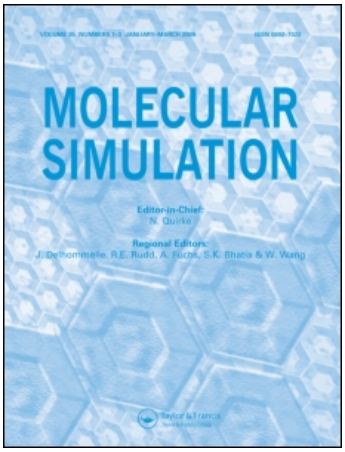

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AN INTRODUCTION TO *Ab-INITIO* MOLECULAR DYNAMICS SCHEMES

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We present some of the basic concepts and procedures which allow to perform ab-initio molecular dynamics calculations. The emphasis is given on writing the basic density functional theory equations and derive them for plane wave norm conserving pseudo-potential applications. The main features of the conjugate gradient minimisation procedure to access the total energy of periodic systems are presented and a brief conclusive introduction to dynamical calculations is given.

Keywords: Ab-initio molecule dynamics; conjugate gradients

I. INTRODUCTION: THE HARTREE-FOCK AND DENSITY FUNCTIONAL THEORY POINTS OF VIEW

Computer calculations are now routinely performed on a wide variety of materials to access an understanding of their basic thermodynamical properties. Along with the development of computer power, different theoretical schemes have been developed. Beside the empirical and semi-empirical methods which pre-suppose the nature and the strength of the interactions linking the atoms, several ways of dealing with the Schrödinger equation describing the stability of a set of atoms have been developed. Since they only require the knowledge of the charge of the different nuclei composing the system, these latter types of calculations are often referenced as "ab-initio" calculations. For extended systems, these calculations are based on either the Hartree-Fock approximation (HF) or the Density Functional Theory (DFT) and are generally in agreement with experimental measurements within a few percents of error.

The procedures behind the HF and DFT schemes in order to deal with the time-independent Schrödinger problem present similarities and differences. First of all, they are both based on the Born-Oppenheimer approximation [1] which postulates that since nuclei are much heavier than electrons, the respective motion of both kind of particles can be treated separately: whilst electrons must be treated as quantum particles, nuclei can be fairly well represented by classical points. Though, we should be aware that such an approximation cannot be correct for very low temperature regimes, we must accept that it is a very good way of dealing with the stability of matter for temperatures in the range of chemical reactivity.

The ab-initio calculation problems then reduces to solving the Schrödinger equation for a set of electrons embedded in an external potential generated by coulombic point-charges (see eq. 1).

$$\left(-\sum_i \frac{\hbar^2}{2m}\Delta_i + \sum_i \left[\sum_I -\frac{1}{4\pi\varepsilon_0}\frac{Q_I e}{|R_I - r_i|}\right] + \sum_j \sum_{i\neq j} \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|r_j - r_i|}\right)$$

$$\psi(r_1, \ldots, r_n) = E\psi(r_1, \ldots, r_n) \quad (1)$$

In the time independent Schrödinger equation, m is the electron mass, e is the electron charge, r_i is electron-i position coordinate in three dimensional space Q_I is nucleus I charge, R_I is nucleus I position coordinate in three dimensional space, E is the electronic system total energy and $\psi(r_1, \ldots, r_n)$ is the n-electron wave function.

Though the number of interacting quantum particles is equation 1 is highly reduced, it is still impossible to solve this problem considering more than a few electrons. This is why further theoretical transformations are needed to be able to deal with the electronic structure of extended systems. This is where Hartree-Fock (HF) and Density Functional Theory (DFT) approaches differ.

Since this paper aims to introduce to DFT based calculation methods which have encountered increasing success during the last ten years, we do not wish to give a full introduction to the HF method which can be found in [2]. We will concentrate in giving insights on how HF differs from DFT. Since solving the Schrödinger problem consists in determining a n-electron wave function which satisfies equation (1) in order to find the lowest possible eigen energy E (ground state), one has to explore all the different functions of the positions of n electrons and consider them as possible solutions of the problem. The number of such functions is great and the entire set cannot be explored practically. This is why no exact solution of the Schrödinger equation 1 is actually pursued for extended systems. Since the complexity is too great, in

order to reduce the number of functions to be explored, two ways can be followed: HF or DFT.

