



Modern2023
4-7 Sep 2023 Paris (France)

Vademecum for Quantum Chemistry

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1. Introduction: why do we need Quantum Chemistry?

This document intends to present some of the most important concepts, basic properties and notations found in Quantum Chemistry (QC) and that will be extensively used in the more specific courses of this thematic school. This compendium is obviously very far from being comprehensive. As such, we refer the reader interested in deepening her/his knowledge on QC to the bibliographic references provided in the final section (please, note that neither such advanced knowledge nor mathematical details are requested for mastering the chemical analyses spanned by this formation).

Quantum mechanics (QM) is up to now the only mainstream physical theory that can explain the formation of chemical bonds, a task that classical mechanics (CM) and electromagnetism (EM) theories cannot achieve by themselves. Indeed, these two last theories fail, for instance, in accounting for the attraction of two *neutral* hydrogen atoms to form the dihydrogen molecule. Besides, in EM, the Earnshaw's theorem implies that a system of point charges cannot be maintained in a stable stationary equilibrium configuration solely by the electrostatic interaction, which may seem in apparent contradiction with matter stability that QM succeeds in explaining in a (up to now) unsurpassed way.

This achievement was only possible by a paradigm shift that leads to statements that sometimes contradict the intuitive understanding one can have of allegedly simple physical or chemical processes, as epitomized by the Heisenberg's uncertainty inequality that asserts that we cannot know both the position and speed of a particle with perfect accuracy. Fundamental notions in CM, such as trajectory, had to be abandoned, generating exciting epistemological issues we will not discuss here.

2. Basics of Quantum Mechanics

From an axiomatic point of view (unessential for our purposes), QM is based on several postulates, the primary one being that at any instant t , the state of a pure quantum *state* is fully determined by a normalized vector in a suitable Hilbert space, notated $|\Psi(t)\rangle$ in Dirac's notation. In practice, $|\Psi(t)\rangle$ is almost exclusively *represented* in QC by a complex-valued function, called *wavefunction*, whose variables are the spatial coordinates \vec{r}_m and the intrinsic spins \vec{s}_m associated to each of the N particles belonging to the studied system.¹

Gathering these variables into the $\vec{x}_m = (\vec{r}_m, \vec{s}_m)$ generic ones, $|\Psi(t)\rangle$ will thus be represented by the $\Psi(\{\vec{x}_m\}, t)$ function, whose time-evolution is governed by the celebrated Schrödinger equation (SE, 1926) that overlooks Schrödinger's grave in the Alpbach's cemetery in Austrian Tyrol:

¹ An alternative, fully equivalent, sometimes found in physics, is the *momentum* representation. The two representations are linked by Fourier transforms.

$$i\hbar \frac{\partial}{\partial t} \Psi(\{\vec{x}_m\}_{1 \leq m \leq N}, t) = \hat{H} \Psi(\{\vec{x}_m\}_{1 \leq m \leq N}, t), \quad (1)$$

where \hat{H} is called the *Hamiltonian*, which will be described more in detail below. The use of SE implies that *relativistic* effects have not to be taken into account, an assumption that can become arguable for chemical elements after the third period of the periodic table for which the velocity of the core electrons is not anymore negligible with respect to the speed of light.²

It is fundamental to notice that only **one** function of several variables is needed, in strong contrast with a Newtonian description in which the same system would be described by a set of N **coupled** differential equations, each of them describing the trajectory of each particle. To quote Feynman, “the effect of the entire History on the future of the universe could be obtained from a single gigantic wavefunction”.

Mathematically, \hat{H} is an *operator*. This means that its action on a function will generate another function. More generally, in QM, every physical quantity P that can be measured is associated to a dedicated operator \hat{P} , called an *observable* which is linear: it transforms any linear combination of functions into the same linear combination of the function images ($\hat{P}(\lambda f + \mu g) = \lambda \hat{P}f + \mu \hat{P}g$). Coming back to the SE, \hat{H} is actually nothing more than the observable corresponding to the total energy of the system.

An important case (and the only one that we will discuss here) is the class of stationary Hamiltonians, \hat{H}^{st} , that do not explicitly depend on the time variable (this assumption for instance excludes the cases of a molecule in interaction with an external oscillating electromagnetic wave), for which the wavefunction can be exactly separated into a function A depending only on t and a function ψ depending only on the \vec{x}_m variables according to:

$$\Psi(\{\vec{x}_m\}, t) = A(t) \times \psi(\{\vec{x}_m\}_{1 \leq m \leq n}). \quad (2)$$

The last function is solution of the so-called *stationary* SE (SSE):

$$\hat{H}^{st} \psi(\{\vec{x}_m\}) = E \psi(\{\vec{x}_m\}_{1 \leq m \leq n}), \quad (3)$$

where E is a *real* number. From a mathematical point of view, ψ is an eigenvector of the Hamiltonian operator. It can also be shown that, for real chemical systems, the eigenvalue E cannot be any number, but should belong to a precise *countable* set of allowed values, \mathcal{E} . This is the famous *quantization* of the total energy. Furthermore, it can be proven that \mathcal{E} admits a *minimal* value, $E^{(0)}$. This last one is called the *ground state* (GS) energy of the system, and the corresponding wavefunction is called the GS wavefunction, $\psi^{(0)}$. All other possible values for E will correspond to *excited* states.

