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"Car-Parrinello study of the
structural and vibrational
properties of the
Dimethyldisulphide molecule"

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Introduction

This work is devoted to the DFT ab-initio approach to the study of vibrational properties in molecules. It is motivated by a renewed interest in the questions arising from the increasing time scale reachable with computer simulations, and by a practical and immediate interest in the study of the vibrational properties of the molecules deposited on surfaces in Self Assembled Monolayers of Dimethyldisulfide. The sulphur-metal reactivity is basic in the construction of Self Assembled Monolayers on metal surfaces and in particular of the Alkanethiols, whose role has been of huge interest relating to surface functionalization: wettability control, electrocatalysis, electron transport mediation (organic diodes and organic electronics), nanotechnology of the secondary functionalization for molecular magnets and metal nanocrystals. The study of single molecule adsorption allows one to understand, in a well-controlled situation, the functionality related to the anchorage of the methyl groups. In the last few years it was recognized that the principal mechanism in the short-range molecules' adsorption is the interaction with the surface, so that the interchain interaction is negligible. However a very rich phenomenology attracted experimental and theoretical attention [1],[2],[3]. In this sparkling experimental situation, the computational capability is evolving at an ever faster rate, and the development of new ideas is essential in order to understand old experiments, predict new phenomena and suggest new experiments . This thesis is devoted to the study and the application of the Density Functional Approach to these adsorption phenomena. The interplay between statistical methods and deterministic quantum mechanics has played an increasingly powerful role in the explanation of adsorption. More generally, the DFT methods and the time dependent DFT, in interaction with Many Body theory, have shown impressive potentiality in the understanding of the nano-world.

Chapter 1

The Ab Initio molecular dynamics methods

1.1 Introduction

The history of ab initio molecular dynamics, namely the derivation of the time evolution from quantum mechanics, saw one of the first successful approaches in the Born-Oppenheimer paper in 1927, but dates back to Ehrenfest and his pioneering approach to the problem of making a bridge from the newest quantum mechanics and the atomistic world to the old macroscopic and classical picture. Since then the development of computational methods has brought about the concrete possibility to make ab-initio quantum calculations. The original difficulties related to this ab initio approach to molecular dynamics were partially avoided and partially overcome, bringing the classical interatomic interaction near to the quantum one, by exploring a potential energy landscape for sets of configurations fixed in advance. Typically the description of the system is obtained by breaking the full interaction up into several few and many body contributions and matching long and short range behaviors. This approach drove theorists to consider very non trivial questions relating to representing analytically the more relevant physical aspects and the more suitable computational tools. Despite the overwhelming success of this approach a separate course is needed to study systems in which the electronic structure and thus the bonding pattern may change during the simulation. So the full ab initio methods appear on the scene of molecular dynamics. The more intriguing aspect of adjusting the potential in order to trace back the properties of the system is less evident and more difficult in ab initio methods of molecular dynamics. On the other hand the ab initio molecular dynamics show a bigger predictive power in cases in which physi-

cal phenomena arising from quantum mechanics are relevant. So the anharmonic or the non adiabatic quantum corrections appear in the full quantum approach shedding light on genuine quantum phenomenology. Despite the development of computational tools the full quantum calculations are out of reach. A lot of methods such as Montecarlo simulations, full Hartree Fock, density functional theory, were developed in order to understand the quantum behavior of the electronic cloud. Born-Oppenheimer and other adiabatic quantum and semiclassical methods, classical evolution of the mean quantum value for observables starting from Heisenberg's equations, like in the Ehrenfest picture, or quantum trajectory summation on the history, like in the Feynman path integral method, were developed in order to include the emergence of the classical mechanics in the quantum description. Here we want to develop a gradual introduction to the more relevant of these tools, in order to introduce to the Car Parrinello Molecular Dynamics (CPMD) and First Principle Molecular Dynamics (FPMD) package we used. First we discuss the Born-Oppenheimer tool starting from a naive introduction and moving to the finest points of the original paper. The Born-Oppenheimer approximation is in fact relevant in order to introduce our different approach to molecular dynamics. Starting from the familiar Born-Oppenheimer approximation it will be clear that in order to apply the full quantum mechanics to molecular dynamics it will be necessary to add other approximations. In the FPMD-CP approach the key steps are in effect: a mean field approximation combined with the density functional theory (DFT) in order to simplify the electron energetic, the Hellman Feynman theorem in order to calculate the forces from the energies saving the DFT rigor, the Car-Parrinello approximation in order to integrate the equations of motion.

1.2 Born-Oppenheimer approximation

In our approach the Born-Oppenheimer approximation is derived directly from the Schroedinger equation (though for more refined applications it may be derived from the Dirac-Schroedinger equation - our approach will be fully non relativistic at this level, but in some cases relativistic effects will be accounted in the pseudopotential choice, regarding the electronic degree of freedom). We will consider in the following an N-atoms molecule neutral in charge. The first index indicated with a capital Latin letter is running over the set $1, \dots, N$ and labels the nuclei: the atomic mass and the atomic number of the I^{th} nucleus are indicated respectively with A_I and Z_I . The second index, labeling the electrons, runs over the set $1, \dots, E$ where $E = \sum_{I=1}^N Z_I$. The electron mass is indicated with m and the electron charge with e , the

momenta with p , the positions with r . The Hamiltonian of the molecule is

$$\begin{aligned}
 H(r_I, r_i, p_I, p_i) = & \sum_{I=1}^N \frac{p_I^2}{2M_I} + \sum_{i=1}^E \frac{p_i^2}{2m} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} + \\
 & \sum_{I>J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0} \frac{1}{r_{IJ}} - \sum_{I=1}^N \sum_{j=1}^E \frac{Z_I e^2}{4\pi\epsilon_0} \frac{1}{r_{Ij}} \quad (1.1)
 \end{aligned}$$

Physically, the Born-Oppenheimer approximation proceeds from this observation: since the velocity of the electrons is bigger than the velocity of a nucleus so the variation regarding the electron degrees of freedom is very little with respect to the variation related to the nuclear degrees of freedom and because the nuclear masses are bigger than the electron mass, the Heisenberg principle suggests that we consider the nuclei more localized than electrons. However, because the electron gas is “running around” the localized nuclei with energy that varies when the nuclear positions vary, the nuclei feel the charge density produced by the electron distribution like an effective potential. The Born-Oppenheimer approximation, as we will show, is a full quantum mechanical approximation though for some practical purpose it is possible to treat the nuclei like classical particles: this actually occurs in the Car-Parrinello approach. In practice the route we will explore is this: (i) we shall consider a picture larger than the Born-Oppenheimer approximation, namely the Born-Huang approximation, (ii) we will exploit the adiabatic approximation, in order to decouple the equation for the two factors of a trial function, (iii) we will change the electronic wave function searching for the minimum of the functional given from a properly defined mean value of the energy with respect to the electrons coordinates. In order to solve the variational principle for each nuclear position we have one electronic configuration and one energy related to it. After that we shall consider the non adiabatic corrections due to the nuclei-electrons coupling, and briefly we will survey another approach to the decoupling which leads to a Schroedinger equations system including non adiabatic terms.

Because it will be implicit in the following, when we will speak about the adiabatic character of the Born-Oppenheimer approximation for the electrons, we state here the adiabatic theorem:

The adiabatic theorem: Consider a family of Hamiltonians $H(s)$ parameterized with $s \in (0, 1)$. If the Hamiltonian is smoothly varying in s and if the minimum eigenvalue $E(s)$ of $H(s)$ is also smoothly varying in s , then the solution $\psi_T(t)$ of the time dependent Schroedinger equation $id\psi_T(t)/dt = H(t/T)\psi_T(s)$ with $\psi_T(0) = \varphi_0$ where $H(0)\varphi_0 = E(0)\varphi_0$ has the property that as $T \rightarrow \infty$, $\psi_T(T) \rightarrow \varphi_1$ where $H(1)\varphi_1 = E(1)\varphi_1$.

