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# Quantum Mechanics in Earth Sciences: a one century-old story

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Abstract Nowadays it is possible to calculate, at the *ab initio* level, any property of condensed matter, from its crystal structure and mechanical properties, to its thermodynamics, and therefore its stability in a given environment and in a range of temperature and pressure conditions. Predictions from calculations of this type can be used to estimate geophysical properties like densities of mantle rocks as they change along geoterms, the geotherms themselves, phase transitions and their properties, seismic velocity profiles to be compared with models derived from other paradigms and techniques. Moreover, known facts and observations concerning structure, behaviour, properties of materials and properties of whole complex systems of materials can be *explained* or at least rationalized within a common and very general frame that is at the basis of all the currently known physics and chemistry. However, the development of ideas, paradigms and related techniques did not come out all of a sudden, but steadily proceeded from the early days till now, without a real solution of continuity. During the time, quantum mechanics heavily contributed to create a language, a set of basic ideas and a frame of mind that is extensively used by chemists and crystallographers to interpret the relevant facts. What we know today, and how we currently apply quantum mechanics to systems of our interest, is largely dependent upon the path followed during the years to implement the theory in practical and efficient algorithms to make calculations for *real* systems. This paper will present a brief review of the paths followed, along with their motivations, since those early and heroic days of physics at the beginning of the last past century. The aim is to provide the reader with a general view of the subject that could possibly drive her/him toward the choice of more specific papers from the huge literature, concerning more restricted and specialized topics.

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#### 1 Introduction

The present paper is intended for scientists working in the Earth Science field, who do not have a strong background in quantum mechanics, but that are nevertheless interested to discover what contribution such discipline could bring in their field. My choice was to present the evolution of the quantum mechanical based approach in the field of the Earth Sciences, by showing the conceptual tenets and milestones, together with the practical calculation techniques, from an historical perspective. By no means the paper pretends to be an exaustive account of the history of the ideas, their motivations and advancements; rather, the material here presented reflects the view of the author, based as it is on his personal knowledge, interests and experience. The material is organized following a *logical* scheme that might not always coincide with the actual historical line of development, as it is well known that very often scientific research does not proceed linearly in its evolution, so that the real chronological sequence of steps undertaken could be somewhat dissimilar from what could be expect from a strictly logical point of view.

Quantum mechanics born out of classical mechanics to solve some peculiar problems that were discovered by the end of the  $XIX^{th}$  century. The approach followed to solve such problems was deeply interconnected with the previous classical physical building. In this view, a shot of what was classical physics at that early time is due, and will be provided in section one, together with a perhaps too brief presentation of the foundation of the *new physics* that was built up to answer those problems.

The second section is devoted to the development and the advancement of quantum chemistry: the specialized field of quantum mechanics applied to *many electrons* systems (atoms and molecules). Indeed, from the computational techniques employed for the difficult practical solution of the equation of motion (the Schrödinger equation) for such systems, a whole conceptual frame arose to interpret the chemical bond, its properties, the energetic, the stability and the reactivity of molecules. Such *wave function* based frame still dominates the *chemical thinking* in case an explanation of molecular properties is wanted, at the fundamental level of physics.

The transfer to condensed matter, crystalline state in particular, of the quantum-chemical technologies developed for molecules was particularly troublesome, especially due to the *infinite* size of crystals. Thus, instead of a wave function based approach, which is typical of the molecular quantum-chemistry world, methods based on the electron density were developed, thank also to the efforts made to study the problem of the *homogeneus electron gas*, which later found its rather *obvious* model in materials like the metals. The resulting *Density Functional Theory* (DFT), which continues to be a very active field of research, is the subject of a third section. DFT is nowadays largely employed

even in molecular quantum chemistry, due to its good effectiveness at a limited *cost* of calculation (*cost* in terms of power of computers and computing time). Since the literature concerning DFT is huge, for reasons of space, scope of the present paper and experience of the author, the examples discussed will be limited to the hybrid Hartree-Fock/Density Functional approch, as it will be explained in the relavant section.

Starting from the '80s, the focus on the electron density, which is a real and measurable scalar function of position, rather than on the wave function which, instead, is a *non*-measurable function *living* in an infinite dimensional Hilbert space, stimulated a new way of interpreting bonds, their classification and properties. The Quantum Theory of Atoms in Molecules (and Crystals), QTAIM (QTAIMC) was developed by Richard Bader working at the McMaster University in Canada, and will be briefly addressed in section four.

A last fifth section deals with the computation of properties at the macroscopic scale, like whole crystals in the case of solid state systems, starting from properties determined at the molecular level, or at the level of the unit cell of a crystal. The method discussed is firmly grounded to the quantum statistical approach which is the formal link between the *microscopic* and the *macroscopic* worlds, the latter being described within the frame offered by thermodynamics.

# 2 The early days, the crisis of physics and the quantum-mechanical picture

#### 2.1 The Classical World

By the end of the XIX<sup>th</sup> century, what we now call *classical* physics reached a very high and sofisticated level, believed to be capable, at least in principle, to explain every possible fact of the physical world. Starting from Galilei, the World knew giants like Newton, Lagrange, Hamilton and Maxwell, to name just a few of them, that set up physics and its formalism to describe and predict the behavior of mechanical systems, and electric and magnetic phenomena. Meanwhile, heath was recognized as a form of energy and thermodynamics arose as the formal physical frame suitable to explain heath transfer, its transformation in mechanical work and, perhaps mostly important from the conceptual point of view, as the theory under which the problem of the arrow of time could be formalized and discussed. Maxwell theory and, in particular, its prediction of a unique speed for electromagnetic waves (the speed of light) did not agree with the relativity principle in the form stated by Galilei, and this fact together with a bunch of experimental observations and considerations (e.g. the Michelson and Morley experiment) led Albert Einstein to develop the theory of special relativity. The Einstein theory was then incorporated in a more general principle from which the whole (relativistic) classical physics can be derived: the *principle of least action*. More precisely, given a system and its Lagrangian  $L(q_i, \dot{q}_i, t)$  [a function depending upon generalized coordinates  $(q_i)$ , velocities  $(\dot{q}_i)$  and time (t)] the space-time trajectory followed by the system in a given time interval  $[t_i, t_f]$  is the one that minimizes the action (S):

$$S = \int_{t_i}^{t_f} L(q_i, \dot{q}_i, t) \mathrm{d}t \tag{1}$$

by keeping fixed the end points  $q(t_i)$  and  $q(t_f)$  of the trajectory. In fact, it can be easily demonstrated that the Lagrange equations of motion do directly follow as a consequence of such least action principle. By requiring the Lagrangian to be a Lorentz scalar (that is, *invariant under Lorentz transformations*) and gauge invariant, all of the classical relativistic physics can be derived. Indeed the same action principle is also at the basis of quantum mechanics, and of quantum field theory (QFT) as well, from which all of the current modern physics is systematically developed. In this respect, the action principle is either the unifying principle of the classical, relativistic and quantum physics, or a formidable operational tool to derive *theories* which are consistent with the basic principles of relativity, gauge invariance, *locality* and *continuity*.

In spite of the great success reached by classical physics around the turn of the XIX<sup>th</sup> century, new facts hardly explainable by the dominant paradigma, at that time, started to emerge: the most significant ones were probably the failure of the classical law of radiation from the *black body* at any finite temperature (the failure is known with the name of *ultraviolet catastrophe*); the difficulties of the classical theory of specific heat; the nature of the emission spectra of gases; the stability of atoms according to the model proposed in those years by Ernest Rutherford. The black body problem was solved by Max Planck by assuming that the energy associated with each frequency of the infinite set of oscillators constituting the ideal black body, was restricted to a *discrete* set of values of the form  $E_n = nh\nu$  where n is an integer number,  $\nu$  is the frequency of the given oscillator and h is a constant having the dimension of the *action* (energy  $\times$  time), which is known as the *Planck constant*. The black body problem was the first example of quantization of energy (the energy) of each oscillator cannot assume arbitrary values related to the amplitude of vibration as, instead, it was possible at the classical level of description) and its solution led to the Planck's formula for predicting the shape and the intensity of the electromagnetic spectrum emitted by bodies at any given temperature. Concerning the stability of atoms, the Rutherford model was very attractive due to its similarity with the *planetary* model: a positively charged nucleus around which negatively charged electrons orbit like planets around their star: the Coulomb force had only to be sostituted for the Newtonian gravitational force, the two forces having the same functional form. The point was that orbiting electric charges were also *accelerated charges*, that were predicted to emit electromagnetic radiation (and, therefore, energy) by the already established Maxwell classical theory of electromagnetism. The Rutherford atom was then not stable, and the electrons had to fall on the nucleus in a very short time.

A first solution to both the atomic stability and the nature of the atomic emission spectra was formulated by Niels Bohr (with the contribution of other scientists like A. Sommerfeld). Essentially, the idea was to accept the de Broglie hypothesis of a link between the momentum p of a particle and the wavelength  $\lambda$  of an associated *pilot wave driving its motion*, in the form of  $\lambda = h/p$ , where h is the Planck's constant. Indeed the de Broglie hypothesis stemmed from a parallelism drawn between massive particles and massless particles like the photon whose energy E can be expressed as  $E = h\nu$  from the Planck theory, and E = pc from the Einstein relativity (where c is the speed of light):  $h\nu = pc \rightarrow \lambda = c/\nu = h/p$ . The de Broglie hypothesis was experimentally confirmed in 1927 by Davisson and Germer, who were able to produce diffraction effects by firing electrons against a nickel crystal. The idea of pilot waves was then incorporated by Bohr in a model of the quantum atom, in which electrons where confined to move around the nucleus along orbits whose lengths had to be multiple integers of the wavelength of the associated pilot wave, thereby establishing a precise link between the radius of each allowable orbit and its energy. The Bohr (or the Bohr-Sommerfeld) model has a clear historical importance, but by no means it represents the picture of the atom that emerged afterward from the Schrödinger work (despite it is often presented as the model of the *modern* atom in too many High School textbooks).

Subsequent crucial developments came out from the works of Erwin Schrödinger, Werner Heisenberg, Paul A.M. Dirac, Wolfang Pauli and others, who were able to lay down the principle of quantum mechanics by suitably crafting the formalism already available for classical systems, to derive the equation of motions and the *rules* necessary to translate every classical dynamical variable into the corresponding quantum-mechanical one. It is important to give here some details of the theory at the very basic level, in order to understand the more advanced applications. So, let's take our time to discuss at least the principles, in the most simple and straighforward way.