² One should then shift towards the more intricate Dirac equation.

3. Basics of Quantum Chemistry

3.1. The molecular Hamiltonian

Up to now, these generalities are valid for any quantum system. We will now restrict our attention to chemical ones, consisting in n_α nuclei of charge $Z_\alpha e$ (where $e = 1.602 \cdot 10^{-19}$ C is the elementary charge), with spatial coordinates \vec{r}_α and in n_e electrons (charge $-e$) with coordinates \vec{r}_i (in other words, $\{\vec{r}_m\}_{1 \leq m \leq N} = \{\{\vec{r}_\alpha\}_{1 \leq \alpha \leq n_\alpha}, \{\vec{r}_i\}_{1 \leq i \leq n_e}\}$).

Most QC calculations are then based on a further approximation, the Born-Oppenheimer (BO) one, which can break down in case of light nuclei or if electronic states are closed in energy, but which reveal robust for main applications in organic chemistry where the error induced by the BO approximation is much lower than those stemming from the other QC computational parameters. BO separates nuclei and electrons roughly based on the fact that the first ones being heavier exhibit a much lower velocity. The molecular wavefunction is then approximated by the following ansatz:

$$\psi(\{\vec{x}_m\}_{1 \leq m \leq n}) = \psi_v(\{\vec{x}_\alpha\}_{1 \leq \alpha \leq n_\alpha}) \times \psi_e(\{\vec{x}_i\}_{1 \leq i \leq n_e}; \{\vec{r}_\alpha\}_{1 \leq \alpha \leq n_\alpha}), \quad (4)$$

where the nuclear ψ_v wavefunction describes rotational and vibrational effects, while the *electronic wavefunction*, ψ_e , is computed for each $\{\vec{r}_\alpha\}_{1 \leq \alpha \leq n_\alpha}$ configuration (in other words, the coordinates of the nuclei are considered as fixed *parameters* to determine ψ_e)³ and is solution of the *electronic SE*:

$$\widehat{H}_e^{st} \psi_e^{(n)}(\{\vec{x}_i\}_{1 \leq i \leq n_e}; \{\vec{r}_\alpha\}_{1 \leq \alpha \leq n_\alpha}) = E_e^{(n)} \times \psi_e^{(n)}(\{\vec{x}_i\}_{1 \leq i \leq n_e}; \{\vec{r}_\alpha\}_{1 \leq \alpha \leq n_\alpha}), \quad (5)$$

where $n = 0$ corresponds to the *electronic GS* and $n \geq 1$ to the various electronic excited states. If one adds the electrostatic nuclei repulsion energy (given by Coulomb's law and that is constant for a given electronic state within the BO approximation), one ends up with the GS molecular energy:⁴

$$E_{mol}^{(0)} = E_e^{(0)} + \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{\|\vec{r}_\alpha - \vec{r}_\beta\|}. \quad (6)$$

Coming back to eq. 5, the *electronic Hamiltonian* \widehat{H}_e^{st} can be expressed as the sum of the electronic kinetic operator \widehat{T}_e and the potential energy operator \widehat{V} . The first one involves the Laplacian operator with respect to all electronic position coordinates:

$$\widehat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n_e} \nabla_i^2, \quad (7)$$

where $\hbar = h/(2\pi)$ is the reduced Planck constant, m_e the electron mass and (in Cartesian coordinates) $\nabla_i^2 f = \frac{\partial^2 f}{\partial x_i^2} + \frac{\partial^2 f}{\partial y_i^2} + \frac{\partial^2 f}{\partial z_i^2}$. The potential energy operator can be divided into two contributions, that

³ This does mean that nuclei cannot move: in a so-called BO molecular dynamics (BOMD) calculation, **once** ψ_e has been determined, all forces, including those exerted by the electrons on the nuclei, can be computed, and the nuclei will then be displaced according to them, leading to another nuclei configuration on which a new ψ_e will be determined.

