Quantum Chemistry II   2022

Text book   Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 2. Hartree-Fock (Cramer: chapter 6)

The molecular (non-relativistic) Hamiltonian for the electrons is known

$$H = \left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{iI} \frac{Z_I e^2}{4\pi\varepsilon_0 |r_i - R_I|} + \sum_{j<i} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{I>J} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0 |R_I - R_J|} \right] \quad (2.1)$$

In this we need to know the atomic type and positions. The positions do not need to be exact but they need to be reasonable. The molecular geometry can be optimized later. The exact wave functions cannot be solved and thus some approximations are needed. We also utilize the variational principle to find the best **trial wave functions** from the chosen function class.

Note: the general wave function is extremely complex. It is general 3N-6 dimensional functions: $\Psi(r_1, r_2..r_N)$. If we use grid of 10 points in every dimension the wave function of a single water molecule (10 electrons) contain 10^{24} numbers, which is 10^9 PB which by far exceeds the worlds data storage.

Variational principle

The closer to the true wave function the trial function is the lower the energy expectation $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$ value is. For exact wave functions this is

$$E = \langle H \rangle = \frac{\int \Psi(r_1...r_N) H \Psi(r_1...r_N) d^3r...d^3r_N}{\int \Psi(r_1...r_N) \Psi(r_1...r_N) d^3r...d^3r_N} \quad (2.2)$$

but the more interesting case is when this equation is used for a wave function like functions $\tilde{\Psi}$. The $\tilde{\Psi}$ can be almost any reasonable function. The energy is now

$$\tilde{E} = \frac{\int \tilde{\Psi}(r_1...r_N) H \tilde{\Psi}(r_1...r_N) d^3r...d^3r_N}{\int \tilde{\Psi}(r_1...r_N) \tilde{\Psi}(r_1...r_N) d^3r...d^3r_N} \qquad (2.3)$$

we can show that $\tilde{E} \geq$ E. The = sign appears only when $\tilde{\Psi} = \Psi$.

Proof:

We can expand $\tilde{\Psi} = \sum_n a_n \Psi_n$ where $a_n = \langle \tilde{\Psi} | \Psi_n \rangle$ (we do not know Ψ's but this does not matter, also $\delta_{mn} = \langle \Psi_m | \Psi_n \rangle$, $\epsilon_n | \Psi_n \rangle = H | \Psi_n \rangle$)) when this is inserted to (2.3) we get

$$\tilde{E} = \frac{\sum_n \epsilon_n a_n^2}{\sum_n a_n^2} \qquad (2.4)$$

This equation is always larger or equal than ε_0 = E.

This is a very powerful statement. It can be used to approximate Ψ with single Slater determinant (SD) or many SD's (the CI methods) or to find parameters of Ψ. We can determine the quality of the trial wave function $\tilde{\Psi}$ by comparing the energy $\tilde{E}$. **The lower energy the better wave functions and thus better results.**

Hartree-Fock equations

The **simplest** anti-symmetric product function is the Slater determinant

$$\Psi(r_1, r_2,.., r_N) = \frac{1}{\sqrt{N!}} \det | \varphi_1(r_1) \varphi_2(r_2)..\varphi_N(r_N) |$$

Where the φ(r)'s is an atomic type orbital. We "ignore" here the spin or more precisely we assume that all states are doubly occupied so the number of electrons are 2N! The φ_i(r)'s are orthonormal, $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$.

The data requirement of the Slater determinant is $N*g^{3N}$, where the g is data in one dimension. With grid of 10 points and for water (N=10) this will be 10^4 which is very small.