#### 2.2 Quantum mechanics in a nutshell

Probably the most clear account of the foundation of quantum mechanics was given by Dirac himself in his book (Dirac, 1930a). One of the key points at the base of the new physics, which also is our entry point in the theory, was the recognition of the possible *interference* of an *observer* with the system being *observed*; therefore, a theory had to be established that formalized the description of the *state of the system*, so that the state itself became an active part of the theoretical formal building. Dirac invented the notion of the *ket* vector  $| \rangle$  that represents the state of the system (kets may be labelled to represent a specific state: *e.g.*  $|A\rangle$ ). Kets can be acted upon by operators  $\hat{F}$ representing dynamical variables (classical *observables*) to give, in general, a different state:  $\hat{F}|A\rangle = |B\rangle$ ; this action of the operator on a ket, to give a *different* ket, is just the mathematical way to describe the interference of the observer (which measures the observable F) on the observed state: indeed, at the end of the measurement process, the system is found in a final state  $|B\rangle$  different from the initial state  $|A\rangle$ . Of particular importance is the case where the two vectors involved are actually *parallel* (they differ at most by a multiplicative scalar f):  $\hat{F}|A\rangle = f|A\rangle$ ; in words: the action of the operator  $\hat{F}$  on the ket vector  $|A\rangle$  produces the same vector multiplied by a scalar. In this case  $|A\rangle$  is said to be an eigenvectors of  $\hat{F}$ , and f is the corresponding eigenvalue. The equation (*eigenvalue equation*) is interpreted as follow: the scalar f is the result of the measurement of the observable F, represented by the operator  $\hat{F}$ , on a system that is in a state described by the ket  $|A\rangle$  that happens to be an *eigenvector* of the operator  $\hat{F}$ . It is important to note that if the state of the system is an *eigenstate* of the observable being measured, the act of measurement does not change it; moreover it is important to emphasize that the result of the measurement is *certainly* f. On this basis, to cut a long story short (actually, jumping too soon to a conclusion), the *time independent* Schrödinger equation:

$$\hat{H}|\psi\rangle = E|\psi\rangle \tag{2}$$

can be understood exactly in the same way: the act of measuring the energy (that is, the *Hamiltonian* H), represented by the operator  $\hat{H}$ , of a system that is in a state represented by an eigenvector of  $\hat{H}$  ( $|\psi\rangle$ ), provides the value of the energy (E), and the state of the system remains unaltered.

It is interesting to consider the case of the measurement of an observable Ffor a system that is in a state which is *not* represented by an eigenvector of the relevant operator; to this end, let's call  $|B\rangle$  the vector representing the system,  $\hat{F}$  the operator,  $|F_i\rangle$  the set of its eigenvectors and  $f_i$  the set of the associated eigenvalues (that is, for each *i*, the following equations hold:  $F|F_i\rangle = f_i|F_i\rangle$ ): it is *postulated* that the result of the measurement of F is *one* of the possible eigenvalues  $f_i$  and, at the end of the process, the system will be found in the corresponding state  $|F_i\rangle$ . Which one of the particular  $f_i$ 's will come out from the measurement process is not known: only a *probability* distribution of possible outcomes can be defined. In particular, it is postulated (under the name of superposition principle) that whatever  $|B\rangle$  is, it can be expanded as a linear combination of eigenvectors of whatever operator  $\hat{F}$  representing an observable:  $|B\rangle = \sum_i b_i |F_i\rangle$ , where the coefficients  $b_i$ 's are, in general, complex numbers. The square module of each  $b_i$  is the probability that a measurement of F will provide the value  $f_i$ . The average value of measurements of F on a large set of *identical systems*  $|B\rangle$  is indicated with the symbol  $\langle F \rangle_B$ . It can be shown that:

$$\langle F \rangle_B \equiv \langle B | \hat{F} | B \rangle = \sum_i |b_i|^2 f_i$$
 (3)

Thus, each measure provides an eigenvalue of  $\hat{F}$ ; the average of such measures eventually coincides with the *classical* expectation from a single measurement on the same system.

In case the operator F is the one that measures the position x of a particle in some state  $|B\rangle$ , the set of coefficients b's assumes the form of a *continuous*  function of  $x \ [\psi_B(x)]$  called *wave function*. The quantity  $\ |\psi_B(x)|^2 dx$  is interpreted as the probability of finding the particle in the volume element dx. Also, the wave function  $\psi_B(x)$  is said to be the *representation* of the ket  $|B\rangle$  in the space of coordinates (*Schrödinger representation*).

Now, imagine to have two observables F and G, and imagine the system be initially in a state represented by an eigenvector  $|F_i\rangle$  of  $\hat{F}$ . Let's take two measures: the first one of the observable F, followed by the G measurement. The measurement of F will certainly provide the value  $f_i$  and the system will be left unaltered in the state  $|F_i\rangle$ ; the second measurement of G on  $|F_i\rangle$ will provide one of the  $g_i$  eigenvalues of  $\hat{G}$  with a probability that depends by the coefficients of the expansion of  $|F_i\rangle$  into the eigenvectors  $|G_i\rangle$  of  $\hat{G}$ . If the two measures are reversed, the outcome of the G observation will be again an eigenvalue  $g_i$  of  $\hat{G}$ , with the same probability distribution discussed above, but the measure of F will not any longer be certainly  $f_i$ , as after the G measurement the system will be left in one of the  $|G_j\rangle$  state, that in general is not an eigenvector of  $\hat{F}$ , too; thus the second measurement will provide one of the possible  $f_i$  with a distribution of probability that dependes upon the coefficients of the expansion of  $|G_i\rangle$  into the  $|F_i\rangle$ 's. The moral is that the order of the measurements matters:  $\hat{G}\hat{F} \neq \hat{F}\hat{G} \rightarrow \hat{G}\hat{F} - \hat{F}\hat{G} \equiv [\hat{G}, \hat{F}] \neq 0$ . It has been here introduced the *commutator* of two operators  $[\hat{G}, \hat{F}]$  which is by definition the difference  $\hat{G}\hat{F} - \hat{F}\hat{G}$ : it plays a key role in quantum mechanics: a given quantum state can be associated with a definite set of values of a corresponding set of observables if, and only if, all of the corresponding operators *commute*: be  $\{\hat{F}_i\}_{i=1,N}$  a set of N commuting operators, states exist that can be represented by the simultaneous eigenvectors of all the operators in the set; such states can be given definite values of all the corresponding observables. The most important examples are the atomic orbitals for the hydrogen atom, which are simultaneous eigenvectors of the Hamiltonian (for the hydrogen atom) and of the operators of the module of the total angular momentum, and of only one component of the angular momentum vector in a given spatial direction. Such reasoning justifies the three quantum numbers (generally indicated with  $n, \ell$ and  $m_{\ell}$ ) assigned to each orbital.

Commutation relations are important for another aspect: given a classical observable F, what are the *rules* necessary to define the corresponding quantum operator  $\hat{F}$ ? Indeed, since classical mechanics correctly works for *macroscopic* systems, where the effect of the observer on the observed object is neglibible, a connection should be established between classical and quantum operators, so that classical mechanics could naturally emerge from quantum mechanics as the size of the system grows at the macroscopic scale. At variance with the classical case where two observations always *commute*, in the quantum theory operators generally do not commute and thus, in the quest of translation rules between the two worlds, some mathematical structure of the classical formalism had to be identified that could map commuting classical observables onto *non*-commuting quantum operators. Such classical structure was chosen to be the *Poisson bracket*: reducing for simplicity to just one coordinate q and conjungate momentum p (it should be noted that, in the classical Hamiltonian formalism, q and p are two independent variables), given two observables F and G, functions of q and p, their Poisson bracket is:

$$\{F,G\} = \frac{\partial F}{\partial q}\frac{\partial G}{\partial p} - \frac{\partial F}{\partial p}\frac{\partial G}{\partial q}$$
(4)

The value of the Poisson bracket of two observables is invariant with respect to all the possible equivalent pairs of coordinates and conjungate momenta that can be chosen to describe the system, so it must reflect some intrinsic quality of the physics describing it: a quality that is independent by the way the system is described. For precisely this reason, the classical Poisson bracket of two observables F and G was identified with the quantum commutator of the corresponding two operators  $\hat{F}$  and  $\hat{G}$ . In the particular case where F is q and G is p, equation (4) gives  $\{q, p\} = 1$  and, therefore,  $[\hat{q}, \hat{p}] = 1$ . One the one hand, such not null commutator immediately tells about the Heisenberg uncertainty principle for which it is impossible to assign definite values of position and momentum to a particle; on the other hand, it justifies the reason why the representation of the momentum operator p, in the space of the coordinate q, is proportional to -d/dq: indeed, given any differentiable function f(q),

$$[q, -d/dq]f(q) = -\left[q\frac{df(q)}{dq} - \frac{d}{dq}qf(q)\right] = f(q) \rightarrow [q, -d/dq] = 1 \quad (5)$$

Thus the operator -d/dq shows the same commutation relation with q as p does and, therefore, it could be taken as the representation of the momentum operator p in the space of the coordinate q. On the basis of some other rather technical considerations, the actual form of the quantum momentum operator (in the Schrödinger representation, that is in the representation of the coordinates  $q_i$ ) is  $\hat{p}_i = -i\hbar d/dq_i$ , where  $\hbar$  is  $h/2\pi$ . Knowing the form of  $\hat{p}$  is enough to derive the form of many other quantum operators: for instance the non-relativistic classical Hamiltonian for a free particle of mass m and momentum p (the Hamiltonian reduces to the kinetic energy  $E = p^2/2m$ ) is transformed into the operator

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \equiv -\frac{\hbar^2}{2m} \nabla^2 \tag{6}$$

Wanting to describe a single electron bound to a nucleus by the Coulomb potential V (that's the case of the hydrogen atom), the time independent Schrödinger equation to solve is:

$$\hat{H}|\psi\rangle = (\hat{T} + \hat{V})|\psi\rangle = E|\psi\rangle \rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{r}\psi = E\psi$$
(7)

in some *appropriate* units of the electric charge (e). This is a second order differential equation with partial derivatives; it can be solved *exactly*: the solutions  $\psi$  are the well known atomic orbitals.

Such set of rules to derive quantum operators from classical observable was named *the correspondence principle*. It can be derived from other assumptions and considerations, together with the equation of motions, as Schrödinger did, as well as Dirac himself (or later by Schwinger, 1951): indeed it can be shown that, at the basic level, quantum mechanics can be derived from the least action principle.