⁴ This is not the internal energy at 0K since zero-point vibrational contributions are missing. More generally, the calculation of thermodynamical contributions are outside the scope of this document.

corresponding to the attraction of each electron by each nucleus (\widehat{V}_{ne}) and the bielectronic repulsion (\widehat{V}_{ee}) between each atom pair, and whose expression directly follows from Coulomb's law (v_{ne} and v_{ee} functions) translated in the language of operators (\widehat{V}_{ne} , \widehat{V}_{ee}) in accordance with the correspondence principle:

$$\widehat{V} = \underbrace{-\frac{e^2}{4\pi\epsilon_0} \sum_{\alpha=1}^{n_\alpha} \sum_{i=1}^{n_e} \frac{Z_\alpha}{\|\vec{r}_\alpha - \vec{r}_i\|}}_{\widehat{V}_{ne}} \times + \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{n_e-1} \sum_{j>i} \frac{1}{\|\vec{r}_i - \vec{r}_j\|}}_{\widehat{V}_{ee}} \times, \quad (8)$$

where the \times symbol (generally omitted in the specialized literature) explicitly stresses the *multiplicative* nature of these operators (i.e. $\widehat{V}_{ne}\psi_e = V_{ne} \times \psi_e$). It is common practice in the QC literature to use *atomic units* (a.u.) in order to simplify such expressions. In this unit system, $e = \hbar = m_e = 4\pi\epsilon_0 = 1$, and it will be used exclusively in the following unless otherwise stated. The electronic Hamiltonian then reads:

$$\widehat{H}_e^{st} \Big|_{a.u.} = -\frac{1}{2} \sum_{i=1}^{n_e} \nabla_i^2 - \sum_{\alpha=1}^{n_\alpha} \sum_{i=1}^{n_e} \frac{Z_\alpha}{\|\vec{r}_\alpha - \vec{r}_i\|} \times + \sum_{i=1}^{n_e-1} \sum_{j>i} \frac{1}{\|\vec{r}_i - \vec{r}_j\|} \times. \quad (9)$$

Energies are then expressed in *Hartree*, the usual conversion factors being: $1 E_h = 27.21 eV = 627.51 kcal/mol = 2625.5 kJ/mol$.

It should be underlined that, as we are not dealing with magnetic properties and for the sake of simplicity, we have not included potential operators involving spins (for instance spin-orbit coupling) even if the presented methodology allows for integrating them into a straightforward way.

The main goal of QC is to solve eq. 5. Unfortunately, it can be exactly done only for very few systems, so that approximation methods are needed. They can be roughly classified in two main families: *WaveFunction Methods* (WFMs) and *Density Functional Theory* (DFT). Among the most widespread WFMs, one finds Hartree-Fock (HF), Møller-Plesset (MP), Configuration Interaction (CI) and Coupled-Cluster (CC) approaches. DFT will be the topic of a following section.

3.2. Hartree-Fock approximation and the correlation energy problem

All these methods take into account some constraints on the wavefunction. The first one is the *normalization* condition. Indeed, in the probabilistic interpretation (Born rule), the elementary probability to find at the same time t electron 1 inside an infinitesimal volume d^3r_1 centered at point \vec{r}_1 , electron 2 inside an infinitesimal volume d^3r_2 centered at point \vec{r}_2 and so on... is equal to (for the sake of clarity, spin variables have been not considered here and notations have been simplified) $|\psi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{n_e})|^2 d^3r_1 d^3r_2 \dots d^3r_{n_e}$. As the sum of all these probabilities should be equal to 1 when all possible space positions are considered,

$$\int \int \dots \int |\psi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_{n_e})|^2 d^3r_1 d^3r_2 \dots d^3r_{n_e} = 1, \quad (10)$$

where all integrals extend over whole space. More precisely, in QM, only the square of the wavefunction has a physical meaning. As a consequence, dephasing ψ_e by a constant real angle θ ($\psi_e \rightarrow \psi_e \times e^{i\theta}$) will lead to the *same* quantum state.

The second important condition comes from the fact that all electrons are *indistinguishable*. This implies that if two particles are exchanged in the wavefunction, the electronic *state* should remain the same. In virtue of our previous remark, electron permutation can actually only generate dephasing. As electrons are half-integer-spin particles, the spin-statistics theorem gives that the dephasing is exactly equal to π . In other words, ψ_e must be *antisymmetric* with respect to electron permutation (please note that electron spin variables here have to be taken into account), here illustrated on electrons 1 and 2:

$$\psi_e(\vec{x}_2, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_{n_e}) = -\psi_e(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_{n_e}). \quad (11)$$

As a first illustration, we now consider the electronic GS of the H₂ molecule in its GS state as discussed in undergraduate courses. By convention, the eigenfunctions of the \widehat{S}_z electronic spin operator⁵ are denoted α (for the +1/2 eigenvalue in atomic units) and β (for the -1/2 eigenvalue). More colloquially, α corresponds to the “spin *up*” orientation and β to the “spin *down*” one. In the molecular orbital (MO) formalism, two electrons occupy the (normalized) σ_g bonding MO, described by the real function $\sigma_g(\vec{r})$ defined in the 3D-space, with opposite spins. At first sight, the corresponding molecular electronic wavefunction may read as a simple product, $\psi_e(\vec{r}_1, \vec{r}_2, s_1, s_2) = \sigma_g(\vec{r}_1)\sigma_g(\vec{r}_2)\alpha(1)\beta(2)$, but this does not fulfil the antisymmetry condition. The antisymmetry is recovered if the spin contribution is actually replaced by $\alpha(1)\beta(2) - \alpha(2)\beta(1)$. Interestingly, the obtained wavefunction can be conveniently put in a determinantal form according to:

$$\psi_e(\vec{r}_1, \vec{r}_2, s_1, s_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g(\vec{r}_1)\alpha(1) & \sigma_g(\vec{r}_1)\beta(1) \\ \sigma_g(\vec{r}_2)\alpha(2) & \sigma_g(\vec{r}_2)\beta(2) \end{vmatrix}, \quad (12)$$

where the $1/\sqrt{2}$ prefactor is the so-called normalization constant.

