Master de Chimie, M1

Quantum Chemistry

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Avertissement : _this lecture intends to introduce quantum theory starting from the principles of quantum mechanics. Important notions such as orbitals, the construction of molecular orbitals are introduced to analyse electronic structures from a theoretical point of view._

Bilbiography :

- T. Albright, J. K. Burdett, M. Whangbo : _Orbital Interaction in Chemistry._

- P. W. Atkins and R. S. Friedman : _Molecular Quantum Mechanics._

- J. K. Burdett : _Chemical Bonding in Solids._

- J. L. Rivail : _Eléments de Chimie Quantique à l'Usage des Chimistes._

- C. Cohen-Tannoudji, B. Diu, F. Laloë : _Mécanique Quantique._

1. **Quantum mechanics basics**

   (a) Fundamental principles

   In quantum mechanics, the point of view is radicaly different from the dominant one in classical mechanics. For instance, a particle of charge q and mass m positioned in $\mathbf{r}$ in space is described by a function, named wavefunction $\varphi(\mathbf{r})$.

   Observable quantities are formulated as operators and one refers to as representations, usually _r representation_. In one dimension, position, momentum and kinetics energy operators read :

   $$\begin{aligned} x &\rightarrow x \times \\ p_x &\rightarrow \frac{\hbar}{i}\frac{\partial}{dx} \\ T = \frac{p_x^2}{2m} &\rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \end{aligned}$$

   Note : these expression can be extended to three dimension-space.

   The Hamiltonian $\hat{H}$ is associated to the total energy. An electron moving in the field of a fixed nucleus can be written :

   $$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{dx^2} - \frac{Ze^2}{4\pi\epsilon_0 x}.$$

The second term is the electrostatic potential energy.

In the following, we shall make extensive use of the so-called atomic units (a.u.) where formally $e = 1$, $m_e = 1$, $\hbar = 1$, $\frac{1}{4\pi\epsilon_0} = 1$.

(b) <u>Quantum mechanics postulates</u>

- The state of a system is fully captured by a mathematical function $\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots, t)$. where the $\mathbf{r_1}, \mathbf{r_2} \ldots$ stand for the particle coordinates.

- Position x and momentum p_x operators satisfy particular rules featuring the Heisenberg uncertainty principle

$$[x, p_x] = x p_x - p_x x = i\hbar$$

- The mean value of an operator $\hat{\Omega}$, $\langle \hat{\Omega} \rangle$, in a normalized state Ψ (*i.e.*, $\langle \Psi | \Psi \rangle = \int \Psi^* \Psi d\tau = 1$) reads :

$$\langle \hat{\Omega} \rangle = \int \Psi^* \hat{\Omega} \Psi d\tau.$$

Interpretation : Let us first assume *discretisation* of levels. Ψ can be decomposed as a linear combination of $\hat{\Omega}$ eigenvectors Ψ_n associated to eigenvalue ω_n one can easily show that :

$$\Psi = \sum_n c_n \Psi_n$$
$$\langle \hat{\Omega} \rangle = \sum_n |c_n|^2 \omega_n.$$

$\langle \Omega \rangle$ is mean value weighted by the appearance of the eigenstates in the expansion of Ψ.

- Born suggested the following interpretation of the wavefunction. The probability of finding the system in "position" $\mathbf{r_1}, \mathbf{r_2} \ldots$ is given by $|\Psi(\mathbf{r_1}, \mathbf{r_2}, \ldots)|^2 d\tau$.
  Such interpretation imposes some restrictions on the wavefunction $\int |\Psi|^2 d\tau < \infty$. *Important :* from now on, we shall impose the normalization condition $\int |\Psi|^2 d\tau = 1$.

- The wavefunction satisfies the time-dependent Schrödinger's equation :

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi.$$

Assuming separability between time and space variables, $\Psi(x, t) = \psi(x)\theta(t)$. The Schrödinger's equation splits in two :

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi,$$
$$i\hbar \frac{\partial \theta}{\partial t} = E\theta.$$

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The first equation is the *time-independent Schrödinger's equation.*
Note : the second equation can be easily solved and $\theta \sim e^{-iEt/\hbar}$.
Let us recall that the eigenvalues of any observables are quantized. In particular, the energy levels of a quantum system are discrete (*i.e.* integers can be used to label them). Finally, the eigenvectors form an orthogonal basis set. This property will be frequently used in the following.

(c) Matrix representation

From algebra, it is known that matrix multiplication is, in general, not commutative (*i.e.*, $A.B \neq B.A$). This property is relected in quantum mechanics such as $[x, p_x] = i\hbar$.

Note : The Dirac's notation "bracket" is very useful in quantum mechanics. Let us recall that $\langle \Psi_m | \hat{\Omega} | \Psi_n \rangle = \int \Psi_m^* \hat{\Omega} \Psi_n d\tau$. In the following, we shall write $\Omega_{mn} = \langle \Psi_m | \hat{\Omega} | \Psi_n \rangle$ as the matrix element.

Let us assume a $\{|n\rangle\}$ basis set. Any Ψ can be decomposed onto that basis and the Schrödinger's equation reads :

$$\hat{H} |\psi\rangle = \hat{H} \sum_n c_n |n\rangle = E\psi = E \sum_n c_n |n\rangle.$$

By multiplying by the bra $\langle m|$,

$$\sum_n c_n \langle m | \hat{H} | n \rangle = E \sum_n c_n \langle m | n \rangle.$$

Since the $\hat{H}$ eigenvectors are orthogonal, $\langle m | n \rangle = \delta_{mn}$, one gets :

$$\sum_n H_{mn} c_n = E c_m$$

Let us suppose that all off-diagonal matrix elements are zero, $H_{mn} = 0$. Then, the energy E is simply the diagonal element H_{mm}. Therefore, solving the Schrödinger's equation is just a diagonlization problem.