The HF way consists in writing that the n-electron wave function should exhibit the form of a "Slater determinant". This Slater determinant is a function of the coordinates of the n different electrons which is built as a product of n single-electron wave functions. Such product is built in order to verify the basic property of fermions which is the antisymmetry of the n-particle wave function upon particle permutation. That is to say that whatever i and j two different electrons, the n-particle wave function verifies $\psi(\ldots,r_i,\ldots,r_j,\ldots) = -\psi(\ldots,r_j,\ldots r_i,\ldots)$.

The writing of a Slater determinant wave function considerably simplifies the search of a solution. Indeed, instead of searching all possible n-particle wave functions, one only has to search n times all possible single-electron wave functions. The laws of combination conclude that in the first case the complexity grows as the factorial of the number of particles (n) and in the second case, the complexity grows as n only. For increasing numbers of electrons, this makes rapidly a difference. Consequently, if one can reasonably deal with only single-electron wave functions, this is definitely a good start in the direction of practically solving the n-electron Schrödinger problem.

Like HF, DFT only deals with single-electron wave functions. The difference lies in the fact that with DFT, one does not attempt to calculate the n-electron wave function but only tries to access the electronic energy (E eq. [1]) and the global electronic density distribution ($\rho(r)$, r refers to three dimensional space coordinate). Indeed, the demonstration that the ground state properties (electronic energy E) can be related in a rigorous fashion to the global electronic density distribution $\rho(r)$ was first given by Hohenberg and Kohn [3] in 1964. In 1965, Kohn and Sham [4] have applied the Hohenberg and Kohn theorem to the n-electron problem in the presence of the external influence of coulombic nuclei. They showed that the ground state electronic energy in Schrödinger equation 1 can be formally obtained from the resolution of n single-particle equations. These equations are now known under the name of Kohn-Sham (KS) equations (eq. 2). In equation 2, the different single-electron wave functions are reported as $\psi_i(r)$. The first term is the kinetic energy of electron i, the second term is the interaction energy between electron i and the external coulombic potential due to the nuclei. The third term is known as the Hartree energy. It measures the coulombic interaction energy between electron i and the global electronic density distribution $\rho(r)$. The last term called Exchange and Correlation term measures the energy which is related to the correlation between the motion of the different electrons. Since the different electrons exhibit a charge $-e$, they are interacting

and their respective motion must reflect such interaction. The Exchange and Correlation also includes the excess in energy which is related to the fact that the electrons are fermions and then should interact as so (because of the antisymmetrical nature of the n-particle wave function, electrons exchange [2]). The Hohenberg and Kohn theorem ensures that this last term only explicitly depends on $\rho(r)$.

$$\forall_i \in [1, \ldots, n]$$

$$\left(-\frac{\hbar^2}{2m}\Delta_i - \sum_I \frac{1}{4\pi\varepsilon_0}\frac{Q_I e}{|R_I - r_i|} + \frac{2}{4\pi\varepsilon_0}\int \frac{e^2\rho(r_j)}{|r_j - r_i|}d^3r_j + V_{XC}(\rho(r))\right)\psi_i(r_i) = \varepsilon_i\psi_i(r_i) \tag{2}$$

In the Kohn-Sham equations, m is the electron mass, e is the electron charge, r_i is electron-i position coordinate in three dimensional space, Q_I is nucleus I charge, R_I is nucleus-I position coordinate in three dimensional space, ε_i is the electronic system total energy and $\psi_i(r_i)$ is the single-electron wave function related to electron i.