Such wavefunctions can be easily extended to the general case of n_e electrons according to:

$$\psi_e(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_{n_e}) = \frac{1}{\sqrt{n_e!}} \begin{vmatrix} \varphi_1(\vec{x}_1) & \dots & \varphi_{n_e}(\vec{x}_1) \\ \vdots & \ddots & \vdots \\ \varphi_1(\vec{x}_{n_e}) & \dots & \varphi_{n_e}(\vec{x}_{n_e}) \end{vmatrix}, \quad (13)$$

where the $n_e \varphi_i$ are called spin-molecular orbitals, and the wavefunction defined by eq. 13 a *Slater determinant* (SD). Finding the SD determinant that provides the lowest total energy (in other words, optimizing the $\{\varphi_i\}$ set for that its energy is minimal) corresponds to a (unrestricted) *Hartree-Fock* (HF) calculation.⁶

⁵ which are also eigenfunctions of the \widehat{S}^2 operator.

⁶ Alternatively, the HF theory can be constructed as a *mean-field* approximation of the electronic potential.

However, while the HF wavefunction is correctly normalized and antisymmetric, it is never the exact electronic wavefunction for a molecule with more than one electron. It is thus inaccurate to state that the H₂ molecule is in the $(\sigma_g)^2$ electronic configuration.⁷ This is only an approximation, whose error is measured by the so-called correlation energy (always *negative*, as a consequence of the so-called *variational principle*) defined by:

$$E_e^{corr} = E_e^{exact} - E_e^{HF}. \quad (14)$$

In the H₂ case, $E_e^{corr} \approx -0.04 E_h \approx -25 \text{ kcal/mol}$, which is not at all negligible with respect to H₂ bond energy ($\approx 100 \text{ kcal/mol}$). In fact, standard MO approaches only provides a crude estimate of bonding in molecules. Of course, HF theory can be improved by post-HF methods. However, we will here focus on an alternative already mentioned, DFT, which is certainly the most used one to theoretically study real chemical systems, since it can now be routinely applied to systems of hundreds of atoms.

4. Density Functional Theory

4.1. The electron density

DFT starts from the observation that, due to the wavefunction antisymmetry, ψ_e encodes redundant information, so that one can wonder whether a simpler function embodying only necessary information present in $|\psi_e|^2$ could be sufficient to describe the electronic states. Such a condensation can be achieved by integration over some variables. The *electron density* (ED) is the prototype of such operation, where $|\psi_e|^2$ is integrated over all electrons except one:

$$n(\vec{r}_1) = n_e \int \dots \int |\psi_e(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_{n_e})|^2 ds_1 d^4x_2 \dots d^4x_{n_e}. \quad (15)$$

In eq. 15, only the spatial coordinates of electron 1 have been kept. Due to the electron indiscernibility, the same function will be fortunately obtained if integration has been instead performed on electrons 1, 2, ..., $n_e - 1$, keeping only the coordinates of electron n_e . At variance with the electronic wavefunction whose number of variables increases linearly with the system size (making it intractably huge even for relatively small molecules), ED is a 3D-function for any chemical system. It can thus be easily visualized.

Moreover, it has a simple physical interpretation, as follows from its integrated values over whole space:

$$\int n(\vec{r}_1) d^3r_1 = n_e. \quad (16)$$

⁷ This is also true at the atomic level. Considering that the He atom is in its $(1s)^2$ configuration at the GS induces an error of more than 25 kcal/mol on the helium atom energy.

More precisely, the average number of electrons inside an infinitesimal volume d^3r_1 centered at point \vec{r}_1 equals $n(\vec{r}_1)d^3r_1$. ED thus counts the *number of electrons per volume*.⁸ Among the important ED properties are the following: for real chemical systems,

- n is strictly *positive* at any space point;
- n exhibits *cusps* at nuclear positions, whose slope depends on the nuclear charge (Kato's theorem);
- in non-periodic systems, n is exponentially decreasing far from the nuclei, the asymptotic decay being controlled by the ionization potential of the system;
- for atoms, n is monotonic decreasing with maximal values at nuclei;
- n can be *experimentally measured* by means of X-ray diffraction techniques: it can be directly obtained by Fourier-transform of the structure factor.

This last property is particularly appealing since this is **not** the case of the wavefunction that cannot be experimentally accessed.