2. Two-level problem

(a) Perturbation treatment

This is a rather common situation in quantum chemistry. Let us start from $\hat{H}^0$ holding two known eigenvectors and eigenvalues :

$$\hat{H}^{(0)} |i\rangle = E_i^{(0)} |i\rangle \text{ with } E_1^{(0)} < E_2^{(0)}$$

And let us write the exact Hamiltonian as $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$.
Note : this is typically the situation when one has to build molecular orbitals (several nuclei acting on a given electron) starting from atomic orbitals (a single nucleus acting on an electron).

Any solution ψ can be decomposed as a linear combination of $|1\rangle$ and $|2\rangle$:

$$|\psi\rangle = a_1|1\rangle + a_2|2\rangle.$$

Since ψ is a solution of the Schrödinger's equation, one gets :

$$a_1(H - E)|1\rangle + a_2(H - E)|2\rangle = 0.$$

Projections onto $\langle 1|$ and $\langle 2|$ lead to the following equations :

$$a_1(H_{11} - E) + a_2 H_{12} = 0 \quad \text{and} \quad a_1 H_{21} + a_2(H_{22} - E) = 0$$

The solution $\psi = 0$ is not compatible with $\int |\psi|^2 d\tau = 1$. Therefore, one wants to avoid the solution $a_1 = a_2 = 0$, and this is done by setting the determinant to zero. One refers to the *secular determinant* :

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0.$$

The second-order equation is easily solved and leads to the energies :

$$E_\pm = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\left[(H_{11} - H_{22})^2 + 4H_{12}H_{21}\right]^{1/2}.$$

Let us recall that H is hermitian. Therefore, $H_{12}H_{21} = H_{12}H_{12}^* = |H_{12}|^2$, positive real value. Then, if the diagonal elements are not affected (*i.e.* $H_{ii}^{(1)} = 0$), $H_{ii} = E_i$. This assumption allows for a simplification of the following discussion. Let us define $\Delta E = E_2^{(0)} - E_1^{(0)}$ the energy difference between the interacting levels (see Figure 1). Assuming $|H_{12}| \ll \Delta E$, the solution can be expanded as :
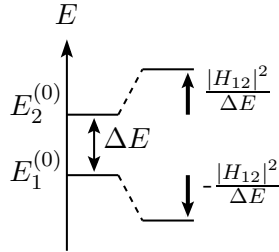

FIG. 1: Avoided crossing between two interacting levels.

$$E_+ \approx E_1^{(0)} - \frac{|H_{12}|^2}{\Delta E} \quad \text{and} \quad E_- \approx E_2^{(0)} + \frac{|H_{12}|^2}{\Delta E}$$

Let us comment on these results :

- The low-lying level is lowered in energy, whereas the high-lying one is pushed higher in energy. This is the so-called *avoided crossing* (see Figure 1).

- The *avoided crossing* is enhanced as the energy difference ΔE goes to zero. Evidently, the expansion is invalidared as soon as $\Delta E = 0$. However, for $\Delta E = 0$, $E_\pm = \frac{1}{2}\left(E_1^{(0)} + E_2^{(0)}\right) \pm |H_{12}|$.
- This general result is at the orgini of the core/valence separation.
- The wave functions expression can be obtained from the secular determinant and the expression of the eigenvalues. One can show that

$$|\psi_+\rangle \approx |1\rangle - \frac{|H_{12}|}{\Delta E}|2\rangle$$

$$|\psi_-\rangle \approx |2\rangle + \frac{|H_{12}|}{\Delta E}|1\rangle.$$

One often says that starting from the unperturbed Hamiltonian, both states get *contaminated* by the introduction of the perturbation.

(b) Variational method : generalisation

Another strategy consists in building the wave function, say a trial wavefunction Ψ, and to progressively modify $\Psi \to \Psi + \delta\Psi$ in order to minimize the energy. The Raleigh ratio is defined as :

$$\mathcal{E} = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle},$$

and one wants to reach $\delta\mathcal{E} = 0$ (stationnary condition).

The variational theorem states that the ground state energy E_0 is a lower bound for any function Ψ, $\mathcal{E} \geq E_0$. The equality holds as soon as Ψ is an eigen value of H.

In practice, one uses the Raleigh-Ritz method. We shall see how a variational problem (*mathematical minimisation*) is transformed into an algebra one (*secular determinant*).

Again, the idea is to expand the trial function Ψ on a basis set $\{\Psi_i\}$, $\Psi = \sum_i c_i \Psi_i$. The unknowns are now the coefficients of the expansion. For the sake of simplicity, let us assume that all coefficients are real values :

$$\mathcal{E} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{ij} c_i c_j S_{ij}},$$

where $H_{ij} = \langle\Psi_i|H|\Psi_j\rangle$ and $S_{ij} = \langle\Psi_i|\Psi_j\rangle$ (*overlaps* matrix).

The minimization of $\mathcal{E}$ is achieved by imposing $\partial\mathcal{E}/\partial c_k = 0$. As a result, a set of coupled linear equations must be solved :

$$\sum_i c_i \left(H_{ik} - \mathcal{E}S_{ik}\right) = 0$$

Again, to exclude the unacceptable solution $(c_1, c_1, \ldots) = (0, 0, \ldots)$, the *secular determinant* must be set to zero :

$$det|H_{ik} - \mathcal{E}S_{ik}| = 0.$$

The solutions of this polynomial in $\mathcal{E}$ are the eigenvalues, defining the spectroscopy. This is a very standard way of solving a problem in quantum chemistry. The trick is the introduction of a basis set.