#### 2.3 Identical particles and spin

At the *non*-relativistic level, to explain fine details of the hydrogen emission spectrum (Zeeman effect), scientists were forced to admit the existence of spin: a property of particles related to an intrinsic magnetic moment and an intrinsic angular momentum that particles may have. Spin is quantized following exactly the same quantization rules derived for the orbital angular momentum, and it can assume integer or half integer values in units of  $\hbar$ . In particular, for the electrons in an atom, spin had an impact on the fine structure of atomic emission spectra, suggesting that each energy level computed by the (non-relativistic) Schrödinger equation was further splitted in several sub-levels according to simple rules related to the *spin coupling* among different electrons. Later on, spin emerged *naturally* from the relativistic formulation of the quantum theory of the *free* electron given by Dirac but, before of that, its very existence and features had to be postulated. By Looking at the structure of the atomic emission spectra, at the *structure* of the Periodic Table of Elements, and on the basis of very general considerations concerning systems of *identical* particles, Wolfang Pauli postulated the so called *antisymmetry principle*: let's take  $|ab\rangle$  to be the ket describing two *identical* particles, the first one (a) occupying the position  $x_1 = (s_1, r_1)$ , in the four-dimensional spin-spatial coordinates space, and the second one (b) being in the position  $x_2$ in the same space<sup>1</sup>; then  $|ab\rangle = -|ba\rangle$  if the spin s is half integer, whereas, if s is integer,  $|ab\rangle = |ba\rangle$ . The particles belonging to the first type (half integer spin) are named *fermions*; particles of the second type are named *bosons* (e.g. the photon). Electrons are fermions and therefore they satisfy the principle with the negative sign:  $\psi(x_1, x_2) = -\psi(x_2, x_1)$  (kets are here represented in the space of the 4D spin-spatial coordinates space).

The antisymmetry principle plays a key role in determining the energetic of a system of identical particles. Let's take two electrons having identical spin

<sup>&</sup>lt;sup>1</sup> Two electrons have always the same total spin; however their spin vectors may differ in the orientation; the latter one is specified by the three components of the vector along the axes of a cartesian frame. Due to the commutation rules of the angular momentum operators, only one component of the spin vector can be precisely assigned and, by convection, this is the z component. The variable s given in the text is exactly such component, and it can assume only two possible values: 1/2 or -1/2 in units of  $\hbar$ . In the jargon, when it is said that two electrons have the same spin (*spin parallel* electrons), the z component of it is meant; the same is true for *spin paired* electrons: they have different (*opposite*) values of the z component.

(*parallel spins* as it is often said): the relation holds:

$$\psi(x_1, x_2) = -\psi(x_2, x_1) \rightarrow \psi(r_1, s_1; r_2, s_1) = -\psi(r_2, s_1; r_1, s_1)$$
(8)

Now, keep the position  $r_1$  of the first particle fixed and gradually change the spatial position  $r_2$  of the second particle towards  $r_1$ : when the condition  $r_1 = r_2$ is met, one also has  $x_1 = x_2$ , and  $\psi(x_1, x_1) = -\psi(x_1, x_1) = 0$ . Recalling the interpretation of the meaning of the wave function:  $|\psi(x_1, x_2)|^2 dx_1 dx_2$  is the probability to find the particle 1 in the volume element  $dx_1$  and the particle 2 in the volume element  $dx_2$ , it is deduced that the probability to find two spin-parallel identical particles in the same  $dr_1$  spatial volume element must be zero. Moreover, since wave functions are continuous and are required to have no sharp changes with r, even the probability to find two spin-parallel particles in close volume elements  $dr_1$  and  $dr_2$  must be small. That is, two electrons having the same spin avoid each other. It is most important to notice that such avoidance has nothing to do with the electrons, being charged, repel each other, nor it has to do with any other possible repulsion force (and the associated energy): simply, the wave function of two electrons is *shaped* in such a way that it is small the probability of having two spin-parallel electrons close to one another. Note also that things are different for two electron having different spin (they are spin paired), as in this case  $x_1$  is always different from  $x_2$  even if  $r_1 = r_2$ .

When Coulomb interaction is considered by integrating the 1/|r| Coulomb potential over all the spatial positions assumed by the two electrons, weighted by the relevant probability:

$$V_{ee} = \int \mathrm{d}r_1 \mathrm{d}r_2 \, \frac{e^2}{|r|} \, |\psi(r_1, r_2)|^2 \tag{9}$$

it turns out that, if the two electrons have the same spin, such interaction energy  $V_{ee}$  is lower than the energy for two spin-paired electrons. This fact is called *electronic exchange* and the energy difference between the two cases is named *exchange energy*.

#### 2.4 The Hartree-Fock method

In spite of its fairly simple look, the time independent Schrödinger equation can be exactly solved in very few cases. The hydrogen atom is one of those, but with just the two electrons case (the helium atom, for instance) an exact solution is impossible and approximated methods of solution had to be devised. Many of them relied upon the variational theorem which will be here stated without a proof (that can be easily found on many basic textbooks): given an approximate wave function  $\phi$  of an exact wave function  $\psi$ , the energies  $E_{\phi} = \langle \phi | H | \phi \rangle$  and the exact  $E_{\psi}$ , from the equation  $H | \psi \rangle = E_{\psi} | \psi \rangle$ , are such that  $E_{\phi} \geq E_{\psi}$ , and  $E_{\phi} = E_{\psi}$  if and only if  $\phi = \psi$ . In words, the energy correspondent to whatever approximated wave function will be always greater than the exact energy associated to the exact wave function. The *trick* is then to make the approximate wave function  $\phi$  dependent upon some parameter a(or upon a set of parameters), and minimizing the resulting  $E_{\phi}(a)$  function with respect to a: the particular value of a that minimize  $E_{\phi}$  (let's call it  $a_0$ ) will provide the closest possible energy  $E_{\phi}(a_0)$  and wave function  $\phi(x; a_0)$  to the correspondent exact  $E_{\psi}$  and  $\psi(x)$ . Such procedure is named the *variational method*.

Let's see how the variational method is employed in the solution of a twoelectron system (like the helium atom). This simple system alone will show many of the key points and issues that we find when quantum mechanics is applied in the derivation of properties of many-electron atoms, molecules and crystals. First, one has to express the (exact) two-electron wave function  $\psi(x_1, x_2)$  in terms of *one*-electron functions  $\eta(x)$ : a common choice for the  $\eta$  are the atomic spin-orbitals of hydrogen. In fact, any *complete* set of functions  $\eta$ can be used for the purpose, and a theorem from mathematics says that the set of eigenfunctions of any operator related to whatever observable (technically, any *Hermitian* operator) is complete. The atomic spin-orbitals of hydrogen do indeed constitute a complete set, since they are the eigenfunctions of an Hamiltonian. The expansion of a two-electron function in terms of one-electron functions can always be done exactly, as assured by the Boys' theorem:

$$\psi(x_1, x_2) = \sum_{i,j=1}^{\infty} c_{ij} \eta_i(x_1) \eta_j(x_2)$$
(10)

where the  $c_{ij}$  are scalars. By introducing the antisymmetry principle [that is,  $\psi(x_1, x_2) = -\psi(x_2, x_1)$ ] in equation (10), one easily derives that  $c_{ij} = -c_{ji}$ ,  $c_{ii} = 0$  and the whole sum can be expressed as an infinite series of determinants (Slater determinants, or detors):

$$\psi(x_1, x_2) = \sum_{i,j \neq i}^{\infty} c_{ij} [\eta_i(x_1) \eta_j(x_2) - \eta_j(x_1) \eta_i(x_2)] =$$

$$= c_{12} \left| \begin{array}{c} \eta_1(x_1) \eta_2(x_1) \\ \eta_1(x_2) \eta_2(x_2) \end{array} \right| + c_{13} \left| \begin{array}{c} \eta_1(x_1) \eta_3(x_1) \\ \eta_1(x_2) \eta_3(x_2) \end{array} \right| + \cdots$$
(11)

It must be emphasized that such infinite expansion is an *exact* representation of the original two-electron wave function. Since, when doing real calculations, it is practically impossible to work with infinite series, the above Boys' series must be truncated. One way to do such truncation is to build all the possible detors from a *finite* subset of the, otherwise infinite, set of one-electron  $\eta$ functions. The resulting approximated wave function will depend upon the  $c_{ij}$ scalars  $[\phi(x_1, x_2; c) \approx \psi(x_1, x_2)]$  and, by following the variational method, the most effective approximation can be found by minimizing  $E_{\phi}$  with respect to the c's. Such technique is known with the name of *Full CI* where *CI* stands for *Configuration Interactions*. The energy minimization process (common in all the variational techniques) reduces to the diagonalization of the *Hamiltonian matrix* which is the representation of the Hamiltonian operator in the space spanned by the detors. The lowest eigenvalue of such a matrix is the energy of the lowest energy state, and the corresponding eigenvector gives the c's coefficients of the polydetor representing the same state. Each detor represents an electronic configuration, and the *polydetor* somehow incorporates their interactions. To clarify the point, if  $\eta_1$  and  $\eta_2$  represent the 1s electrons with spin up and down respectively, and  $\eta_3$  is the 2s electron with spin up, then the first detor in expression (11) is the configuration with the two electrons paired in the 1s orbital; the second detor represents an *excited* configuration: two spin-parallel electrons, one of which occupying the 1s orbital, and the second one occupying the 2s orbital. The resulting  $\phi$  wave function is a mix of of the two configurations with weights determined by the variationally optimized c's coefficients. In a case like the one considered (the helium atom),  $c_{12}$ will be very large compared to the coefficient associated to the excited configuration, thus we say that the ground state electronic configuration of He is reasonably well described by the electrons occupying the two 1s hydrogenoid spin-orbitals, with spins paired<sup>2</sup>. The Full CI method is very effective (actually is one of the most accurate techniques developed) but it is really very costly in terms of computer power and computing time, as the number of detors to be considered in the calculation increases very rapidly with the number of one-electron functions and the number of electrons in the system. In fact, Full CI is usually applied for atoms and small molecules only. On the same line, the CAS-CI (Complete Active Space CI) or RAS-CI (Restricted Active Space CI) techniques are less expensive and based on truncation criteria of the Full CI polydetor.

