Factors Affecting the Accuracy of the Hartree-Fock Method

There are two factors that limit the accuracy of the Hartree-Fock method. One is the accuracy with which one actually solves the HF equations and the second is the intrinsic limitation of the model. The accuracy with which on solves the HF equations is determined by the completeness of the expansion basis. For example the geometry of formaldehyde and the vibrational frequencies calculated using the HF method and various basis sets is shown below.

Basis	cont/prim*	R(CO)Å	R(CH)Å	A(O-C-H)	Energy(au)
sto-3g	12/36	1.2169	1.1014	122.73	-112.354347
3-21g	22/36	1.2071	1.0833	122.51	-113.221820
sto-6g	12/72	1.2163	1.0981	122.61	-113.440775
6-31g	22/52	1.2103	1.0816	121.69	-113.808366
D95	24/56	1.2170	1.0843	121.57	-113.830712
D95v*	34/70	1.1887	1.0935	121.96	-113.891726
6-311g**	48/78	1.1787	1.0949	122.09	-113.899154
6-311++g**	58/88	1.1797	1.0943	121.97	-113.902874
apvtz	138/206	1.1786	1.0927	121.94	-113.915337
experimental		1.210	1.102	121.1	

*number of contracted basis functions/number of primitive basis functions

Note that the 6-31g basis is closer to experiment than the larger and more complete basis sets. The error in the HF model itself and the error due to a limited basis set are canceling to some degree. It's clear from the last two entries (6-311++g** and apvtz) that the HF model is converging to R(CO)=1.180, R(CH)= 1.09 and A(O-C-H)= 122 degrees which differs (as it should) from the experimental results.

Basis	B1	B2	A1	A1	A1	B2	dipole (D)
sto-3g	1278	1397	1767	2099	3499	2099	1.537
sto-6g	1282	1396	1762	2096	3490	3639	1.597
3-21g	1337	1378	1692	1914	3161	3232	2.659
6-31g	1329	1374	1673	1909	3207	3298	3.044
6-311g**	1337	1372	1656	2006	3091	3160	2.651
D95	1324	1350	1651	1878	3223	3315	3.190
D95v*	1334	1373	1667	2010	3180	3256	2.775
6-311++g**	1336	1363	1650	1995	3096	3168	2.806
apvtz	1335	1367	1648	1991	3086	3155	2.717
experiment	1191	1299	1529	1778	2978	2997	2.33

Once again the last two entries (6-311++g** and apvtz) are close enough to suggest that they represent the model limit and this limit is far from the experimental values. The limitation of the model means that even when one solves the Hartree-Fock equations

exactly one has not solved the Schrodinger equation but has simply produced an approximate wavefunction. Improving this approximation, i.e. going beyond the Hartree-Fock approximation is a subject of intense research interest. The basic idea is that the exact wavefunction can be written as

$$\psi = (\psi_{HF} + \lambda\psi_{correlation})/\sqrt{1+\lambda^2}$$

where

$$\langle\psi_{HF}|\psi_{correlation}\rangle = 0$$

One attempts to approximate $\psi_{correlation}$ using a variety of techniques that are collectively known as correlated methods. We will discuss these latter but for now it suffices to note that these correlated methods have well understood limitations and one knows, in principle, how to determine $\psi_{correlation}$ rather accurately. The following table summarizes these ideas. The computational method is listed vertically while the basis set is horizontal. The higher the computational level, the larger the basis set, the more accurate the result.

method	STO-3g	6-31g**	Basis set 6-311++g**	6-311g(2d,p)	6-311++g(3df,3pd)	…	complete
HF							
MP2							
CISD							
CCSD							
CISDTQ							
CCSD(T)							
CCSDT							
CCSDTQ							
MRCI							
…							
Full CI							Exact solution to Schrodinger equation