



!empirical potential for molecular modeling and dynamics Studies of  
!proteins. Journal of Physical Chemistry B, 1998, 102, 3586-3616.

The first set of entries in the parameter file are those for bonds, indicated by the BONDS keyword. Each entry consists of a pair of atom types, a spring constant, and an equilibrium length. The bond potential function is  $K_b(b-b_0)^2$ , where  $b$  is the bond length in Angstroms. Bonds are a stiff degree of freedom in biomolecules, so the energy function is only accurate for values near the equilibrium length. Entries are present for every type of bond present in the topology file. The beginning of the bonds section is shown below:

```

BONDS
!
!V(bond) = Kb(b - b0)**2
!
!Kb: kcal/mole/A**2
!b0: A
!
!atom type Kb          b0
!
C    C    600.000    1.3350 ! ALLOW ARO HEM
          ! Heme vinyl substituent (KK, from propene (JCS))
CA   CA   305.000    1.3750 ! ALLOW  ARO
          ! benzene, JES 8/25/89
CE1  CE1  440.000    1.3400  !
          ! for butene; from propene, yin/adm jr., 12/95
CE1  CE2  500.000    1.3420  !
          ! for propene, yin/adm jr., 12/95
CE1  CT2  365.000    1.5020  !
          ! for butene; from propene, yin/adm jr., 12/95
CE1  CT3  383.000    1.5040  !
          ! for butene, yin/adm jr., 12/95
CE2  CE2  510.000    1.3300  !
          ! for ethene, yin/adm jr., 12/95

```

The CHARMM potential function is designed to confuse physicists, as the form is  $K_b(b-b_0)^2$ , rather than the traditional  $\frac{1}{2}k_b(b-b_0^2)$ , and therefore the  $K_b$  given in the parameter files is half the value of a traditional spring constant. Also, while the units kcal/mol for energy, Angstroms for length, atomic masses, electron charges, and either fs or ps for time may be convenient for input and output, tortuous unit conversions are required to express the equations of motion.

The next section gives parameters for every type of angle present in the topology file, indicated by the ANGLES keyword. The angle potential function is  $K_\theta(\theta-\theta_0)^2$ , where  $\theta$  is the measure of the angle in degrees. Angles are a stiff degree of freedom in biomolecules as well, so the energy function is only accurate for values near the equilibrium angle. Since angles are formed from combinations of bonds, there are many more types of angles than types of bonds. Each entry consists of three atom types, a spring constant, and an equilibrium

angle. A small minority of entires also contant Urey-Bradley parameters, which are a spring constant and equilibrium length for a bond-like term between the first and third atoms in the angle. The beginning of the angles section is shown below, with a Urey-Bradley term in the first entry only:

```

ANGLES
!
!V(angle) = Ktheta(Theta - Theta0)**2
!
!V(Urey-Bradley) = Kub(S - S0)**2
!
!Ktheta: kcal/mole/rad**2
!Theta0: degrees
!Kub: kcal/mole/A**2 (Urey-Bradley)
!S0: A
!
!atom types      Ktheta      Theta0      Kub        S0
!
CA  CA  CA      40.000     120.00     35.00     2.41620 ! ALLOW  ARO
! JES 8/25/89
CE1 CE1 CT3     48.00     123.50     !
! for 2-butene, yin/adm jr., 12/95
CE1 CT2 CT3     32.00     112.20     !
! for 1-butene; from propene, yin/adm jr., 12/95
CE2 CE1 CT2     48.00     126.00     !
! for 1-butene; from propene, yin/adm jr., 12/95
CE2 CE1 CT3     47.00     125.20     !
! for propene, yin/adm jr., 12/95

```

The next section gives parameters for every type of dihedral present in the topology file; there are even more dihedrals than there are angles. Since dihedrals represent the energy of rotation around a covalent bond, which is the source of most conformational flexibility in biomolecules, they must provide a smooth energy for 360 degrees. This is done in most cases with a single sinusoid,  $K_\chi(1 + \cos(n(\chi - \delta)))$  where  $\chi$  is the angle between the plane containing the first three atoms in the dihedral and the plane containing the last three. The “multiplicity”  $n$  is typically 1, 2, or 3, although for a small number of cases two or three terms with different values of  $n$  are provided for the same atom types. You may can observe in the excerpts below that the dihedral spring constants are one to two orders of magnitude lower than for angles, with an order of magnitude difference between flexible and inflexible dihedrals.

```

DIHEDRALS
!
!V(dihedral) = Kchi(1 + cos(n(chi) - delta))
!
!Kchi: kcal/mole
!n: multiplicity
!delta: degrees