A simply way of writing equation 2 is shown in equation 2B in which the different terms are schematised by KE_i for kinetic energy operator of electron i, $V_{\text{ion}}(r)$ for the nuclei-electrons interaction, $V_H(r)$ for the Hartree term and $V_{XC}(r)$ for the exchange and correlation term.

$$\forall_i \in [1, \ldots, n]$$

$$(KE_i + V_{\text{ion}}(r) + V_H(r) + V_{XC}(r))\psi_i(r_i) = \varepsilon_i\psi_i(r_i) \tag{2B}$$

Finally, Kohn and Sham showed that the global electronic density distribution $\rho(r)$ can be deduced from the single electron wave function appearing in eqs. 2 (see eq. 3). They also showed that the ground state global electronic energy can then deduced in a straight forward way from the single-electron eigen energies ε_i (see eq. 4).

$$\rho(r) = \sum_{i=1}^{n} \psi_i(r)\psi_i^*(r) \tag{3}$$

$$E = \sum_{i=1}^{n} \varepsilon_i - \frac{1}{2}\int \frac{2\rho(r)\rho(r')}{|r - r'|}d^3r.d^3r' - \frac{1}{4}\int V_{XC}(\rho(r))\rho(r)d^3r \tag{4}$$

Since the potentials V_H and V_{XC} are built using the charge density distribution $\rho(r)$, one notices that KS equations have to be solved self consistently.

Indeed, the electronic states which are eigen functions for these equations must generate the charge density distribution which is used to write these very same equations. In practice, one chooses a trial set of initial wave functions in order to write a first set of KS equations. Solving this first KS problem, one deduces a new charge density distribution which will help writing a new set of KS equations. This process has to be repeated until the global charge density distribution remains unchanged.

At the first glance DFT equations seem to be an easy way of finding ground state properties of atom built systems. Unfortunately, though we know such equations exist, we are not able to practically write them in an explicit way. The difficulty arises from the fact that the explicit dependence of the Exchange and Correlation potential upon the global charge density distribution is not known. In practice, one has to choose an explicit but approximate form for V_{XC}. At the moment two main approximations to the Exchange and Correlation potential are currently in use: the so called local density approximation (LDA) [5] and the generalised gradient approximation (GGA) [6]. Both potentials derive from the only case for which one is practically able to calculate the actual Exchange and Correlation potential: the constant density Fermi-liquid or homogeneous electronic distribution. The LDA consists in "locally" identifying the Exchange and Correlation potential of a non-homogeneous density distribution of electrons $\rho(r)$ with the Exchange and Correlation potential of the homogeneous electronic gas having the same density. That is to say that for each different position (r), $V_{XC}(\rho(r))$ is identified to $V_{XC}^{\text{(constant density liquid)}}$ previously calculated for a density ρ which equals $\rho(r)$. The GGA is an extension of the LDA which takes into account effects related to the local changes of the density. GGA calculations are also called gradient corrected calculations.

In HF theory, one has to simplify the writing of n-electron distribution wave functions. In DFT, one has to assume a certain form of the global Exchange and Correlation energy. In principle, no one is able to determine which between HF and DFT gives better results. Beyond this, no one is even able to know if these approximations can work and only the final confrontation between experiment and calculation results will help.

Several years of successful investigations considering different types of compounds have led to the general belief that both HF and DFT provide total energy differences and structural equilibrium parameters which are in error by a few percents only [7]. As far as covalent structures are concerned, it seems that DFT is doing better that HF. Considering hydrogen-type bonding, HF seems to be closer to experiments than DFT. In that sense, no one is able to determine which scheme is the best. However, as far computer time and memory consuming is concerned, DFT schemes appear to be far more cheaper

than HF ones. This is certainly why DFT calculations have encountered such a success. However further simplifications are actually needed in order to solve DFT equations considering condensed state systems. In the next section, we wish to point out a few of them which are commonly used in the solid state physics community. These further approximations are: the pseudo-potential approximation and the periodic boundary conditions.