4.2. The Hohenberg-Kohn theorems

Henceforth, the electron density already presents attractive assets, but one can now wonder if it can also provide useful information on electronic state? The answer is given by the celebrated Hohenberg-Kohn (HK) theorems (1964) that are the pillars of DFT. In brief, the first of the two theorems (the second one being the variational version of the first) can be formulated as follows (we recall that, see eq. 8, v_{ne} is the potential generated by the nuclei, very often called *external potential* in the DFT community):

“The ground-state density $n(\vec{r})$ determines the potential $v_{ne}(\vec{r})$, which in turn determines the Hamiltonian, and thus everything about the many-body problem.”

In summary, we can in principle determine any physicochemical property of the system from the **sole** electron density. Two caveats should be associated to this generalized statement: it is only valid for stationary states and restricted to the electronic GS. Extensions to excited states exist (these are the Runge-Gross theorems, foundations of Time-dependent DFT), but they will not be discussed here.

We now introduce additional terminology. Very crudely speaking, a *function* maps a number to another number; an *operator* maps a function to another function; a *functional* will map a function to a number. Examples are given below:

⁸ When multiplied by the opposite elementary charge, one obtains the negative charge density $\rho_e(\vec{r}_1) = -en(\vec{r}_1)$. If the positive charge distribution carried by the nuclei, $\rho_{nuc}(\vec{r}_1)$, is added, one gets the (total) charge density ρ according to $\rho(\vec{r}_1) = \rho_{nuc}(\vec{r}_1) - en(\vec{r}_1)$. It is this ρ that, for instance, is used in the Maxwell's equations governing the electromagnetic fields. It should be noticed that this is common practice not to distinguish between n and $-\rho_e$ in the DFT literature.

$$\text{function: } x \mapsto x^2, \text{ operator: } f(x) \mapsto f'(x), \text{ functional: } f(x) \mapsto \int_{-\infty}^{\infty} f'(x) dx. \quad (17)$$

Using this vocabulary, one can thus conclude that **the electronic ground state energy is a functional of the electron density**, which can be notated by $E_e^{(0)} = E_e^{(0)}[n]$. This is also true for any component of $E_e^{(0)}$, such as the total electronic kinetic energy T and the bielectronic repulsion energy V_{ee} , so that:

$$E_e^{(0)} = T[n] + V_{ee}[n] + \int n(\vec{r}) v_{ne}(\vec{r}) d^3r, \quad (18)$$

where the last integral is the electron density functional for the energy of attraction of the electrons by nuclei. Conversely, the $T[n] + V_{ee}[n]$ sum does not depend on v_{ne} ; for this reason, it is coined the HK “*universal functional*” generally denoted F_{HK} . Unfortunately, while HK theorems prove that F_{HK} exists, they do not provide any analytical formula for it. It is precisely the difficulty to find accurate approximations for this term that led Kohn and Sham to reformulate DFT within the so-called KS framework.

4.3. The Kohn-Sham approach

To this aim, Kohn and Sham introduced one year later a *fictitious non-interacting* electronic system that gives the *same* electron density as that of the interacting system of interest.⁹ As electrons do not interact in this KS system, its wavefunction is *exactly* given by a Slater determinant involving the so-called KS orbitals ($\psi_e^{KS} = \det(\{\varphi_i^{KS}\})$), while *differing* from the exact electronic wavefunction. The electronic kinetic energy of this fictitious system, T_s , can then be exactly expressed as a functional of the occupied orbitals (here assume to be real-valued, while spin variables are once more omitted for clarity):

$$T_s[\{\varphi_i^{KS}\}] = -\frac{1}{2} \sum_i \int \varphi_i^{KS}(\vec{r}) \nabla^2 \varphi_i^{KS}(\vec{r}) d^3r = \frac{1}{2} \sum_i \int \|\vec{\nabla} \varphi_i^{KS}(\vec{r})\|^2 d^3r. \quad (19)$$

For the electron-electron repulsion energy, KS extracts the classical part (also known as the Hartree term) J . Consider two points \vec{r} and \vec{r}' in space, and two infinitesimal volumes d^3r and d^3r' around them. The infinitesimal electronic charges inside each of them are equal to $\delta q = -en(\vec{r})d^3r$ and $\delta q' = -en(\vec{r}')d^3r'$. The electrostatic interaction energy between them is given by Coulomb’s law (in SI units): $\delta^2 J = \frac{1}{4\pi\epsilon_0} \frac{\delta q \delta q'}{\|\vec{r} - \vec{r}'\|}$, hence, in atomic units, $\delta^2 J = \frac{n(\vec{r})n(\vec{r}')}{\|\vec{r} - \vec{r}'\|} d^3r d^3r'$. The total corresponding energy is obtained by summing all these infinitesimal contributions for all possible values of \vec{r} and \vec{r}' . This is nothing else than the $J = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{\|\vec{r} - \vec{r}'\|} d^3r d^3r'$ integral where the 1/2 factor prevents from double-counting. Obviously, $J[n]$ is an ED functional.