3. Goals and objectives

(a) <u>Electrons behaviours</u>
The problem is multiple since different interactions, of same nature though, are to be treated :

- Nuclei have their own degrees of freedom. One may factorize the wave function, or simply consider nuclei as fixed particles.
- Electrons repel each other. Any independent picture might be invalidated
- Electrons do have an intrinsic magnetic moment. The wave function must include such property, possibly as a total spin.

(b) <u>Electronic density</u>
The density ρ is defined as the amount of charge per volume unit. The nuclear contribution is easily calculated since nuclei are considered as point charges :

$$\rho_{nuc}(\mathbf{r}) = \sum_A Z_A \times \delta(\mathbf{r} - \mathbf{R_A}),$$

with $\rho(\mathbf{r}) = \rho_{nuc}(\mathbf{r}) + \rho_{elec}(\mathbf{r})$. The electronic contribution ρ_{elec} must then be added.

(c) <u>Approximations and standard methods (semi empirical, DFT, ab initio)</u>
The objective is to evaluate ρ_{elec}.

- Most recent methods directly focus on the density and the method is named *Density Functional Theory*. This is the leading methodology, despite the need for some parametrization. The electron-electron interaction energy is described as a function of the density (and the density is a function of space. That is the origin of "functional").
- Historically, the Hartree-Fock method was first developed starting from original Hartree's views. The idea is to describe each electron dynamics in a mean field generated by the other electrons. There is a strong similariy with the concept of screening in atomic theory (see Figure 2). Unfortunately, fluctuations are not taken into account. The movements of electrons are not independent, and one must account for a description that goes beyond Hartree-Fock picture. These are called Configurations Interaction *CI* methods, where several configurations are explicitely included (in contrast with Hartree-Fock theory where a unique configuration is considered).
- Finally, *semi empirical* methods are based on a limited number of parameters to build up the electronic density. Most of these methods are mono-electronic in essence, projecting the complexity of electron-electron
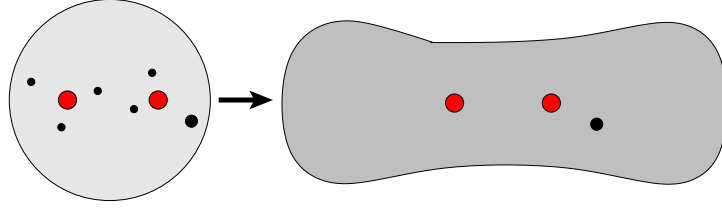
FIG. 2: Left : schematic view of the electronic structure of dinuclear system. Right : mean-field description of the dynamics of a single electron.

interactions into these parameters. Transferability of any parametrization is a central issue. Let us mention *Hückel* and *extended Hückel* theories which have been extensively used for conjugated polyenes.

4. Hydrogen atom quantification

(a) Description of the system
The system is just two interacting particles, a proton and an electron. It is known that the problem can be decomposed into a fictitious reduced mass positionned by the relative coordinates and a global movement of the center of mass. Let us concentrate on the fictitious particle and leave out the global movement :

- Since $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M_N}$ et $M_N \sim 2000 \times m_e$, $\mu \approx m_e$.
- Therefore, the center of masse is almos located on the nucleus and the problem has spherical symmetry.

In atomic units, the Schödinger's equation reads :

$$-\frac{\nabla^2}{2}\psi - \frac{1}{r}\psi = E\psi.$$

(b) Resolution of the Schrödinger's equation : *spherical harmonics*
It is rather tempting to separate the radial part from the angular by writing $\psi(r, \theta, \phi) = R(r).Y(\theta, \phi)$. The R function is the so-called *radial part* of the wave function. Let us first look into the equation the *angular part* Y obeys :

$$\left[\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}\right]Y = -E_lY.$$

The Y functions are the so-called spherical harmonics, traditionally denoted Y_{l,m_l} with $m_l = -l, -l+1, \ldots, 0, \ldots l-1, l$. Besides, the eigenvalues are $E_l = l(l+1)$.

- These *spherical harmonics* are solution of the particle on a sphere problem.
- For a given quantum number l value, the magnetic quantum number m_l has $2l + 1$ values.

- Since E_l does not depend on m_l, each level is $(2l + 1)$ degenerated.
  Examples : for $l = 0$, $m_l = 0$ is the unique possible value. It is an *s*-type orbital. For $l = 1$, m_l can be -1, 0 or +1. These orbitals p_x, p_y, p_z are in fact linear combinations of the spherical harmonics $Y_{1,-1}$, $Y_{1,0}$ et $Y_{1,1}$.
- Let us note L_z the projection of the angular momentum L on a quantification axis. The spherical harmonics are also eigenvectors of L_z, with eigenvalues m_l, $L_z Y_{l,m_l} = m_l Y_{l,m_l}$.

Attention : atomic units were used through out these manpulations. Do keep in mind that the unit of $[x, p_x]$, L is the one of $\hbar$.

By writing $R = \frac{u}{r}$, the u function satisfies a one-dimensional type Schrödinger's equation :

$$-\frac{d^2 u}{dr^2} + V_{eff}(r)u = Eu,$$

where $V_{eff}(r) = -\frac{1}{r} + \frac{l(l+1)}{2r^2}$ is an effective potential. The second term is named *centrifugal potential.* The problem can be analytically solved, and the n quantum number naturally appears. One can show that :

$$R(r) = R_{n,l}(r) \text{ and } n = 1, 2, \ldots \quad l = 0, 1, \ldots, n - 1$$

Definition : The solutions of a monoelectronic problem are called *orbitals.* The radial part of atomic orbitals are dominated by an exponentially decaying function :

$$R_{n,l}(r) = P(r).e^{-r/r_n} \text{ with } r_n = n^2 a_0.$$

P is a polynoma of degree $n - 1$ (Laguerre's polynoma) and $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius ($a_0 = 0.529$ Å).