```

```

!
!atom types          Kchi    n    delta
!
C   CT1 NH1 C        0.2000  1   180.00 ! ALLOW PEP
! ala dipeptide update for new C VDW Rmin, adm jr., 3/3/93c
C   CT2 NH1 C        0.2000  1   180.00 ! ALLOW PEP
! ala dipeptide update for new C VDW Rmin, adm jr., 3/3/93c
C   N   CP1 C        0.8000  3    0.00 ! ALLOW PRO PEP
! 6-31g* AcProNH2, ProNH2, 6-31g**/3-21g AcProNHCH3 RLD 4/23/93
CA  CA  CA  CA       3.1000  2   180.00 ! ALLOW  ARO
! JES 8/25/89
CA  CPT CPT CA       3.1000  2   180.00 ! ALLOW  ARO
! JWK 05/14/91 fit to indole

```

Because of the large numbers of dihedral terms required to describe a complete protein, the wildcard atom type X is occasionally used. These parameters will be used in NAMD if a more specific match is not found elsewhere in the parameter file.

```

X   C   C   X        4.0000  2   180.00 ! ALLOW HEM
! Heme (6-liganded): substituents (KK 05/13/91)
X   C   NC2 X        2.2500  2   180.00 ! ALLOW  PEP POL ARO
! 9.0->2.25 GUANIDINIUM (KK)
X   CD  OH1 X        2.0500  2   180.00 ! ALLOW  PEP POL ARO ALC
! adm jr, 10/17/90, acetic acid C-OH rotation barrier
X   CD  OS  X        2.0500  2   180.00 ! ALLOW  PEP POL
! adm jr. 3/19/92, from lipid methyl acetate
X   CE1 CE1 X        5.2000  2   180.00 !
! for butene, yin/adm jr., 12/95
X   CE2 CE2 X        4.9000  2   180.00 !
! for ethene, yin/adm jr., 12/95

```

The final bond-like terms in the parameter file are impropers, which are used exclusively and explicitly in the molecular topology to maintain planarity. As such, the harmonic form  $K_\psi(\psi - \psi_0)^2$  with a large spring constant and  $\psi_0$  typically zero is used to restrain deformations among an atom and three atoms bonded to it. As with dihedrals,  $\psi$  is angle between the plane containing the first three atoms and the plane containing the last three. Notice below that wildcard atom types occur in the second and third positions, rather than the first and fourth as in dihedrals.

```

IMPROPER
!
!V(improper) = Kpsi(psi - psi0)**2
!
!Kpsi: kcal/mole/rad**2
!psi0: degrees
!note that the second column of numbers (0) is ignored
!

```

```

!atom types          Kpsi          psi0
!
CPB CPA NPH CPA    20.8000          0      0.0000 ! ALLOW HEM
      ! Heme (6-liganded): porphyrin macrocycle (KK 05/13/91)
CPB X  X  C     90.0000          0      0.0000 ! ALLOW HEM
      ! Heme (6-liganded): substituents (KK 05/13/91)
CT2 X  X  CPB   90.0000          0      0.0000 ! ALLOW HEM
      ! Heme (6-liganded): substituents (KK 05/13/91)
CT3 X  X  CPB   90.0000          0      0.0000 ! ALLOW HEM
      ! Heme (6-liganded): substituents (KK 05/13/91)
HA  C  C  HA    20.0000          0      0.0000 ! ALLOW PEP POL ARO
      ! Heme vinyl substituent (KK, from propene (JCS))