We can look the kinetic energy part

$$T = -\frac{\hbar^2}{2m_e}\sum_k \int \Psi^*(r_1, r_2.., r_N)\nabla_k^2\Psi(r_1, r_2.., r_N)\, d\tau =$$

$$-\frac{\hbar^2}{2m_e N!}\sum_{IJk} \epsilon_I\epsilon_J \int \varphi_1(r_1)\varphi_2(r_2)..\varphi_N(r_N)\nabla_k^2\; \varphi_1(r_1)\varphi_2(r_2)..\varphi_N(r_N)d\tau =$$

$$-\frac{\hbar^2}{2m_e}\sum_n \int \varphi_n(r)\nabla^2\; \varphi_n(r)d^3r$$

The ε is a shorthand of the determinant also $d\tau$ will contain all the dr's. As one can see the expression is rather simple.

As an example this can be done for two states. The orthogonality is important.

$$\Psi(r_1, r_2) = \frac{1}{2}\left[\varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1)\right]$$

$$T = -\frac{\hbar^2}{4*2m_e}\sum_{k=1,2} \int [\varphi_1(r_1)\varphi_2(r_2) - \varphi_1(r_2)\varphi_2(r_1)]\nabla_k^2[\varphi_1(r_1)\varphi_2(r_2)$$
$$- \varphi_1(r_2)\varphi_2(r_1)]dr_1 dr_2$$
$$= -\frac{\hbar^2}{4*2m_e}\int [\varphi_1(r_1)\varphi_2(r_2)\nabla_1^2\varphi_1(r_1)\varphi_2(r_2)]\, dr_1 dr_2 + \cdots$$
$$= -\frac{\hbar^2}{4*2m_e}\int \varphi_1(r_1)\nabla_1^2\varphi_1(r_1)dr_1 \underbrace{\int \varphi_2(r_2)\,\varphi_2(r_2)dr_2}_{=1} + \cdots$$
$$= -\frac{\hbar^2}{2m_e}\left[\int \varphi_1(r_1)\nabla_1^2\varphi_1(r_1)dr_1 + \int \varphi_2(r_1)\nabla_1^2\varphi_2(r_1)dr_1\right]$$

The Coulomb part is more complex,

$$C = \frac{e^2}{4\pi\varepsilon}\int \frac{\Psi^*(r_1, r_2.., r_N)\Psi(r_1, r_2.., r_N)}{|r_1-r_2|}d\tau =$$

$$\frac{e^2}{4\pi\varepsilon N!}\sum_{IJ} \epsilon_I\epsilon_J \int \frac{\varphi_1(r_1)\varphi_2(r_2)..\varphi_N(r_N)\varphi_1(r_1)\varphi_2(r_2)..\varphi_N(r_N)}{|r_1-r_2|}d\tau$$

The last integral is delicate since the r_1 and r_2 are twice in the product wave functions and the Slater determinant will have all the **permutations** of the orbitals. This lead to two contributions.

$$J = \frac{e^2}{4\pi\varepsilon\,2}\sum_{nm}\int\frac{|\varphi_n(r_1)|^2|\varphi_m(r_2)|^2}{|r_1-r_2|}dr_1dr_2 = \frac{e^2}{4\pi\varepsilon\,2}\int\frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}dr_1dr_2$$

$$K = -\frac{e^2}{4\pi\varepsilon\,2}\sum_{nm}\int\frac{\varphi_n(r_1)\varphi_m(r_1)\varphi_n(r_2)\varphi_m(r_2)}{|r_1-r_2|}dr_1dr_2$$

The J is simple. It is the Coulomb interaction of the electron density, $\rho(r) = \sum_n|\varphi_n(r)|^2$. The K is more complex it is the Fock (or exchange) term which arises from the fact that the electrons can be exchanged.

These are the **Hartree-Fock equations**. They are still impractical since the wave functions are hard to handle.