Finally, the energy is directly controlled by the principal quantum number n :

$$E_n = -\left(\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\right)\frac{1}{n^2} = -\frac{13,6}{n^2} \ (eV).$$

(c) <u>Radial distribution</u>

The orbitals can be written as $\psi_{n,l,m} = R_{n,l}.Y_{l,m}$. Following Bohr's view, the probability of finding the electron in an elementary volume $d\tau$ is given by $|\psi_{n,l,m}|^2 d\tau$, where $d\tau = r^2 \sin\theta dr d\theta d\phi$ using spherical coordinates. Thus, the probabilyt of finding the electron at a given distance r is given by integrating over θ et ϕ :

$$P(r)dr = \int_0^\pi d\theta \int_0^{2\pi} d\phi R_{n,l}^2(r)|Y_{l,m}|^2 \sin\theta dr.$$

Spherical harmonics being normalized,

$$\int_0^\pi d\theta \int_0^{2\pi} d\phi |Y_{l,m}|^2 \sin\theta = 1.$$

$P(r) = R_{n,l}(r)^2 r^2$ is called the *radical distribution function*.

Note : extrema of this function give a classical view. One can show that r_{max} grows as n^2. Thus, the electrostatic energy being proportionaal to $1/r_{max}$, the $1/n^2$ law for the energy levels is recovered.

5. Polyelectronic atoms : the Helium case

(a) Analysis of the problem

In a system such as helium atom (nuclear charge $Z = +2$), an extra contribution arising from the electron-electron repulsion V_{ee} must be taken into account.
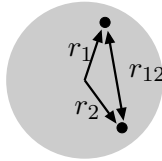

FIG. 3: Caracteristic distances in helium atom.

The Hamiltonian in atom units reads :

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

No analytical solution of the Schrödinger's equation can be found because of the presence of the $V_{ee}(r_{12}) = 1/r_{12}$ term.

(b) Orbital approximation

One can start considering V_{ee} as a perturbation. In that case, $\hat{H}^{(0)} = \hat{h}_1 + \hat{h}_2$ where $\hat{h}_1$ and $\hat{h}_2$ are *hydrogenoïd* Hamiltonians for which solutions are known. As a mater of fact, the resolution is rigorously the same as for the hydrogen atom, by changing the nucleus charge from $Z = 1$ to $Z = 2$. From the independency of the electrons, the solutions of $\hat{H}^{(0)}$ have the following form:

$$\psi\left(\mathbf{r_1}, \mathbf{r_2}\right) = \psi_{n_1,l_1,m_1}\left(\mathbf{r_1}\right).\psi_{n_2,l_2,m_2}\left(\mathbf{r_2}\right).$$

Let us stress that ψ is an approximate solution though, since the exact Hamiltonian reads $\hat{H}^{(0)} + \hat{V}_{ee}$. Such approximation is called the *orbital approximation*.

Let us insist on this definition : an orbital is monoelectronic wavefunction solution of a monoelectronic wave equation. Thus, the tota energy can be approximated as :

$$E = \epsilon_{n_1} + \epsilon_{n_2} \sim \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right).$$

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The energy correction δE to the previous energy is given by the mean value of V_{ee} in state ψ (*cf* perturbations theory) :

$$\delta E = \langle \psi_{n_1,l_1,m_1}.\psi_{n_2,l_2,m_2} | \frac{1}{r_{12}} | \psi_{n_1,l_1,m_1}.\psi_{n_2,l_2,m_2} \rangle$$

$$= \int |\psi_{n_1,l_1,m_1}|^2 \left(\frac{1}{r_{12}} \right) |\psi_{n_2,l_2,m_2}|^2 d\tau_1 d\tau_2 = J.$$

This quantity named as *Coulomb integral* is usually written in a compact way $J = (\psi_{n_1,l_1,m_1}\psi_{n_1,l_1,m_1}, \psi_{n_2,l_2,m_2}.\psi_{n_2,l_2,m_2})$. Numerically, J is of the order of a few eV and $E = 2E_{1,0,0} + J$ provides an estimation of the ground state energy of helium atom.

The situation is somewhat different when one examines excited states. Let us consider excited states ψ^* generated from the $1s^1 2s^1$ configuration. By exhanging the $\mathbf{r_1}$ et $\mathbf{r_2}$ coordinates (1 and 2 for simplicity), two functions can be generated, $\psi_1(1,2) = a(1)b(2)$ et $\psi_2(1,2) = a(2)b(1)$. One can immeditaly build the secular determinant from the linear expansion of ψ^* on ψ_1 et ψ_2. Let us evaluate the required matrix elements :

$$H_{11} = \langle a(1)b(2) | \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} | a(1)b(2) \rangle = \epsilon_a + \epsilon_b + J = H_{22}$$

$$H_{12} = \langle a(1)b(2) | \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} | a(2)b(1) \rangle$$

$$= \langle a(1)|\hat{h}_1|b(1)\rangle.\langle b(2)|a(2)\rangle + \langle b(2)|\hat{h}_2|a(2)\rangle.\langle a(1)|b(1)\rangle + K$$

$$H_{12} = H_{21},$$

where $K = \langle a(1)b(2) | \frac{1}{r_{12}} | a(2)b(1) \rangle$ is the *exchange integral*. Using the compact notation for the Coulomb integral, $K = (ab, ba)$: the terminology "exchange" is understood. The K integral is behind the famous *Hund'rule*.