To recap, the following procedure is legitimate: we first calculate the electronic configuration such as the nuclei are fixed, then (adiabatic approximation) we calculate the nuclear wave function assuming the nuclear energy potential is dictated by the energetic eigenvalues of the electronic configuration. Now at work: we simplify eq. 1.1 by using the compact notation:

$$T_N = \sum_{I=1}^N \frac{p_I^2}{2M_I} \quad (1.2)$$

$$T_e = \sum_{i=1}^E \frac{p_i^2}{2m} \quad (1.3)$$

$$V = \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{I>J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 r_{IJ}} - \sum_{I=1}^N \sum_{j=1}^E \frac{Z_I e^2}{4\pi\epsilon_0 r_{Ij}} \quad (1.4)$$

In order to apply the variational principle and the adiabatic approximation we choose the following trial ground state wave function:

$$\Psi(R, r) = \Phi_N(R)\psi_e(R, r) \quad (1.5)$$

where R indicates the set of nuclei positions and r refers to the set of electrons positions. We will determine the nuclear wave function using the variational principle and the electronic wave function assuming that the electrons are strictly confined in the given energy surface even when the nuclei are delocalized and slowly moving. This is the adiabatic aspect in the Born-Oppenheimer approximation. The nuclear kinetic energy term act on this trial wave function answering:

$$T_N(\Phi_N\psi_e) = \sum_{I=1}^N \frac{1}{2M_I} ((p_I^2\Phi_N)\psi_e + 2(p_I\Phi_N)(p_I\psi_e) + \Phi_N p_I^2\psi_e) \quad (1.6)$$

The Born-Oppenheimer approximation consists in this: we consider negligible the second and the third terms because they involve derivation with respect to nuclear degrees of freedom of the electronic wave function. (Watch for the phases factors, we will come back on this point later)

$$T_N(\Phi_N\psi_e) = (T_N\Phi_N)\psi_e \quad (1.7)$$

The change of the parenthesis order implements the key step of Born-Oppenheimer approximation.

The complete Schroedinger equation:

$$[T_N + T_e + V(R, r)]\psi(R, r) = E\psi \quad (1.8)$$

can be recast in the variational form:

$$\min_{\psi} \iint \psi^*(R, r)[T_N + T_e + V(R, r) - E]\psi(R, r)dRdr \quad (1.9)$$

where the constraint of normalization:

$$\iint \psi^*\psi dRdr \quad (1.10)$$

is accounted by the Lagrange multiplier E . Substituting ψ with the trial function $\Phi\psi_e$ and adopting the adiabatic approximation we obtain the new variational problem:

$$\min_{\Phi\psi} \left\{ \int \Phi^*(R)[T_N - W]\Phi(R)dR + \iint \Phi^*(R)\psi_e^*(R, r)[T_e + V(R, r) - Z]\psi_e(R, r)\Phi(R)dRdr \right\} \quad (1.11)$$

where the normalization constraints for the wave-functions are accounted by the W and Z Lagrange multipliers.

$$\begin{aligned} & \delta \left\{ \int \Phi^*(R)[T_N - W]\Phi(R)dR + \int \Phi^*(R) \left(\int \psi_e^*(R, r)[T_e + V(R, r) - Z]\psi_e(R, r)dr \right) \Phi(R)dR \right\} \\ = & 2 \left\{ \begin{array}{l} \int \delta\Phi^*(R)[T_N - W + \\ (\int \psi_e^*(R, r)[T_e + V(R, r) - Z]\psi_e(R, r)dr)]\Phi(R)dR + \\ + \int \Phi^*(R) (\int \delta\psi_e^*(R, r)[T_e + V(R, r) - Z]\psi_e(R, r)dr) \Phi(R)dR \end{array} \right\} \quad (1.12) \end{aligned}$$

In this way we should obtain the two equations:

$$[T_e + V(R, r) - Z]\psi_e(R, r) = 0 \quad (1.13)$$

$$[T_N - W + U(R, \psi_e)]\Phi(R) = 0 \quad (1.14)$$

where constraints fix the normalization and:

$$U[R, \psi] = \int \psi_e^*(R, r)[T_e + V(R, r) - Z]\psi_e(R, r)dr \quad (1.15)$$

Anyway the last functional is irrelevant to the solution of the first equation and it isn't so far very useful. Born and Oppenheimer suggested another approach: namely, fixing the optimum conditions:

$$U(R) = \min_{\psi_e} \int \psi_e^*(R, r)(T_e + V)\psi_e(R, r)dr \quad (1.16)$$

where ψ_e varies but in the set of normalized (with respect to r integration) functions. They consider the optimum problem:

$$\min_{\Phi} \iint \Phi^*(R)\psi^*(R,r)[T_N + T_e + V(R,r)]\Phi(R)\psi(R,r)dRdr \quad (1.17)$$

with the constraint of normalization for Φ and that ψ satisfies the first constraint. The stationary points are given by

$$\delta \int \psi_e^*(R,r)(T_e + V(R,r) - U(R))\psi_e(R,r)dr = 0 \quad (1.18)$$

$$\delta \iint \Phi^*(R)\psi^*(R,r)[T_N + T_e + V(R,r) - W]\Phi(R)\psi(R,r)dRdr = 0 \quad (1.19)$$

from which we obtain:

$$[T_e + V(R,r) - U(R)]\psi_e(R,r) = 0 \quad (1.20)$$

$$[T_N - W + U(R)]\Phi(R) = 0 \quad (1.21)$$

This is implicitly an infinite system of equations. The Lagrange method permits to obtain the system from the stationary point of the functional:

$$\begin{aligned} & \iint \Phi^*(R)\psi^*(R,r)[T_N + T_e + V(R,r)]\Phi(R)\psi(R,r)dRdr \\ & - W \iint \Phi^*(R)\Phi(R)dRdr \\ & - Z \left[\int \psi_e^*(R,r)(T_e + V(R,r))\psi_e(R,r)dr - \right. \\ & \left. \int \psi_e^*(R,r)(U(R))\psi_e(R,r)dr \right] \end{aligned} \quad (1.22)$$

which isn't invariant with respect to phase changes. Only the first term is in fact invariant with respect to the simultaneous change: $\psi_e \rightarrow \psi_e e^{i\alpha(R)}$ and $\Phi \rightarrow \Phi e^{-i\alpha(R)}$ so that the equations aren't invariant. In order to overcome this problem Grosso suggested to introduce the non adiabatic term:

$$\Lambda(R) = \sum_I -\frac{\hbar^2}{M_I} \int (\psi_e^* \frac{\partial^2}{\partial R^2} \psi_e^* + \psi_e^* \frac{\partial}{\partial R} \psi_e \frac{\partial}{\partial R}) dr \quad (1.23)$$

In fact Born and Oppenheimer didn't neglect this term but they considered it as a perturbation term. Then equation 1.29 will become:

$$\begin{aligned}
& T_N \Phi + (U(R, \psi_e) - E_g) \Phi + \left(\sum_I -\frac{\hbar^2}{M_I} \int \psi_e^* \frac{\partial^2}{2\partial R^2} \psi_e \right) \Phi \\
& - \left(\sum_I \frac{\hbar^2}{M_I} \int \psi_e^* \frac{\partial}{\partial R} \psi_e dr \right) \frac{\partial}{\partial R} \Phi = 0
\end{aligned} \tag{1.24}$$

However this doesn't suffice for the exact cancellation of the gauge terms. In the case in which the non adiabatic terms are really negligible another approach is possible which consists in the introduction of "fictitious" generalized forces into the Hamiltonian, namely the terms arising from the covariant derivatives which are of the form: $-i\nabla_I A - 2iA \cdot \nabla_I + A^2$. The non adiabatic term effect in this case introduces into the Schroedinger equation a term proportional to Berry's phase, and a term proportional to the gradient of the gauge phase. However the Born-Oppenheimer system determines a complete system which permit to approach perturbatively the exact solution from the approximated one. A direct way to obtain the basis system is this: in the Schroedinger equation we put the trial function

$$[T_N + T_e + V(R, r)]\psi_e(R, r)\Phi(R) = E\psi_e(R, r)\Phi(R) \tag{1.25}$$

Now we use the Born-Oppenheimer approximation:

$$[(T_N \Phi)\psi_e + (T_e \psi_e)\Phi + (V(R, r) - E)\Phi\psi_e = 0 \tag{1.26}$$

easily recast in the form:

$$\frac{T_N \Phi}{\Phi} + \frac{T_e \psi_e}{\psi_e} + V(R, r) - E = 0 \tag{1.27}$$

