

Quantum Chemistry

Lecture 20

Applications of Hartree-Fock
Effect of Configuration Interaction

NC State University

Basis set dependence of E

The total energy is the most basic quantity that can be obtained from a calculation. Because of the variational approach we can say with certainty that the “better” the basis set, the lower will be the energy. “better” typically means more complete.

In the early 1970s computer codes were advanced enough to permit calculation of the energies of typical small molecules. For example, for H₂ the energy (in Hartrees) is:

STO-3G	-1.117
4-31G	-1.127
6-31+G(p,d)	-1.131
HF limit	-1.134

Schulman and Kaufman J. Chem. Phys. 1970, 53: 477

Comparison up to the HF Limit

The absolute energies are only of interest to the aficionados who try to develop better computation methods. What started in the 1970s with a few a molecule has developed into libraries of hundreds of molecules.

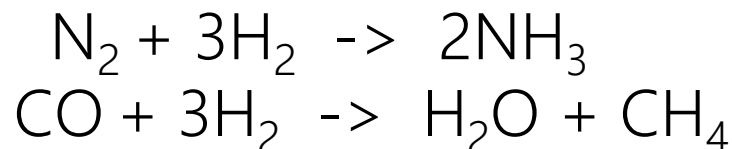
A few further examples are given below (in Hartrees).

	CH ₄	NH ₃	H ₂ O	HF
STO-3G	-39.727	-55.454	-74.963	-98.571
4-31G	-40.140	-56.102	-75.907	-99.887
6-31+G(p,d)	-40.202	-56.184	-76.023	-100.011
HF limit	-40.225	-56.225	-76.065	-100.071

Hariharan and Pople *Theor Chim Acta*, 1973, 28: 213

Using HF calculations for thermochemistry

Comparison of N₂ and CO is interesting because these two molecules are isoelectronic. While the absolute energies are important to benchmark different methods, we are most interested in the energetics of chemical reactions. Based on the information on these slides one could estimate the energies of



	N ₂	CO	(in Hartrees)
STO-3G	-107.496	-111.225	
4-31G	-108.754	-112.552	
6-31+G(p,d)	-108.952	-112.737	Huo J Chem Phys
HF limit	-108.997	-112.791	1965, 43: 624

Ionization potential for H₂

The ionization potential is theoretically equal to the calculated molecular orbital energy level (Koopman's theorem).

This theorem ignores relaxation and correlation effects.

relaxation lowers the energy of the final oxidized state and correlation lowers the energy of ground state. These two effects tend to cancel out, which is why the approximation works so well. For H₂ the values are (in Hartrees)

STO-3G	0.578
4-31G	0.596
6-31+G(p,d)	0.595
Experiment	0.584

Ionization potential for N₂

The N₂ ionization potentials are not even qualitatively correct in HF theory. The ordering of the bonding orbitals in the pσ system is clearly affected by the lower σ orbitals (from 1s and 2s linear combinations) since the 3σ_g orbital is the HOMO in N₂. However, HF theory misses this. Only the STO-3G is qualitative correct in the ordering and this is clearly an accidental agreement since STO-3G is the least inclusive basis set.

	² Σ	² Π
STO-3G	0.540	0.573
4-31G	0.629	0.621
6-31+G(p,d)	0.630	0.612
Near-HF	0.635	0.616
Experiment	0.573	0.624

Equilibrium geometries

Unlike energy where there is a road map based the Variational method and Koopman's theorem, the agreement (or disagreement) of computation with geometry is difficult to rationalize. The first example is the bonding in H_2 , shown in the table below. The bond lengths are given in atomic units (Bohrs):

STO-3G	1.346
4-31G	1.380
6-31+G(p,d)	1.385
Experiment	1.401

Bond lengths for CO and N₂

Equilibrium bond lengths are calculated using a geometry optimization procedure that we will discuss in a future lecture. For N₂ and CO there is greater difficulty in getting an accurate value than for the X-H type bonds. This is because of the fact that these molecules both have triple bonds.

