Molecular properties – dipole moment, atomic charges, etc.

By default at the HF level

To get e.g., MP2 properties, need density = current

HF, usually pretty good for charges, dipole moments, polarizabilities, etc. (assuming a decent basis set is used)

E.g., for H_2O

μ(HF) = 2.2 D μ(MP2) = 1.85 D

observables – dipole moment, quadrupole moment

non-observables – atomic charges

Pop = reg – print five highest occ. MOs, 5 lowest unoccup MOs.

= full – print all MOs

Pop = esp (or MK)

espd – esp plus dipole

chelp (or chelpg)

nbo

Atomic charges can vary appreciable between methods, and from basis set to basis set

Two other approaches

Atoms in molecules (AIM) (removed from code)

Distributed multipole analysis (DMA)

Charges, dipoles, quadrupoles associated with various centers

Prop =

Potential – electrostatic potential

Field – esp plus field

efg – esp, field, and field gradient

Grid – evaluate potential over a grid of points

Energy of molecule in an electric field

$$E(\varepsilon) = E(0) + E'\varepsilon + 0.5E''\varepsilon^2 + \ldots.$$

$$E(\varepsilon) = E(0) + \mu_0\varepsilon + -0.5\alpha\varepsilon^2 +$$

$$\mu_{ind} = \alpha\varepsilon$$

Thus one can calculate polarizabilities from dependence of dipole or energy on electric field strength

In general, α is a “tensor”, with nine components, not all of which are independent

The next term in the series gives β, the hyperpolarizable

Field = x+10 dipole field of strength 10*.0001 au

Field = xy-2 quadrupole filed of strength –10*.0001 au

Polar = analytical (RHF, UHF, DFT, MP2)

= numerical (uses analytical derivatives)

= enonly (uses energies)

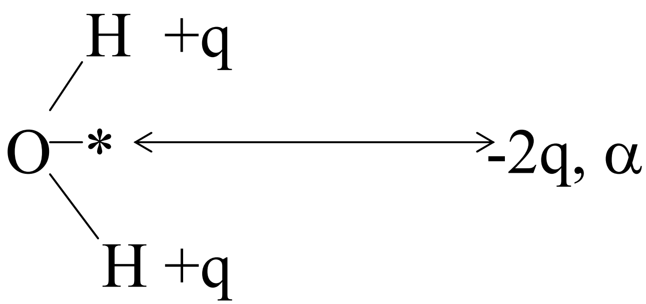
= step=N (field in 0.0001*N au)

Polarizability can be defined as

$\alpha = \Sigma|\langle 0|x|i\rangle|^2/(E_0 - E_i)$, sum over dipole allowed states $|i\rangle$

Low-lying dipole-allowed states → large polarizability

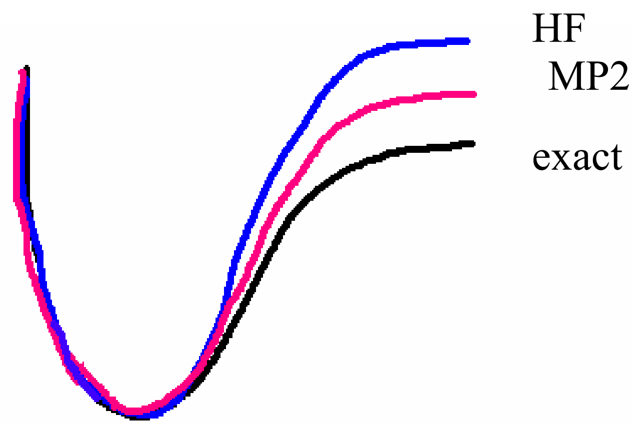
Polarizabilty important in model potentials for molecules



Dang-Chang model for water

Also includes O-O Lennard-Jones interactions

Vibrational frequencies



$$\frac{\partial^2 E}{\partial x_i \partial x_j} \rightarrow \text{force constant matrix}$$

HF frequencies ~ 10% too high

MP2 frequencies ~ 5% too high

} Experimental frequencies include anharmonicity

IR intensities $\propto |d\mu/dQ_i|^2$. Q_i = normal mode

$$\frac{\partial^2 E}{\partial x_i \partial \varepsilon_a} \rightarrow \text{to get IR intensities}$$

Can do isotopic substitution for very little extra computational cost (readisotopes)

Expression for vibrational /rotational levels of a diatomic molecule

$$E(v,J) = E_0 + \widetilde{\omega_e}(v+\frac{1}{2}) - \widetilde{\omega_e x_e}(v+\frac{1}{2})^2 + \ldots$$

$$+\widetilde{B_e} J(J+1) - \alpha_e [J(J+1)](v+\frac{1}{2}) + \ldots$$

$$-D_e [J(J+1)]^2 + \ldots$$

$\widetilde{\omega_e x_e}$ – Leading correction for anharmonicity