Because Φ depend only on the R coordinates we will separate the equations as follows

$$\frac{T_e \psi_e}{\psi_e} + V(R, r) = U(R) \tag{1.28}$$

$$\frac{T_N \Phi}{\Phi} + U(R) - E = 0 \tag{1.29}$$

The complete derivation of Born-Oppenheimer approximation dating to the Born and Oppenheimer paper accounted for an hierarchy of perturbation corrections, the perturbation parameter relating to the fourth order root of electron mass divided by the mean nuclear mass. Later Hagedorn using the multiple scales method and factorizing the ψ_e wavefunctions in terms of the polar Euler form $e^{iS(x)}\psi_e^{real}$ was able to distinguish the phase dependent

terms from the genuine non adiabatic terms. He recognized that the Born-Oppenheimer paper accounts in the right way for this distinction, although the perturbative development is stopped to fourth order in the parameters. In order to use the Born-Oppenheimer approximation in a more general setting it is necessary to implement the other electronic terms and decouple the equations with the usual variational technique, but searching the minimum with the constraints arising from a complete observable set for the electronic degrees of freedom supplying the Hamiltonian. For each electronic term we obtain a different landscape. So we need a double set of indexes in order to enumerate the electron wave functions $\psi_e^{(m)}(R, r)$, the potential $U_m^{BO}(R)$, the nuclear wave functions $\Phi_N^{mn}(R)$, the nuclear Schroedinger equation eigenvalues E_g^{mn} . The different energy landscapes in the second equation of the Born-Oppenheimer approximation point out some doubts about the orthonormality of the set of the eigenfunctions generated by the system. Three observations answer this question.

First: for each fixed value of R the $U_m(R)$ function is just a number entering a Schroedinger equation whose eigenfunctions will be orthogonal to each other. So that the products of functions $\psi_e \Phi_N$ will be orthogonal with respect the double integration in R and r because are orthogonal with respect the single integral in r .

Second: the nuclear wave functions with different m effectively aren't orthogonal. In fact, when a deactivation occurs in a molecule the fact that the nuclear functions are not orthogonal is responsible for the Franck Condon factor. However for each fixed electronic level index m , the nuclear wave functions are obtained calculating the spectrum of a self-adjoint hamiltonian.

Third: because, in practice, the nuclear motion description rarely will involve excited configurations with local nuclear minima very far from one another, and because the energy separation of the vibronic energy is a thousand times smaller than the electron excitation energy, we can treat the nuclear motion as a continuum. This is the spirit of the Car-Parrinello approximation to the molecular dynamics.

Coming back to the original paper, Born and Oppenheimer defined the perturbative parameter $k = (m/M)^{1/4}$ and the zero order energetic term as the electronic energy with nuclei at the optimal configuration obtained by the variational method. In order to understand the way followed by Born-Oppenheimer we need to introduce in the equations 1.28, 1.29 the variable $R + ku$, where R are the positions at which $U_m(R)$ has a minimum, and then we develop with respect to ku . Now the first order correction to energy in k is null, the second order correction term in k is the energy of the harmonic approximation to the vibrational motion of the nuclei. The third term again

is null, and the fourth order term contains the energy of the rotational motion, anharmonic corrections to the nuclear vibrations, and the non-adiabatic one. The spectra of small molecules reflect this structure. Electronic transitions are typically in the ultraviolet or visible range, vibrational transition are one order below in the infrared, rotational transitions are in the microwave range, the anharmonic and non adiabatic corrections to the electron energy are too in this bottom range of energy, so that in the solid bulk and in the deviations from statistical quantities for gases, we can meaningfully quantify these energetic corrections by experimental settings. Now we will explicitly derive the Born-Oppenheimer perturbative corrections up to second order. Assuming:

$$R_I = R_{0I} + k u_I \quad (1.30)$$

we will obtain:

$$T_N = \sum_{I=1}^N \frac{\hbar^2}{2M_I} \nabla_I^2 = -k^2 \sum_{I=1}^N \frac{M}{M_I} \frac{\hbar^2}{2m} \nabla_{u_I}^2 \quad (1.31)$$

and defining:

$$H_1 = \sum_{I=1}^N \frac{M}{M_I} \frac{\hbar^2}{2m} \nabla_{u_I}^2 \quad (1.32)$$

we rewrite the total Hamiltonian as:

$$H_0 + k^2 H_1 \quad (1.33)$$

We then consider the projection of the wave functions in the factorized Born-Oppenheimer base:

$$\Psi(u, r) = \sum_{n, \nu} \Phi_{n\nu}(u) \psi_n(u, r) \quad (1.34)$$

where the $\psi_n(u, r)$ minimize the Born-Oppenheimer functional satisfying the equation:

$$H_0 \psi_n = U_n(u) \psi_n \quad (1.35)$$

and U is the potential landscape for the Born-Oppenheimer function. Now the partial expectation value of the Hamiltonian obtained by tracing out the electronic positions is:

$$(k^2 H_1 + U_n + C_n) \phi_{n\nu} + \sum_{m \neq n} C_{nm} \phi_{m\nu} = E_{n\nu} \phi_{n\nu} \quad (1.36)$$

where:

$$C_n(u) = k^2 \frac{M}{M_I} \frac{\hbar^2}{2m} \int \psi_n^*(u, r) \nabla_{u_I}^2 \psi_n(u, r) dr \quad (1.37)$$

$$\begin{aligned} C_{nm}(u) &= k^2 \frac{M}{M_I} \frac{\hbar^2}{2m} \int \psi_n^*(u, r) \nabla_{u_I} \psi_m(u, r) dr \nabla_{u_I} \\ &\quad - k^2 \frac{M}{M_I} \frac{\hbar^2}{2m} \int \psi_n^*(u, r) \nabla_{u_I}^2 \psi_m(u, r) dr. \end{aligned} \quad (1.38)$$

Here $\psi_m(u, r)$ minimizes the Born-Oppenheimer functional. Because the electron wave functions are more broadened than the nuclear ones, it is not surprising to find out that the real order of the C_n terms is the fourth order in k and that C_{nm} terms are of third order in k . Now we will consider the Taylor series for $U_n(R(u))$ and the related perturbative wave functions sequence:

$$U_n(R(u)) = U_n^0 + kU_n^1 + k^2U_n^{(2)} + o(k^2) \quad (1.39)$$

$$\psi_n(u, r) = \psi_n^{(0)}(u, r) + k\psi_n^{(1)}(u, r) + k^2\psi_n^{(2)}(u, r) \quad (1.40)$$

and we will find out the terms $E_{n\nu}$ and $\phi_{n\nu}$ in terms of powers of k :

$$E_{n\nu} = E_{n\nu}^0 + kE_{n\nu}^1 + k^2E_{n\nu}^2 \quad (1.41)$$

$$\phi_{n\nu} = \phi_{n\nu}^0 + k\phi_{n\nu}^1 + k^2\phi_{n\nu}^2 \quad (1.42)$$

In this way we derive the perturbative equations:

$$U_n^0 \phi_{n\nu}^0 = E_{n\nu}^0 \phi_{n\nu}^0 \quad (1.43)$$

$$U_n^1 \phi_{n\nu}^0 + U_n^0 \phi_{n\nu}^1 = E_{n\nu}^1 \phi_{n\nu}^0 + E_{n\nu}^0 \phi_{n\nu}^1 \quad (1.44)$$

$$(H_1 + U_n^2) \phi_{n\nu}^0 + U_n^1 \phi_{n\nu}^1 + U_n^0 \phi_{n\nu}^2 = E_{n\nu}^2 \phi_{n\nu}^0 + E_{n\nu}^1 \phi_{n\nu}^1 + E_{n\nu}^0 \phi_{n\nu}^2 \quad (1.45)$$