Orbitals a and b are eigenvectors of a hermitian operator : they are orthogonal. Thus, the extradiagonal term is simply $H_{12} = K = H_{21}$ and the secular determinant reads :

$$\begin{vmatrix} \epsilon_a + \epsilon_b + J - E & K \\ K & \epsilon_a + \epsilon_b + J - E \end{vmatrix} = 0,$$

with finally

$$E_\pm = \epsilon_a + \epsilon_b + J \pm K.$$

The corresponding wavefunctions can be developped onto $a(1)b(2)$ et $a(2)b(1)$

$$\psi_\pm = \frac{1}{\sqrt{2}} \left(a(1)b(2) \pm a(2)b(1) \right).$$

- As expected the degeneracy between ψ_1 and ψ_2 functions is lifted by the electron-electron repulsion and the energy difference is just $2K$.

- For $\mathbf{r_1} \sim \mathbf{r_2}$, $\psi_-(\mathbf{r_1}, \mathbf{r_2}) \sim 0$. One refers to the *Fermi hole*, the presence of an electron in some region of space excluding the presence of any other electron. Thus, the electron-electron repulsion is reduced in ψ_-. This is to be contrasted with what is observed in ψ_+ since $\psi_+(\mathbf{r_1}, \mathbf{r_1}) \neq 0$. The electron-electron repulsion is larger in ψ_+ than in ψ_- and one can understand that $E_+ \geq E_-$.

- One can easily check that $\psi_-(\mathbf{r_1}, \mathbf{r_2}) = -\psi_-(\mathbf{r_2}, \mathbf{r_1})$ whereas $\psi_+(\mathbf{r_1}, \mathbf{r_2}) = \psi_+(\mathbf{r_2}, \mathbf{r_1})$. ψ_- and ψ_+ are said to be *antisymmetric* et *symmetric*, respectively.

(c) Electron spin

The wavefunction behaviour by permutation of electrons coordinates is crucial in quantum mechanics. Evidently, the intrinsic orbital momentum of electron has been omitted up to now.

Let us recall the algebra of kinetic moments coupling J_1 and J_2 leading to a total kinetic moment $J = J_1 + J_2$ with :

$$|J_1 - J_2| \leq \quad J \quad \leq J_1 + J_2$$
$$\text{or} \quad J = |J_1 - J_2|, |J_1 - J_2| + 1, \ldots, J_1 + J_2 - 1, J_1 + J_2$$
$$\text{and} \quad M_J = M_{J_1} + M_{J_2}.$$

Example : the electron holds a kinetic spin moment $s = 1/2$. If the electron evolves in a d orbital ($l = 2$) then the total kinetic moment $j = l + s$ has values ranging from $|l - s|$ to $l + s$, $j = 3/2, 5/2$. In a two-electron system, the total spin S can be either $S = 0$ (singlet state) or $S = 1$ (triplet state). Usually, α stands for the $|s = 1/2, m_s = 1/2\rangle$ spin state and β for $|s = 1/2, m_s = -1/2\rangle$ and the total spin wavefunctions read :

$$|S = 0, M_S = 0\rangle = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) - \alpha(2)\beta(1) \right)$$

and

$$|S = 1, M_S = -1\rangle = \beta(1)\beta(2)$$
$$|S = 1, M_S = 0\rangle = \frac{1}{\sqrt{2}} \left(\alpha(1)\beta(2) + \alpha(2)\beta(1) \right)$$
$$|S = 1, M_S = +1\rangle = \alpha(1)\alpha(2).$$

The three $S = 1$ components are symetrical upon $1 \leftrightarrow 2$ exchange. In contrast, the singlet spin function is antisymetric.

Note: the eigenvalues of the spin operator S^2 (valid for any kinetic moment) are $S(S + 1)$, that is 0 et 2.

(d) Determinantal structure of the wavefunction

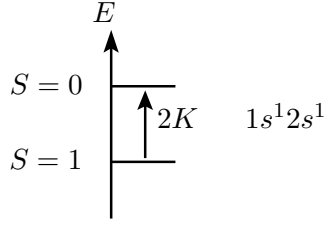*Pauli's principle :* the wavefunction of any electron system must be antisymetric

FIG. 4: Singlet-triplet splitting of the $1s^1 2s^1$ configuration : Hund's rule.

upon electron pair coordinates transposition. By coordinates, one refers to both space and spin components. Thus, the singlet wave function $S = 0$ must be associated to the symmetric space part ψ_+. In other words, the $1s^1 2s^1$ configuration of helium gives rise to a fundamental triplet state and a $2K$ higher in energy singlet state (see Figure 4). This is the origin of Hund's rule, a strictly non-classical phenomenon.

Extension : the spin degree of freedom allows us to introduce *spin-orbitals*. From any orbital (one-electron wavefunction) $\psi_{n,l,m}$ which is a function of space coordinates $\mathbf{r}$, we build two *spin-orbitals* :

$$\psi_{n,l,m}^{\alpha}(1) = \psi_{n,l,m}(\mathbf{r_1})\alpha(1) \quad \text{and} \quad \psi_{n,l,m}^{\beta}(1) = \psi_{n,l,m}(\mathbf{r_1})\beta(1)$$

Notations : $\psi_{n,l,m}^{\beta} = \overline{\psi_{n,l,m}}$ and $\psi_{n,l,m}$ the α spin-orbital.

From spin-orbitals, the antisymetry is automaticaly fulfilled if the wavefunction is written as a determinant, named *Slater's determinant* :

$$\psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix} = |ab|.$$

Such structure obeys the laws of quantum mechanics but remains an approximation. If electron 1 occupies orbital a, the electron 2 must be in orbital b. The double occupancy of a given orbital is not (configurations $|a\bar{a}|$ and $|b\bar{b}|$) are not taken into account, whereas they might appear at least in the singlet state. Several Slater's determinants must be included to progressively build up the exact state.