We need to write there using some **basis functions** $\xi(r)$ (simple known functions that contain adjustable parameters. Typically the basis functions are centered to atoms, $\xi(r-R)$.

$$\varphi_n(r) = \sum_m c_{n,m}\xi_m(r)$$

Now we can insert to the Slater determinant and the basis functions to variation equation (or to Schrödinger equation). After a bit of math we can write the Roothaan-Hall (R-H) equation

$$\boldsymbol{FC} = \varepsilon\boldsymbol{SC}$$

Where **C** contain all the molecular coefficients, **F** is the Fock matrix and **S** is the overlap matrix. The Fock matrix is

$$F_{nm} = H_{nm} + J_{nm} - K_{nm}$$

$$H_{nm} = \int\xi_n(r)\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon}\sum_I\frac{Z}{|r-R_I|}\right]\xi_m(r)\,d\tau$$
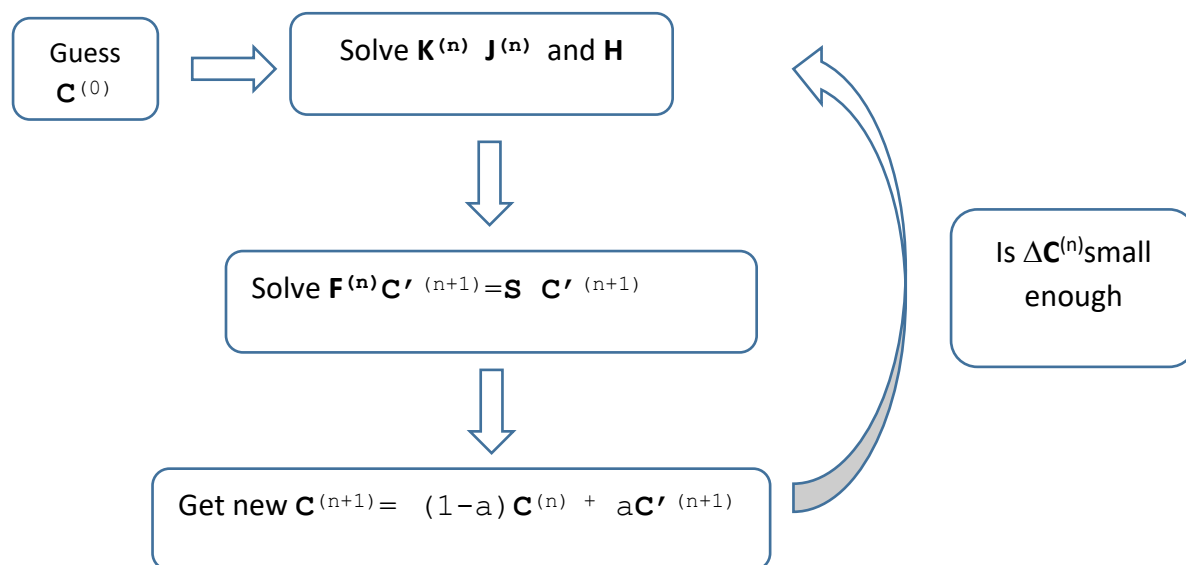
$$J_{nm} = \sum_{kl}P_{kl}(nm|kl) \qquad K_{nm} = \sum_{kl}P_{kl}(nk|ml)$$

$$(nm|kl) = \iint \frac{\xi_n(r_1)\xi_m(r_1)\xi_k(r_2)\xi_l(r_2)}{|r_1 - r_2|} d\tau_1 d\tau_2 \qquad P_{nm} = \sum_i c_{n,i} c_{m,i}$$

$$S_{nm} = \int \xi_n(r)\xi_m(r)d\tau$$

This is quite complex equation since the solution of the R-H equation is hidden to the coefficients J and K. Also the integrals (nm|kl) contain 4 functions (and they are 6 dimensional). The J can be simplified but K not. If there is M basis functions the computations scale as M^4. These together are the Hartree-Fock (HF) equations. They cannot be solved directly. One need to make a guess of $\mathbf{C}^{(0)}$ and solve $\mathbf{K}^{(0)}$, $\mathbf{J}^{(0)}$ and $\mathbf{F}^{(0)}$ matrixes with this guess. Then the R-H equation can be solved and a new set of coefficients $\mathbf{C}^{(1)}$ can be solved. Usually one have to adjust the new C's a bit but this self-consistent loop usually converges quite well (at least if there is a large HOMO-LUMO gap).

