3 | Hartree–Fock Theory

3.1 Hartree–Fock theory and the independent particle approximation

The simplest quantum chemistry method is the Hartree–Fock approach. This method relies on an independent particle approximation, where the wave function is expressed as a product of wave functions of single electron (orbitals). We will indicate orbitals with the lower-case Greek letter phi (ϕ). An orbital is a function of the coordinate vector $\mathbf{r} = (x, y, z)$ for an electron. To distinguish between different orbitals, we will label them with an index and write them as

$$\phi_i(\mathbf{r}) \qquad (3.1)$$

In the Hartree–Fock approach we approximate the wave function of N electrons as a product of the orbitals for each electron

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N) \qquad (3.2)$$

This approximation reduces the problem of solving the Schrödinger equation for a wave function of $3N$ coordinates into a simpler problem: we only need to determine N wave functions that depend on 3 spatial coordinates.[1] This simplification makes Hartree–Fock theory much more affordable than a direct solution of the Schrödinger equation!

3.2 Spin and the Pauli principle (antisymmetry)

The wave function form of Eq. (3.2) is still missing two important ingredients: 1) it does not account for the spin of electrons and 2) it does not obey the Pauli exclusion principle. Spin can be easily introduced by recognizing that the wave function of each electron must be accompanied by a spin function, that is, a label for the spin of the electron. As you have learned from previous classes, the spin of an electron can be either up (alpha, α) or down (beta, β).[2] So if we want to specify that an electron occupies the orbital ϕ_i and has spin alpha, we write the wave function $\phi_i(\mathbf{r})\alpha$. We can represent this wave function graphically with an orbital diagram in which one electron with up spin occupies the level i

$$\phi_i(\mathbf{r})\alpha \equiv \ \uparrow\!\!-\!\!-\ i \qquad (3.3)$$

[1] For example, imagine representing the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ using a grid that has 10 points along each dimension. For N electrons, this grid will have a total of 10^{3N} points since Ψ depends on $3N$ coordinates. In comparison, if we represent each orbital with the same grid, each orbital requires only 10^3 grid points, and the total number of grid points is $N10^3$. Even for as little as six electrons the exact wave function required already 10^{18} points, while the Hartree–Fock approach requires only 6000!

[2] This is not rigorously true.

In the case of beta electron, the graphical representation is similar but with a down arrow

$$\phi_i(\mathbf{r})\beta \equiv \ \downarrow \ i \tag{3.4}$$

When we do not want to be specific about the spin of the electron (and thus allow for both options), we will use instead the **spinorbital** notation based on the Greek letter psi $[\psi(x)]$ and use the variable $x = \{\mathbf{r}, \sigma\}$ to represent both the position vector ($\mathbf{r}$) and one spin coordinate (ω). For the moment, we can think of spin orbitals as always coming in alpha/beta pairs that share the same spatial orbital. To distinguish between alpha/beta orbitals we place a bar above the orbital index

$$\psi_i(x) = \phi_i(\mathbf{r})\alpha \tag{3.5}$$
$$\psi_{\bar{i}}(x) = \phi_i(\mathbf{r})\beta \tag{3.6}$$

Now we can be more precise and write the product wave function as

$$\Psi(x_1, x_2, \ldots, x_N) \approx \psi_1(x_1)\psi_{\bar{1}}(x_2)\cdots \tag{3.7}$$

Equation (3.7) is still not fully correct. To make sure that the wave function satisfies the Pauli exclusion principle, we have to enforce that the sign of $\Psi(x_1, x_2, \ldots, x_N)$ changes if we exchange the labels of any two particles. To illustrate this point, consider two electrons. The wave function $\Psi(x_1, x_2)$ depends on the position and spin of each electron (x_1, x_2), and it must change sign when we replace x_2 with x_1 and vice versa, which means[3]

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1) \tag{3.8}$$

It is easy to write down a wave function built from orbitals that satisfies this condition, it just requires making the product antisymmetric with respect to the coordinates. Such a wave function is called a **Slater determinant**[4] and for the two electron case is it written as[5]

$$\Psi_{\text{SD}}(x_1, x_2) = |\psi_i\psi_j\rangle = \frac{1}{\sqrt{2}}\left[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)\right] \tag{3.9}$$

Stater determinants correspond exactly to the orbital diagrams with orbitals filled with electrons (represented by arrows). For example, the electron configuration with two electrons filling the same orbital corresponds to the following Slater determinant

$$|\psi_1\psi_{\bar{1}}\rangle = |\phi_1\alpha\phi_1\beta\rangle \equiv \ \underset{\uparrow\downarrow}{\overline{}} \ \begin{matrix} 2 \\ 1 \end{matrix} \tag{3.10}$$

This electron arrangement is called a **closed shell**, because all the electrons are paired. It corresponds to a **singlet** electronic state.