From these equations it follows that the zero order energy is the electronic energy with the nuclei in an optimal configuration. The first order says that each nucleus occupies its minimum equilibrium position, the second order says the nuclear motion is approximated by an harmonic motion with equation:

$$[H_1 + U_n^2] \phi_{n\nu}^0 = E_{n\nu}^2 \phi_{n\nu}^0 \quad (1.46)$$

The third order is null. The fourth order is required to describe rotational levels, because the inertia moment is of the fourth order in the parameter k . But at this order we meet a new quantum phenomenon: namely the non adiabatic corrections arising from the C terms are of the same order as the rotational level. When the Berry phase may be chosen freely because the

connection in the manifold is not singular we have the same levels with or without the non adiabatic corrections, otherwise there may be some slightly but structurally very relevant differences. Coming back to the description of a molecule in this frame we can ask, for example: how can we describe the oscillation of a simple pyramidal molecule? We can think this: because the electronic ground state will describe a double minimum potential landscape we can consider a simple superposition of nuclear wave functions describing a nucleus localized in one of the two minima. Namely:

$$\left(\sum_{n=1}^{\infty} \Phi_{n,0}(R)\right)\psi_0(R, r) \quad (1.47)$$

In order to restate this naive proposition in a more rigorous frame we can follow Hagedorn [4], which start with a coherent state expressed from a semi-classical wave packet concentrated near a given point in the nuclear phase space, times the electronic eigenstate: $f_{coherent}^{\{R_0, P_0\}}(R)\psi_0(R, r)$ (really Hagedorn just supposes there exists an isolated eigenvalue $E(R)$ for each R in a given open set and roughly we can change 0 with an other integer index, where the electronic factor is an eigenvector for the eigenvalue $E(R)$; moreover the discrete enumerable sum is improper because the nuclear spectrum for a fixed electron configuration has a continuous part).

Hagedorn [4] shows an estimation for the transitions to orthogonal electron wave parts of the spectrum in the exact evolution of the Schroedinger equation and for the delocalization in the nuclear positions determining a time scale on which the nuclei are localized. These transitions are controlled by the square of the non-adiabatic Born-Oppenheimer k parameter. However we must stress that in almost all classical applications of Born-Oppenheimer the interference terms between different electronic terms aren't accounted. In order to make practical use of the Born-Oppenheimer approximation we need a more critical approximation, because, as we said before, the superposition of nuclear wave functions can generate a compact wave packet so that we will assume the nuclear coordinates are effectively localized from an essentially unknown mechanism and are classical points. This is an approximation, not the true story, however on the time scale of molecular dynamics it works well except when we want to study finer effects than vibrations. This isn't intrinsic to the Born-Oppenheimer approximation and introduces a systematic deviation from the right quantum evolution when electron configuration changes are possible. We generally need to vary the positions and to estimate the forces from energy variations, but the Born-Oppenheimer estimate of the energy differs from the right energy because of the neglected interference terms. On the other hand the Hellman-Feynman theorem will

ensure the significativity of the forces calculated from the ground state energy variation in the case the motion is really slow with respect to electronic transitions. Physical coupling with the electromagnetic radiation is neglected in the Born-Oppenheimer approach, but this coupling forces the electronic system to stay near the ground state, so that the Hellman-Feynman hypothesis is generally fulfilled for any slow initial state we will meet in very low (vibrational range) energy.

1.3 Berry's phase

Here we briefly describe the mathematical tool named as Berry's phase and some of its more intriguing applications. Let M be a manifold describing the parameter space of the nuclei position vector R . At each point R of M we will consider the normalized n^{th} eigenstate of the Schroedinger equation 1.28. As we show in 1.24 a phase change in each of the solutions of 1.28 will give a linked phase in the nuclear wave function. The additional terms are necessary in order to guarantee the independence of the Born-Oppenheimer functions with respect to the phase change of the equations. However we now shall fix attention on 1.28 and we shall learn a lot about the phase independent $U(R)$ function structure. Because the trial function can be chosen to be real, the phase can be fixed and we shall say the gauge is fixed. However if the $U(R)$ term shows a cusp the partial phases cannot change continuously when we change the parameters R . This was shown in the clearest way by Berry [5] who related the continuous phase variation induced from an adiabatic change of the parameters (R in this case) to a differential form whose exterior derivative is related to a curvature in the parameter space manifold: Berry showed, very generally, that given a Hamiltonian which is differentiable with respect to R , if we require the phase factor of the eigenfunction to vary smoothly with R , then along a closed path γ the integral:

$$i\lambda(R) = \beta[\psi_e, \gamma] = i \oint_{\gamma} \left(\int \psi_e^* \frac{\partial}{\partial R} \psi_e dr \right) dR \quad (1.48)$$

is well defined and phase independent. The generalized differential form for the eigenfunction $|n, R\rangle$ associated with the eigenvalue $E_n(R)$ of a parametric Hamiltonian $H(R)$ is written as $\langle n, R | \nabla | n, R \rangle dR$. Berry's proof is very simple, but tricky: the differential form has an exterior derivative, namely:

$$\sum_{i < j} Im \left(\int (\partial_i \psi_e^*) (\partial_j \psi_e) dr \right) dx_i \wedge dx_j \quad (1.49)$$

and, in the customary Dirac notation:

$$\sum_{i<j} Im \langle \nabla_i n | \nabla_j n \rangle dx_i \wedge dx_j \quad (1.50)$$

can be recast in the form

$$\sum_{m \neq n} \sum_{i<j} Im \langle \nabla_i n | m \rangle \langle m | \nabla_j n \rangle dx_i \wedge dx_j \quad (1.51)$$

in fact

$$Im \langle \nabla_i n | n \rangle \langle n | \nabla_j n \rangle = Im |\langle \nabla_i n | n \rangle|^2 = 0 \quad (1.52)$$

now we write down

$$\begin{aligned} \langle m | (\nabla H | n \rangle) &= \langle m | (\nabla H) | n \rangle + \langle m | H \nabla | n \rangle = \\ \langle m | (\nabla H) | n \rangle + E_m(R) \langle m | \nabla | n \rangle & \end{aligned} \quad (1.53)$$

and

$$\begin{aligned} \langle m | (\nabla H | n \rangle) &= \langle m | (\nabla E_n(R) | n \rangle) = \\ \langle m | (\nabla E_n(R)) | n \rangle + E_n(R) \langle m | \nabla | n \rangle &= E_n(R) \langle m | \nabla | n \rangle \end{aligned} \quad (1.54)$$

so that

$$(E_n(R) - E_m(R)) \langle m | \nabla | n \rangle = \langle m | (\nabla H) | n \rangle. \quad (1.55)$$

Finally then:

$$\langle m | \nabla | n \rangle = \frac{\langle m | (\nabla H) | n \rangle}{E_n(R) - E_m(R)} \quad (1.56)$$

and so:

$$\begin{aligned} \langle n R | \nabla | n, R \rangle dR &= \sum_{i<j} Im \langle \nabla_i n | \nabla_j n \rangle dx_i \wedge dx_j = \\ \sum_{m \neq n} \sum_{i<j} Im \langle \nabla_i n | m \rangle \langle m | \nabla_j n \rangle dx_i \wedge dx_j &= \\ \sum_{m \neq n} \sum_{i<j} \frac{Im \langle n | (\nabla_i H) | m \rangle \langle m | (\nabla_j H) | n \rangle}{(E_n(R) - E_m(R))^2} dx_i \wedge dx_j & \end{aligned} \quad (1.57)$$

The last expression doesn't depend on the phases because each phase will appear with its complex conjugate. If we can choose all the functions real simultaneously, the exterior derivative of the Berry differential form is null

where the derivatives are well defined, and when the phase space is non-degenerate the Berry's phase is null because of the Stokes theorem. If the manifold shows a cusp the curvature gets an irreducible non-null value at a point, where the Stokes theorem maybe fails. However the Berry phase $\Lambda(R) = e^{i\lambda(R)}$ in a loop γ doesn't depend on the loop if it can be deformed continuously without meeting the singular point. When can a cusp occur in the parameter space? Of course, when the Schroedinger eigenvalue is degenerate. To help imagination we can think the case of a conical intersection in a simple one parameter space in which two functions intersecting in a given point have two minima in two different points of the manifold. Though very naive this argument was shown to be right, in the twofold degenerate case, where Berry's phase is π .

