Ch121a Atomic Level Simulations of Materials and Molecules

Room BI 115
Lecture: Monday, Wednesday Friday 2-3pm
Lab Session:

Lecture 3, April 6, 2015
FF1: valence, QEq, vdw

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Homework and Research Project

First 5 weeks: The homework each week uses generally available computer software implementing the basic methods on applications aimed at exposing the students to understanding how to use atomistic simulations to solve problems.

Each calculation requires making decisions on the specific approaches and parameters relevant and how to analyze the results.

Midterm: each student submits proposal for a project using the methods of Ch121a to solve a research problem that can be completed in the final 5 weeks.

The homework for the last 5 weeks is to turn in a one page report on progress with the project.

The final is a research report describing the calculations and conclusions.
The full Quantum Mechanics Hamiltonian:

\[ H = -\sum_{k}^{M} \frac{\hbar^2}{2M_k} \nabla^2 - \sum_{i}^{N} \frac{\hbar^2}{2m_i} \nabla^2 + \sum_{k}^{M} \sum_{l>k} Z_k Z_l e^2 R_{kl} + \sum_{i}^{N} \sum_{j>i} e^2 r_{ij} - \sum_{k}^{M} \sum_{l}^{N} Z_k e^2 r_{kj} \]

Born-Oppenheimer approximation, fix nuclei \((R_k=1..M)\), solve for \(\Psi_{el}(1..N)\)

\[ H_{el}(1..N_{el}) \Psi_{el}(1..N_{el}) = E_{el} \Psi_{el}(1..N_{el}) \]

\[ H_{el}(1..N_{el}) = -\sum_{i}^{N} \frac{1}{2} \nabla^2 - \sum_{k}^{M} \frac{Z_k}{r_{kj}} + \sum_{i}^{N} \sum_{j>i} \frac{1}{r_{ij}} \]

\(\Psi_{el}(1..N_{el})\) and \(E_{el}(1..M_{nuc})\) are functions of the nuclear coordinates.

Next solve the nuclear QM problem

\[ H_{nuc}(1..M_{nuc}) \Psi_{nuc}(1..M_{nuc}) = E_{nuc} \Psi_{nuc}(1..M_{nuc}) \]

\[ H_{nuc}(1..M_{nuc}) = -\sum_{k}^{n} \frac{\hbar^2}{2M_k} \nabla^2 + E_{el}(1..M_{nuc}) + \sum_{k}^{M} \sum_{l>k} \frac{Z_k Z_l e^2}{R_{kl}} \]

FF is analytic fit to this \(E_{PE}(1..M_{nuc})\)
The Bending potential surface for CH$_2$

Note that $E(\pi-\theta) = E(\pi+\theta)$
Symmetric about $\theta = \pi=180^\circ$
The Force Field (FF) is an analytic fit to such expressions but formulated to be transferable so can use the same parameters for various molecules and solids.

General form: \[ E = E_{\text{valence}} + E_{\text{nonbond}}. \]

\[ E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{inversion}} + E_{\text{cross-terms}} \]

Involves covalent bonds and the coupling between them (2-body, 3-body, 4-body, cross terms)

\[ E_{\text{nonbond}} = E_{\text{vdw}} + E_{\text{electrostatic}} \]

Involves action at a distance, long range interactions
**Bond Stretch Terms: Harmonic oscillator form**

Taylor series expansion about the equilibrium, $R_e$, $\delta = R - R_e$

$E(\delta) = E(R_e) + \frac{dE}{dR}_e[\delta] + \frac{1}{2}(\frac{d^2E}{dR^2})_e[\delta]^2 + \frac{1}{6}(\frac{d^3E}{dR^3})_e[\delta]^3 + O(\delta^4)$

Ignore zero

$E(R) = \frac{k_e}{2}(R - R_e)^2,$

Simple Harmonic

$K_e = 700 \text{ (Kcal/mol)/Å}^2$

Units: multiply by 143.88 to convert mdynes/ Å to (Kcal/mol)/Å$^2$

QM eigenstates, $E_v = v + \frac{1}{2},$ where $v = 0, 1, 2, \ldots$

Ground state wavefunction (Gaussian)