However, we could also arrange the electrons in two different orbitals both with alpha spin in an **open-shell** configuration

$$|\psi_1\psi_2\rangle = |\phi_1\alpha\phi_2\alpha\rangle \equiv \ \begin{matrix} \uparrow \ 2 \\ \uparrow \ 1 \end{matrix} \tag{3.11}$$

[3] This wave function satisfies the Pauli principle in the sense that if the two electron have the same **space and spin** coordinates ($x_1 = x_2 = x$), then the wave function is zero because the condition

$$\Psi(x, x) = -\Psi(x, x)$$

can be satisfied only if $\Psi(x, x) = 0$.

[4] The Slater determinant is named after John C. Slater, who introduced the determinant in 1929 as a means of ensuring the antisymmetry of a many-electron wave function, although the wave function in the determinant form first appeared independently in Heisenberg's and Dirac's articles three years earlier. (Source: Wikipedia)

Fig. 3.1: John C. Slater.

[5] Here I use the symbol $|\psi_i\psi_j\cdots\rangle$ to indicate a general Slater determinant.

In this state, the spin of the electrons add up and we get what is called a **triplet state**.

We have covered a lot of details in this section, so I want to make sure that the important message comes across: **in the Hartree–Fock method the wave function of many electrons is approximated with a single Slater determinant**. This approach accounts for spin and satisfies the Pauli exclusion principle. We can also conveniently represent Slater determinants graphically with orbital diagrams.

3.3 The Hartree–Fock equation

The main goal of the Hartree–Fock method is to find the orbitals that give the "best" possible wave function. Here by "best" we mean precisely the one that minimizes the expectation value of the energy, which is given by the integral

$$E_{SD} = \int \Psi_{SD}^* \hat{H} \Psi_{SD} \tag{3.12}$$

The **variational** theorem guarantees that the energy of an approximate wave function $\tilde{\Psi}$ is always greater than the exact energy, $\tilde{E} \geq E_{exact}$, and the closer we get to the exact energy E_{exact}, the better our wave function $\tilde{\Psi}$ approximate the exact solution Ψ_{exact}.

The orbitals that minimize the energy satisfy the **Hartree–Fock equations**

$$\hat{f}\psi_i(x) = \varepsilon_i \psi_i(x), \quad \text{for all } \psi_i(x) \tag{3.13}$$

where $\hat{f}$ is the **Fock operator**. This is an eigenvalue equation like the Schrödinger equation, but it is simpler because it only involves one orbital at the time (a functions of 3 coordinates only). However, it is important to remember that this equation is valid only in the Hartree–Fock approximation. The quantity ε_i is called the **orbital energy** and it is the eigenvalue corresponding to the orbital ψ_i.

The physical interpretation of the Hartree–Fock equation is that we can approximate the interaction (repulsion) of an electron in orbital ψ_i with all the remaining $N - 1$ electrons via an average potential. The Fock operator is defined as

$$\hat{f} = \underbrace{-\frac{1}{2}\nabla^2}_{\text{kinetic}} + \underbrace{-\sum_i^{\text{nuclei}} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|}}_{\text{electron-nuclear}} + \underbrace{\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}}_{\text{Coulomb interaction}} + \text{exchange interaction} \tag{3.14}$$

and it contains two terms that depend on the distribution of electrons. One of these two terms is the **Coulomb interaction** of an electron with all the other electrons and it is proportional to the density of electrons (ρ). This term has a classical interpretation: it represents the Coulomb interaction of an electron with a charge distribution.[6] The electron density is in turn given by the sum of the square of the occupied orbitals, which for a closed-shell molecule is given by

$$\rho(\mathbf{r}) = 2 \sum_i^{\text{occupied}} |\phi_i(\mathbf{r})|^2 \tag{3.15}$$

[6]The term labeled **exchange interaction** is a bit more complicated to write down. It comes from imposing the Pauli principle and it does not have a classical interpretation.