II. DFT EQUATIONS AND CONDENSED MATTER STABILITY

The pseudo-potential approximation [8] reduces the actual number of electrons associated with a set of atoms. Only a reduced number of atoms has to be considered in order to access the differences in the total energy of different structures. The construction of a pseudo-potential is based on the assumption that core electrons which are tightly bonded to the atomic nuclei do not participate in the formation of chemical bonds. Indeed, core electron states do not expand far from the atomic nucleus and the potential that they experience is only very slightly modified by the presence of neighbouring atoms. Replacing the total number of electrons by the valence electrons only is generally a good approximation to the chemical bond. Within the pseudo-potential approximation, the real atoms are substituted by pseudo-atoms which have only valence electrons. The pseudo-potentials created by these pseudo-atom nuclei are constructed so that the valence electrons are scattered in an identical way either by the real nucleus with the core electrons nor by the pseudo-potential. In practice, creating such a pseudo-potential one also wants the eigen-functions to be as smooth as possible. For many electron atoms, the valence electrons wave functions (orbitals) strongly oscillate close to the atomic nucleus. This is due to the fact that valence orbitals are orthogonal to core orbitals. However, a great part in these oscillations are atomic structure related and are not characteristic of the chemical bond which is the main fact we are interested in here. When close enough to the nucleus (let us say in a region which is included in a sphere of radius r_c around the nucleus), the pseudo-potential is then constructed so as the valence pseudo-wave functions do not exhibit these oscillations. Far from the nucleus (outside the sphere of radius r_c), the pseudo-potential is then the potential which exactly matches the scattering properties of both the nucleus and the core electrons. Such construction involving a core and an outcore region should be done in a proper way. Mainly, the integration over space of both the real valence and pseudo wave-functions must lead to the same number of valence electrons. In practice, all these requirements can be achieved. A precise description of the construc-

tion of these so-called 'norm-conserving' pseudo-potentials is given in ref. [9]. Let us quote that other ways of constructing pseudo-potentials have also been developed. We do not wish to enter these so-what more complex constructions. Some of these can be found in [10]. Finally, let us notice that other ways of dealing with the separation between core and valence electrons are commonly used. Some are based on the so called Muffin-Tin approximation and some examples are found in [11].

Usual condensed matter systems contain about 10^{24} atoms. Obviously, no one can actually deal with such a great number of associated electrons. Dealing with condensed matter implies the use of further approximations. Since they were primarily concerned with crystals, solid state physics are using the so-called periodic boundary conditions. One considers the system as infinite crystals built out of the infinite repetition of a unit-cell. This approximation to disordered matter becomes exact when the unit-cell is large enough to encompass the 10^{24} atoms. In actual calculations, we are restricted to unit-cell composed with a few hundreds of atoms. The periodic boundary condition allows the building of infinitely large systems of atoms which are subdivided in only a few sub-sets which are independent from one another. All the atoms, in these subsets are identical and identically coordinated.

Formally, the use of these boundary conditions allows the treatment of the electronic structure of condensed matter systems using the classical solid state theory tools. In particular, the use of the reciprocal lattice together with Bloch's theorem will help in reformulating in a practical way the basic equations of DFT.

III. DFT EQUATIONS FOR PERIODIC SYSTEMS DEVELOPING WAVE FUNCTIONS IN PLANE-WAVE (PW) EXPANSIONS

Bloch's theorem [12] states that in a periodic system each single-electron KS wave function can be written as the product of a cell periodic part and a plane wave part (eq. 5). According to completion rules, the cell periodic part $f_i(r)$ in equation 5 can be expanded using a discrete set of plane wave (PW) whose wave vectors are reciprocal lattice vectors of the periodic system (eq. 6) (reciprocal lattice vectors G are defined by $G.1 = 2^1 m$ where l is a lattice vector of the system and m is an integer.). In principle, the number of G vectors to be used is infinite. However in practice, one only has to use G-vectors which are associated to rather low energy PWs: one only takes into account PWs whose associated energy is less than a chosen so-called cut-off energy which

varies typically from 100 to 700 eV. Indeed, PWs exhibiting very high energies will lie energetically very far away from the wave functions describing the chemical bond. Hence, they do not contribute substantially to the expansion of the occupied state wave-functions (using pseudo-potentials instead of real potential allows the use of lower cut-off energies).