The most popular and widely used method, at least in the past, due to its reasonable cost and accurate enough results (for at least a set of systems, as it will be seen below) is the *Hartree-Fock* one: it is based on a very *crude* truncation of expression (11): one determinant only! To reduce the generally very large truncation error that would result, the trick is to modify (and variationally optimize) the one-electron spin-orbitals  $\eta$  used to build the determinant. In practice, every  $\eta$  is substituted with a new one-electron function  $\xi$  which, in turn, is defined through a linear combination of one-electron hydrogenoid wave function  $\eta$ 's. In formula, the exact two-electron wave function  $\psi$  is approximated by a two-electron function  $\phi$ :

$$\begin{cases} \psi(x_1, x_2) \approx \phi(x_1, x_2) = c \begin{vmatrix} \xi_1(x_1) & \xi_2(x_1) \\ \xi_1(x_2) & \xi_2(x_2) \end{vmatrix} \\ \xi_i(x) = \sum_{j=1}^N a_{ij} \eta_j(x) \end{cases}$$
(12)

where c is a normalization constant, N is the number of hydrogenoid functions used to expand each function  $\xi$ , and the  $a_{ij}$  scalars are the set of coefficients to be variationally optimized to get the best possible approximated wave function  $\phi$  together with its energy. In the case of helium we could, for instance, decide to use the 1s and 2s hydrogenoid spin-orbitals as  $\eta$  functions (four

<sup>&</sup>lt;sup>2</sup> In systems having no spin unpaired electrons, in a non-relativistic approximation, an *orbital* ( $\zeta$ ) gives rise to two spin-orbitals ( $\eta_1$  and  $\eta_2$ ) having the same orbital part ( $\zeta$ ) and two different spin function ( $\sigma_1$  and  $\sigma_2$ ):  $\eta_i(x) = \zeta(r) \cdot \sigma_i(s)$ .

functions, considering the spin variable). The Hamiltonian operator will then be represented in the space of such four functions, and the diagonalization of the resulting 4x4 H matrix will provides the four eigenvalues and the corresponding eigenvectors. Such four eigenvalues are the energies of the four one-electron atomic spin-orbitals ( $\xi$ ) of helium expressed in terms (a linear combination of) the one-electron hydrogenoid spin-orbitals ( $\eta$ ). In terms of orbitals, the two electrons occupy the same orbital with opposite spins (the first two spin-orbitals are degenerate: they have the same energy; likewise the third and fourth spin-orbitals).

When extended to the case of molecules, such  $\xi$  functions are called *molecular orbital* (MO) expressed as Linear Combination of Atomic Orbitals ( $\eta$ ; LCAO), centered on each nucleus of the atoms constituting the molecule; the whole Hartree-Fock (HF) procedure (HF-MO-LCAO) is the core of the model used for the interpretation of the molecular structure and molecular properties, in terms of *bonds* properties inferred from the nature (*spatial extension*, *shape*, *nodes*) and energies of the molecular orbitals.

It is both interesting and important to take a look at the energy of a multielectronic system in the frame of the Hartree-Fock approximation. Given the *exact* Hamiltonian H with nuclei *standing still* (no kinetic energy terms for nuclei) in the form of:

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i,a=1}^{n,N} \frac{Z_a e^2}{r_{ia}} + \frac{1}{2} \sum_{a,b\neq a}^N \frac{Z_a Z_b e^2}{r_{ab}} + \frac{1}{2} \sum_{i,j\neq i}^n \frac{e^2}{r_{ij}}$$
(13)

where n is the number of electrons, N in the number of nuclei; the indices aand b run on nuclei, whereas i and j run on electrons;  $Z_a e$  and  $Z_b e$  are nuclear charges,  $r_{ia}$ ,  $r_{ab}$  and  $r_{ij}$  are respectively electron-nuclear, inter-nuclear and inter-electron distances. The first term in (13) accounts for the kinetic energy of electrons [see equation (6)]; the second term is the nuclei-electrons interaction; the third and fourth terms are respectively the nuclei-nuclei and electrons-electrons interactions. It is precisely the last term that creates problems in the solution of the Schrödinger equation, even within the Hartree-Fock approximation. Anyway such problems can be overcome with the recourse to an iterative approach called *Self Consistent Field* (SCF). When the operator H is represented in the space of the molecular orbitals (to variationally solve the Schrödinger equation) several contributions arise: kinetic  $(T_e)$ and electrons-nuclei  $(V_{Ne})$  one-electron terms; two-electron terms due to the electrons-electrons interaction  $(V_{ee})$ . The  $V_{NN}$  nuclei-nuclei interaction term is just a fixed contribution for a fixed nuclear spatial configuration. After some algebraic manipulations and after *integration* over the spin variable, it can be shown that (within the Hartree-Fock frame) the  $V_{ee}$  term for two electrons in the i and j spin-orbitals consists of two contributions: a *Coulomb* contribution  $J_{ij}$ :

$$J_{ij} = \int dr_1 dr_2 \rho_i(r_1) \rho_j(r_2) \frac{e^2}{r_{12}}$$
(14)

and an exchange contribution  $X_{ij}$ :

$$X_{ij} = -\delta_{s_1 s_2} \int \mathrm{d}r_1 \, \mathrm{d}r_2 \, \zeta_i^*(r_1) \zeta_j^*(r_2) \zeta_j(r_1) \zeta_i(r_2) \frac{e^2}{r_{12}} \tag{15}$$

In expression (14),  $\rho_i$  is the distribution of the  $i^{th}$  electron; likewise for  $\rho_j$ . Thus  $J_{ij}$  is nothing else than the Coulomb interaction of the two electrons i and j described by their respective charge distributions  $\rho$ . Note the absence of *pointwise* interactions: the interaction is calculated by averaging over the positions of the two electrons, each one being subjected to the *mean field* created by the other electron. This fact is at the core of the *correlation problem* (lack of pointwise electronic interactions) which will be discussed below.

The term X of expression (15) is known with the name of *electronic exchange*. It is a direct consequence of the antisymmetry principle as it is declined in the Hartree-Fock approximation. Symbols  $\zeta$ 's represent the orbital part of the spin-orbitals, and the \* in  $\zeta^*$  denotes complex conjugation. The electronic exchange has essentially three important features: (*i*) it is *non local*, due to the presence of products like  $\zeta_i(r)\zeta_j^*(r)$  that cannot be reduced to *local* electron densities as it was for the J term; (*ii*) it is not zero only if the spins of the two electrons are parallel (the Kronecker  $\delta_{s_1s_2}$  assures that); (*iii*) it has a negative sign. The *total* electrostatic interaction term between the two electrons is then:  $V_{ij} = J_{ij} + X_{ij}$ . Due to the sign of X, the interelectronic potential energy is lower for electrons having parallel spins, compared to spin paired electrons: (it costs energy to pair two electrons: this is at the base of the well known Hund's rule). It must be emphasized that the *exchange energy* is not a *new kind of energy*: it is just a corrective term to the way the electrostatic interaction is evaluated (through the J term) to take antisymmetry into account.

By the way, a point that could seem just technical and fundamentally unimportant at this level of discussion (but that, instead, will result to be crucial in the density functional approach discussed in the next section) has to do with the practical implementation of the Hartree-Fock technique. The term  $J_{ij}$  can be written as:

$$J_{ij} = \int dr_1 \,\zeta_i^*(r_1) \left\{ \int dr_2 \,\zeta_j^*(r_2) \frac{e^2}{r_{12}} \zeta_j(r_2) \right\} \zeta_i(r_1) \equiv \int dr_1 \,\zeta_i^*(r_1) \hat{J}_j \zeta_i(r_1) \tag{16}$$

where a one-electron operator  $\hat{J}_j$  has been defined. Likewise, a similar oneelectron operator  $\hat{X}_j$  is defined for the exchange term. After some manipulation, the electronic potential  $V_{ee}$  can be expressed in the form

$$V_{ee} = \frac{1}{2} \sum_{i} \int dr_1 \, \zeta_i^*(r_1) (\hat{J} - \hat{X}) \zeta_i(r_1) \tag{17}$$

where, for each i term of the summation, the  $\hat{J}$  and  $\hat{X}$  operators are defined as

$$\hat{J} = \sum_{j \neq i} \hat{J}_j \text{ and } \hat{X} = \sum_{j \neq i} \hat{X}_j$$
 (18)

The condition  $j \neq i$  in the two summations (18) means that the operators  $\hat{J}$  and  $\hat{X}$ , to be plugged in the expression (17), are different for each *i* of the summation occuring in (17). This is not practical for the coding of an automated algorithm written to solve the equations. The way out is to remove the condition  $j \neq i$  in the summations (18), and this can be done with no harm as, when j = i,  $J_{ii} = X_{ii}$  so that the two terms cancel out exactly in (17). Note that  $J_{ii}$  would mean the interaction of the *i*<sup>th</sup> electron with itself. The Hartree-Fock exchange term ensures that such self-interaction error (SIE), introduced in the algorithm, is exactly zero.

#### 2.4.1 Some examples

Let's consider an hydrogen molecule  $(H_2)$  and, by using the Hartree-Fock method, let's calculate the total energy and its separate contributions, for different values of the distance between the two nuclei (see figure 1).



Fig. 1 Total, kinetic and potential energy terms [in atomic units (*hartree*)] of the H<sub>2</sub> molecule as a function of internuclear separation (H-H distance in Å). The scale on the left refers to the total energy; kinetic (electronic) and the  $V_{NN}$  potential energies refer to the scale on the right; the total potential energy  $(V_{NN} + V_{ee} + V_{Ne})$  refers to the farthermost scale on the right.

The total energy (continuous curve) has a minimum for an H-H distance of 0.72Å: that is the estimated equilibrium internuclear separation. By looking at the left energy scale it can be noted how small is the variation of the total energy, as the H-H distance is changed, in comparison to the relative variations of the kinetic energy of the electrons (their kinetic energy increases significantly as the two nuclei are squeezed together) and of the total electrostatic potential (the sum  $V_{NN} + V_{ee} + V_{Ne}$ ), that decreases toward more negative values as the H-H distance is reduced. The total energy is thus the small difference between two large contributions of opposite sign: a positive kinetic energy contribution and a negative electrostatic one. From the computational point of view, this has the consequence that even small relative errors in the evaluation of the separate contributions can result in large relative errors of their difference, having therefore a dramatic impact on the prediction of the equilibrium geometry and on the binding energy (thermochemistry). From the physical-chemical point of view, it is interesting to note that the rapid increase of the total energy, at H-H distances lower than the equilibrium one, is not due to an increased electrostatic repulsion, nor to the presence of a mysterious short range force of quantum origin (as it is sometimes written is basic chemistry textbooks): it is rather due to the rapid increase of the kinetic energy of the electrons. Indeed, the total potential is still decreasing at the equilibrium distance (see the dotted curve in figure 1) due to the dominance of the  $V_{ne}$  (negative) energy term over the (positive)  $V_{NN}$  and  $V_{ee}$  ones. These facts are not at all new: they were already clearly pointed out by Slater (1967), for instance, in one of his masterpieces on quantum chemistry.