The argument of Berry was generalized by Barry Simon [6], who was able to connect Berry's paper to a paper of Thouless et al. [7] and to the old paper of Von Neumann [8] about the conical intersections intrabands. One of the key results of Barry Simon is this: each singularity (i.e. degenerate point) is associated with a charge. The Thouless result was that each band in a continuous level system, like the solid state bands, is labelled by an integer number. Barry Simon showed this integer is equal to the sum of the singularity charges. This is a very surprising phenomenon relating the molecular dynamics to the esoteric Berry phase.

When a molecule or a crystal shows a singular degeneracy in some level of the Born-Oppenheimer energy landscape and the degeneracy is characterized as a conical intersection we call it Jahn-Teller intersection. If the interaction occurs in a symmetric point this is the signature of an instability regarding this symmetric configuration, and the result is a Jahn-Teller distortion: in fact the minimum of the ground state will be in a non symmetric configuration, far away the conical intersection where an upper level intersects the ground state. So that, when Berry's phase is π in a twist of ground state configurations, this is the signature of a Jahn-Teller distortion. However, more complex situations can occur because the spin degrees of freedom of the electron gas. Berry's argument is in fact very general, although it was developed initially for a restricted class of systems. As stated originally by Berry, all that's needed is the possibility to identify, in the physical system, a quantity that plays the role of a slowly varying parameter. This enables the application of Berry's argument to the study of an electronic system in the Born-Oppenheimer approximation, with the nuclear coordinates playing the role of parameters. However, the validity of the results is not restricted to the regime of adiabatic variation of the nuclear degrees of freedom, because the existence of a degeneracy in the energy landscape, or equivalently of a conic intersection, is structurally stable against small perturbations.

If we treat the spins of the system like internal degrees of freedom, though we will speak about other than the Born-Oppenheimer approximation, we can still apply Berry's phase to detect the singularities. However, not all the asymmetric ground state configurations arise from a Jahn-Teller distortion associated with a conical intersection. For example, the NH_3 molecule is asymmetric, but this asymmetry isn't associated with a conical intersection in the ground state. The dimethyl disulfide molecule $(SCH_3)_2$ is also asymmetric, as we will see, and we can reproduce this asymmetric configuration in the DFT non polarized frame. The more common kind of asymmetries is due to the simplest broken symmetry, the angular momentum broken symmetry. For an atom we know that all the systems show a broken symmetry in the electronic configuration with order parameter given by the multipole tensor. Though not all the asymmetric ground states arise from Jahn-Teller effect, when the degeneracy occurs in an excited level near the ground-state or when there is a quasi-degeneracy resembling an avoided crossing in the energy landscape, but the simplest symmetry arguments do not suggest any degeneracy, we refer to it sometimes as a pseudo-Jahn-Teller distortion. A typical example of pseudo-Jahn-Teller effect arises in the C_4H_4 molecule, where in the square symmetric geometry the molecule has two degenerate antibonding molecular orbitals partially occupied, and so Hund's rule predicts a triplet state, but in the rectangular geometry the degeneracy is broken and the antibonding orbital whose energy is lowered hosts two electrons in a singlet state. In such a system no degeneracy occurs in the ground state, in the symmetric configuration, however if we constrain the electrons in the antibonding orbitals to stay in a singlet state we can observe a degeneracy.

The Jahn-Teller distortion occurs, of course, in the NH_3^+ molecule, which differently from NH_3 shows a real Jahn-Teller distortion. Like in the CH_4 ionized molecule, this occurs because the triangular and tetrahedral symmetry, combined with the Floquet theorem, implies a generalized Bloch factor multiplied by the symmetric wave function. This function isn't globally symmetric, so that the kinetic term is increased with respect to the symmetric function case and the ionization stabilizes the E representation with respect to the A representation, so inducing a conical intersection. This function has, in fact, irreducible representation class E (two dimensional) and the same symmetry class occurs in the vibrational modes, because the Born-Oppenheimer approximation fails near the degeneracy and the coupling between terms of the same symmetry stabilizes the asymmetric configurations. Regarding the non planar configuration, what happens? If we consider the Born-Oppenheimer planar configuration of NH_3^+ , we see that the N has oxidation number -3 and has 3 electrons in p orbitals. This implies that the two p orbitals in the plane of the molecule hybridize with s orbitals giving

a triangular fully symmetric ground state configuration. However, the third p orbital changes sign under planar reflection, so that an occupation of this orbital is kinetically unfavorable but has lower Coulombic energy, because it permits an increased dislocation of the charge. So the energy landscape of the ground state in the NH_3 molecule shows two minima when N occupies two mirroring symmetric positions in the direction orthogonal to the hydrogens' plane.

1.4 Mean field approach

In 1930 Dirac suggested another method to approximate the quantum evolution of a system, nowadays referred to as time dependent self consistent fields method (TDSCF) [9]. In this approach the Born-Oppenheimer ansatz is replaced with a simpler one:

$$\Psi(R, r, t) = \Phi_N(R, t)\psi_e(r, t)e^{\frac{i}{\hbar} \int_{t_0}^{t_1} dt' E_e(t')} \quad (1.58)$$

where the nuclear and electronic wavefunctions are separately normalized to unity at every instant of time, and a phase factor is introduced in order to simplify the self consistent equations deriving from the Schroedinger equation. In this phase $E_e(t')$ is just the mean value of the electronic term of the Hamiltonian in the approximate state. Calculating the mean value and imposing the energy conservation we obtain the following relations:

$$i\hbar \frac{\partial \psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \psi + \left(\int dR \phi^*(R, t) V(R, r) \phi(R, t) \right) \psi \quad (1.59)$$

$$i\hbar \frac{\partial \psi}{\partial t} = - \sum_I \frac{\hbar^2}{2m_I} \nabla_I^2 \psi + \left(\int dr \psi^*(r, t) H_e(R, r) \psi(r, t) \right) \psi \quad (1.60)$$

These are the self consistent coupled equations introduced by Dirac: the nuclei and the electrons move in time-dependent effective potentials averaged over the other degrees of freedom. In this sense Dirac spoke of mean field description of the coupled nuclear electronic quantum dynamics. As the reader will notice in this scheme the initial conditions are, until now, undefined. The simplest choice we can make in order to derive a classical molecular dynamics approximation is to treat the nuclei as classical point particles. But at this stage we have a quantum description, so the natural choice in order to reduce

to classical dynamics is to implement the semiclassical WKB approximation. We write the nuclear wavefunction in the polar Euler form:

$$\Phi(R, t) = A(R, t)e^{iS(R, t)/\hbar} \quad (1.61)$$

then we obtain the full Schroedinger system for the mean field nuclear equation 1.60:

$$\begin{aligned} & \frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \int dr \psi^*(r, t) H_e \psi(r, t) = \\ & = \hbar^2 \sum_I \frac{1}{2M_I} \frac{\nabla_I^2 A}{A} \end{aligned} \quad (1.62)$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I A)(\nabla_I S) + \sum_I \frac{1}{2M_I} A (\nabla_I^2 S) = 0 \quad (1.63)$$

Now we can immediately recognize the second equation as the continuity equation for the probability density $\rho = A^2$ and the current density $Im(\sum_I \frac{\hbar}{M_I} \psi \nabla_I \psi^*) = A^2 \sum_I \frac{1}{M_I} (\nabla_I S)$.