	N ₂	CO	(in Bohrs)
STO-3G	2.143	2.166	
4-31G	2.050	2.132	
6-31+G(p,d)	2.039	2.105	
HF limit	2.013	2.081	
Experiment	2.074	2.132	

Cade, Sales, Wahl J Chem Phys, 1966, 44: 1973

Population analysis

One can use the equation:

$$\rho(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \Phi_{\mu} \Phi_{\nu}^*$$

to calculate the electron density. The density is difficult to describe on paper. It is the shape of the electron contours that surround the nuclei. It is useful to conceptually reduce the density to quantities such as atomic charge (which cannot actually be measured) and dipole or quadrupole moments, which can be measured.

We will discuss (later) how to decompose the charge into Mulliken charge. There are a number of different schemes for assigning charge to nuclei. These are not unique.

Dipole moments

The dipole moment is calculated as the expectation value of the dipole operator. In the general case there are three dipole moments (one along x, y and z). For a diatomic, such as CO, there is only one. CO has an interesting history since it has an anomalous dipole moment.

Basis set	Dipole moment (a.u.)
STO-3G	0.066
4-31G	-0.237
6-31+G(p,d)	-0.131
HF-limit	-0.110
Experiment	0.044

Frequencies

Vibrational frequencies can be calculated using the Hessian Matrix (force constant matrix). This can be obtained numerically by pulling each atom away from its equilibrium position along x, y and z or analytically (in Gaussian) by taking the second derivative of the energy.

The frequencies assume that the harmonic approximation is used, which is not necessarily accurate for vibrational modes that have large anharmonic corrections. For example, X-H stretching vibrations are high frequency modes with significant cubic anharmonicity. -NH_2 out-of-plane modes have significant quartic anharmonicity.

Frequencies of H₂O

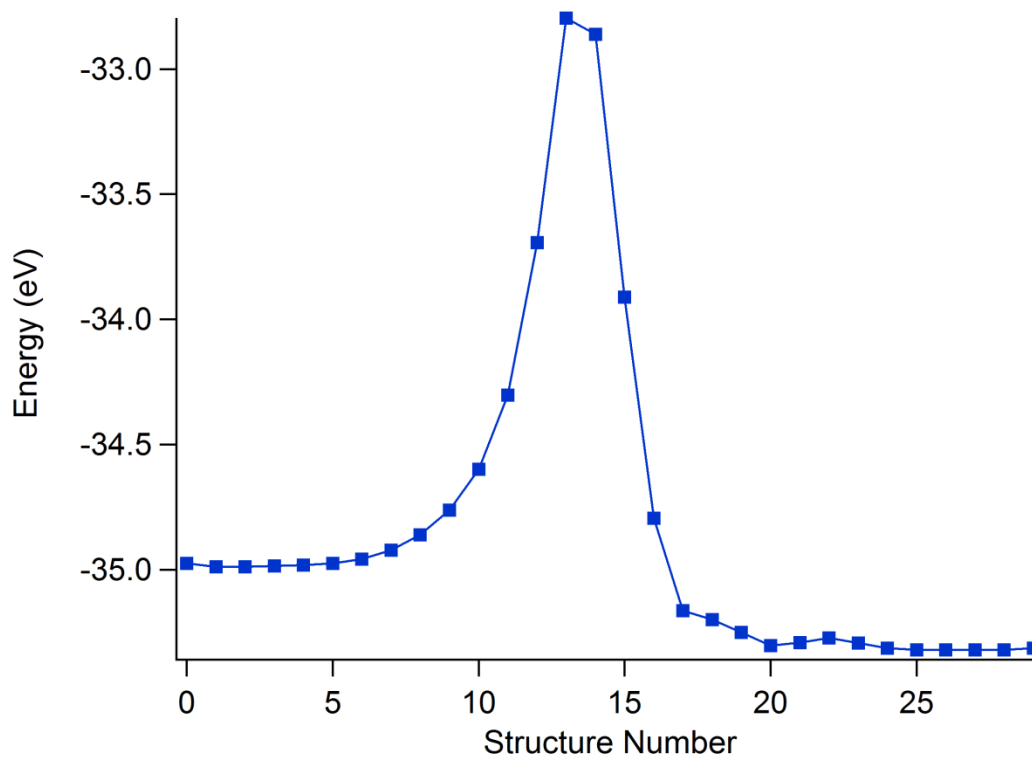
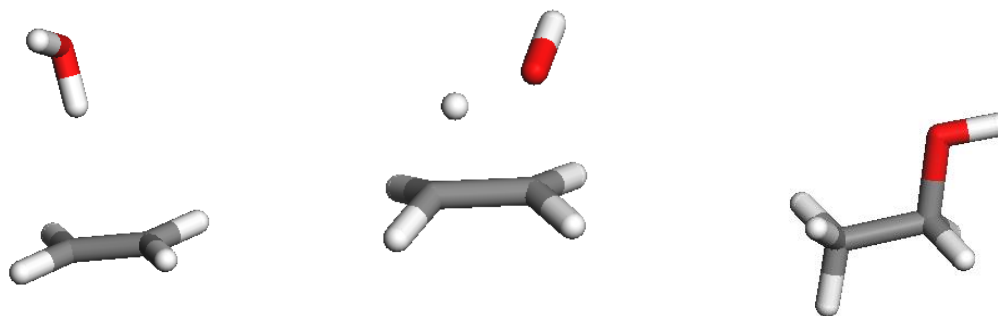
As a test case we consider the frequencies of H₂O calculated using Gaussian09 and using DMol3 (PBE column).