$$\psi_i(r) = f_i(r) \cdot \exp(ik \cdot r) \tag{5}$$

$$\psi_i(r) = \sum_G c_{i,k+G} \exp(i(k+G) \cdot r) \tag{6}$$

Because of Bloch's theorem, it has been shown that KS electronic wave functions can be written as a sum of plane waves. Bloch's theorem also states that all the different single-electron eigen wave functions in a periodic system are obtained by calculating the wave functions in a unit-cell large system and by varying k vectors all around the first Brillouin zone in reciprocal space. In fact, Bloch's theorem changes the problem of calculating an infinite number of electronic wave functions into the problem of calculating a finite number of wave functions at an infinite number of k-points. However, since two wave functions calculated for two nearby k-points will be almost identical, it is possible to properly calculate the global electronic density distribution $\rho(r)$ using only a finite set of k-points. Therefore, the use of Bloch's theorem has allowed us to transform the KS general problem into a PW related KS problem. Moreover, the number of PW to be considered appears to be finite.

Our problem is now to write the KS equations including the Bloch's transformation as explained above. This is easily done by introducing equation 6 into equations 2 and by subsequent integration over real space variable r. Consequently, the KS equations assume a particularly simple form (eq. 7) [13].

$$\sum_{G'} \left[\frac{\hbar^2}{2m} |k+G|^2 \delta_{G,G'} + V_{\text{ion}}(G-G') + V_H(G-G') + V_{XC}(G-G') \right] c_{i,k+G'} = \varepsilon_i c_{i,k+G} \tag{7}$$

In the brackets, the first term is the Fourier transform of the kinetic energy and the 3 last terms are Fourier transforms of the interaction terms as described in equation 2B. δ is the Kronecker symbol which equals zero if $G \neq G'$ and 1 if $G = G'$.

In equation 7, the kinetic energy is a diagonal term and the various potentials are introduced as Fourier transforms. These equations appear to be secular equations related to a Hamiltonian-type Matrix whose element $H_{k+G,\ k+G'}$ are the in bracket terms in equation 7. A classical way for finding a solution to the above problem is to proceed by diagonalisation. The size of the matrix is determined by the PW cut-off energy. A typical matrix size is given by $(100.n) \times (100.n)$ where n is the number of atoms in the unit cell). Because of the large memory requirement and long lasting procedures to diagonalise matrices, PW pseudo-potential calculations using diagonalisation techniques are restricted to unit cells containing less than 20 atoms. However, in 1985 R. Car and R. Parrinello [14] have proposed a new way of solving the KS problem which does not involve a diagonalisation procedure but a minimisation procedure of the KS total energy functional. This new way appeared to increase by a factor of 10 the size of the unit-cells which can be considered in PW pseudo-potential calculations. In the next section, we shall introduce a direct minimisation procedure which is not the original Car and Parrinello method, but an evolution proposed by M.P. Teter, M.C. Payne and D.C. Allan in 1985 [15] and which is now widely used.

IV. A DIRECT MINIMISATION PROCEDURE USING CONJUGATE GRADIENT TECHNIQUES TO SOLVE THE PW PSEUDO-POTENTIAL KS PROBLEM

In the first section, we showed how the KS equations are related to the electronic total energy and consequently to the total energy of the system which is the sum of both the electronic energies and coulombic repulsion energies between the classical ions. In the latter section, we have shown how the KS equations could be written in reciprocal space as a function of PW coefficients. In a straight forward way, one can consequently calculate the explicit dependence of the system ground state total energy (E_{GS}) upon both the PW coefficients ($c_{i,k+G'}$, i denotes the band number, k and G' are reciprocal lattice vectors) and the positions of the different nuclei (R_I). The actual form of E_{GS} is given in equation 8. Since both V_H and V_{XC} explicitly depend on a set of input PW coefficients, one must remember that this search for the ground state has to be performed in a self consistent way (see section 1).

$$E_{GS} = \sum_{\substack{i \\ \text{occ}}} \varepsilon_i - \left[\frac{1}{2} \sum_G V_H(G)\rho(G) - \frac{1}{4} \sum_G V_{XC}(G)\rho(G) \right] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$$

with

$$\rho(r) = \left[\sum_G c_{i,k+G} \exp\left(i(k+G)\cdot r\right)\right]\left[\sum_G c_{i,k+G} \exp\left(-i(k+G)\cdot r\right)\right] \tag{8}$$

Since the ground state is the minimum energy state, a search for the KS wave function coefficient can be pursued minimising the above functional. We are now going to present an efficient computational method that allows a direct minimisation of the KS energy: the conjugate gradient method [15, 16].