The Hartree-Fock wave function  $\phi$  (12) is not an eigefunction of the *exact* Hamiltonian (13); it is however the eigenfunction of the *Hartree-Fock Hamiltonian* ( $H_{HF}$ ): the non-exact nature of  $\phi$  is transferred onto the Hamiltonian, and thus we have an exact solution of an approximated Hamiltonian rather than an approximated solution of an exact Hamiltonian. Formally:

$$H_{HF}\phi = E_{HF}\phi \tag{19}$$

where  $E_{HF}$  is the Hartree-Fock energy. The difference between the two Hamiltonian operators  $H_c = H - H_{HF}$  is the definition of the *correlation Hamiltonian*, and the corresponding energy difference  $(E_c = E - E_{HF})$  is the *correlation energy*. It has to do with the short range pointwise electronic interactions that are neglected in the mean field Hartree-Fock approach. A fraction of such interactions is responsible for the *dispersion energy* and the associated *dispersion force*. However small, such correlation energy can have a magnitude comparable with the binding energy of a system, so that its neglection can lead to relatively large errors in geometry and termochemistry.

Correlation lays in those neglected determinants of the truncated Boys expansion (11) and, since each of those determinants would correspond to an excited electronic configuration, dispersion forces are often *pictorially* described as if they were due to the coupling of fluctuating dipole moments, the latter being generated by fluctuations of the electron density, in turn due to random electronic excitations. Of course, there cannot be real fluctuations in whatever model based on the *time independent* Schrödinger equation [nor the time is a variable entering in the exact Hamiltonian (13) at all].

The electronic correlation is generally negligible in those systems having a small number of electrons and a large binding energy. That is at the core of the success of the Hartree-Fock method in quantum-chemistry, for the modeling of a very large number of molecules, expecially organic compounds.

Traditionally, quantum mechanical calculations for crystals did follow a different path: rather than a *wave function* based approach, the one based

on the *electron density* was developed (the Density Functional Theory, DFT, as it will be discussed in the next section). However, in the '80s, a program (CRYSTAL) was developed at the University of Torino that applied the Hartree-Fock method to crystals (see for instance Pisani and Dovesi, 1980). Since then, CRYSTAL has been applied to study a very large set of covalent and ionic compounds, many of them being of mineralogical interest. In this respect, looking at the Hartree-Fock calculations only (actually, CRYSTAL applies DFT and hybrid HF/DFT approaches, too), the literature is huge and a list of works can be found on the CRYSTAL web site, at the address http://www.crystal.unito.it/elementi/node1.html. Here I only report the early calculations on  $\alpha$ -quartz (Dovesi et al., 1987) and corundum (Causà et al., 1987), as well as the systematic application of the method to the alkali halides as an example of application to ionic compounds [Prencipe M, 1990: Master thesis, University of Torino, Italy; Prencipe et al., 1995]. Other examples of application of the Hartree-Fock technique to minerals can be found in Prencipe (2002) and Prencipe et al. (2003), dedicated to beryl and spodumene respectively.

Concerning alkali halides, calculations provided results in reasonable agreement with experimental measurements if the elements involved had a low atomic number, due to the low correlation error. Discrepancies with respect to the experiments increased with the atomic number. Looking at the results for NaCl, and to the bulk modulus  $(K_0)$  in particular, the Hartree-Fock datum from the second derivative of the energy-cell volume curve, at the equilibrium volume, gave 22.3 GPa (Prencipe et al., 1995). An estimation of the same quantity (this work) from a volume-integrated third order Birch-Murnaghan (BM3) equation of state, gave 24.0 GPa (K' = 4.6), not too far from the older result. These estimations are however at the *static level*: they do not take into account the effect of atomic vibrations within the solid that have a role in generally *decreasing* the elastic moduli (this point will be further discussed in the last section; see also Prencipe et al., 2011). When such dynamic effects are properly taken into account, at a temperature of  $300 \,\mathrm{K}$ ,  $K_0$  decreases to 20.6 GPa (and K' = 4.0; this work). The experimental estimation of the bulk modulus of NaCl provides a value of 23.7 GPa [from a BM3 fit of P(V) data; K' = 5.14; see Matsui et al., 2012]. Thus the Hartree-Fock estimation of  $K_0$  is somewhat underestimated with respect to the experiment. An hybrid HF/DFTapproach, that corrects for some correlation effects (see next section), provides a bulk modulus at 300 K of 23.05 GPa and K' = 5.2 (this work) which is very close to the experimental value at the same temperature.

There are *limiting* cases where the Hartree-Fock method is useless: as said above, when the binding energy (due essentially to the accumulation of electronic charge in the binding regions of a molecule; see Berlin, 1951) is so low to become comparable to the correlation energy, computed results could be very far from *reality*. That is the case of dimers of noble gases whose very weak binding is attributed to *dispersion forces*, which means that it is correctly described only with the recourse to a generally very large number (millions) of Slater determinants in the Boys' expansion above. Figure (2) illustrates the point in the case of the helium dimer where the energy variations, with He-He distance, are about one hundredth of the corresponding variations in  $H_2$  [compare the left energy scales of figures (1) and (2)]. The continuous curve in figure (2) has



**Fig. 2** Total energy (in hartree) of the  $\text{He}_2$  dimer as a function of the He-He nuclear distance (in Å). The continuous curve refers to a coupled cluster calculation [CCSD(T); see text for explanations]; the dashed curve is evaluated with a Density Functional approach (see next section) and the dotted curve is the Hartree-Fock one

been obtained (this work) by using a version of the *coupled cluster* technique (see for instance Crawford and Schaefer, 2007); coupled cluster is a very efficient and accurate quantum chemical technology: it is comparable to the Full CI method, but it is faster and significantly less expansive than the latter. It is our reference here. Coupled cluster predicts a bound state having an equilibrium distance of 2.97 Å which is the same value proposed by Ogilvie and Wang (1991), whereas Hartree-Fock does not find a minimum in the energy curve (no bound state). A Density Functional calculation (this work) made by using one of the most recent functional developed ( $\omega$ -B97X-D; Chai and Gordon, 2008) also predicted a bound state but overestimates the equilibrium distance and shows a too sharp increase of the energy at small He-He distances, compared to the coupled cluster calculation. Systems like those of noble gases (or even clusters or crystals of apolar organic molecules) are limiting cases where the Hartree-Fock method is surely not the right choice. Other cases are less extreme; however, to reach an accuracy level comparable to what experimental measures do provide, it is necessary to move beyond Hartree-Fock and to deal with the electron correlation problem. This is discussed in the next section.

#### 3 The Density Function Theory (DFT)

As seen in section 2, at the molecular level the approch followed to solve the Schrödinger equation was the Hartree-Fock one or other wave function based technologies like the Full CI, the coupled cluster or even other methods not quoted in this paper (a very popular one is the Møller-Plesset perturbative method - MP2). In the solid state field, historically, scientists proceeded differently. As soon as quantum mechanics was established at a very basic level, scientists tried to deal with problems like the electrical conductivity in metals and their optical properties. Metals were particularly actractive as the reasonable hypothesis of a substantially free electron gas, which could be modelled in a relatively easy way, seemed to be a good starting point to *explain* their conductivity. Textbooks like the Ashcroft and Mermin (1976) provide really good accounts of the early ideas and attemps to apply quantum mechanics to metals. Anyhow rather than on the wave function, the focus was on the electron density function  $[\rho(r)]$  that can easily be related to the wave function. In fact, for a two-electron system one has:

$$\rho(r) = 2 \int dr' \, |\psi(r, r')|^2 \tag{20}$$

(the dependence upon a spin variable is here neglected). Indeed, integrating  $\rho(r)$  over all the space, one gets 2 (the number of the electrons in the system), as the wave function  $\psi$  is normalized (its double integral over all the space is 1). A relation was found relating the kinetic energy of the homogenous free electron gas and its electron density (which is a constant in such a gas) and this fact was used to successfully *explain* some properties of the metals of the first group of the Periodic Table (with some good luck due to errors cancellation).

Since those early attemps, Density Functional Theory (DFT) had a huge development and it is the technique invariably employed at the solid state level as, by insisting on a wave function based approach, it proved to be extremely difficult and expansive to go beyond the Hartree-Fock approximation [see however the CRYSCOR project (Pisani et al., 2008) that applies the perturbative MP2 technique to crystals]. Its foundations rest on the Hohenberg-Kohn theorem (Hohenberg and Kohn, 1964) that was proved to be true somewhat later than many applications of DFT to real problems were already published. As it is generally stated today, the theorem says that, given an external potential (for instance the electrostatic potential due to a specific configuration of nuclei), the electron density is uniquely determined and, viceversa, the electron density uniquely determines the nuclear potential and thus the total Hamiltonian of the system. Thereby, there must exist a *functional* of  $\rho$  ( $\varepsilon[\rho]$ ) whose knowledge allows the calculation of the total energy of the system:

$$\begin{cases} E_{tot} = E[\rho] + \frac{1}{2} \sum_{a,b \neq a} \frac{Z_a Z_b e^2}{|R_a - R_b|} \\ E[\rho] = \int dr \, \rho \, \varepsilon[\rho] \end{cases}$$
(21)

where  $E[\rho]$  is the total electronic energy. If the functional  $\varepsilon[\rho]$  were known, then the correct electron density  $\rho$ , for a system having a given nuclear configuration, could be found by minimizing  $E[\rho]$ , without the recourse to the Schrödinger equation at all. In the practical implementation of DFT, the electron density is still *strumentally* calculated, through integrals like (20), from a wave function depending upon some parameters, as in the Hartree-Fock method discussed in the previous section, and then the energy is *variationally* minimized with respect to those parameters. The important point here is that the Hohenberg-Kohn theorem does not provide the form of  $\varepsilon$ : the functional must exist but nobody knows what it is.