$\psi_0(\delta) = (m\omega/\pi\hbar) \exp[-(m\omega/2\hbar)\delta^2]$

Some force fields, CHARMM, Amber use $k = 2K_e$ to avoid multiplying by 2

Problem: cannot break the bond, $E \rightarrow \infty$
Bond Stretch Terms: Morse oscillator form

Want the E to go to a constant as break bond, popular form is Morse function

\[ E_{vdw} (R_{ij}) = D_e [\chi^2 - 2\chi] \]

where \( \chi = \exp[-\alpha (R - R_e)] = \exp[-(\gamma/2)(R/R_e - 1)] \)

Note that \( E(R_e) = 0 \), the usual convention for bond terms

- \( D_e \) is the bond energy in kcal/mol
- \( R_e \) is the equilibrium bond distance
- \( \alpha \) is the Morse scaling parameter
- calculate from \( K_e \) and \( D_e \)

\[ \alpha = \sqrt{k_e/2D_e}, \]

where \( k_e = \frac{d^2E}{dR^2} \) at \( R = R_e \) (the force constant)

\[ E = 0 \]
**Morse Potential – get analytic solution for quantum vibrational levels**

\[ E_{\text{Morse}}(R_{ij}) = D_e[x^2 - 2x] \]

where \( x = \exp[-\alpha(R-R_e)] = \exp[-(\gamma/2)(R/R_e -1)] \)

\[ \alpha = \sqrt{k_e/2D_e}, \text{ where } k_e = \frac{d^2E}{dR^2} \text{ at } R=R_e \text{ (the force constant)} \]

\[ E_v = h\nu_0(\nu + 1/2) - \left[h\nu_0(\nu + 1/2)^2\right]/4D_e \]

\[ \nu_0 = (\alpha/2\pi)\sqrt{2D_e/m} \]

**Level separations decrease linearly with level**

\[ E_{v+1} - E_v = h\nu_0 - (\nu+1)(h\nu_0)^2/2D_e \]

Write

\[ E_n/hc = \omega_e(\nu + 1/2) - x_e\omega_e(\nu + 1/2)^2 \]
Angle Bend Terms: cosine harmonic

Expand $E(\theta)$ as Fourier series.

Note only $\cos(n\theta)$ since must be symmetric about $\theta=0$ and $\pi$

$$E(\theta) = C_0 + C_1 \cos(\theta) + C_2 \cos(2\theta) + C_3 \cos(3\theta) + \ldots.$$ 

$$E(\theta) \sim \frac{1}{2} C_h [\cos \theta - \cos \theta_e]^2$$

$E=0$ at $\theta = \theta_e$

$$E'(\theta) = \frac{dE(\theta)}{d\theta} = - C_h [\cos \theta - \cos \theta_e] \sin \theta = 0 \text{ at } \theta = \theta_e$$

$$E''(\theta) = \frac{d^2E(\theta)}{d\theta^2} = - C_h [\cos \theta - \cos \theta_e] \cos \theta + C_h (\sin \theta)^2$$

$$k_\theta = E''(\theta_e) = C_h (\sin \theta_e)^2$$

Using $\cos(2\theta) = 2 \cos^2\theta - 1$
The Bending potential surface for CH₂

Note that \( E(\pi-\theta) = E(\pi+\theta) \)
Symmetric about \( \theta = \pi = 180° \)

9.3 kcal/mol
Barriers for angle term

The energy is a maximum at $\theta = \pi$.
Thus energy barrier to “linearize” the molecule becomes

$$E_{\text{barrier}} = \frac{1}{2}C[1 + \cos(\theta_0)]^2 = \frac{1}{2}K_\theta \left(\frac{1 + \cos(\theta_0)}{\sin(\theta_0)}\right)^2$$

By symmetry the angular energy satisfies

$$E(\pi - \theta) = E(\pi + \theta)$$
$$E(-\theta) = E(+\theta)$$

This is always satisfied for the cosine expansion but

A second more popular form is the Harmonic theta expansion

$$E(\theta) = \frac{1}{2}K_\theta [\theta - \theta_e]^2$$

However except for linear molecules this does NOT satisfy the symmetry relations, leading to undefined energies and forces for $\theta = 180^\circ$ and $0^\circ$. This is used by CHARMM, Amber, ..
Angle Bend Terms for linear molecule,