Guess $\mathbf{C}^{(0)}$ → Solve $\mathbf{K}^{(n)}$ $\mathbf{J}^{(n)}$ and $\mathbf{H}$

Solve $\mathbf{F}^{(n)}\mathbf{C}'^{(n+1)}=\mathbf{S}$ $\mathbf{C}'^{(n+1)}$

Get new $\mathbf{C}^{(n+1)}=$ $(1-a)\mathbf{C}^{(n)}$ + $a\mathbf{C}'^{(n+1)}$

Is $\Delta\mathbf{C}^{(n)}$ small enough

Basis functions

The next issue is the basis functions, $\xi(r)$. There are several possibilities but the most natural basis functions would be the Slater functions. They are very close to the solutions of the hydrogen atoms.

$$\xi_k(r) = P_n(r)\exp\left(-\zeta_k r\right)Y_{lm}(\theta,\varphi)$$

The $P_n(r)$ is some polynomial to make the functions more atomic like and Y_{lm} are the spherical harmonic functions. These atomic type functions are not very practical since the **J** and **K** integrals become tedious with them but they are still important for also other basis functions. The J and K matrixes can be solved numerically and at least one quantum chemistry (DFT) code ADF will use them as basis. One the other hand Gaussian functions can be used as basis functions.

$$\xi_k(r) = P_n(r)\exp\left(-\alpha_k r^2\right)Y_{lm}(\theta,\varphi)$$

With Gaussians the J and K integrals can be done analytically but we need more Gaussians to get good accuracy. It is close to an art to make a good Gaussian basis. The normal strategy is to optimize the Slater type function for an atom and then use several Gaussians (typically around 6) to present the Salter functions. Note that it is difficult to get the orbitals to match at origin.
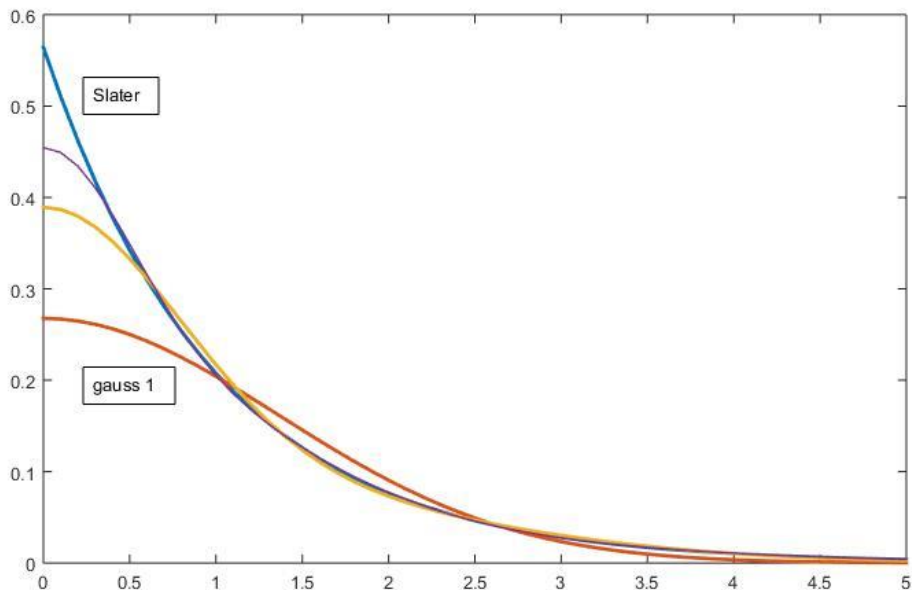
It is also difficult to fit the Slater function at larger distances. Below is the $r^2\xi_{1s}(r)$ orbitals plotted
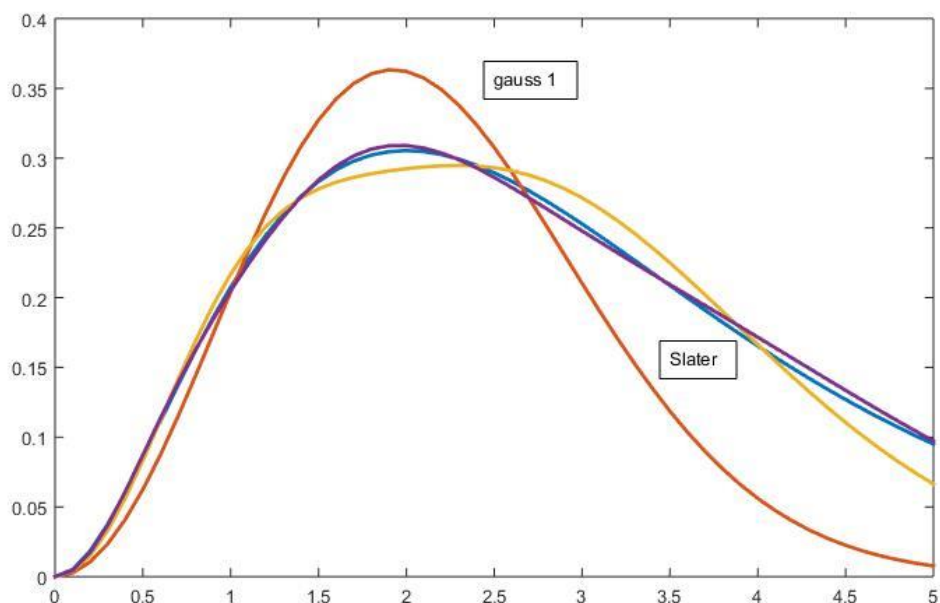