The quest for effective and general functionals is a never-ending story. A good account of it, from the basic to the advanced level, can be found in chapter 11 of the Trindle and Shillady book (Trindle and Shillady, 2008). Here we just note the key points. One of the first model proposed for the electronic energy  $[E_{TFD}]$  was the Thomas-Fermi-Dirac one:

$$E_{TFD}[\rho] = T_{TF}[\rho] + E_{ne}[\rho] + J[\rho] - X_D[\rho]$$
(22)

where  $T_{TF}$ ,  $E_{ne}$ , J and  $X_D$  are respectively the kinetic energy of electrons, the nuclei-electrons potential energy, the electrons-electrons potential energy and the exchange (electronic) energy as proposed by Dirac (Dirac, 1930b). For the *curious* reader, the expressions of the functionals are:

$$\begin{cases} T_{TF} = \frac{3(3\pi^2)^{2/3}}{10} \int \rho^{5/3}(r) \, \mathrm{d}r \\ E_{ne} = \sum_a^N \int \frac{Z_a \rho(r)}{|R_a - r|} \, \mathrm{d}r \\ J = \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r - r'|} \, \mathrm{d}r \mathrm{d}r' \\ X_D = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(r) \, \mathrm{d}r \end{cases}$$
(23)

One of the important aspects concerning the expressions of the various components of the total electronic energy is that they are all *local*: they depends only upon the electron density at any given point and not on its derivatives. All of the subsequent developments of *local* functionals proposed by other more modern Schools fall under the LDA category (Local Density Approximation; Trindle and Shillady, 2008). The problem with *locality* is essentially that exchange [which is *non*-local, as discussed in section (2.4)] and *long range* correlation effects (dispersion forces) are not properly described. On the other hand, *short range* correlation effects<sup>3</sup> are taken into (approximated) account. More advanced functionals try to go beyond *locality* by introducing, in their

<sup>&</sup>lt;sup>3</sup> Although pointwise correlation effects are short ranged if compared to mean field effects described at the Hartree-Fock level, they can be classified in two categories: *short range* and *long range* effects, where the adjectives *short* and *long* have here a relative meaning inside this further classification. Dispersion forces are ascribed to such long range correlation effects, and are generally not properly accounted for by DFT functionals; DFT correlation functionals are instead effective in dealing with the short range effects.

expressions, dependences upon the gradient of the electron density: they fall under the GGA category (Generalized Gradient Approximation). However, apart some very recent formulations, even GGA functionals are generally not effective in dealing with dispersion forces.

The density functional approach is applied not only to solids, but at the molecular level too, to study large systems and bio-molecules, due to its limited cost compared to more advanced Full CI or coupled cluster calculations. To this end, many advanced functionals has been developed and one example of the most recent formulations is provided by the  $\omega$ -B97X-D functional (Chai and Gordon, 2008) used above for the calculation of the equilibrium distance in the He<sub>2</sub> dimer (this formulation also includes a parametrization to deal with dispersion energy at the *classical* level). As crystals are concerned, however, the most popular functionals which are systematically employed are those from the Becke and Perdew Schools, and they only will be briefly reviewed here (although many of the modern functionals are nowadays coded in programs for crystals, too; see for instance the last release of the CRYSTAL program; Dovesi et al., 2018).

The two Becke and Perdew Schools developed different functionals to describe the GGA electronic exchange to be associated, as a correction, to the original Dirac LDA exchange (Dirac, 1930b): Becke developed the *B*88 gradient term (Becke, 1988) to be added to the LDA part; Perdew developed the PBE gradient corrections to be *multiplied* to the same Dirac LDA exchange (Perdew et al., 1996). Note that the expressions for electronic exchange, formulated at the DFT level, are always approximations of the exact *non*-local Hartree-Fock exchange.

In the Becke approach, electronic exchange must be coupled to an appropriate formulation of electronic correlation (absent, by definition, at the Hartree-Fock level). To this end, the LDA Vosko, Wilk and Nusair functional (VWN, from the expression derived for the homogeneous electron gas; Vosko et al., 1980) or the GGA Lee, Yang and Parr functional (LYP, derived from the knowledge of the one-electron and two-electron density matrices, calculated at the Hartree-Fock level; Lee et al., 1988) are often employed. On the Perdew side, the PBE functional provides both exchange and correlation.

Many other functionals for both exchange and correlation do exist, and they can be combined following some criteria to get the best results for some classes of systems. However, note that exchange and correlation functionals are generally developed together following some *philosophy*, and thus it is not wise to combine them randomly.

A first procedure, attempting to introduce correlation effects to correct the Hartree-Fock predictions, was to plug in the Hartree-Fock electron density in a correlation functional in order to calculate the correlation energy; an example was the set of alkali halides from LiF to RbBr (Prencipe M, 1990: Master thesis, University of Torino, Italy): the correlation PW86 functional (Perdew, 1986) was employed, but the results were not very satisfactory. In particular, the correction was somewhat too *rigid*: the cell parameter, for instance, was *over-corrected* for light compounds like LiF or NaF (that, in fact, need not

to be corrected), whereas it was not corrected enough for heavier compounds (RbBr). The reasons of such partial failure had to be searched in the wrong exchange-correlation coupling (the exchange was the exact Hartree-Fock one) and in the fact that the electron density was obtained without taking correlation into account. Concerning the first point, it seems to be a bad idea to couple the (total) Hartree-Fock exchange with some correlation functional (Prencipe and Nestola, 2005).

#### 3.1 The *hybrid* functionals

One of the problem of the DFT approach has to do with the Self Interaction Error (SIE) discussed at the end of section (2.4). Precisely, the pratical implementation of a DFT algorithm closely parallels the Hartree-Fock procedure and, in particular, the Coulomb operator  $\hat{J}$  is calculated with the same method already discussed above [equation (18)] by removing the condition  $j \neq i$  in the summation (we recall that the added i = j term is equivalent to the interaction of an electron with itself). This gave no problem at the Hartree-Fock level as, for each i, the corresponding exchange term  $\hat{X}_i$  exactly canceled such unphysical  $\hat{J}_i$  contribution. At the DFT level the situation is different as the exchange is evaluated through an approximate functional  $X[\rho]$ , so that the cancellation of SIE is not complete. As the SIE increases with the electron density, the atomic core regions are those where the error is larger and, as a consequence, their volumes are expanded (to reduce  $\rho$ , and hence SIE and the total energy). This leads to an overestimation of the geometrical parameters (interatomic distances and lattice constants). Not only, but another *possibility* that the DFT model has, in order to reduce the SIE, is to shift electrons out of the core regions to the valence part of the atoms (Cremer, 2001): this decreases the energy but creates *spurious* forces that *simulates* dispersion effects, generally in a not *proper* way (indeed, it can be said that the apparent success that some GGA functionals have, in dealing with dispersion forses, is due to the self interaction error in the core region).

The SIE can be reduced by adding a fraction of the Hartree-Fock exchange to the corresponding DFT term. This strategy led to the development of the so called *hybrid* HF/DFT functionals. One of the most popular is the B3LYP functional, developed by the Becke group (Becke, 1993) and extensively applied to molecules and crystals (Koch and Holthausen, 2000). Its formulation consists of a fraction (20%) of Hartree-Fock exchange, added to LDA e GGA exchange functionals; precisely, such formulation is:

$$E_x(\text{B3LYP}) = E_x(\text{LDA}) + a_0[E_x(\text{HF}) - E_x(\text{LDA})] + a_x[E_x(\text{GGA}) - E_x(\text{LDA})]$$
(24)

where  $E_x(\text{LDA})$  is the Dirac LDA exchange (Dirac, 1930b);  $E_x(\text{HF})$  is the Hartree-Fock exchange, and  $E_x(\text{GGA})$  is the Becke GGA exchange (Becke, 1988). The coefficients  $a_0 = 0.2$  and  $a_x = 0.72$  specify the weights of the Hartree-Fock and of the GGA contributions, respectively, to the total ex-

change. The correlation part of B3LYP is formulated as:

$$E_c(B3LYP) = E_c(LDA) + a_c[E_c(GGA) - E_c(LDA)]$$
(25)

where  $E_c(\text{LDA})$  is the VWN LDA correlation (Vosko et al., 1980), and  $E_c(\text{GGA})$  is the LYP GGA functional (Lee et al., 1988); the value of the  $a_c$  coefficient is 0.81. The values of the three coefficients  $a_0$ ,  $a_x$  and  $a_c$  were set by best fit of the computed results against the experimental ones, for a number of properties (atomization energies, ionization potentials, affinities, and total atomic energies) of a set of atoms (Becke, 1993).

Another more recent hybrid formulation that provides very good results, expecially concerning compressibilities and vibrational properties (computed frequencies and relative intensities in Raman and infrared spectra) of carbonates and silicates, is the WC1LYP functional, which employs the Wu-Cohen GGA exchange functional (Wu and Cohen, 2006). The weight of the Hartree-Fock exchange in WC1LYP amounts to 16%.

#### 3.2 Some examples

The examples shown here do not pretend to review the overall range of possibilities and applications of the DFT techniques published in literature (not even a whole book would be enough to cover every aspect). Rather, the discussion and the supporting examples are mainly focused on comparisons of results from different functionals concerning the calculation of vibrational frequencies. The choice of such observables is due to several reasons: (*i*) they are one of the first outputs from quantum-mechanical calculations (after the estimation of the geometrical structure under a specific space group); (*ii*) vibrational frequencies are quantities subtle enough to reveal weakness and strength points of the chosen DFT functionals; (*iii*) they are *immediately* useful in the interpretation of infrared and Raman spectra; (*iv*) they serve as a basis for the estimation of thermo-elastic and thermodynamical properties within a statistical-thermodynamical frame (discussed in the last section).

The relative performances of various DFT and HF/DFT formulations has been tested in a number of cases and, generally, the HF/DFT results are more accurate than those from *pure* DFT. For instance, in Prencipe et al. (2012) the Raman spectrum of diopside was calculated by using several functionals: WC1LYP, B3LYP, PBE0, PBE, WCPBE, LDA and the Hartree-Fock. Besides WC1LYP and B3LYP, PBE0 is the hybrid version (25% of HF exchange) of the purely DFT GGA PBE functional by Perdew et al. (1996); WCPBE is the original version of the Wu-Cohen exchange-correlation functional (WC functional for exchange, and PBE functional for correlation; Wu and Cohen, 2006). With reference to the experimental wave numbers, the best agreement was obtained with WC1LYP (average discrepancy  $3.2 \text{ cm}^{-1}$ ), followed by B3LYP ( $4.7 \text{ cm}^{-1}$ ) and PBE0 ( $6.5 \text{ cm}^{-1}$ ); of the purely DFT GGA functionals, the worst was PBE ( $18.0 \text{ cm}^{-1}$ ) with WCPBE performing better ( $9.7 \text{ cm}^{-1}$ ). LDA performed better than GGA ( $7.3 \text{ cm}^{-1}$ ). Hartree-Fock was definitely the worst with its  $40.6 \text{ cm}^{-1}$  of average discrepancy. Note the performance of LDA which is better than GGA, in spite of the fact that LDA represents a lower level of approximation with respect to GGA (this fact probably reflects some error cancellation in LDA, that is removed in GGA, thereby worsening the results; Cremer, 2001).