The first equation is the quantum version of the Hamilton-Jacobi classical equation. We can trace back to the classical equation with the limit $\hbar \rightarrow 0$ and the replacement $P_I = \nabla_I S$. This gives:

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (P_I)^2 + \int dr \psi^*(r, t) H_e \psi(r, t) = 0 \quad (1.64)$$

whose gradient leads to:

$$\frac{dP_I}{dt} = -\nabla_I \int dr \psi^*(r, t) H_e \psi(r, t) \quad (1.65)$$

i.e. the Newton cardinal equation of the dynamics! The careful reader will notice that the initial condition isn't fixed by the Dirac self consistent mean field system. But the found Newton equation suggests to consider a new approximation: if we choose a concentrated density for the nuclear wave functions the 1.59 equation assumes the simpler form:

$$i\hbar \frac{\partial \psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \psi + V(R, r) \psi = H_e(R, r) \psi \quad (1.66)$$

The last two equations, namely: 1.65 and 1.66, are referred as the Ehrenfest molecular dynamics equations. In order to solve these equations there are

usually two main routes. The first, the more expensive one, is to solve simultaneously the two equations; the other takes advantage of the fact that it is easy to solve a time-independent Schroedinger equation, by pinning down the eigenvalues and then finding the wave functions with an iterative fixed point algorithm. In this method, the time dependent equation is conveniently recast in the “on the fly” adiabatic basis as follows. For each fixed value of the nuclear coordinates we solve the time-independent Schroedinger equation:

$$E_k(R)\psi(r, R) = H_e(R, r)\psi \quad (1.67)$$

and we assume the uniquely determined expansion:

$$\psi(r, R) = \sum c_k \psi^k(r, R) \quad (1.68)$$

Now, because R as well as the expansion coefficients are varying in time, we write more properly:

$$\psi(r, R(t), t) = \sum c_k(t) \psi^k(r, R(t)) \quad (1.69)$$

Inserting this sum in the time dependent Schroedinger equation and considering the scalar product of this equation with each $\psi_k(r, R(t), t)$ we obtain:

$$i\hbar \dot{c}_k = c_k E_k(R) + \sum_l \dot{R} \int dr \psi_k^*(r, R) \nabla_R \psi_l(r, R) c_l \quad (1.70)$$

and equation 1.65 becomes:

$$M_I \ddot{R}_I = - \sum_k |c_k(t)|^2 \nabla_R E_k - \sum_{k,l} c_k^* c_l (E_k - E_l) \int dr \psi_k^*(r, R) \nabla_R \psi_l(r, R) \quad (1.71)$$

The time dependent formalism reduces to the time independent one when the interferences between electronic terms are negligible. In this case as in the Born-Oppenheimer dynamics the force is just evaluated as the gradient of the ground state energy. Namely:

$$M_I \ddot{R}_I = -\nabla \langle \psi_0 | H_e | \psi_0 \rangle \quad (1.72)$$

1.5 Car-Parrinello

As we sketch at the end of the section in which we discuss the Born-Oppenheimer approximation, and as we remark at the end of the last section, the true point in the practical use of ab initio methods in molecular

dynamics is related to the extraction of the forces acting on nuclei. The force is a definition of classical mechanics, the status of the force in quantum theory emerges from approximations, and as a mean concept. For example, the motion of the mean value of the observable position in a quantum oscillator satisfies the Heisenberg equation and the classical force appears in the Heisenberg equation. So in the Dirac-Ehrenfest self consistent field equations the forces arise from the classical approximation. In order to match the Born-Oppenheimer approximation with the Dirac-Ehrenfest time dependent approximation, we need to consider the coupling between the electrons and the electromagnetic radiation and we need to build on the Hellman-Feynman theorem. But because the Hellman-Feynman theorem implies the loss of all information about electron dynamics (the electrons follow the nuclei and should stay in the ground state related to the Born-Oppenheimer surface), Car and Parrinello suggested to switch on a thermodynamics of the electron cloud and to account for the electron dynamics by the following ad hoc effective Lagrangian:

$$\begin{aligned}
L_{CP} = & \sum 1/2M_I\dot{R}_I^2 + \sum 1/2\mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle - \langle \Psi_0 | H_e | \Psi_0 \rangle \\
& + \text{constraints}
\end{aligned}
\tag{1.73}$$

Despite the apparent simplicity of this Lagrangian here is a revolution in molecular dynamics. The key point is this: the Lagrangian approach permit to use the multiple time scale operator factorization techniques and the symplectic algorithms of integration, in order to guarantee the full verification of the relevant physical constraints in the dynamics. Introducing to a phase space and using the Liouville operator arising from the Hamiltonian associated with the Car-Parrinello Lagrangian, it is possible to make transparent the dialogue between quantum and classical pictures. In the spirit of the KMS theorem [10] the electron cloud may be viewed as a cold system in equilibrium with a thermal bath dissipating the energy surplus coming from the coupling with the nuclear degrees of freedom. Thus in the fictitious electron dynamics, which has a semiclassical character, a temperature lower than the bath's is required in order to guarantee agreement with the quantum picture. This is achieved by assigning a large fictitious mass to the electrons. It is necessary to stress that in Car-Parrinello this thermal dissipation is not physical, but external and fictitiously imposed; moreover in practical uses the Car-Parrinello dynamics requires a simplification in the quantum description of the electronic structure, and so the electron dynamics is really fictitious. However, because the characteristic evolution of the electronic degrees of freedom is faster than the nuclear vibrations, the temperature of the electronic bath is decoupled from the nuclear energy scale. We can then assume two

different temperatures, with the electronic fictitious temperature colder than the nuclear one. The full operativity of the Car-Parrinello approach depends on the density functional theory applied to electron degrees of freedom in the Kohn Sham arrangement. We will discuss this scheme in greater depth. Before the Car Parrinello method a question was unsolved: how to combine the evaluation of ground state electronic properties of large and disordered systems at the level of state-of-art electronic structure calculations, with the ab initio MD simulations where the only assumptions are the validity of classical mechanics to describe ionic motion and the Born-Oppenheimer approximation? So following Kohn and Sham, Car and Parrinello in their pioneering work of 5 August 1985 [11] wrote the electron density in terms of occupied single particle orthonormal orbitals $n(r) = \sum_i |\psi_i(r)|^2$. A point of the Born-Oppenheimer potential energy surface is given by the minimum with respect to $\psi_i(r)$ of the energy functional $E[\psi_i, R_I, \alpha_\nu]$. So since the origin the Car-Parrinello method permits to fix, in the α_ν variables some external constraints to the system, like the volume, the stress tensor, an electrical field, Hartree and exchange correlation contributions. The minimization of the energy functional with respect to the orbitals ψ_i is the core of the Car-Parrinello dynamics and is done by using “dynamical simulated annealing” not only because it permits an efficient exploration of the minimum of the energy landscape associated to the objective functional, but also in order to study the finite temperature properties. The Car-Parrinello Lagrangian generates a dynamics for the parameters $\psi_i(r, t), R_I, \alpha_\nu$. The dynamical equations are

$$\mu \ddot{\psi}_i(r, t) = -\delta E / \delta \psi_i^*(r, t) + \sum_k \lambda_{ik} \psi_k(r, t) \quad (1.74)$$

$$M_I \ddot{R}_I = -\nabla_{R_I} E \quad (1.75)$$

$$\mu_\nu \ddot{\alpha}_\nu = -(\partial E / \partial \alpha_\nu) \quad (1.76)$$

In the original paper Car and Parrinello stressed that only the ion dynamics may have a real physical meaning, whereas the dynamics associated with the Kohn Sham orbitals and with the additional parameters is fictitious and has to be considered only as a tool to perform the dynamical simulated annealing. In order to minimize the functional the Newtonian dynamics may be replaced by Langevin dynamics. Notwithstanding the fictitious nature of the Kohn-Sham parameters, a metastable situation is realized, in which the kinetic energy associated with the ψ_i remains always very small compared to the typical variations of the potential energy of the system. If this temperature remains very small, the ion dynamics provides a good representation of the actual dynamics of a physical system, saving the goodness and the

validity of all the approximations: adiabatic following, classical nuclei, Kohn Sham density functional. However, if the temperature is too small the low velocities of the electronic variational parameters might lead to intolerably long relaxation times. In order to obtain the optimized wave functions we could start the optimization procedure from a random wavefunction which certainly does not minimize the electronic energy. Thus we need to extract energy from the system. This may be obtained adding to the Car-Parrinello Lagrangian a Routhian dissipative term, in the same spirit of the simulated annealing.