If $\theta_e = 180^\circ$ then we write $E(\theta) = K_\theta [1 + \cos(\theta)]$

since for $\theta = 180 - \delta$ this becomes

$E(\delta) = K_\theta [1 + (-1 + \frac{1}{2} \delta^2)] \sim \frac{1}{2} K_\theta \delta^2$
For an Octahedral complex
The angle function should have the form
\[ E(\theta) = C \left[ 1 - \cos 4\theta \right] \]
which has minima for
\[ \theta = 0, 90, 180, \text{ and } 270^\circ \]
With a barrier of \( C \) for
\[ \theta = 45, 135, 225, \text{ and } 315^\circ \]
Here the force constant is
\[ K_\theta = 16C = CP^2 \]
where \( P=4 \) is the periodicity, so we can write
\[ C = K_\theta / P^2 \]
Simple Periodic Angle Bend Terms

For an Octahedral complex

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However if we wanted the minima to be at

\( \theta = 45, 135, 225, \) and \( 315^\circ \) with maxima at

\( \theta = 0, 90, 180, \) and \( 270^\circ \)

then we want to use \( E(\theta) = \frac{1}{2} C \left[ 1 + \cos 4\theta \right] \)

Thus the general form is

\[ E(\theta) = \left( K_\theta/P^2 \right) \left[ 1 - (-1)^B \cos 4\theta \right] \]

Where \( B=1 \) for the case with a minimum at \( 0^\circ \) and
\( B=-1 \) for a maximum at \( 0^\circ \)
Dihedral barriers

HOOH

$\phi_e \sim 111^\circ$

7.6 kcal/mol Cis barrier

Part of such barriers can be explained as due to vdw and electrostatic interactions between the H’s.

But part of it arises from covalent terms (the $p\pi$ lone pairs on each S or O)

This part has the form

$$E(\phi) = \frac{1}{2} B \left[1+\cos(2\phi)\right]$$

Which is

$E=0$ for $\phi=90,270^\circ$ and $E=B$ for $\phi=0,180^\circ$

HSSH: $\phi_e \sim 92^\circ$

5.02 kcal/mol trans barrier

7.54 kcal/mol cis barrier
**dihedral or torsion terms**

Given any two bonds IJ and KL attached to a common bond JK, the dihedral angle φ is the angle of the JKL plane from the IJK plane, with cis being 0.

\[ E(\phi) = C_0 + C_1 \cos(\phi) + C_2 \cos(2 \phi) + C_3 \cos(3 \phi) + \ldots \text{which we write as} \]

\[ E(\phi) = \sum_{n=1}^{p} \frac{1}{2} [k_n (1 - d \cos(n\phi))] \]

Where each \( k_n \) is in kcal/mol, \( n = 1 \), is the periodicity of the potential and \( d=+1 \) the cis conformation is a minimum, \( d=-1 \) the cis conformation is the maximum. Input data is \( k_n \) and \( d_n \) for each \( n \).
Consider the central CC bond in Butane

There are nine possible dihedrals: 4 HCCH, 2 HCCC, 2 CCCH, and 1 CCCC. Each of these 9 could be written as

\[ E(\phi) = \frac{1}{2} B \left[ 1 + \cos(3 \phi) \right], \]

For which \( E=0 \) for \( \phi = 60, 180 \) and \( 300^\circ \) and \( E=B \) the rotation barrier for \( \phi = 0, 120 \) and \( 240^\circ \).
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For ethane get 9 HCCH terms.

The total barrier in ethane is 3 kcal/mol but standard vdw and charges of +0.15 on each H will account for ~1 kcal/mol.

