N, C', and C β (in that order) to define an improper angle that measures the chirality of Ca.

```

topology
  residue ALA
    group
      atom HA type=HA end
      atom N type=NH1 end
      atom C type=C end
      atom CB type=CH3E end
      ...
    improper HA N C CB ! chirality CA
  end
end

```

According to the CORN rule, the spatial arrangement of H α , N, C', and C β corresponds to a positive improper angle (clockwise rotation).



(pic32391.jpg)

The parameter component of the force field therefore assigns a positive value to this improper angle. Its absolute value is smaller than the ideal value of 70.5° because the bond Ca-Ha is shorter than the bonds connecting C α to N, C', or C β .

```

parameter
  improper HA NH1 C CH3E 500.00 0 65.9907
end

```

You can invert the configuration of any chosen amino acid from L- to D-form by assigning atom-based improper angle parameters and reversing the sign of the equilibrium value.

```

parameter
  improper
    (resid 4 and name HA) (resid 4 and name N)
    (resid 4 and name C) (resid 4 and name CB) 500.00 0 -65.9907
end

```

Force fields comprising unified atoms only contain polar hydrogens, or in some cases no hydrogen atoms at all. Most force fields used for crystallographic computations belong to this category. In the absence of explicitly defined Ha atoms, the improper angle describing the chiral center Ca must use the atom Ca instead of Ha.

```

topology
  RESIDue ALA
  GROUp
    ATOM N      TYPE=NH1    ...    END
    ATOM CA     TYPE=CH1E   ...    END
    ATOM CB     TYPE=CH3E   ...    END
    ATOM C      TYPE=C      ...    END
    ...
  IMPRoper CA   N   C   CB !tetrahedral CA
END
End

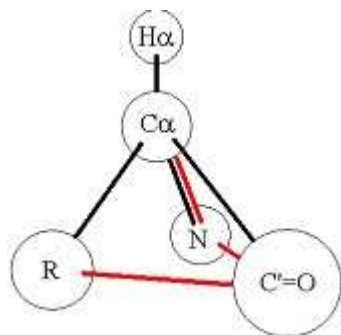
```

The target value for this improper angle is obviously different from the one used in an all-hydrogen force field. Fortunately, the value can be extracted from the second figure without additional derivations. The atom $C\alpha$ coincides with the center of the tetrahedron, which is located on the line EF. The ideal value corresponding to the improper angle $C\alpha-N-C'-C\beta$ is therefore $\Phi/2 = 35.3^\circ$. As in the all-hydrogen case, the L-configuration corresponds to a clockwise rotation and therefore to a positive improper angle value.

```

parameter
  impr CH1E X   X   CH3E 750      0      35.26439
end

```



(pic14604.jpg)

Caution: the actual value of the improper angle depends on the order of atoms. If you permute the order, the sign will change with the parity of the permutation.

Use `pick improper` to examine the current improper parameterization and `print improper` to list all dissatisfied improper angles.

```

pick improper
  (name N and residue 3)
  (name C and residue 3)
  (name CB and residue 3)
  (name HA and residue 3)
  equilibrium constant delta energy

```

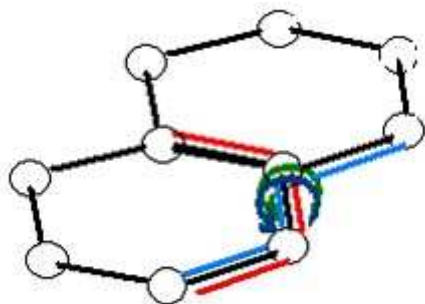
```

print threshold=D improper

```

The most frequently used improper potentials are harmonic wells with a single minimum. This is understandable, considering the fact that improper angles usually describe rigid configurations and serve to prevent

deviations from the desired target value. However, in conjugated, planar rings, cosine improper potentials of the second order (with two minima, $n = 2$) are often beneficial. The reason for this is the possibility to have both cis- and trans-configurations involving the same chemical types; a single minimum would favor either cis- or trans-structure, but would be unable to allow both of them simultaneously. Remember to set d to 180° , since the value of 0° will enforce right angles and ruin ring planarity. The notoriously shallow minima of the cosine function can be made sharper by increasing the value of the force constant for the improper potential.



(pic03902.jpg)

Admittedly, improper angles are not ideal tools to enforce planarity of large groups of atoms, such as conjugated rings. A much better approach would specify all the atoms that belong to a planar group and then penalize their movements away from the plane that best fits all of them. That treatment would significantly reduce the number of parameters relative to improper angle approach. It would also benefit from treating all coplanar atoms as a single group, whereas improper angles break the whole collection of atoms into clusters of four atoms. However, parameterization for a least-square plane is currently not available in CNS, whereas improper angles are on hand.

----- Yahoo! Groups Sponsor ----->
In low income neighborhoods, 84% do not own computers.
At Network for Good, help bridge the Digital Divide!
<http://us.click.yahoo.com/EA3HyD/3MnJAA/79vVAA/CBYolB/TM>
----->

List information at <http://groups.yahoo.com/group/cnsbb>.
Posting is only allowed for members of this list.

Yahoo! Groups Links

<*> To visit your group on the web, go to:
<http://groups.yahoo.com/group/cnsbb/>

<*> To unsubscribe from this group, send an email to:
cnsbb-unsubscribe@yahoogroups.com

<*> Your use of Yahoo! Groups is subject to:
<http://docs.yahoo.com/info/terms/>