Even an atom might be well described with very few Slater functions (minimal basis set) a reliable description of molecules needs larger basis. Typically, higher angular momentums than the valence electrons have are needed, e.q. d-orbital for C, O, N etc. and p-orbitals for H. We need two (or more) exponents since in the molecule the wave functions decay from the nucleus is not symmetric.

For example the optimal zeta for hydrogen atom is =1 but for H_2 it is 1.19. In general we need a basis that will describe the atom in all bonding geometries and it will be impractical (difficult and time consuming) to develop an individual basis for each problem.

Polarization functions: basis functions with higher angular momentum

Double-zeta (DZ), triple-zeta (TZ) functions: basis functions with different exponents

Diffuse functions: very broad gaussians, needed for inter-molecular interactions.

The naming convention of is rather messy but the modern basis functions are usually named with zeta-functions (DZ,TZ, etc). Take a look of the Orca manual for further details.

cc-pVTZ   Dunning correlation concisistent polarized triple zeta
cc-(p)VTZ   Same but no polarization on hydrogen
Aug-cc-pVTZ   Same but including diffuse functions

Historically the first basis set's have been fitted to HF theory but almost all calculations include the correlation so it is better to tune the basis to correlated calculations. The cc-basis above takes correlation into account.

Extrapolation

As it is tedious to do calculations with several basis functions most of the quantum chemical codes include some automatic extrapolation methods. Usually the extrapolation methods that goes beyond TZ are very reliable.