Thus only need explicit dihedral barrier of 2 kcal/mol.
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Can do two ways. Incremental: treat each HCCH as having a barrier of 2/9 and add the terms from each of the 9 to get a total of 2 (Amber, CHARRM) Or use a barrier of 2 kcal/mol for each of the 9, but normalize by the total number of 9 to get a net of 2 (Dreiding)
The ground state (N) of ethene prefers $\phi=0^\circ$ to obtain the highest overlap of the $p_\pi$ orbitals on each C. The rotational barrier is 65 kcal/mol. We write this as $E(\phi) = \frac{1}{2} B [1-\cos 2\phi]$. Since there are 4 HCCH terms, we calculate each using the full $B=65$, but divide by 4.

The triplet excited state (T) prefers $\phi=90^\circ$ to obtain the lowest overlap.
When an atom I has exactly 3 distinct bonds IJ, IK, and IL, it is often necessary to include an explicit term in the force field to adjust the energy for "planarizing" the center atom I.

\[ E(\theta) = \frac{1}{2}C(\cos(\omega) - \cos(\omega_0))^2 \]

Where the force constant in kcal/mol is

\[ K_\omega = C\sin^2 \omega_0 \]

Umbrella inversion: \( \omega \) is the angle between the IL axis and the JIK plane.
AMBER Improper Torsion JILK

Amber describes inversion using an improper torsion.

\[ E(\psi) = \frac{1}{2}K_\psi \cos[n(\psi - \psi_o)] \]

n=2 for planar angles (\(\psi_o = 180^\circ\)) and n=3 for the tetrahedral Angles (\(\psi_o = 120^\circ\)).

Improper Torsion: \(\psi\) is the angle between the JIL plane and the KIL plane
In the CHARMM force field, inversion is defined as if it were a torsion.

\[ E(\phi) = \frac{1}{2}K_\phi [\phi - \phi_o]^2 \]

For a tetrahedral carbon atom with equal bonds this angles is \( \phi = 35.264^\circ \).

Improper Torsion: \( \phi \) is the angle between the IJK plane and the LJK plane.
### Summary: Valence Force Field Terms

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<tr>
<th>Description</th>
<th>Example</th>
<th>Typical Expressions</th>
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<tr>
<td>Bond Stretch</td>
<td>Harmonic Stretch</td>
<td>( E(R) = \frac{K_b}{2} (R - R_o)^2 )</td>
</tr>
<tr>
<td>Angle bend</td>
<td>Harmonic-cosine ( E_\theta = \left[ k_\theta / 2 \sin(\theta_o) \right] \left[ \cos(\theta) - \cos(\theta_o) \right]^2 )</td>
<td></td>
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<tr>
<td>Torsion</td>
<td>dihedral</td>
<td>( E(\phi) = \frac{1}{2} B \left[ 1 - \cos(3 \phi) \right], )</td>
</tr>
<tr>
<td>Inversion</td>
<td>Umbrella inversion</td>
<td>( E_\omega = \left[ 1 / 2 k_\omega / \sin(\omega_o) \right] \left[ \cos(\omega) - \cos(\omega_o) \right]^2 )</td>
</tr>
</tbody>
</table>
Coulomb (Electrostatic) Interactions

Most force fields use fixed partial charges on each nucleus, leading to electrostatic or Coulomb interactions between each pair of charged particles. The electrostatic energy between point charges $Q_i$ and $Q_k$ is described by Coulomb's Law as

$$E_Q(R_{ik}) = C_0 \frac{Q_i Q_k}{\varepsilon R_{ik}}$$

where $Q_i$ and $Q_k$ are atomic partial charges in electron units.

$C_0$ converts units:
if $E$ is in eV and $R$ in Å, then $C_0 = 14.403$
If $E$ is in kcal/mol and $R$ in Å, then $C_0 = 332.0637$
$\varepsilon = 1$ in a vacuum (dielectric constant)
How estimate charges?

Even for a material as ionic as NaCl diatomic, the dipole moment $\Rightarrow$ a net charge of $+0.8$ e on the Na and $-0.8$ e on the Cl not the idealized charges of $+1$ and $-1$

We need a method to estimate such charges in order to calculate properties of materials.

A side note about units.