The conjugate gradient (CG) method is a classical method which is used to locate the minimum of a function $F(x)$ where x is a multidimensional space vector. Though we will not discuss the CG algorithm which can be found elsewhere [16, 17], we wish to outline the basic and simple ideas on which it is built. In the absence of information about the function $F(x)$, the optimum direction to move from a starting point x_1 is the steepest descent direction down to the point x_2. In order to optimise the process, the displacement must be proportional to the descent. Iterating such process a certain number of time should lead to the minimum. However, in order to minimise $F(x)$, there is a more efficient way which reduces the number of direction to move x at each step and ensures that the search will not end up oscillating between two sides of the minimum valley: the CG minimisation. The CG procedure uses the same idea as the steepest descent (ST) method to move from the starting point down to the minimum but opposite to ST, the moves are subject to constraints related to all the previous minimisation moves which have already been done. At the nth iteration, the conjugate gradient minimisation procedure consists in moving x_n along the steepest descent direction in the sub space which is perpendicular to all the previous minimisation move directions. If N is the dimensionality of x-space, this ensures that the procedure will end in N iterations. No over lasting oscillating moves are possible. The application of the CG procedure to the minimisation of the KS energy requires another extra constraint which is related to the quantum nature of the underlying particles. Since they are eigen vectors of the KS hamiltonian matrix, the electronic wave functions are required to be orthogonal to one another. The CG minimisation of the KS energy must take this fact into account by constantly orthogonalising the wave-functions with respect to one another.

In general, one single CG procedure does not lead to the minimum. The process has to be repeated several times. However, in order to speed up the convergence, the technique of preconditioning can be used [16, 18]. High energy eigen states are dominated by PW states whose kinetic energy lies close to the eigen energy of the state. To reduce the size of the space which needs to

be actually searched, one has to remove the effect of the kinetic energy operator in order to make these high energy states degenerate. In practice, this is achieved by the multiplication of the steepest descent vector by a diagonal preconditioning matrix which is essentially the inverse of the kinetic operator. In general, such preconditioning procedure speeds the convergence up by a factor of two.

In conclusion of this section, let us summarise the different steps needed to be done in order to access the KS total energy of the system. First one has to choose trial coefficient for the band wave functions. This is usually achieved using a random generator. From this, one has to calculate a charge density distribution and construct the corresponding KS energy functional. Using the preconditioned CG procedure described above, one deduces a second set of coefficient for the band wave functions. This new set is then used to repeat the complete operation. This operation is repeated until no change in the total energy is found.

V. THE HELLMANN-FEYNMAN THEOREM AND THE MOLECULAR DYNAMIC SCHEME

Up to this point, only the determination of the ground state properties of a set of electrons considering a given static set of atomic positions have been considered. We have proposed a self-consistent scheme that allows to determine a numerical expression of the KS ground state total energy which depends also on the position of the nuclei in an explicit way. Since we have an energetic functional of the system which depends on the position of the nuclei (based on the Born Oppenheimer approximation), it is now possible to modelise the dynamics of nuclei using classical mechanics. This scheme is much simpler than the determination procedure of the electronic structure.

The position of ions and the coordinate that define the size and shape of the unit-cell can be included in the dynamical variables that one takes into account. Indeed, when the system undercomes a drastic change in its structure the volumic mass is subject to changes which must also be included in dynamical descriptions. Two different set of Newtonian equations should be written. The first one concerns the position of the nuclei (R_I, M_I is the mass of nuclei I) and the second one the unit-cell coordinate (α_v, β is a fictive mass describing the cell dynamics).

$$M_I \frac{d^2 R_I}{dt^2} = -\frac{dE_{GS}}{d\mathrm{R}_I} \tag{9}$$

$$\beta \frac{d^2\alpha_v}{dt^2} = -\frac{\partial E_{GS}}{\partial \alpha_v} \tag{10}$$

The equations of motions for the different degrees of freedom can be integrated at the same time as the search for a minimum for the electronic states. This provides an accurate basic scheme in order to perform ab-initio dynamical simulations. However, this integration is not as straight forward as it first seems and so, because ground state forces on the ions and stresses on the unit cell cannot be calculated in an arbitrary way. They must obey the Hellmann-Feynman theorem [19].