(e) Screening effect

One wishes to maintain the framework of orbitals even in polyelectronic atoms. Let us concentrate on electron **1**. One may to to account for electron-electron repulsion by introducing some approximation to recover a central potential :

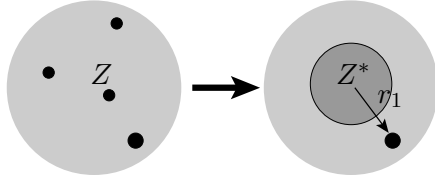$$V = \sum_{i \neq 1} \frac{1}{r_{1i}} \approx \frac{\sigma}{r_1}.$$

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FIG. 5: A given electron undergoes a *central potential* arising from an effective charge $Z^* = Z - \sigma$.

σ is an effective charge localized on the nucleus that should account of the presence of all the other electrons acting on electron **1**. The problem is significantly simplified since it is turned into a single electron problem moving in the field of a $Z^* = Z - \sigma$ nucleus (see Figure 5). Empirical and variational methods can be used to evaluate the screened charge.

6. Polynuclear system: study case of H_2

In a molecule, each individual electron feels the presence of several nuclei, breaking down the central character of the potential.

(a) Nature of the problem

Let us consider the H_2 molecule characterized by the R distance between the nuclei. For large distance separation, the total energy E is simply twice the one of a single hydrogen atom, that is -27.2 eV. At shorter distances, the nucleus-nucleus repulsion (at least !) contribute to the divergence of E. The dissociation curve displayed in Figure 6 gives the variation of E with respect to R. First, the move-
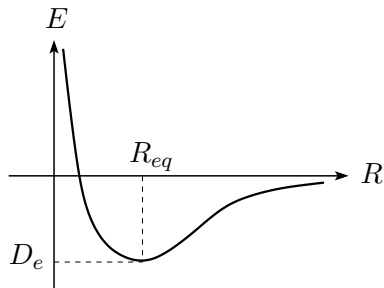

FIG. 6: *Dissociation* curve of a diatomic molecule. D_e stands for the dissociation energy.

ments of nuclei and electrons are separated following the Born-Oppenheimer's approximation. The variables **R** of the "heavy" particules (nuclei) are separated from the ones of the "light" particules (electrons) $\mathbf{r_i}$ in the expression of the total wavefunction $\Psi(R, r_1, r_2)$:

$$\Psi(R, r_1, r_2) = \psi(R, r_1, r_2)\xi(R).$$

By neglecting certain contributions, one can show that ψ a Schrödinger's equa-

tion, R being a parameter :

$$-\frac{\nabla^2}{2}\psi + V(R, r_1, r_2)\psi = E(R)\psi$$

The total energy E_{tot} simply reads $E_{tot} = E(R) + 1/R$.

(b) Linear combination of atomic orbitals

Let us A and B be the two protons separated by R. Qualitatively, the *linear combination of atomic orbitals* (LCAO) method can be illustrated on the H_2^+ cation. In the vicinity of nucleus A, the Hamiltlonian can be approximated by :

$$-\frac{\nabla^2}{2}\psi - \frac{1}{r_A}.$$

One recognizes the hydrogen atom Hamiltonian on A nucleus, the solutions of which are known. Thus the solution of our problem should behave as an atomic orbital in the vicinity of A (and B as well !). Acceptable solutions should be $\phi_A \pm \phi_B$ where ϕ_A et ϕ_B are the atomic orbitals localized on nucleus A and B, respectively.

More generaly, the molecular orbitals are written as linear combinations of the atomic orbitals :

$$\psi_{OM} = \sum_i c_i \phi_{OA,i}$$

The optimization of the c_i coefficients leads us back to the secular determinant. The so-called *overlap integrals* $S_{ij} = \langle \phi_i | \phi_j \rangle$ play a major role along this procedure. Atomic orbitals centered on different nuclei are not necessarily orthogonal.

Let us concentrate on the H_2 molecule to understand the notion of "overlap". This terminology can be understood by looking into the strucutre of the atomic orbitals localized on A and B (see Figure 7).
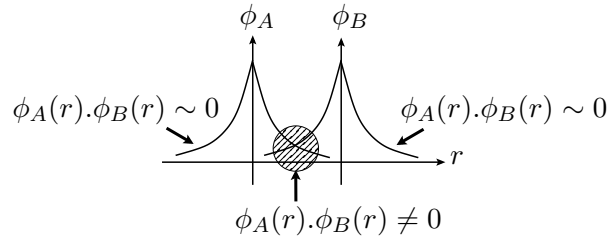

FIG. 7: *Overlap* concept : the grey zone corresponds to a domain where the product $\phi_A(r).\phi_B(r)$ has noticeable values. The orbitals "overlap" in such region of space.

Note : the atomic orbitals being normalized, $S_{AA} = S_{BB} = 1$ et we shall write $S = S_{AB}$ for the sake of simplicty. Overlap is a dimensionneless quantity.

Traditionally, the following short-hand notations are introduced $\alpha = H_{AA} = H_{BB}$ *Coulomb integral*, and $\beta = H_{AB} = H_{BA}$ *resonance integral* ($\beta \leq 0$). The solutions of the secular determinant 2×2 are readily accessible :

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$$

- Let us stress that in absolute value the destabilization is larger than the stabilization. This is contrasted with the approximate perturbative treatments.
- Is is easily shown that $S \to 0$ when $R \to 0$.
- A similar behaviour is expected for the resonance integral.
- Consequently, $E_+ \to \alpha$ and $E_- \to \alpha$ in the dissociation limit.
- The molecular orbitals can be fully expressed, using again the normalization condition :

$$c_A = c_B = \frac{1}{\sqrt{2(1+S)}} \quad \text{for} \quad E = E_+$$

$$c_A = -c_B = \frac{1}{\sqrt{2(1-S)}} \quad \text{for} \quad E = E_-.$$

These orbitals satisfy some symmetry properties g et u characteristic of systems holding a center of inversion.