The relative performance of the B3LYP and PBE functionals was also tested in the case of the vibrational spectrum of lizardite (Prencipe et al., 2009): PBE systematically provided lower frequencies with respect to B3LYP even if, in the comparison with experimental data (infrared and Raman spectra), the two functionals were almost equivalent. The comparison with the experiments was however complicated by the presence of several anharmonic modes involving hydrogen: it was possible to correct the frequencies of the O-H stretching modes for the anharmonic effect, but the same could not be done for the bending modes (due to the coupling among modes falling in the same spectral range). Significant differences in the frequencies of at least some vibrational modes (with respect to both experimental values and B3LYP or PBE calculations) were instead observed in the computational work of Balan et al. (2002): the latter Authors used the PBE functional along with a plane waves basis set, instead of localized hydrogenoid orbitals, to represent the wave function used to work out the electron density. This fact is quite common in solid state calculations: the set of one-electron functions employed in the representation of the multi-electronic wave function [Boys' expansion (10)] can be any set satisfying the *completeness* condition: in short, every function satisfying very general requirements can be represented as a linear combination of functions of a *complete* set, more or less like every vector of a vector space can be represented as a linear combination of a set of basis vectors; in turn, every set of functions that happen to be eigenfunctions of whatever Hermitian operator is complete. For this reason, the set of hydrogenoid atomic spin-orbitals is complete, as indeed they are the eigenfunctions of the Hamiltonian (Hermitian operator) of the hydrogen atom. The same is true for plane waves as they are eigenfunctions of the Hamiltonian for the free electron (of course, the set of plane waves is complete for other mathematical reasons too, but the explanation given here puts orbitals and plane waves on equal footing). Plane waves are employed by the majority of codes for the quantum-mechanical calculations for crystals essentially because they simplify the calculation of the Coulomb integrals, but have two important drawbacks: (i) it is pratically impossible to describe the highly localized electron density of atomic core regions by using plane waves, so that rigid *pseudopotentials* for the cores must be employed: the latter are *effective* potentials that make the job of taking into account both the nuclear and the core electrons charges and imposing, at the same time, suitable mathematical conditions to avoid the penetration of the valence electron wave function into the core region (a requirement that is ultimately motivated by the Pauli antisymmetry principle); (*ii*) the estimation of the Hartree-Fock exchange requires extremely long computing times if a plane waves basis is employed; thus plane waves are generally coupled to purely DFT functionals only, thereby giving up the benefits derived from the hybrid HF/DFT approaches. As discussed in Prencipe et al. (2009) the problems in the Balan et al. (2002) computation are probably related to the use of plane waves (and of the *pseudopotential* for H), more than to the use of the PBE functional.

For extensive comparisons of performances of different functionals, concerning structures at equilibrium, vibrational properties and relative stability of some minerals, see also the works by De La Pierre et al. (2011), Demichelis et al. (2010a,b) and Maschio et al. (2011). Other examples of *ab initio* computations of vibrational frequencies relevant for Earth Sciences, which employ hybrid functionals, can be found in Aliatis et al. (2015); Corno et al. (2006); De La Pierre and Belmonte (2016), Noel et al. (2006), Pascale et al. (2005), Prencipe et al. (2004, 2006, 2014a); Stangarone et al. (2016, 2017); Tosoni et al. (2006). As a *rule of thumb* it can be said that, as demonstrated in nearly all of the quoted papers, the performance of the hybrid HF/DFT functionals in predicting the frequencies of vibrational modes in crystals is very good, the average discrepancy between the computed wave-numbers and those measured in Raman, or IR, spectra being generally within  $5 \,\mathrm{cm}^{-1}$ .

#### 4 The Atoms In Molecules theory

The electron density function  $\rho(r)$  of molecules and crystals, which is one of the key ingredients and output from the DFT methodologies (and that can, of course, even be measured experimentally) is at the core of a review of the chemical bond definition, and its related properties, developed by Richard Bader, at the McMaster University in Hamilton (Canada), since the eighties onward (Bader, 1994). Fundamentally the theory proposes to base every possible definition and interpretation of bond and its properties, in chemistry, on observable quantities (and  $\rho$  is one of those) rather than on a wave function which is not an observable, but an object *living* in an *infinite-dimensional* Hilbert's space (whatever an Hilbert's space might be, let's say it is not the ordinary space used to describe the experimentally accessible *reality*). To this end, Bader proposed a method for partitioning the space occupied by a given system [a molecule or a (unit cell of a) crystal] based on some features of the total electron density, in order to *identify* the atoms *inside* the system. This point is not trivial: given a biatomic molecule, for instance, where is the surface of contact between the two bonded atoms? Is an atomic radius definable? Moreover, in more complex structures, which atoms are bonded together and which are not? Is the energy of an atom within the molecule a measurable quantity? What is the *real* charge of an ion within a molecule or crystal? Is it definable? Everyone having some experience in mineralogy, immediately realizes that all these questions have to do with the definition of ionic radius, the coordination number and, in general, with the Pauling's rules which dominated the *classical* thinking in crystal-chemistry for years. Curiously, David Brown, whose contributions to crystal-chemistry are widely acknowledged in the mineralogial community, had his room close to the Bader's one at the McMaster University, but the two scientists did not interact too much (Brown, personal communication), though they worked for years on the same subject, even if from two different perspectives.

It must be strongly emphasized that the Bader's partitions of the electron density function into *atomic basins* is not just one of the many possible schemes that can be devised to partition a given domain in several subdomains: at variance with all of the other possibile schemes, the Bader's partitioning has a sound physical basis and clear motivations. To understand the importance of Bader's work, putting it in the appropriate frame, it must be premised that, in 1951, Julian Schwinger (Schwinger, 1951) published a milestone paper where he showed how the whole quantum-mechanics could be derived from an *action principle* [see section (2.1) above]; in particular, the equation of motions and the correspondence principle [discussed above, in section (2.2)] where obtained from the minimization of a *quantum* action formulated in terms of a quantum Lagrange operator. The Schwinger formulation, that was subsequently used as a building block of important conceptual advancements of quantum-mechanics (ending in the developments of the quantum field theory or the string theory) unified both classical and quantum mechanics under the common principle of least action. In the Schwinger work, the general quantum system considered, whose time evolution was considered, is *isolated* (e.q, a particle, a system of particles, a molecule or a whole crystal, with no interactions with the surrounding).

Bader extended the Schwinger approach to non-isolated systems, for instance to the atoms *within* a molecule, which interact with all of the surrounding atoms (Bader, 1994). Such extension of quantum-mechanics to open systems is possible if, and only if, each open subsystem (quantum atom) of the total system (molecule) is bounded by a surface  $(\Omega)$  defined by the condition of zero flux of the gradient of the electron density:  $\nabla \rho(r) \cdot n(r) = 0$  for each point of the  $\Omega$  surface [n(r)] is a unit vector normal to the surface, at each point r]. That is the Bader's partitioning: a subdivision of the total system in interacting subdomains, each one being bounded by an  $\Omega$  surface satisfying the property stated above. Apart from being consistent with the most general principle of least action, such partitioning has the great advantage of being the only one for which it is possible to assign definite values to several physical key quantities: for instance, it can be shown (Bader, 1994) that it is possible to assign a definite value of energy to a given (atomic) subdomain of a molecule, only if the subdomain is bounded by such  $\Omega$  surface. Starting from the total electron density, the Bader's topological analysis of a molecule or a crystal identifies the atomic interaction lines, the bonds, the interatomic surfaces, the critical points of  $\rho$  together with key features assigned to each of such points (electron density, Laplacian, Hessian matrix, energy density, etc.) that can be used to build physically consistent schemes for the classification of atomic interactions (in terms of *observable* quantities; Bader and Essen, 1984); moreover, by integrating the relevant quantities over each atomic basin, the charge or the energy of each atom can be calculated, or the forces that the electrons belonging to that atom exert on the nucleus of the same atom, or on the nuclei

of nearby atoms. In this way it is possible to describe and rationalize the force schemes, the mechanics and the dynamics of deformation of a crystal structure under stress, in a consistent physical framewok (see for instance Prencipe and Nestola, 2007). Moreover, the Bader's picture resumed and extend the idea of Theodore Berlin of the chemical bond being the result of accumulation of electron charge in the *binding region* between the nuclei (Berlin, 1951), putting it on a firm physical and quantitative basis. In addition, a strong connection was found between the *minima of the Laplacian of the electron density* and the positions of the *electron pairs* in a molecule, the latter being predicted by the well known Valence Shell Electron Pair Repulsion model (VSEPR) of Ronald Gillespie, also working at the McMaster University, which is useful for the prediction and the interpretation of molecular geometries (Bader et al., 1988; Gillespie and Robinson, 1996).

A pioneer in the application of the Bader's theory to mineralogy was Gerald V. Gibbs at the Virginia Tech. His many works on the subject, so well written and clear even for *non*-specialists, greatly contributed to the formation of a view of crystal-chemistry that is alternative to the one merely based on geometric interpretations about how sets of essentially spherical, rigid and charged ions (that do not *really* exist) should arrange themselves in space, and react to external stresses. See for instance Bader and Austen (1997), Gibbs et al. (1994, 2001, 2006, 2008, 2014), Prencipe (2002); Prencipe et al. (2003); Prencipe and Nestola (2007), and the interesting work by Merli and Pavese (2018) on catastrophe theory (also based on the Bader's analysis) to predict and characterize instability in crystal structures, and used to discuss about phase transitions in rutile, periclase and corundum. See also Gatti (2015) for a comprehensive review of the applications of the Bader's theory in crystal-chemistry.

## 5 Quantum statistics and applications to thermodynamics of minerals and rocks

The Hamiltonian formulated in equation (13) lacked of the kinetic term of nuclei that were considered fixed in a given configuration; however, nuclei move and contribute, with their kinetic energy, to the total energy of the molecule or crystal. The kinetic energy of the nuclei is generally accurately estimated by using the *harmonic approximation*: the equation of motion is solved for a system of nuclei moving in an *effective* potential  $V_{eff}(R)$  [which is the sum of  $V_{ee}$ ,  $V_{NN}$ ,  $V_{Ne}$  and the kinetic energy of electrons, evaluated at the nuclear configuration described by the R vector<sup>4</sup>; see subsection (2.4.1)]; the potential  $V_{eff}(R)$  is then Taylor-expandend around the nuclear equilibrium configuration

 $<sup>^4</sup>$  This is at the core of the *Born-Oppenheimer* approximation that separates the nuclear motion from the electron motion, justified by the large difference of mass of the two types of particles.