The Hartree–Fock equations and these last two equations tell us that to find the orbital we need to know $\hat{f}$, but to know $\hat{f}$ we need to know the density, which is determined by the orbitals

$$\psi_i \leftarrow \hat{f} \leftarrow \rho \leftarrow \psi_i \tag{3.16}$$

In practice this means that the Hartree–Fock equations have to be solved via a **self-consistent-field (SCF) procedure** where one first starts with a guess for the orbitals and then proceeds to improve the solution iteratively.

The SCF procedure consists of the following steps:

1. Forming an initial guess. At beginning of an SCF procedure we need to start from orbitals that are close to the optimal ones. Common ways to guess the orbitals include neglecting electron repulsion or forming the average potential from a superposition of atomic densities.

2. Updating the Fock matrix. Using the current set of orbitals, the average potential and the Fock operator are built.

3. Determining the orbitals and orbital energies. Using the current Fock matrix, the Hartree–Fock equations are solved to obtain one set of orbitals and orbital energies and an updated value for the total energy.

4. Convergence check. The program checks if the change in energy and orbitals with respect to the previous iteration is less than a predefined convergence threshold. If the computation has converged, we stop. Otherwise, we go back to step 2. and use the new set of orbital to compute a new Fock operator.

The following is the output of a Hartree–Fock computation on water. In this example, the iterations start with a guess of the density given by the superposition of atomic densities (SAD)[7] As the iterations progress, the energy becomes lower and lower (in accordance with the variational principle) and we reach convergence in eight iterations to the final value $-76.02665366185\ E_{\mathrm{h}}$. Note that in the last step the energy is converged to $-5.4 \times 10^{-10}\ E_{\mathrm{h}}$.[8]

[7]Computational chemists love acronyms. With time you will become conversant with this language.

[8]Quantum chemistry computations are usually converged to high accuracy. It is not uncommon to see the energy optimized to less than 10^{-7}–$10^{-8}\ E_{\mathrm{h}}$, and in certain cases down to even $10^{-12}\ E_{\mathrm{h}}$.
The quantity labeled "RMS |[F,P]|" measures the derivative of the energy, and it is another way to monitor the convergence (remember that at a minimum, the gradient is zero). The label "DIIS", indicates that the code is using the direct inversion of the iterative subspace (DIIS) algorithm to accelerate the convergence.

```
 Water/Hartree-Fock
 ==> Iterations <==
                     Total Energy        Delta E      RMS |[F,P]|

@RHF iter SAD:    -75.50773245935    -7.55077e+01    0.00000e+00
@RHF iter   1:    -75.95378451304    -4.46052e-01    3.03072e-02 DIIS
@RHF iter   2:    -76.00708060915    -5.32961e-02    1.73589e-02 DIIS
@RHF iter   3:    -76.02624491762    -1.91643e-02    1.58426e-03 DIIS
@RHF iter   4:    -76.02663310976    -3.88192e-04    3.65265e-04 DIIS
@RHF iter   5:    -76.02665270339    -1.95936e-05    6.70876e-05 DIIS
@RHF iter   6:    -76.02665363515    -9.31757e-07    1.06688e-05 DIIS
@RHF iter   7:    -76.02665366131    -2.61654e-08    1.50538e-06 DIIS
@RHF iter   8:    -76.02665366185    -5.39330e-10    3.50179e-07 DIIS
   Energy and wave function converged.
```

3.4 Interpretation of the orbital energies

It is important to understand the precise meaning of the orbital energies ε_i because it is slightly different than our intuition as chemists. **Koopmans' theorem** shows that the orbital energies are related to the energy necessary to remove or add electrons to an orbital. More precisely, for orbitals that are occupied by electrons, Koopmans' theorem says that $-\varepsilon_i$ correspond to the energy necessary to remove one electron (ionize) from the system

$$M \longrightarrow M^+ + e^-$$
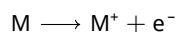
Koopmans' theorem can be stated as

> Ionization potential for electron in $\psi_i = \text{IP}_i = E^{N-1} - E^N = -\varepsilon_i.$ \hfill (3.17)

If an occupied orbital has a negative energy, then we have to put energy into a molecule to remove that electron (the IP is positive).

Similarly, for orbitals that are not occupied, the orbital energy ε_a corresponds to the energy released when an electron is added to form an anion (if the starting molecule is neutral)

$$M + e^- \longrightarrow M^-$$
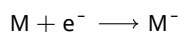
In this case, Koopmans' theorem helps us quantify the electron affinity

> Electron affinity for electron in $\psi_a = \text{EA}_a = E^N - E^{N+1} = -\varepsilon_a.$ \hfill (3.18)

Therefore, if an unoccupied orbital has a negative energy (positive EA), a molecule will attach an electron and form a stable negative ion. If instead ε_a is positive, a molecule will not accept an electron, and its anion will be unstable with respect to self ionization (the anion will spontaneously loose an electron in a finite amount of time).