In QM calculations the unit of charge is the magnitude of the charge on an electron and the unit of length is the bohr ($a_0$)

Thus QM calculations of dipole moment are in units of $ea_0$ which we refer to as au. However the international standard for quoting dipole moment is the Debye $= 10^{-10}$ esu A

Where $\mu(D) = 2.5418 \, \mu(au)$
QEq Electrostatics energy

- Self-consistent Charge Equilibration (QEq)
- Describe charges as distributed (Gaussian)
- Thus charges on adjacent atoms shielded (interactions $\rightarrow$ constant as $R \rightarrow 0$) and include interactions over ALL atoms, even if bonded (no exclusions)
- Allow charge transfer (QEq method)

$$E(\{q_i\}) = \sum_{i<j} J_{ij}(q_i,q_j,r_{ij}) + \sum_i \left( \chi_i q_i + \frac{1}{2} J_i q_i^2 \right)$$

- Hardness (IP-EA)
- Electronegativity (IP+EA)/2

Three universal parameters for each element:
1991: used experimental IP, EA, $R_i$;
ReaxFF get all parameters from fitting QM
Charge dependence of the energy (eV) of an atom

\[ E = \frac{1}{2}(\text{IP} + \text{EA}) = \chi_A^0 = 8.291 \]

\[ \text{IP} - \text{EA} = J_{AA}^0 = 9.352 \]

Harmonic fit

Get minimum at \( Q = -0.887 \)

\( E = -3.615 \)

\( E = 0 \)

\( E = 12.967 \)

\( Q = -1 \)  \( Q = 0 \)  \( Q = +1 \)

The 2\textsuperscript{nd} order expansion in \( Q \) is ok

\( E_{\text{min}} = -3.676 \)
QEq: the optimum charges lead to Equilibration that is, equal chemical potential

Expand the energy of an atom in a power series of the net charge on the atom, $E(Q)$

$$E_A(Q) = E_{A0} + Q_A \left( \frac{\partial E}{\partial Q} \right)_{A0} + \frac{1}{2} Q_A^2 \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A0} + ... \tag{1}$$

Including terms through 2nd order leads to

$$E_A(+1) = E_{A0} + \left( \frac{\partial E}{\partial Q} \right)_{A0} + \frac{1}{2} \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A0}$$

$$E_A(0) = E_{A0}$$

$$E_A(-1) = E_{A0} - \left( \frac{\partial E}{\partial Q} \right)_{A0} + \frac{1}{2} \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A0}$$

$$\left( \frac{\partial E}{\partial Q} \right)_{A0} = \frac{1}{2} (\text{IP} + \text{EA}) = \chi_A^0 \tag{2}$$

$$\left( \frac{\partial^2 E}{\partial Q^2} \right)_{A0} = \text{IP} - \text{EA} = J_{AA}^0 \tag{3}$$

Charge Equilibration for Molecular Dynamics Simulations;
A. K. Rappé and W. A. Goddard III;
J. Phys. Chem. 95, 3358 (1991)
<table>
<thead>
<tr>
<th>element</th>
<th>χ, eV</th>
<th>J, eV</th>
<th>R, Å</th>
<th>ζ, au</th>
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<tr>
<td>Li</td>
<td>3.006</td>
<td>4.772</td>
<td>1.557</td>
<td>0.4174</td>
</tr>
<tr>
<td>C</td>
<td>5.343</td>
<td>10.126</td>
<td>0.759</td>
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<tr>
<td>N</td>
<td>6.899</td>
<td>11.760</td>
<td>0.715</td>
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<td>13.8904</td>
<td>0.371</td>
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</tbody>
</table>
**Interpretation of J, the hardness**

\[ E_A(Q) = E_{A0} + \chi_A Q_A + \frac{1}{2} J_{AA}^0 Q_A^2 \]  

(1')

Define an atomic radius as

\[ J_{AA}^0 = \frac{14.4}{R_A^0} \quad \text{or} \quad R_A^0 = \frac{14.4}{J_{AA}^0} \]

<table>
<thead>
<tr>
<th>Element</th>
<th>( R_A^0 )</th>
<th>( R_e(A_2) )</th>
<th>Bond distance of homonuclear diatomic</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.84</td>
<td>0.74</td>
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<td>C</td>
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<td>O</td>
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<tr>
<td>S</td>
<td>1.60</td>
<td>1.63</td>
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</tr>
<tr>
<td>Li</td>
<td>3.01</td>
<td>3.08</td>
<td></td>
</tr>
</tbody>
</table>