7. A semi empirical method : the Hückel method

(a) σ/π separation

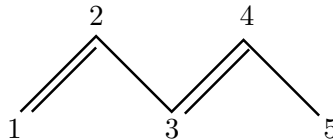In a conjugated polyene (see Figure 8), carbon atoms are all sp^2 hybridized. The

FIG. 8: Conjugated polyene : pentadiene.

network is defined by the interaction of orbitals which display cylindrical revolution along the bonds : one refers to the σ network. The three directions around a trigonal carbon are generated by linear combinations of atomic orbitals (LCAO) on a given site. One referes to *hybrid orbitals*. The fourth valence atomic orbital is availabe for the π network construction, more polarizable and reactive. From their s character, the σ orbitals lie lower in energy and a qualitative molecular orbitals spectrum is given in Figure 9.

The Hückel method concentrates on the valence part (see the highlighted window energy Figure 9), and more generaly upon the π system constructed upon a basis

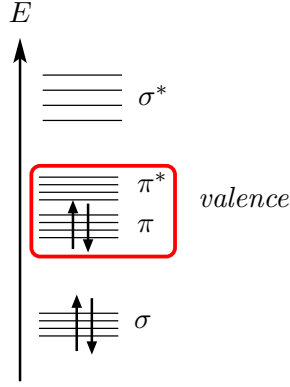FIG. 9: $\sigma - \pi$ separation in conjugated polyenes.

of $2p$-type atomic orbitals $\{\varphi_i\}$. Besides, the Hamiltonian is monoelectronic, a significant assumption that consists in adpating the parameters to reproduce some experimental evidence.

(b) <u>Resonance and Coulomb integrals</u>
The parametrization is derived from UV spectroscopy of thermodynamics, or from more elaborated calculations. *Transferability* of a set of parameters is a central issue, and more importantly the transferability of the resonance integral $h_{ij} = \langle \varphi_i | h | \varphi_j \rangle$. It is then assumed that $h_{ij} = \beta$ is independent of the i et j sites. In its simplest version (*Hückel*), it is supposed that this integral is zero for non-neigbhouring atoms, *i.e.* $h_{ij} = 0$ as soon as i et j are not nearest-neighbours. Besides, the overlaps S_{ij} being usually rather small, they are set to zero, $S_{ij} = 0$ for $i \neq j$. Finally, the Hückel method can be summarized as follows :

$$h_{ij} = \beta \quad \text{if} \quad i \text{ et } j \text{ are connected,}$$
$$h_{ij} = 0 \quad \text{otherwise, and}$$
$$S_{ij} = \delta_{ij}.$$

Example : For the system given in Figure 8, $h_{23} = \beta$ but $h_{24} = 0$.

However, β is very sensitive to the the relative orientation (see Figure 10).
One way to account for the angular dependency is to write :

$$\beta = \langle 2p_z | h | 2p_z \rangle = \beta_0 cos\left(\theta\right),$$

where the θ angle is given Figure 10.

Let us now examine the diagonal terms of the secular determinant. $h_{ii} = \langle \varphi_i | h | \varphi_i \rangle = \alpha$ is named *Coulomb integral* and corresponds to the energy of an electron staying in such orbital. Therefore, α is the ionization potential of the element.
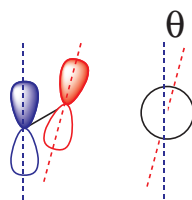
FIG. 10: Relative orientation of $2p$ type atomic orbitals that modulates the resonance integral.

Since in the Hückel method one concentrates on the π system, $\alpha = 0$ eV can be imposed by a simple change of the origin of the energies.

As an estimate, $\alpha/\beta \sim 1/10$ and all energies are measured with respect to β.

(c) <u>Construction of the secular determinant</u>
In the simplest version of the Hückel method, the construction is much simplified owing to the approximations. As an example, the secular determinant of the polyene represented in Figure 8 reads :

$$
\begin{vmatrix}
\alpha - E & \beta & 0 & 0 & 0 \\
\beta & \alpha - E & \beta & 0 & 0 \\
0 & \beta & \alpha - E & \beta & 0 \\
0 & 0 & \beta & \alpha - E & \beta \\
0 & 0 & 0 & \beta & \alpha - E
\end{vmatrix} = 0,
$$

and one traditionally introduces $x = \frac{\alpha - E}{\beta}$:

$$
\begin{vmatrix}
x & 1 & 0 & 0 & 0 \\
1 & x & 1 & 0 & 0 \\
0 & 1 & x & 1 & 0 \\
0 & 0 & 1 & x & 1 \\
0 & 0 & 0 & 1 & x
\end{vmatrix} = 0.
$$

Note : an order n equation arises, n being the number of carbon atoms. Once the energies $\{E_i\}$ are determined, by setting $E = E_i$ in the set of equations the molecular orbitals can be fully expanded remembering the normalization condition.

(d) <u>Advantages/drawbacks of the method</u>
It is very attractive for qualitative interpretation, giving quite reasonable a description of electronic densities. Orbital analysis can be carried out along with *electrophilicity* et *nucleophilicity*.

Evidently, electron-electron interactions are not taken into account. Besides, overalp integrals are all set to zero which makes the splitting between two degenerate levels strictly symetrical, $\alpha + \beta$ et $\alpha - \beta$. Reality is different and some precautions should be taken.

8. Quantitative approach of electronic structure

(a) <u>Setting the problem</u>
The difficulty lies in the the presence of the electron-electron repuslion term in the Hamiltonian.

    i. First, no analytical resolution is possible, and one would like to start with the orbital picture. Thus, electrons are "confined" in boxes the dimension of which are related to the electronic density.

    ii. The treatement of the instantaneous electron-electron interactions is a difficult task, and though gives rise to intriguing properties.

(b) <u>Mean field</u>
Evidently, some approximations must be made in view of the difficulties of the problem.