The Hellmann-Feynman theorem states that since the electronic system is in the ground state then the global derivation of the ground state energy with respect to the position of ion should equal the partial derivation (eq. 11).

$$f_I = -\frac{dE_{GS}}{dR_I} = -\frac{\partial E_{GS}}{\partial R_I} \tag{11}$$

As an ion moves to a new position, the KS energy functional must be changed self-consistently to a new functional which corresponds to the new position of the atom. If no updating is performed then there is no chance that the Hellmann-Feynman theorem is verified. The calculated forces are then "wrong" and do not represent the actual physical forces experienced by the nuclei. So, at each step in the dynamics of nuclei, the electronic energy must be recalculated. If using small time steps (typically in the order of a few tenth of femto-second), the changes in the electronic configuration is small enough so that convergence of the electronic configuration is easily achieved using a few conjugate gradient steps. However, the computational cost of dynamical simulation appears to be mostly due to keeping the electronic configuration in the ground state.

There is an enormous amount of literature concerning dynamical simulations which are based on an incredible large number of different schemes [20]. The interest in the field include diffusion, melting, phase transitions, calculations of free energies and so on. Ab-initio molecular dynamics calculations cannot be performed on a "statistical number of atoms" (at present a few hundreds) but offer reliable potentials which can be trusted when empirical ones fail. This mostly happens when the structure is very different from the perfect structure from which the empirical potentials have been obtained. The poor statistics is certainly one major problem in using ab-initio schemes: true phase transitions cannot be seen and the range of correlation will be limited by the size of the unit cell. A second problem arises from the description of

thermal excitations which cannot be accurately calculated using a simple schemes like LDA or GGA. More complicated computer time consuming schemes which reduce the actual number of atoms taken into account must be used [21]. In the latter case, no proper statistics can be considered.

VI. CONCLUSION: APPLICATIONS AND EXISTING CODES

Despite the limitations quoted above, the DFT ab-initio molecular dynamics schemes based on the direct minimisation of the KS energy functional provide a reliable way of dealing with the stability of extended systems. Mainly it allows to deal with the energetics of non conventionally coordinated structures which cannot be safely held using classical methods. It is now a safe way of investigating the structure of amorphous materials for which no classical potential is able to deal with the wide range of extreme distortions which is experienced by the atomic coordinations in these systems.

As far as existing codes are concerned, their number is important and a complete list cannot be given. However, we wish to give a few references of people which have been working in the field and who have developed Car and Parrinello type related codes. In order to classify these different codes according to their specificity, we shall divide our list into 'classical codes' which mainly apply the well troden techniques described above and 'evolution codes' which depart from the above description from the fact that they rely on different DFT formulations or include different kinds of approximation. However, such classification does not underline any connotations related to up date or old fashion type codes. Evolution codes are often based on classical ones and develop new formalisms.

Many groups have been working on developing classical codes which are based either on conjugate gradients or original Car and Parrinello molecular dynamics minimisation schemes. Some related references are found in [16]. Some of these codes have reached the commercial standards and some have been developed by the ones who are applying them to actual chemical or physical problems. Notice that some of these codes can be run on parallel computers [22].

Some evolutions like algorithms which update all orbitals simultaneously are proposed but successful applications are still rare [23–25]. Other developments are also proposed and are usually designed in order to perform calculations which can hardly be done using classical codes. For instance some codes go beyond the pseudo-potential approximation or use an other approximation [26]. Other codes go beyond the LDA or GGA approximations [27].

At this end let us mention an approach [28] which is based on the diagonalization of the KS Hamiltonian for fixed potential and the determination of a self-consistent charge density. Although based on a traditional scheme, this approach turns out to be very efficient for metallic systems.

It can be easily seen that the application of Density Functional Theory to the problem of electronic stability has been the subject of many developments and applications. It has proven to be a reliable and efficient way of solving a wide range of problem based on the Schrödinger equation.

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