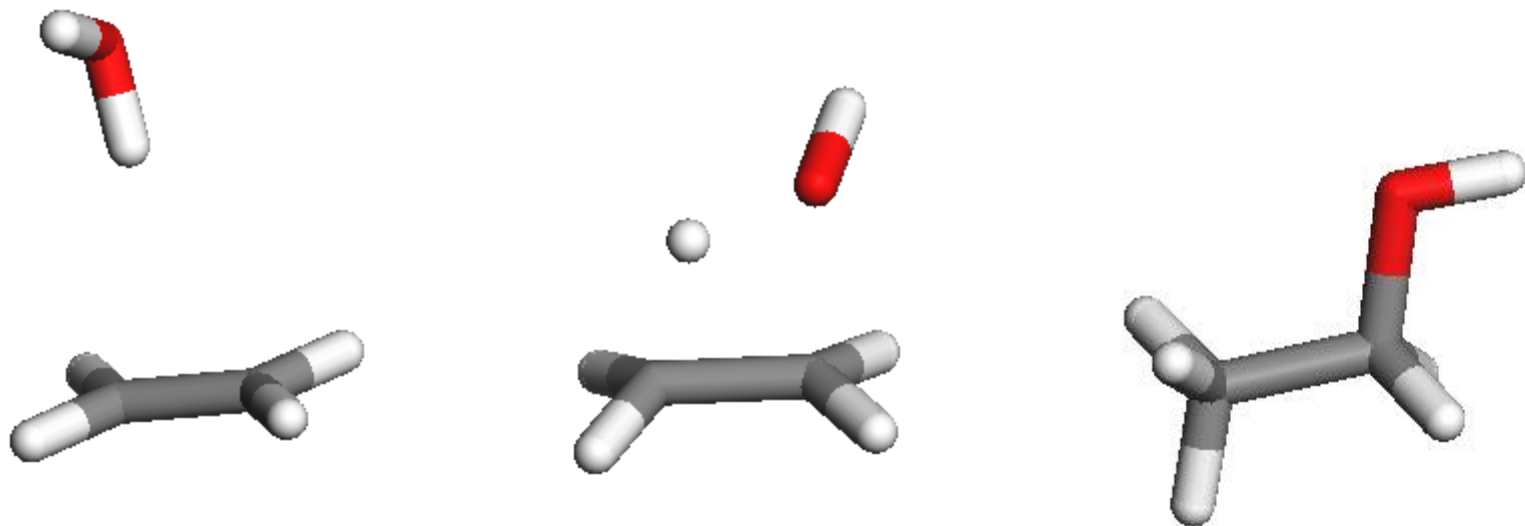
Note that we have used two density functional theory methods in this calculation and we will explain those methods next.