We have now in hand two exact functionals for approximations of the kinetic energy and of the bielectronic repulsion. The missing energy is called the *exchange-correlation energy* E_{xc} that

⁹ The conditions so that it is possible are known to constitute the *n-representability* problem.

represents about 10% of the total electronic energy but that is fundamental to account for bonding and reacting. According to HK, it can be written as a functional of the ED of the real system. As this one is also the ED of the fictitious system by construction, E_{xc} is also a functional of ED of the fictitious system than can be directly calculated from KS orbitals (here again chosen real for simplicity):

$$n(\vec{r}) \equiv n^{KS}(\vec{r}) = \sum_i \varphi_i^{KS}(\vec{r})^2. \quad (20)$$

One can then write:

$$E_e^{(0)} = T_s[\{\varphi_i^{KS}\}] + \int n(\vec{r})v_{ne}(\vec{r})d^3r + \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r}')}{\|\vec{r}-\vec{r}'\|} d^3r d^3r' + E_{xc}[n]. \quad (21)$$

The $E_{xc}[n]$ functional is thus made of two components that gather the main quantum effects: the *correlation kinetic energy* that is the difference between the exact electronic kinetic energy and that of the KS system (in principle, all density functionals according to HK) and the bielectronic exchange-correlation correction that one has to add to the Hartree energy to recover the full bielectronic repulsion energy (note that in KS DFT, the correlation energy is different from that defined by eq. 14):

$$E_{xc}[n] = (T[n] - T_s[n]) + (V_{ee}[n] - J[n]). \quad (22)$$

By minimizing the total GS electronic energy (variational DFT), it can be shown that the φ_i^{KS} obey the so-called KS equations, which take, once more, the form of an eigenvalue problem for each φ_i^{KS} :

$$-\frac{1}{2}\nabla^2\varphi_i^{KS}(\vec{r}) + v_{KS}(\vec{r})\varphi_i^{KS}(\vec{r}) = \varepsilon_i\varphi_i^{KS}(\vec{r}), \quad (23)$$

where v_{KS} is the *KS potential*, which is the sum of the external, electrostatic and exchange-correlation potentials (this last one being defined as the functional derivative of $E_{xc}[n]$ with respect to n):

$$v_{KS}(\vec{r}) = v_{ne}(\vec{r}) + \int \frac{n(\vec{r}')}{\|\vec{r}-\vec{r}'\|} d^3r' + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}. \quad (24)$$

ε_i are the orbital energies. It is important to notice that, in principle, φ_i^{KS} being related to the fictitious system, they are mainly mathematical intermediates with no direct chemical interpretation. Nevertheless, the energy of the highest occupied KS orbital is exactly equal (if the exact exchange-correlation functional is used) to the negative of the ionization potential of the system. However, the energy of the lowest unoccupied orbital is not directly linked to the electron affinity due to the discontinuity of the exchange-correlation potential with respect to the electron number. Furthermore, the electronic energy is not equal to the sum of the energies of the occupied orbitals.¹⁰

4.4. The self-consistent-field algorithm

Coming back to eqs 23, instead of solving only one differential equation (the Schrödinger one) that involves $3n_e$ spatial variables, we now have to solve a system of n_e integro-differential equations of 3 variables, which is fully equivalent, but that is in principle much simpler to solve. It is however

¹⁰ This is also the fact in Hartree-Fock theory due to some double-counting.

fundamental to notice that these equations are actually *coupled* since, as v_{KS} depends on n , it is a function of **all** φ_i^{KS} . The resolution of one of the KS equations thus requires in principle that the solutions of the $n_e - 1$ other equations are known.

It is the reason why they are solved using an *iterative* procedure called the *self-consistent field* (SCF) algorithm. First, initial approximate φ_i^{KS} are generated (this is the *guess*). They allow to build an approximate v_{KS} , from which new φ_i^{KS} can be determined by solving eq. 23. These new orbitals allow for the computation of a (in general) improved v_{KS} , which is reinjected in the KS equations to get new KS orbitals. Usually, at a certain point, the orbital variations between one cycle and the next one become small enough that we can consider that convergence has been reached.

From a technical point of view, KS equations are solved using an expansion on a basis set: each orbital is written as a linear combination of *fixed* functions $\{\chi_\mu(\vec{r})\}$:

$$\varphi_i^{KS}(\vec{r}) = \sum_\mu c_{i\mu} \chi_\mu(\vec{r}). \quad (25)$$

Solving the KS equations is thus reduced to find the $c_{i\mu}$ values, and eq. 23 can then be cast into a matrix form that can be efficiently solved by linear algebra packages and that can be parallelized for use in supercomputing centers. Once the $c_{i\mu}$ are obtained, the ED can be built straightforwardly:

$$n(\vec{r}) = \sum_{\mu,\nu} P_{\mu\nu} \chi_\mu(\vec{r}) \chi_\nu(\vec{r}) \text{ with } P_{\mu\nu} = \sum_i c_{i\mu} c_{i\nu}, \quad (26)$$

the $P_{\mu\nu}$ matrix being called the *density matrix*.

