Computational Chemistry Methods and Programs

Molecular Mechanics

Geometry optimization using classical mechanics and parameterized force fields.
The most common force-field is MM2, which is used by HyperChem, Chem3D and many other chemical structure programs.

Semi-empirical M.O. Methods

LCAO applied to valence electrons only, with parameterized constants for the integrals.
The Hückel Method is simple enough to do with paper and pencil.
HyperChem uses the Extended Hückel Method.
More sophisticated methods include

CNDO, INDO, MNDO, MINDO, MINDO/3, AM1, PM3

They are often included in ab initio quantum chemistry packages and are useful for quick or approximate answers before applying the “big guns”.

Ab initio M.O. Methods

Calculations start from scratch, in principle using all electrons and interactions but then have to invoke various approximations to make the problem tractable.
The best known programs are GAUSSIAN (commercial) and GAMESS (free).

Geometry Optimization

The principles apply to all methods – molecular mechanics, semi-empirical and ab initio.

There are $3N$-6 variables to optimize. The goal is to find the global minimum on a multidimensional potential surface $V(q_j)$.

At the optimum geometry $\dfrac{\partial V}{\partial r_j} = 0$ for each coordinate r_j. bond length, angle, …

The steepest descent method is an efficient algorithm for seeking a stationary point.
At the energy minimum $\dfrac{\partial^2 V}{\partial r_j^2} > 0$ or more generally, $\left(\dfrac{\partial^2 V}{\partial r_k \partial r_i}\right)_{r_k} > 0$

Efficient algorithms vary all coordinates simultaneously, by diagonalizing the Hessian:

$$\begin{pmatrix} \dfrac{\partial^2 V}{\partial r_1^2} & \dfrac{\partial^2 V}{\partial r_1 \partial r_2} & \cdots \\ \dfrac{\partial^2 V}{\partial r_2 \partial r_1} & \dfrac{\partial^2 V}{\partial r_2^2} & \\ \vdots & & \ddots \end{pmatrix} \Rightarrow \begin{pmatrix} \dfrac{\partial^2 V}{\partial q_1^2} & 0 & 0 \\ 0 & \dfrac{\partial^2 V}{\partial q_2^2} & 0 \\ 0 & 0 & \ddots \end{pmatrix}$$

The q_j are normal coordinates and the diagonal elements are force constants.

Transition states have *one* negative force constant, i.e. an imaginary frequency $\omega = \sqrt{\dfrac{k}{\mu}}$

Molecular Mechanics

Treat the molecule as a set of point masses (nuclei) connected by springs (force fields).
Typical force fields include components which represent:

Bond stretching (A-B)	$V(r)=\tfrac{1}{2}k(r-r_0)^2+\tfrac{1}{2}k'(r-r_0)^3+\ldots$
Bond bending (A-B-C)	$V(\theta)=\tfrac{1}{2}k(\theta-\theta_0)^2+\ldots$
Torsion (A-B-C-D)	$V(\phi)=\tfrac{1}{2}\sum_n V_n(1-\cos n\phi)$
Dipole-dipole interactions	$V_r=Dr^{-6}$
van der Waals interactions	$V(r)=A\mathrm{e}^{-r/r_0}+B(r/r_W)^{-6}$ $\quad r_W=$ sum of vdW radii

Atoms are defined according to their bonding, e.g. C(alkane), C(alkene), C(aromatic).
Standard bond lengths and angles are used to "clean up" the initial structure guess.

The molecular geometry is then optimized to give the minimum energy.

Typical output properties are: structure, moments of inertia, bond energies, heat of formation. No "electronic" properties, since wave functions are not computed.

Semi-Empirical Methods

These are based on the Hartree-Fock self-consistent field method, but the Hamiltonian (the Fock matrix) is approximated and parameterized, i.e. various parameters are adjusted to give known results.

CNDO	Complete Neglect of Differential Overlap
INDO	Intermediate Neglect of Differential Overlap
MNDO	Modified Neglect of Differential Overlap
MINDO	Modified Intermediate Neglect of Differential Overlap
AM1	Austin Model 1
PM3	Parameterized Model number 3

Valence electrons are described by 1-electron atomic orbitals constructed from a minimal basis set of *s* and *p* Slater Type orbitals (STOs).

Core electrons are not included in the calculation, except to adjust the effective nuclear charge.

The 2-electron Coulomb and Exchange integrals are taken from tables parameterized for each element.

Basis Sets

Modern ab initio quantum chemistry programs use multiple Gaussian functions to simulate atomic orbitals, because of the relative ease of computing relevant integrals.

The set of atomic orbitals used to construct the molecular orbitals is known as the basis set.

A minimal basis set contains only enough orbitals to accommodate the electrons,
i.e. 1s for H, He; 1s, 2s, 2p, 2p, 2p for Li…Neon; those + 3s, 3p, 3p, 3p, 3p for Na…Ar.
A common example is STO-3G – Slater-type orbitals simulated by 3 Gaussians.
They lack the flexibility to describe MOs which are not spherical and atom-centred.

Split-valence basis sets have different functions for core and valence electrons.
Common examples are 6-31G and 6-311G.
i.e. 6 Gaussians for each core AO, 3 for one valence set and 1 for another valence set.

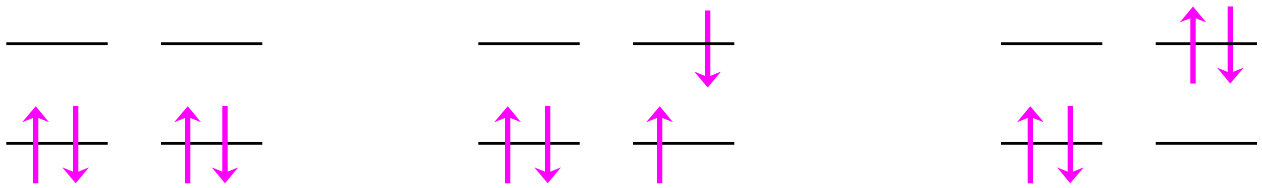
Polarization basis sets have extra functions for directional flexibility: *d* orbitals (*) + *p* (**)
These can be written as either 6-31G* or 6-31G(d), and 6-31G** or 6-31G(d,p).

Extra diffuse functions can be used to account for loosely bound electrons, such as in anions and excited states. They are designated with + or ++, e.g. 6-31++G**.

State-of-the-art Quantum Chemistry Methods

Standard HF procedures use single-determinant molecular orbitals, which are inadequate to deal with the problem of electron correlation.

Configuration Interaction (CI) involves mixing in higher energy electron configurations.



Best known is the Møller-Plesset method, particularly to second-order. MP2

Density Functional Theory provides a different approach.

⇒ 1998 Nobel Prize in Chemistry to Walter Kohn.

The HF exchange integral is replaced with an energy computed from an exchange/correlation functional. e.g. UB3LYP

Development of new, more accurate functionals is a current area of research in computational chemistry.