Thus J is related to the coulomb energy of a charge the size of the atom.
The total energy of a molecular complex

Consider now a distribution of charges over the atoms of a complex: $Q_A, Q_B, \text{etc}$

Letting $J_{AB}(R) =$ the Coulomb potential of unit charges on the atoms, we can write

$$E(Q_1...Q_N) = \sum_A (E_A + \chi_A^0 Q_A + \frac{1}{2} Q_A^2 J_{AA}) + \sum_{A<B} Q_A Q_B J_{AB}$$

Taking the derivative with respect to charge leads to the chemical potential, which is a function of the charges

$$\chi_A(Q_1...Q_N) = \frac{\partial E}{\partial Q_A} = \chi_A^0 + \sum_B J_{AB} Q_B$$

or

$$\chi_A(Q_1...Q_N) = \chi_A^0 + J_{AA}^0 Q_A + \sum_{B \neq A} J_{AB} Q_B$$

The definition of equilibrium is for all chemical potentials to be equal. This leads to

$$\chi_1 = \chi_2 = \ldots = \chi_N$$
The QEq equations

Adding to the N-1 conditions $x_1 = x_2 = \ldots = x_N$

The condition that the total charged is fixed (say at 0)
leads to the condition

$$Q_{\text{tot}} = \sum_{i=1}^{N} Q_i$$

Leads to a set of N linear equations for the N variables $Q_A$.

$$AQ = X,$$

where the NxN matrix $A$ and the N dimensional vector $A$
are known. This is solved for the N unknowns, $Q$.

We place some conditions on this. The harmonic fit of charge to
the energy of an atom is assumed to be valid only for filling the
valence shell.

Thus we restrict $Q(\text{Cl})$ to lie between +7 and -1 and

$Q(\text{C})$ to be between +4 and -4

Similarly $Q(\text{H})$ is between +1 and -1
The QEq Coulomb potential law

We need now to choose a form for $J_{AB}(R)$

A plausible form is $J_{AB}(R) = 14.4/R$, which is valid when the charge distributions for atom A and B do not overlap.

Clearly this form as the problem that $J_{AB}(R) \to \infty$ as $R \to 0$

In fact the overlap of the orbitals leads to shielding.

The plot shows the shielding for C atoms using various Slater orbitals

$$\phi_{n\zeta}^{\text{slat}} = N_n r^{n-1} e^{-\zeta r}$$

$$\zeta_A = \lambda(2n + 1)/(2R_A)$$

And $\lambda = 0.5$
### QEq results for alkali halides

<table>
<thead>
<tr>
<th>metal halide</th>
<th>$Q_{\text{exp}}^a$</th>
<th>$Q_{\lambda=0.5}$</th>
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<tr>
<td>NaCl</td>
<td>0.792</td>
<td>0.776</td>
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<tr>
<td>CsF</td>
<td>0.697</td>
<td>0.660</td>
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</table>
QEq for Ala-His-Ala

Amber charges in parentheses
QEq for deoxy adenosine

Amber charges in parentheses
QEq for polymers

Nylon 66

PEEK
Polarizable QEq

Allow each atom to have two charges:
A fixed core charge (+4 for Si) with a Gaussian shape
A variable shell charge with a Gaussian shape but subject to
displacement and charge transfer
Electrostatic interactions between all charges, including the core and
shell on same atom
Allow Shell to move with respect to core, to describe atomic
polarizability
Self-consistent charge equilibration (QEq)

\[ \rho_i^c (\vec{r}) = \left( \frac{n_i^c}{\pi} \right)^{3/2} Q_i^c \exp\left( -\eta_i^c \cdot | \vec{r} - \vec{r}_i^c |^2 \right) \]

\[ \rho_i^s (\vec{r}) = \left( \frac{n_i^s}{\pi} \right)^{3/2} Q_i^s \exp\left( -\eta_i^s \cdot | \vec{r} - \vec{r}_i^s |^2 \right) \]

Four universal parameters for each element:
Get from QM
All nonbonded atoms and molecules exhibit a very repulsive interaction at short distances due to overlap of electron pairs (Pauli Repulsion) and a weak attractive interaction scaling like $1/R^6$ at long $R$ (London Dispersion). Together these are called van der Waals (vdW) interactions.