In principle, the basis set should be of infinite size, but in practice *finite* basis sets are used. They can be classified into two main categories: *delocalized* (for instance plane waves benefiting from fast Fourier-transform methods, wavelets...) and *localized* (centered at nuclear positions) ones. For these last ones, the most used are Slater functions (acronym STO) and *Gaussian* functions (GTO), inspired by the atomic orbitals (AOs) shape (but that are not AOs):

$$\chi_{\mu,nlm}^{STO}(\vec{r}) = \aleph_\mu S_{lm}(\theta, \phi) r^{n-1} e^{-\zeta_\mu \|\vec{r}-\vec{r}_\mu\|} \quad (27)$$

$$\chi_{\mu,abc}^{GTO}(\vec{r}) = \aleph_\mu x^{a_\mu} y^{b_\mu} z^{c_\mu} e^{-\zeta_\mu \|\vec{r}-\vec{r}_\mu\|^2}, \quad (28)$$

where \aleph_μ is the normalization constant, and ζ_μ the *exponent* controlling the decay rate of the exponential or of the Gaussian function. Eq. 27 is based on spherical coordinates with S_{lm} the angular part built on spherical harmonics. Eq. 28 uses instead a Cartesian representation. For instance, $a_\mu = b_\mu = c_\mu = 0$ corresponds to an isotropic basis function (like a *s*-type OA). Common basis functions are tabulated and are available on online depositories. While Slater functions better mimic the behaviour of the ED at the nuclei and far from it, Gaussian functions have the advantage to lead to more easily calculable integrals thanks to the Gaussian product theorem.

In the case of heavy elements (*e.g.* transition metals, lanthanides, actinides) that contain a large number electrons, two main strategies have been proposed to speed up calculations. The first one (that can be used in popular DFT codes such as Gaussian®) is the approach based on pseudopotentials (also known as effective core potentials (ECPs)) that eliminate core orbitals and simulate their effect on the valence-electron system by adding extra potentials to the electronic Hamiltonian,¹¹ which have been optimized for this particular purpose. Those developed in Los Alamos (LANL ECPs) and in Stuttgart-Dresden (SDD ECPs) are the most frequent ones.

An alternative is that implemented in the ADF® software, which assumes that the core orbitals are unperturbed from the free atom to the molecular environment. These *atomic* orbitals can thus be calculated in a very fast way independently of the molecular system in a separate (and very accurate) calculation. As a consequence, the electrons populating the inner-shells are not included in the variational KS problem, but their electron density can be included in the density analyses (for instance in QTAIM calculations).

4.5. The Perdew's scale of practical DFT

Performing a DFT calculation thus requires choosing two main parameters: the *basis set* (and if needed the pseudopotential/frozen core) and the *exchange-correlation functional*. Indeed, in practice, one has to use an approximation for $E_{xc}[n]$, usually ranked using the *DFT Jacob's ladder* designed by Perdew. The first rung collect the Local Density Approximations (LDAs) than only use $n(\vec{r})$; the second, the Generalized Gradient Approximations (GGAs, known examples are PBE and BLYP) use $n(\vec{r})$ and its gradient $\vec{\nabla}n(\vec{r})$; the third, metaGGAs (such as TPSS, M06L), are based on $n(\vec{r})$, $\vec{\nabla}n(\vec{r})$ and the Laplacian $\nabla^2n(\vec{r})$ (or the KS kinetic energy density). Such ingredients are based on Taylor expansion (involving the two first ED spatial derivatives) of the functional with respect to the ED.

The simplest exchange functional is certainly the *Dirac* one, which is exact for the jellium model (electron gas immersed into a uniform positive background), here in its spin-unpolarized version:

$$E_x^{Dirac}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int n(\vec{r})^{4/3} d^3r. \quad (29)$$

Incidentally, it can be noticed that the KS kinetic energy of this jellium model can also be exactly expressed as a density functional (equivalent, in that very particular case, to the exact orbital functional given by eq. 19), called the Thomas-Fermi (TF) functional:

$$T_s^{TF}[n] = \frac{3}{10}(3\pi^2)^{2/3} \int n(\vec{r})^{5/3} d^3r, \quad (30)$$

which enters the expression of the Electron Localization Function (ELF).

¹¹ ECPs also allows for adding relativistic effects at low cost.