```

Finally we come to the nonbonded interaction parameters. The NONBONDED statement includes a list of parameters which are used as defaults by the program CHARMM, but are ignored by NAMD. Those shown below correspond to the NAMD settings exclude scaled1-4, switching on, pairlistdist 14.0, cutoff 12.0, switchdist 10.0, dielectric 1.0, and 1-4scaling 1.0:

```

NONBONDED nbxmod 5 atom cdie shift vatom vdistance vswitch -
cutnb 14.0 ctofnb 12.0 ctonnb 10.0 eps 1.0 e14fac 1.0 wmin 1.5
      !adm jr., 5/08/91, suggested cutoff scheme

```

Recall that the partial charge of each atom is specified in the topology and PSF files and is independent of the atom type. Therefore the only type-based parameters are for the van der Waals interactions, which are represented by the classic Lennard-Jones potential (expressed in the somewhat unconventional form)  $\epsilon[(r_{min}/r)^{12} - 2(r_{min}/r)^6]$ . Observe that at  $r = r_{min}$  the force is zero and the energy is  $-\epsilon$ . Rather than providing a different value of epsilon could be provided for every possible combination of atom types, only one value is provided per type and inter-type interactions are calculated using the sum of the radii  $r_{min}/2$  and the geometric mean of the well-depths  $\epsilon$ . By convention, the  $\epsilon$  values are negative in the parameter file, as seen here:

```

!
!V(Lennard-Jones) = Eps,i,j[(Rmin,i,j/ri,j)**12 - 2(Rmin,i,j/ri,j)**6]
!
!epsilon: kcal/mole, Eps,i,j = sqrt(eps,i * eps,j)
!Rmin/2: A, Rmin,i,j = Rmin/2,i + Rmin/2,j
!
!atom ignored   epsilon      Rmin/2  ignored   eps,1-4      Rmin/2,1-4
!
C      0.000000  -0.110000    2.000000 ! ALLOW PEP POL ARO
      ! MMA pure solvent, adm jr., 3/3/93
CA     0.000000  -0.070000    1.992400 ! ALLOW ARO
      ! benzene (JES)
CC     0.000000  -0.070000    2.000000 ! ALLOW PEP POL ARO
      ! adm jr. 3/3/92, acetic acid heat of solvation
CD     0.000000  -0.070000    2.000000 ! ALLOW POL

```

```

! adm jr. 3/19/92, acetate a.i. and dH of solvation
CE1  0.000000  -0.068000   2.090000  !
! for propene, yin/adm jr., 12/95
CE2  0.000000  -0.064000   2.080000  !
! for ethene, yin/adm jr., 12/95
CM   0.000000  -0.110000   2.100000  ! ALLOW HEM
! Heme (6-liganded): CO ligand carbon (KK 05/13/91)

```

When the scaled1-4 exclusion policy is used (as it should with the CHARMM force field) nonbonded interactions of atoms separated by three bonds (i.e., atoms 1 and 4 in the chain 1-2-3-4) are modified. Even if the scaling factor for electrostatics is 1.0 (as it should be for modern CHARMM force fields), special modified van der Waals parameters are used for 1-4 pairs of atoms for which they are specified, as in the examples below.

```

!atom  ignored   epsilon   Rmin/2  ignored   eps,1-4   Rmin/2,1-4
!
CP1   0.000000  -0.020000   2.275000  0.000000  -0.010000   1.900000  ! ALLOW  ALI
! alkane update, adm jr., 3/2/92
CP2   0.000000  -0.055000   2.175000  0.000000  -0.010000   1.900000  ! ALLOW  ALI
! alkane update, adm jr., 3/2/92
CP3   0.000000  -0.055000   2.175000  0.000000  -0.010000   1.900000  ! ALLOW  ALI
! alkane update, adm jr., 3/2/92

```

The parameter file ends with a reference to parameters for explicit hydrogen bond energy terms. These are obsolete, no longer present in the CHARMM force field, and therefore not implemented by NAMD.

```

HBOND CUTHB 0.5 ! If you want to do hbond analysis (only), then use
! READ PARAM APPEND CARD
! to append hbond parameters from the file: par_hbond.inp

```

END

For information on how the parameters have been derived, you must consult the corresponding publications referenced in the parameter files themselves or listed on the MacKerell web site <http://www.pharmacy.umaryland.edu/faculty/amackere/research.html>.