Most popular form: Lennard-Jones 12-6

$$E = A/R^{12} - B/R^6$$

$$= D_e[\rho^{-12} - 2\rho^{-6}]$$

where $\rho = R/Re$

Note that $E$ is a min at $Re$, note the 2

A 2nd form for LJ 12-6 is

$$= 4 D_e[\tau^{-12} - \tau^{-6}]$$

where $\tau = R/\sigma$

Note that $E=0$ at $R = \sigma$, note the 1

Here $\sigma = Re(1/2)^{1/6} = 0.89 Re$
van der Waals interaction

What do vdW interactions account for?

- Short range: Pauli Repulsion of overlapping electron pairs
  
  Pauli repulsion:  \( E_{\text{rep}} = \sum_{i<j} e^{-CR_{ij}} \) (where \( C > 0 \))

  Born repulsion: \( E_{\text{rep}} = \sum_{i<j} \frac{1}{R_{ij}^N} \) (where \( N \geq 9 \))

- Long range attraction → London dispersion due to Instantaneous fluctuations in the QM charges

  \[
  E_{\text{disp}} = \sum_{i<j} \left( \frac{C_{6,ij}}{R_{ij}^6} + \frac{C_{8,ij}}{R_{ij}^8} + \frac{C_{10,ij}}{R_{ij}^{10}} + \cdots \right)
  \]

  Dipole-dipole \quad Dipole-quadrupole \quad Quadrupole-quadrupole

  We usually neglect higher order (>\( R^6 \)) terms.
Popular vDW Nonbond Terms: LJ12-6

Lennard-Jones 12-6

\[ E(R) = \frac{A}{R^{12}} - \frac{B}{R^6} \]

\[ = D_{vdw} \{ \frac{1}{\rho^{12}} - \frac{2}{\rho^6} \} \text{ where } \rho = \frac{R}{R_{vdw}} \]

Here \( D_{vdw} \) = well depth,

and \( R_{vdw} \) = Equilibrium distance for vdw dimer

Alternative form

\[ E(R) = 4D_{vdw} \{ [\sigma_{vdw}/R]^{12} - [\sigma_{vdw}/R]^6 \} \]

Where \( \sigma \) = point at which \( E=0 \) (inner wall, \( \sigma \sim 0.89 \) \( R_{vdw} \))

Dimensionless force constant \( \kappa = \{ [d^2E/d\rho^2]_{\rho=1} \}/D_{vdw} = 72 \)

The choice of \( 1/R^6 \) is due to London Dispersion (vdw Attraction)

However there is no special reason for the \( 1/R^{12} \) short range form (other that it saved computation time for 1950’s computers)

LJ 9-6 would lead to a more accurate inner wall.
Buckingham or exponential-6

\[ E(R) = A e^{-CR} - B/R^6 \]

which we write as

\[ E^{x6} = D_0 \left[ \left( \frac{6}{\zeta - 6} \right) e^{\zeta(1-\rho)} - \left( \frac{\zeta}{\zeta - 6} \right) \rho^{-6} \right] \]

where \( R_0 = \) Equilibrium bond distance;
\( \rho = R/R_0 \) is the scaled distance
\( D_0 = \) well depth
\( \zeta = \) dimensionless parameter related to force constant at \( R_0 \)

We define a dimensionless force constant as 

\[ \kappa = \frac{\left( \frac{d^2E}{d\rho^2} \right)_{\rho=1}}{D_0} \]

\( \kappa = 72 \) for LJ12-6

\( \zeta = 12 \) leads to \(-D_0/\rho^6\) at long \( R \), just as for LJ12-6

\( \zeta = 13.772 \) leads to \( \kappa = 72 \) just as for LJ12-6

A problem with exp-6 is that \( E \rightarrow -\infty \) as \( R \rightarrow 0 \). To avoid this, BioGraf, LinGraf, CeriusII calculate the inner maximum and reflect \( E \) about this point for smaller \( R \) so that \( E \) and \( E' \) are continuous. When \( \zeta > 10 \) this point is well up the inner wall and not important
Converting between X-6 and LJ12-6

Usual convention: use the same $R_0$ and $D_0$ and set $\zeta = 12$.