Koopmans' theorem assumes that during the electron ionization/attachment the orbitals do not change, which means that it ignores relaxation effects to the addition or removal of electrons. Koopmans' theorem also neglects electron correlation, so the IP and EA will deviate from experiment. This means that in practice Koopmans' theorem is not a very accurate way to compute the IP and EA of molecules. Nevertheless, it gives physical meaning to the orbital energies and it can be used to qualitatively estimate the IP and EA of molecules.

The importance of Koopmans' theorem is that it build a bridge to experiments that measure the IP and EA of molecules. For example, photoelectron spectroscopy, can measure the ionization potential (also called the binding energy) of electrons in different orbitals. In this spectroscopy, a molecule is ionized with a high energy photon and one electron is released with kinetic energy equal to the energy of the photons ($h\nu$) minus the binding energy, $h\nu - IP$. Therefore, it allows to measure the binding energy of different orbitals. An example of the photoelectron spectrum of water in the gas phase is given in Fig. 3.3.

The example below shows the Hartree–Fock orbital energies of the occupied and unoccupied orbitals of an isolated water molecule in the gas phase.
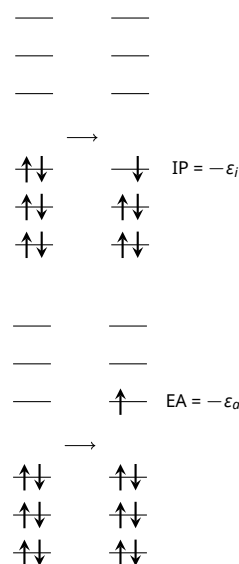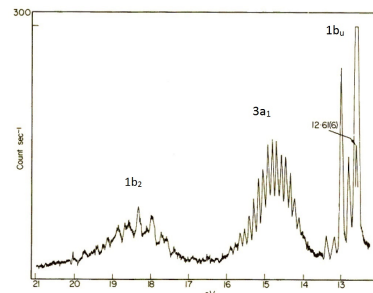

Fig. 3.2: Illustration of Koopmans' theorem.

Fig. 3.3: Photoionization spectrum of water in the gas phase (in eV). Source: Wikimedia Commons.

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Water/Hartree-Fock
Orbital Energies [Eh]
  --------------------
  Doubly Occupied:

     1A1   -20.550918     2A1    -1.335304     1B2    -0.697799
     3A1    -0.566090     1B1    -0.492954

  Virtual:

     4A1     0.185103     2B2     0.255850     3B2     0.787301
     5A1     0.851798     6A1     1.163709     2B1     1.200353
     4B2     1.253480     7A1     1.444918     1A2     1.475588
     3B1     1.674083     8A1     1.867861     5B2     1.931955
     6B2     2.446380     9A1     2.483524     4B1     3.283306
     2A2     3.336170    10A1     3.506961    11A1     3.862825
     7B2     4.144454


  Final Occupation by Irrep:
          A1    A2    B1    B2
  DOCC [    3,    0,    1,    1 ]

 @RHF Final Energy:    -76.02665366185380


  => Energetics <=

  Nuclear Repulsion Energy =              9.1681932964243487
  One-Electron Energy =               -123.1035625229022514
  Two-Electron Energy =                 37.9087155646241101
  Total Energy =                       -76.0266536618537998
```

The lowest ionization potential of water is estimated according to Koopmans' theorem from the energy of the highest occupied MO (HOMO, labeled $1b_1$), which has an energy of -0.493 E_h. The corresponding IP is equal to 0.493 E_h = 13.4 eV, a value that compares well with the experimental gas-phase IP (ca. 12.6 eV, indicated in the figure). The ionization potential for the second orbital (labeled $3a_1$) is 0.566 E_h = 15.4 eV. This corresponds to the middle broad band in the spectrum centered around 15 eV. Note that Koopmans' theorem applied to the Hartree–Fock solution also predicts that the anion H_2O^- is unstable with respect to the process ionization process

$$H_2O^- \longrightarrow H_2O + e^-$$
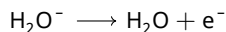
since the energy of the first unoccupied orbital (virtual) is positive (0.185 E_h).