 $R_0$ , and the expansion is truncated at the quadratic term. Schematically:

$$V_{eff}(R - R_0) = \left(\frac{\partial^2 V_{eff}(R)}{\partial R^2}\right)_{R_0} (R - R_0)^2$$
(26)

where the zero of the energy scale is set to  $V_{eff}(R_0)$  and the first order term is also zero, as  $R_0$  is the equilibrium configuration [where  $V_{eff}(R)$  has a minimum]. Such truncated expansion is valid provided that the amplitudes of the nuclear motii are small compared to the internuclear distances (as they generally are). Expression (26) corresponds to an harmonic potential, and thus the equation of motion for nuclei provides 3N solutions (N being the number of nuclei; 3 modes, out of 3N, correspond to rigid translations of the whole crystal along the 3 axes of a cartesian frame) having the form of harmonic oscillators. The frequencies  $\nu_i$  of such oscillators ( $i = 1, \ldots, 3N$ ) are related to the eigenvalues of the Hessian matrix: the matrix of the second derivatives of  $V_{eff}(R)$  with respect to the mass weighted atomic coordinates. Each oscillator contributes a vibrational energy  $E_i = (1/2 + n_i)h\nu_i$  to the total energy of the system, where  $n_i$  is an integer number (actually, it is the vibrational quantum number).

The collection of a large number (of the order of the Avogadro number) of identical molecules, or unit cells of a macroscopic crystal, is dealt with under the framework provided by statistical thermodynamics. In the case of crystals,  $n_i$  is interpreted as the number of phonons associated to the given oscillator i;  $n_i$  is zero at T = 0K and increases with T following the Bose-Einstein statistic: in other words, vibrational excitations are interpreted as *virtual quasi-particles* named phonons, that are *bosons* [see subsection (2.3)] and whose number is a function of the temperature of the crystal. In particular, there are no phonons at 0K but they are created and their number increases at T > 0, thereby creating some sort of *boson gas* confined in the crystal [see Ashcroft and Mermin (1976) for more details]. Such phonon gas can exert a pressure provided that the crystal is not perfectly *harmonic* (see below).

A perfectly harmonic crystal is the ideal one defined by a potential  $V_{eff}(R)$ whose shape (curvature) does not change with the volume of the crystal itself. Real crystals are not harmonic as  $V_{eff}(R)$  is a function of the volume V of the unit cell. However, at each volume V,  $V_{eff}(R)$  can generally be effectively described by the quadratic expression (26) around the corresponding equilibrium nuclear configuration  $R_0(V)$ . This assumption is the so called quasi-harmonic approximation (QHA). The change of  $V_{eff}$  with the volume V reflects in the change of the vibrational frequencies and hence in a change of the vibrational energy  $(E_{vib})$  of the crystal: this amounts to having a pressure  $[-(\partial E_{vib}/\partial V)_T]$ that increases with temperature, and that can be interpreted as due to the phonon gas being created in the crystal as the temperature is increased. The QHA model successfully interprets thermal expansion, thermal effects on the elastic properties and the whole thermodynamics of crystals. Failures of the QHA are however observed in those cases where phase transitions do occur, triggered by soft modes whose frequencies approach zero in the neighborhood of the transition volume, and *intrinsic* anharmonic effects become large [that is, the expression (26) is no longer valid, and higher order terms must be considered].

A precise and clear account of the relevant theory and the QHA model can be found in the classic textbooks by Max Born and Kun Huang (Born and Huang, 1954), or Orson Anderson (Anderson, 1995). However the basic principles are easily recognised and reconducted to the statistical expression for the Helmholtz free energy (F):

$$F(V,T) = -k_B T \ln Z \tag{27}$$

where  $k_B$  is the Boltzmann's constants and Z is the partition function:

$$Z(V,T) = \sum_{i} e^{-\epsilon_i(V)/k_B T}$$
(28)

where the sum on *i* is extended to all the energy levels ( $\epsilon_i$ ) of the crystal. Once vibrational energies have been calculated for a given unit cell volume, the corresponding energies are used to calculate *Z*, following the definition (28), and the free energy (27) is derived. Pressure is obtained from the derivative of *F* with respect to *V*, at constant *T*, so that the Gibbs free energy can also be calculated as a function of pressure and temperature. This is exactly the way how elastic properties (elastic constants, bulk moduli) are being computed at any pressure and temperature conditions. For representative examples (limited to the use of hybrid HF/DTF functionals) see for instance Belmonte (2017a), Erba et al. (2014), Ottonello et al. (2010a), Prencipe et al. (2011, 2014b). With reference to hybrid HF/DFT functionals only, to have an idea of the accuracy reached in the *ab initio* estimation of bulk moduli of minerals, at room temperature, note that the discrepancy with the best experimental results available is often in the range between 1-3 GPa [see for instance Prencipe et al., 2011, 2014b; Ungureanu et al., 2010, 2012].

The interest in the *ab initio* computation of thermodynamics and thermoelastic properties lies not only in the accurate reproduction of already available experimental measures, but in the possibility to provide accurate data at conditions difficult to be achieved or controlled experimentally. Typical it is the case of simultaneous high-pressure/high-temperature conditions (HP/HT): even if such conditions are indeed easily achieved in laser heated diamond anvil cells (LHDAC), the difficulty is in the accurate measure of the obtained actual pressure/temperature. Concerning thermodynamics, another experimental difficulty is related to the possibility to reach real equilibrium conditions during the limited time of a typical experiment of mineral synthesis, or to preserve the synthetized HP/HT mineralogy during the subsequent quencing procedure. In these cases, the *ab initio* methodology provides at least a cross check of experimental data, or it can provide data when experiments are lacking or judged to be inaccurate. An example in this direction is the thermodynamics dataset prepared by Lars Stixrude (Stixrude and Lithgow-Bertelloni, 2005, 2011): the database contains data from both experimental and computational sources, and it was implemented in the PERPLEX program by James Connolly (Connolly, 2005) to model the Earth's mantle, making predictions about mineralogy, phase transitions, density and seismic wave velocities in the mantle, at various depths, to be compared with data derived from seismic tomography (see Bass et al., 2008; Frost, 2008).

#### 6 Conclusions: recent advancements and challenges

In the introductions to many papers it is often written that, in the last decades, the enhanced computer power enabled applications of the quantum-mechanical formalism to problems that were not previously solvable. Of course this is true as many of the calculations described in the previous sections require considerable hardware resources (generally large clusters of processors working in parallels, and several *weeks* of computing time). But computer power is not enough, and new ideas, a variety of new approaches, software technology and engineering are steadily developed. Not only, but also the class of problems under consideration is continuolsly extended, mainly prompted by new requests from the *experimental world*, or problems having difficult experimental solution. This is for instance the case of modeling of fluids, with the purpose to derive consistent thermodynamical datasets to be used in the prediction of the topology of phase diagrams describing rock melting even at high pressure; for accounts on these issues, see Belmonte et al. (2013, 2017b,c); Ottonello et al. (2010b, 2013).

Another point concerns the modeling of minerals under *non*-hydrostatic stress; the more direct and recent application of these calculations is in the predictions of shifts in Raman spectra of non-cubic crystals entrapped, as inclusions, in other minerals from high pressure regions at large depths in the Earth mantle. Raman shifts are widely used to estimate the remnant pressures of inclusions and, from those, the entrapment pressures; however if the generally anisotropic relaxation of the inclusions (resulting from the exumation of the hosting minerals from those depths to the surface), with its peculiar effects on the vibrational spectrum, is not taken in due account, wrong estimations of the remnant pressures might occur. Although it is not easy to experimentally evaluate the effect of anisotropic stress, or strain, on the position of the Raman bands (because it is difficult to characterize the state of stress of generally very small inclusions), such estimation is not particularly difficult at the computational level, provided that sufficiently accurate functionals are available for the calculation of vibrational spectra [these are the hybrid HF/DFT functionals discussed in section (3.1)]. For examples in this direction, see Anzolini et al. (2018); Murri et al. (2018); Nestola et al. (2018).

Important advancements are also in the quantum-mechanical study of surfaces: the traditional and very effective experimental techniques employed to study the bulk properties of minerals, hardly work for their surfaces, so that any contribution from other areas is greatly welcome. Needless to say, the knowledge of surface properties is very important as they control the morphology of minerals and their interactions with the surrounding mineral or biotic worlds. See Aquilano et al. (2015); Bruno et al. (2015, 2016).

One problem that still requires some hard work to be satisfactorily solved is related to the anharmonic vibrations in crystals: at present, the issue is generally limited to the minerals containing hydrogen and, within them, only to those modes directly involving H (in fact, the O-H effective potential curve is strongly anharmonic). Perturbative methods have been implemented in some quantum-mechanical codes for crystal (*e.g.* Dovesi et al., 2018), but at the moment they are not general enough to deal with phonon coupling phenomena. In these cases, mismatches between computed (at the harmonic level) and experimental frequencies can reach 100-150 cm<sup>-1</sup>; see for instance Prencipe et al. (2009).

All the applications to minerals, discussed so far, concern pure end-member phases. Indeed, although some attempts and codes had been written (e.g.D'Arco et al., 2013) to apply the formalism to homogeneous mixtures (solid solutions, for short), at least in the author's view, results are generally not very satisfactory, except for some specific cases. The point is strictly connected with the possibility to model a really disordered crystal, that is a system lacking translational symmetry, at variance with the current computational approaches that build periodic structures out of large supercells *simulating* some disordered configuration in their inside. Such operation generally creates periodic structures having a lower symmetry compared to the real disordered structures, and this can be reflected in a resulting strong anisotropy of the long range Coulomb field, especially in ionic crystals. In turn, such anisotropy can have dramatic effects in the computed vibrational spectra. On the other hand, on the computational side, if some reason justifies a selection of configurations (that is, distributions of ions within a supercell) that maintain the symmetry of the real disordered phase, results may however be of value: see for instance De La Pierre et al. (2013); Lacivita et al. (2014); Scanavino et al. (2012); Scanavino and Prencipe (2013); Zucchini et al. (2012, 2017). Together with melts, disordered systems and solid solutions are probably the challenges for the near future, at least among those fields which are really crucial and relevant to the Earth Sciences.

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