Clearly the CISD and CCSD post-HF calculations are far superior to HF itself. It appears that frequencies are one of the most rigorous tests of a quantum chemical method.

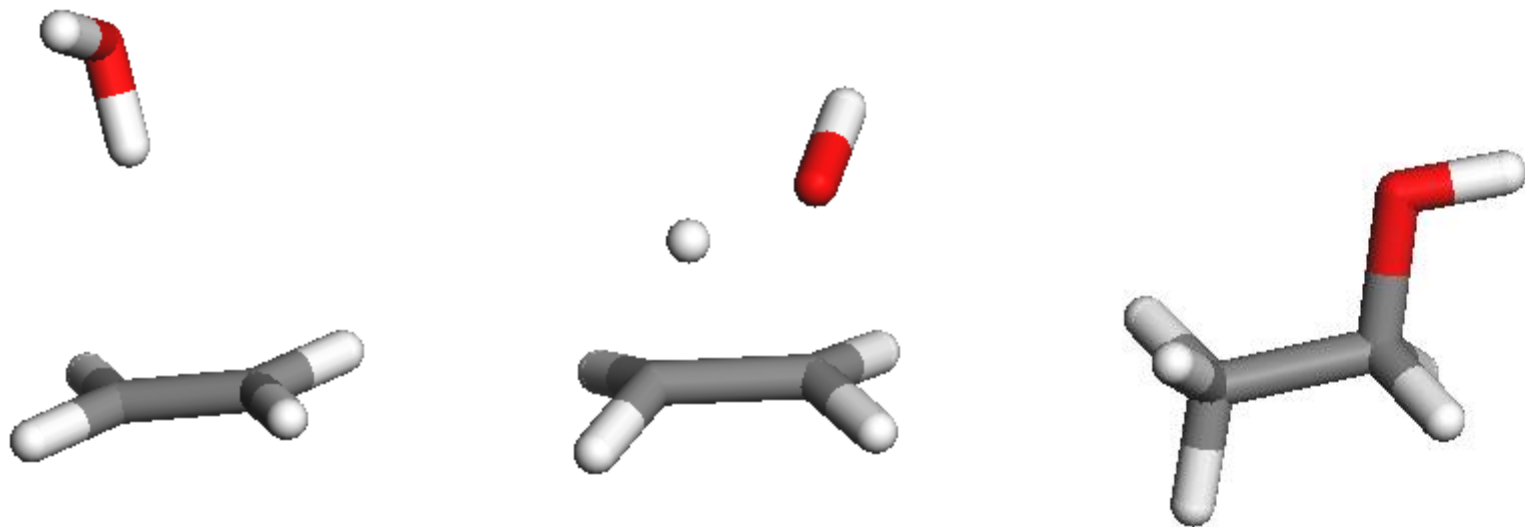
	STO-3G	4-31G	6-31G**	CCSD	CISD	M062X	PBE	Expmt
Bend	2169.9	1742.8	1725.9	1658	1670.3	1604.9	1630.6	1654
Sym Str	4140.6	3958.2	4141.9	3897	3949	3906.3	3718.3	3825
Asym Str	4391.6	4109.9	4244.4	3999	4046.1	4013	3833.7	3935
CPU Time	150	160	345	50100	21700	180	130	

Hydration of ethene: reaction path





Ethene	(STO-3G)	HF (4-31G)	HF	CCSD	CCSD(T)
Reactant	-152.0365	-153.83296	-154.10957	-154.65884	-154.67575
Transition	-151.9177	-153.71891	-153.98526	-154.55514	-154.57819
Product	-152.1295	-153.85441	-154.12934	-154.67857	-154.69491



Ethene	(STO-3G)	(4-31G)	HF	CCSD	CCSD(T)
Reactant	0	0	0	0	0
Transition	311.57	299.27	326.18	272.11	255.99
Product	-244.20	-56.29	-51.89	-51.77	-50.28