Coming back to exchange-correlation, as the ED in molecules is far from being homogeneous, improvements to E_x^{Dirac} have been proposed by introducing a local *enhancement factor* $F_x(\vec{r})$:

$$E_x^{DiracImp}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int n(\vec{r})^{4/3} F_x(\vec{r}) d^3r. \quad (31)$$

Many of them employ the following *reduced density gradient* (RDG) as the primary element:

$$s(\vec{r}) = \frac{1}{2(3\pi^2)^{1/3}} \frac{\|\vec{\nabla}n(\vec{r})\|}{n(\vec{r})^{4/3}}, \quad (32)$$

which is dimensionless and that naturally emerges from the Taylor expansion of the exchange energy for small density variations with respect to jellium. $s(\vec{r})$ is never negative, is equal to zero if ED is locally uniform, and tends toward infinity in the asymptotic ED tail. It is also the basis of the non-covalent index (NCI). In 1988, Becke proposes a simple, but accurate enhancement factor based on this RDG:

$$F_x^{Becke88}(\vec{r}) = 1 + \frac{\delta s(\vec{r})^2}{1 + \gamma s(\vec{r}) \sinh^{-1}(s(\vec{r}))}, \quad (33)$$

where δ and γ are two constant values, independent of the chemical system under investigation. Such coefficients involved in various density functional approximations can be either determined from exact constraints (“first-principles” approach to DFT development) or by fitting to reference values (“pragmatical” approach).¹²

The two last rungs of the DFT scale depart a little bit from the pure ED point of view since they involve the explicit contribution of KS orbitals. Hyper-GGAs (also formerly known as *hybrid* functionals) include information of only occupied KS orbitals. This is in general done by mixing to a GGA or metaGGA exchange functional a certain amount of the so-called exact exchange (xx),¹³ which is *non-local* since it requires the orbital information at two different points \vec{r}_1 and \vec{r}_2 :

$$E_{xx}[\{\varphi_{i,occ}^{KS}\}] = -\frac{1}{2} \sum_{i=1}^{n_e} \sum_{j=1}^{n_e} \int \int \frac{\varphi_i^{KS}(\vec{r}_1) \varphi_j^{KS}(\vec{r}_1) \varphi_i^{KS}(\vec{r}_2) \varphi_j^{KS}(\vec{r}_2) d^3r_1 d^3r_2}{\|\vec{r}_1 - \vec{r}_2\|}. \quad (34)$$

The venerable (but old-fashioned) B3LYP is certainly one of the most celebrated hybrid functionals. Other popular examples are, PBE0 and M06-2X.

In general, these four first rungs fail to correctly account for van der Waals interactions of the dispersion (*i.e.* London) type (for instance, the noble gas dimers, the dimers of methane or of benzene). A popular and very fast way to correct such deficiencies is the semi-empirical scheme proposed by Grimme (leading to the so-called D, D2, D3, and D4 models), based on pair-potentials (that can be, if necessary, complemented by other many-body contributions), as those that can be found in classical force fields:

¹² Obviously, both “first-principles” and “pragmatical” approaches can be mixed.

¹³ The xx functional given by eq. 33 (for real orbitals) is the same *orbital functional* as that used to calculate exchange in HF theory. However, the corresponding KS exact exchange energy in general differs from the HF exchange energy since the KS orbitals and the HF orbitals are different for non-trivial systems.

$$E_{disp} = -\sum_{\alpha < \beta} f_{damp}(R_{\alpha\beta}) \frac{C_6^{\alpha\beta}}{R_{\alpha\beta}^6}, \quad (35)$$

where the double sum is made on all nuclei pair, $R_{\alpha\beta}$ denoting the distance between nucleus α and nucleus β , f_{damp} a damping function that controls the switching of the correction, and the dispersion coefficient $C_6^{\alpha\beta}$ being tabulated or computed following different approaches.

Alternatively, dispersion interactions can also be accurately modelled by density functional approximations belonging to the fifth rung of Perdew's scale, which involve also unoccupied KS orbitals, mainly based on the double hybrid scheme (stemming from second-order perturbation theory: B2P-LYP, PBE-QIDH...) or on the random phase approximation (RPA). While in general more accurate, such approximations suffer from a higher computational time, so that they are not yet routinely used for DFT applications on medium-size or big systems.

In general, all these density functional approximations lead to integrals that cannot be solved in a full analytical way. They are thus evaluated using numerical quadrature techniques. Integrals are thus replaced by a discrete sum using a grid of predefined points \vec{r}_k and integrations weights w_k , according to (for any local $g(\vec{r})$ function):

$$\int g(\vec{r}) d^3r = \sum_k w_k g(\vec{r}_k). \quad (36)$$

As Cartesian grids are not efficient for such purposes, the molecular integrals are approximated as a sum of atomic sub-integrals (often using Becke's partitioning scheme), each of which is then evaluated by quadrature in spherical polar coordinates ($\int g(r, \theta, \phi) d^3r \approx \sum_i w_i^r \sum_j w_j^\Omega g(r_i, \theta_j, \phi_j)$) with a Lebedev angular grid and a radial angular grid. The size of such grids is also an important parameter that controls both calculation accuracy and computational time.

We will not discuss the performances of such proposed functionals (that often rely on more or less spurious *error cancellations*). We instead refer the interested reader to the recent benchmark paper by Goerigk and Mehta cited in the bibliographic section that affords an enlightening and pragmatic overview of the advantages and drawbacks of the most frequent approximations.

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