Automatic basis set extrapolation

Extrapolate(n/m,bas) Extrapolate with basis family bas' (bas=cc,aug-cc ,ano, saug-ano, aug-ano; if omitted 'cc--pVnZ is used) and cardinal Numbers n,m (n<m=2,3,4,5). E.g. Extrapolate(2/3,cc) extrapolates the SCF, MP2 and MDCI energies to the basis set limit

Extrapolate(n,basis)   Calculate the first n---energies for member of the basis set family basis, e.g.Extrapolate(3) is doing calculations with cc--pVDZ, cc--pVTZ and cc--pVQZ

The HF theory and the basis functions will limit the accuracy of the calculations. If the basis is very good and in practice do not cause any practical error to the calculations the results are referred to be at the **HF limit**. With modern computers and rather small molecules it not difficult to get to the HF limit. But even then the results are not very good since the HF itself is not very accurate. Well some quantities, like bond distances,

are good with HF but for example the binding energies are
definitely not.

TABLE 16.2
Homolytic Bond Dissociation Energies (kJ/mol)

Molecule (bond)	Hartree-Fock Limit	Experiment	Δ
Ethane (H_3C—CH_3)	276	406	−130
Methylamine (H_3C—NH_2)	238	389	−141
Methanol (H_3C—OH)	243	410	−167
Methyl fluoride (H_3C—F)	289	477	−188
Hydrazine (H_2N—NH_2)	138	289	−151
Hydrogen peroxide (HO—OH)	−8	230	−238
Fluorine (F—F)	−163	184	−347

Note that even F_2 has negative binding energy (the two F atoms
are more stable than the molecule) it still have a local
minimum.

The geometries are good but most bonds are a bit too short
(about 1 %).

TABLE 16.5
Structures of One-Heavy-Atom Hydrides
(bond distances, Å; bond angles, °)

Molecule	Geometrical Parameter	Hartree-Fock Limit	Experiment	Δ
H_2	r(HH)	0.736	0.742	−0.006
LiH	r(LiH)	1.607	1.596	+0.011
CH_4	r(CH)	1.083	1.092	−0.009
NH_3	r(NH)	1.000	1.012	−0.012
	<(HNH)	107.9	106.7	−1.2
H_2O	r(OH)	0.943	0.958	−0.015
	<(HOH)	106.4	104.5	+1.9
HF	r(FH)	0.900	0.917	−0.017

Even the absolute binding energies are far from good often the relative energies are quite good.

TABLE 16.3

Relative Energies of Structural Isomers (kJ/mol)

Reference Compound	Isomer	Hartree-Fock Limit	Experiment	Δ
Acetonitrile	Methyl isocyanide	88	88	0
Acetaldehyde	Oxirane	134	113	21
Acetic acid	Methyl formate	71	75	−4
Ethanol	Dimethyl ether	46	50	−4
Propyne	Allene	8	4	4
	Cyclopropene	117	92	25
Propene	Cyclopropane	42	29	13
1,3-Butadiene	2-Butyne	29	38	−9
	Cyclobutene	63	46	17
	Bicyclo[1.1.0]butane	138	109	29

Also the vibrational frequencies are reasonable but the error can be more than 10 %. The HF overestimates the frequencies and often computed frequencies are scaled by a factor that is around 0.9. In general the frequencies are difficult quantities to compute since they are based of very small energy differences. The vibrations are computed as the second derivative of the total energy.

TABLE 16.7

Symmetric Stretching Frequencies in Diatomic and Small Polyatomic Molecules (cm^{-1})

Molecule	Hartree-Fock Limit	Experiment	Δ
Lithium fluoride	927	914	13
Fluorine	1224	923	301
Lithium hydride	1429	1406	23
Carbon monoxide	2431	2170	261
Nitrogen	2734	2360	374
Methane	3149	3137	12
Ammonia	3697	3506	193
Water	4142	3832	310
Hydrogen fluoride	4490	4139	351
Hydrogen	4589	4401	188

Spin

Everything above was written for the doubly occupied orbitals. It is easy to take the spin into account. We do not go to the details but the cases the total spin is not =0 one should use so called **Unrestricted HF** method, UHF.

Summary: **(U)HF is the basis of all traditional quantum chemical methods.** HF is not considered to be very accurate and in any serious quantum chemical calculations some "post HF" should be used.