Whatever the nature of the system, atomic or moelcular, one would like to start with orbitals (*i.e.* one-electron wavefunction) to build up electronic configurations from Slater determinants. The concept of screening will be much used (see Figure 5) even if the field is no longer central.

(c) <u>Hartree-Fock method - Self-consistency</u>
For a system consisting of N electrons and M nuclei, the method consists in averaging the interaction of a given electron with the $N - 1$ others. Assuming the Born-Oppenheimer's approximation validity (*i.e.* fixed nuclei), let us write the Hamiltonian in atomic units :

$$\hat{\mathcal{H}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}}$$
$$+ \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

The problematic contribution is the electron-electron interactions term $\sum_{j>i} 1/r_{ij}$. A mean-field approximation does not mean that this term is simply neglected. The objective is rather to average such interactions and to ignore the *fluctuations*. In other words and using a simple writing, the Hartree-Fock approximation consists in substituting the term $\sum_{j>i} 1/r_{ij}$ by $\langle \sum_{j>i} 1/r_{ij} \rangle$. The electrons are then confined in orbitals and the the electronic state Ψ is approximated by a unique electronic configuration.

Let us summarize the Hartree-Fock approach and the search for the so-called *canonical* orbitals :

- Ψ is written as a unique Slater determinant, $\Psi = |a\bar{a}b\bar{b}\cdots|$ where a, b, $\cdots$ are the canonical orbitals

- Ψ makes the energy *stationnary*, that is :

$$\delta E = \delta \langle \Psi | \mathcal{H} | \Psi \rangle = 0$$

This procedure allows to average the interactions of a given electron with the $N-1$ others. It is a *mean field* approach and the method is *self-consistent* since the electronic interactions ruling $\mathcal{H}$ are defined by the orbitals, which are precisely the unknowns.

(d) Electronic correlation : H_2 as a study

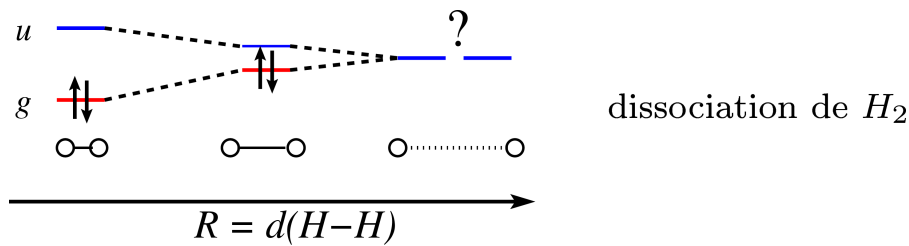A single electronic configuration might not be sufficient to depict the electronic structure.

FIG. 11: H_2 dissociation into $2H^\bullet$: degeneracy and non-validity of the Hartree-Fock method as R increases.

The system may "hesitate" between several electronic configurations. We know from quantum mechanics that in such situation that a superposition is necessary (*cf.* avoided crossing).

Let us examine the dissociation regime of the di-hydrogen molecule starting from the euilibrium geometry $R_{eq} = 0.7$ Å. In a minimal basis set, *i.e.* a single $1s$ type orbital on each hydrogen atom we shall refer to as a and b. The canonical molecular orbitals g et u are the in-phase and out-of-phase linear combinations *gerade* and *ungerade* constructed on a and b. In the vicinity of R_{eq}, the electronic state is fairly well described by the double-occupancy of g, $\Psi = |g\bar{g}|$ (see Figure 11). In contrast, g and u become quasi-degenerate in the limit $R \gg R_{eq}$ and no one can decide on $|g\bar{g}|$ over $|u\bar{u}|$. Therefore, Ψ must be an equal mixture of these two configurations :

$$\Psi = \frac{1}{\sqrt{2}}\Big(|g\bar{g}| - |u\bar{u}|\Big)$$

Note : the superposition of several electronic structures is well-known in organic chemistry, where *mesomerism* is a means to account for the presence of more than one Lewis form. Ψ is to be considered as an *hybrid of resonance* constructed on the *limiting forms* $|g\bar{g}|$ et $|u\bar{u}|$. The negative sign in the previous relation can be understood from the dissociation limit.

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Let us finally switch back to the atomic orbitals basis set, a and b. After a limited algebra, one can find :

$$\Psi = \frac{1}{\sqrt{2}}\Big(|a\bar{b}| + |b\bar{a}|\Big)$$

Attention : to perform the calculations, one should keep in mind the anisymetry character of a determinant (example : $|a\bar{b}| = -|\bar{b}a|$).

This particular regime, so-called *strong correlation*, highlights the limitation of the Hartree-Fock method. Is is very standard for open-shell systems, bond dissociation processes. The active center of biological systems such as hemoglobin (Fe^{2+} vs. Fe^{3+})
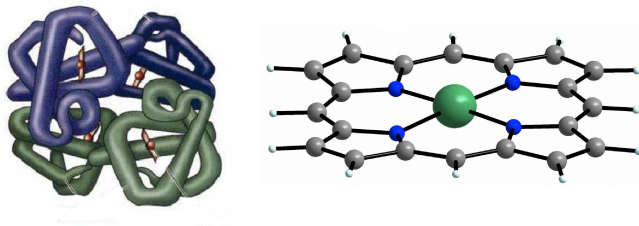

FIG. 12: Left, hemoglobin structure. Right, active center of hemoglobin.

is a prototype of situation where more than one configuration might be necessary (see Figure 12).

The description of electronic structures calls for demanding strategies since particles cannot be treated independently. The latter may invalidate any mean-field approach such as the Hartree-Fock method. Generaly speaking, an electronic state (sometimes accessible from experiments) might not be reduced to a single configuration. It is rather an approximation of a reality that quantum chemists try to build up step by step.