I recall that this leads to small systematic errors.

Second choice: require that the long range form of exp-6 be the same as for LJ12-6 (ie $-2D_0/\rho^6$) and require that the inner crossing point be the same. This leads to

$$\gamma e^{\xi(1-\gamma)} = 1$$

This was published in the Dreiding paper but I do not know if it has ever been used.

$$\frac{D_L}{D_X} = \frac{3\gamma}{2(\xi - 6)}$$

$$\frac{R_L}{R_X} = \left(\frac{\xi}{3\gamma}\right)^{1/6}$$
Popular vdW Nonbond Terms: Morse

\[ E(R) = D_0 \{\exp[-\beta(R-R_0)] - 2 \exp[-(\beta/2)(R-R_0)]\} \]

At \( R=R_0 \), \( E(R_0) = -D_0 \)
At \( R=\infty \), \( E(R_0) = 0 \)

- \( D_0 \) is the bond energy in Kcal/mol
- \( R_0 \) is the equilibrium bond distance
- \( \beta \) is the Morse scaling parameter

I prefer to write this as
\[ E(R) = D_0 [\chi^2 - 2\chi] \] where \( \chi = \exp[(\alpha/2)(1-\rho)] \)
At \( R=R_0 \), \( \rho = 1 \rightarrow \chi = 1 \rightarrow E(R_0) = -D_0 \)
At \( R=\infty \), \( \chi = 0 \rightarrow E(R_0) = 0 \)
\[ \kappa = \{(d^2E/d\rho^2)_{\rho=1}\}/D_0 = \alpha^2/2 \]

Thus \( \alpha = 12 \rightarrow \kappa = 72 \) just as for LJ12-6

Few theorists believe that Morse makes sense for vdw parameters since it does not behave as \( 1/R^6 \) as \( R \to \infty \)
However, the vdw curve matches \( 1/R^6 \) only for \( R>6A \), and for our systems there will be other atoms in between. So Morse is ok.
Generally the vdw parameters are provided for HH, CC, NN etc (diagonal cases) and the off-diagonal terms are obtain using combination rules

\[ D_{0IJ} = \sqrt{D_{0II} \cdot D_{0JJ}} \]
\[ R_{0IJ} = \sqrt{R_{0II} \cdot R_{0JJ}} \]
\[ \zeta_{IJ} = (\zeta_{IJ} + \zeta_{IJ})/2 \]

Sometimes an arithmetic combination rule is used for vdw radii

\[ R_{0IJ} = (R_{0II} + R_{0JJ})/2 \]

but this complicates vdw calculations (the amber paper claims to do this but the code uses geometric combinations of the radii)
1-2 and 1-3 Nonbond exclusions

For valence force fields, it is assumed that the bond and angle quantities include already the Pauli Repulsion and electrostatic contributions so that we do not want to include them again in the nonbond list.

Thus normally we exclude from the vdw and coulomb sums the contributions from bonds (1-2) and next nearest neighbor (1-3) interactions
1-4 Nonbond exclusions

There is disagreement about 1-4 interactions. In fact the origin of the rotational barrier in ethane is probably all due to Pauli repulsion orthogonality effects.

Thus a proper description of the vdW interactions between 1-4 atoms should account for the barrier.

In fact it accounts only for 1/3 of the barrier.

I believe that this is because the CH bond pairs are centered at the bond midpoint not on the H atoms as assumed in the vdw.

Thus using atom centered vdw accounts for only part of the barrier necessitating an explicit dihedral term.

Thus I believe that the 1-4 vdw and electrostatic terms should be included. However some FF, such as Amber, CHARMM reduce the 1-4 interactions by a factor of 2. I do not know of a justification for this.