1.6 Functional density theory

Now we address the problem to solve the electronic configuration in a fixed external potential. As we have seen by now this problem is common in the Ehrenfest molecular dynamics, in the Born-Oppenheimer molecular dynamics and in the Car-Parrinello molecular dynamics. In atoms, molecules, and solids the electrons form a non uniform gas described by a three terms Hamiltonian:

$$H = T + W + V \tag{1.77}$$

The three observables are respectively the electronic kinetic energy, the electron-electron interaction and the external coulombic potential.

$$T = \sum_{i=1}^E -\frac{\hbar^2 \nabla_i^2}{2m} \tag{1.78}$$

$$W = 1/2 \sum_{i \neq j=1}^E \frac{e^2}{|r_i - r_j|} \tag{1.79}$$

$$V = \sum_{i=1}^E v(r, R, \alpha) \tag{1.80}$$

At this stage the notion that ground state properties of quantum many particle systems can be characterized only in terms of the one-particle density isn't obvious. This notion goes back to Thomas, Fermi, Gentile, Majorana, Weiszacker, and Dirac. In fact these hydrodynamic gas models for the electron dynamics were seen as heuristic attempts to simplify the original quantum problems accounting for the Pauli principle and the spin dynamics of electronic states. However in 1964 the Hohenberg and Kohn theorem shed new light in the subject. The original theorem states in essence that an exact representation of the ground state properties of a stationary, non relativistic

many particle system in terms of the ground state density only is possible. We can briefly appreciate the Hohenberg-Kohn theorem as follows. Write down the Hamiltonian in the second quantization formalism:

$$\begin{aligned}
H &= -\hbar^2/2m \sum_{\alpha} \int d^3r \Psi_{\alpha}^{\dagger} \Delta \Psi_{\alpha} + \\
&\sum_{\alpha} \int d^3r \sum_{\alpha} \int d^3r \Psi_{\alpha}^{\dagger} v(r) \Psi_{\alpha} + \\
&\sum_{\alpha, \beta} \Psi_{\alpha}^{\dagger} \Psi_{\beta}^{\dagger} w(r, r') \Psi_{\alpha} \Psi_{\beta}
\end{aligned} \tag{1.81}$$

Solving the associated Schroedinger equation for each fixed $v(r)$ function we obtain one minimum eigenvalue E_{GS} and, in the nondegenerate case, we obtain just one ground state wave function: ψ_{GS} which is associated just to one density function:

$$n(r) = \langle \sum_{\alpha} \Psi_{\alpha}^{\dagger}(r) \Psi(r)_{\alpha} \rangle_{GS} \tag{1.82}$$

If we consider the relation of equivalence $v(r) \sim v'(r) \Leftrightarrow v(r) - v'(r) = k$ where k is a constant, the first part of Hohenberg-Kohn's theorem states: "the map \mathcal{M} connecting the $v(r)$ equivalence class of functions to $n(r)$ functions is invertible". The uniqueness of the wave function immediately follows from comparison between:

$$(T + W + V)|\psi_{GS}\rangle = E_{GS}|\psi_{GS}\rangle \tag{1.83}$$

$$(T + W + V')|\psi'_{GS}\rangle = E'_{GS}|\psi'_{GS}\rangle \tag{1.84}$$

The uniqueness of the density associated with a given wave function follows from the two inequalities:

$$\begin{aligned}
E_{GS} &= \langle \psi | H | \psi \rangle < \langle \psi' | H | \psi' \rangle = \\
&< \psi' | H' | \psi' \rangle + \int d^3r n'(r)(v(r) - v'(r))
\end{aligned} \tag{1.85}$$

$$\begin{aligned}
E'_{GS} &= \langle \psi' | H' | \psi' \rangle < (\langle \psi | H | \psi \rangle = \\
&= \langle \psi | H | \psi \rangle + \int d^3r n(r)(v'(r) - v(r)))
\end{aligned} \tag{1.86}$$

derived from the Ritz variational characterization of the ground state. In fact summing these inequalities we obtain:

$$0 < \int d^3r (n'(r) - n(r))(v(r) - v'(r)) \tag{1.87}$$

when $\psi \neq \psi'$ that implies $n'(r) \neq n(r)$. From Ritz variational characterization of the ground state it follows that

$$\langle \psi | T + W + V | \psi \rangle \quad (1.88)$$

assumes the minimum value when ψ is in the ground state.

But because the Hohenberg Kohn theorem guarantees that we have a one-to-one correspondence between ψ and $n(r)$, we can write $\psi[n]$ meaning that it is the wave function associated to a density n in $\text{Dom}(\mathcal{M})$, and we can also write:

$$E[n] = \langle \psi[n] | T + W + V | \psi[n] \rangle \quad (1.89)$$

This functional defined in the domain of \mathcal{M} is minimized when n is the density for the ground state. The functions in the domain of \mathcal{M} are called "v-representable" because given a function V there exists the $\mathcal{M}(V)$ image in $\text{Dom}(\mathcal{M})$, and vice versa: given a density in $\text{Dom}(\mathcal{M})$ it will be a wave function $\mathcal{M}^{(-1)}[n]$ which solves a ground state problem for some potential V . All the results obtained are extended to the degenerate ground state by just replacing the functions ψ in our discussion with the equivalence class with respect to the equivalence relations "are ground state eigenfunctions of the minimum eigenvalue" in the ground state functions domain. A celebrated Ehrenfest quantum mechanics exercise states: for every definite positive, reasonable, wave function there exists just one potential that generates it. This first old one-dimensional result has been extended to more and more complex problems in the course of time. And in the case of a single particle we easily can show that:

$$v[r] = \frac{(\hbar^2/2m)(\Delta\sqrt{n})}{\sqrt{n}} \quad (1.90)$$

So that when Hohenberg and Kohn stated their result, it was hoped that it could be shown that every density is v-representable. However it is not so simple. Levy and Lieb constructed a class of q-degenerate functions associated to the same density, and more annoyingly Englisch and Englisch showed functions not corresponding to the ground state of any external potential, because the potential may be singular. However in 1982 Lieb and Levy found an extension of the functional principle well behaved in every continuous neighborhood of the density functions, so that Chayes, Chayes and Ruskai showed in 1985 that on a grid every density which is strictly positive, properly normalized, and consistent with the Pauli principle is ensemble "v-representable" [12], [13]. In 1983 E.K.U. Gross and Runge extended these theorems to a time dependent scheme [14]. Briefly described, the conclusion

of all this work is explained thus: starting from the energy functional we can define the Hohenberg-Kohn functional:

$$F_{HK}[n] = \langle \Psi | T + W + V | \Psi \rangle - \int n(r)v([n];r)dr \quad (1.91)$$

where $v([n]; r)$ indicates the v -representation for the $[n]$ density, which exists, by definition, if $[n]$ belongs to $\text{Dom}(\mathcal{M})$. In order to overcome the non degeneracy constraint Lieb and Levy proposed a slightly different variational principle:

$$F_{LL}[n] = \inf_{\Psi \rightarrow n} \langle \Psi | T + W + V | \Psi \rangle - \int n(r)v([n];r)dr = \inf_{\Psi \rightarrow n} \langle \Psi | T + W | \Psi \rangle \quad (1.92)$$

where the Ψ are antisymmetric, normalized N -particle functions whose density is $n[r]$. This variational principle coincides with Hohenberg-Kohn for all pure state N -particle antisymmetric v -representable wave functions, as the Hohenberg and Kohn functional doesn't depend explicitly on the v -functions. Furthermore it doesn't depend on anything other than the condition that $n(r)$ is the density for a non-void set of antisymmetric N -particle functions, where the Hohenberg-Kohn functional is defined in $\text{Dom}(\mathcal{M})$, and minimizes the functional energy:

$$E_{v_0}[n] = F_{LL}[n] + \int n(r)v_0(r)dr \quad (1.93)$$

which is exact for n_0 . The advantage is just in a subtle difference between F_{LL} and F_{HK} : in the first one we don't have the constraint that Ψ is a ground state wave function. However, this advantage is huge: in fact starting from 1975 until 1985 the awareness was gained that all the non-negative n -functions can be represented as the density of some antisymmetric N -particle functions [15], [16],[17]. A theorem due to Coleman [18] guarantees that the restriction to the N -particle antisymmetric wave functions ensemble is less restrictive than it appears, because N -representability constraints to the full spin-density ensemble do not imply any restriction on the minimum sets. Coleman's theory of the representation by density matrix of fermion systems is based on an extension of the Fredholm inverse theory. The inverse problem in potential theory settled by Coleman in the presence of Fermionic constraints is a milestone for the theory of Fermi liquids and gases. A generalization of density functional theory for the spin polarized case is very relevant and is studied in the same general frame of the density matrix formalism, just taking into account the other physical observables like density

of magnetization. The Levy Lieb constrained search is extended to the construction of a density functional from the Schroedinger equation by using the density matrix of N -representations. Finite temperature effects are also included in this scheme by the standard identification of the entropic term $\rho(\ln[\rho])$ and by considering the corresponding functional, namely the free energy functional [19]. However the non-equilibrium case remains generally very challenging and requires time dependent partial differential equations tools and an extension of the multiple time scale operator factorization. In the next chapter we address the problem of a concrete search for the density functional evaluation. Nothing in the theoretical frame we discuss permits to concretely evaluate the functional of Levy and Lieb starting from the density. This will require a dramatic simplification because the minimization with respect to a set of orthonormal all electrons functions will be replaced by a minimization with respect to a set of orthonormal one-particle functions, the so called Kohn-Sham orbitals.

1.7 Kohn-Sham

The origin of the Kohn-Sham scheme is in the heuristic Thomas-Fermi approach. These authors treated for the first time the complex problem to determine the ground state of a complex electronic system as a simpler system in which each electron feels the others via the Coulomb potential of a fixed density. Kohn and Sham generalized this treatment using the density functional theory approach. Let's consider a fictitious system of N non interacting particles:

$$H_s = T + V_s \quad (1.94)$$

For this system, according to the Hohenberg-Kohn theorem, there exists the energy functional:

$$E_s[n] = T_s[n] + \int n(r)v_s(r)dr \quad (1.95)$$

which is minimum for the ground state of density n_s . The Kohn-Sham simplification assumes the existence of a local single particle potential $v_s(r)$ such that the exact ground state density of the interacting system equals the corresponding non interacting ground state density. But this assumption is based on the Kohn-Sham theorem: "The exact ground state density $n(r)$ of an arbitrary interacting system can be obtained by self-consistent solution of the following set of equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v(r) + \int d^3r'w(r,r')n(r') + v_{xc}([n];r)\right]\varphi_i(r) = \varepsilon_i\varphi_i(r) \quad (1.96)$$

with:

$$n(r) = \sum_{i=1}^{\infty} \gamma_i |\varphi_i(r)|^2 \quad (1.97)$$

where γ_i are the occupation numbers whose sum equals the number of electrons in the system". Now we discuss very briefly the reference which leads to this achievement.

As we said above, speaking about Coleman's work, for the general case a density matrix represents the ensemble of states with a given density. This density matrix, as shown by Coleman, exists and isn't a void set. Thus Lieb [20] defined the interacting functional as follows:

$$T_L[n] = \inf_{D \rightarrow n} \text{tr}[DT] \quad (1.98)$$

where D is the density matrix referred to a complete orthonormal set of completely antisymmetric N -particle functions. And Englisch and Englisch [21] showed that this functional is differentiable for all interacting ensemble v -representable densities. For non interacting ground state, which is representable in terms of a single Slater determinant, this functional is shown to be equal to the classical form of Lieb and Levy and so is equal to the Hohenberg-Kohn functional. Now because in the minimum of the energy functional this equation is verified:

$$0 = \delta E_s[n] = \delta T_s[n] + \delta \int v_s(r) n(r) d^3r \quad (1.99)$$

(inserting the normalization constraint this equation changes just by a constant λ that is the Lagrange multiplier) we will obtain:

$$v_s(r) := \left. \frac{\delta T_L[\theta]}{\delta \theta(r)} \right|_{\theta=n} \quad (1.100)$$

Now we can define the exchange correlation potential of the Kohn-Sham equation:

$$v_{xc}([n]; r) = \frac{\delta}{\delta n(r)} \left(F_L[n] - T_L[n] - \frac{1}{2} \iint d^3r d^3r' n(r) w(r, r') n(r') \right) \quad (1.101)$$

where F_L is the Lieb form of the energy functional after we subtract the external potential term. Now we have all the fragments necessary to write

the density functional for the non-interacting equivalent system. Namely:

$$\begin{aligned}
E_{v_0}[n] = & T_s[n] + \int d^3r v_0(r)n(r) + \\
& \frac{1}{2} \iint d^3r d^3r' n(r)w(r,r')n(r') + \\
& \int v_{xc}([n];r)n(r)d^3r
\end{aligned} \tag{1.102}$$

Inserting in this functional the expression for density $n(r) = \sum_i \gamma_i |\varphi_i(r)|^2$, where $\gamma_i = Tr(D\theta_i)$ and θ_i is the number of occupation for the i^{th} single particle orbital, which is a well defined observable in the non interacting picture to which the Lieb density matrix is referred, then, equating to zero the variation of the obtained expression, we will obtain the Kohn-Sham system. We have to stress that, because we need to minimize the energy density functional, γ_i is fixed to one for each single particle wave function except for the occupied states corresponding to the highest occupied eigenvalue. In all this presentation we spoke about very non trivial results. Some other words will be useful. We know the full electron ground state equation isn't separable in a product of single particle wave functions. Generally speaking a full interacting wave function is the sum of Slater determinants of complete single particle wave functions, which include the discrete spins degree of freedom, so that the density correspondent to a single Slater determinant isn't the sum of the single particle squared moduli wave functions, because there are interference terms. However the results here, briefly stated, tell us: "There exists a density matrix of antisymmetric wave functions Slater representable for a non interacting particles system, minimizing a given functional, whose density equals the density of the given full interacting system". Because the density matrix for the non interacting "density equivalent" ensemble is the sum of orthogonal antisymmetric Slater determinants of single particle wave functions, we can express the density as a sum of squared moduli of single particles wave functions.

About the fixing of the occupation number we have to observe this seems an arbitrary choice at first sight, but isn't so, see the section 4.2 of Gross book [19]. However this is a very relevant point when we consider a change in the electron chemistry due to external potential variations, because Janak pointed out these variations may be relevant for the core electron density, so this may be relevant in the study of the pseudopotentials. The question was solved by Von Barth and Gelatt in 1980 and in favor of the Kohn-Sham equations if we consider only the first order of variation, because the frozen core density error is naught at first order. In fact, it turns out that separating the density functional for the core density, we have a constant functional

derivative of this functional so that the error is related to the global charge variation. As we saw the Kohn-Sham system resembles the old Thomas Fermi mean field approximation, however we need to stress that the fictitious system regarding electrons isn't physically significant as in the Thomas Fermi approach, because only the density is physically relevant, though the Kohn-Sham system contains more physical information. This has stimulated also the search for subtle relations between the Thomas Fermi approach and the Kohn-Sham wave functions. In order to better appreciate this point we will cite the Koopman theorem, which states that in the Hartree Fock theory the unrelaxed total energy difference $[E_{HF}(N) - E_{HF}^{unrelaxed}(N - 1_i)]$ is identical with the orbital energy of the i^{th} orbital, so that this is an energy of non adiabatic extraction for the external electron. As the Hartree Fock scheme has been demonstrated to arise from a specialization of the Kohn-Sham system, it follows that this physical interpretation is inscribed in the Kohn-Sham system. But this isn't all. The Thomas Fermi Dirac and Weiszacker systems can be derived from the Kohn-Sham equation with a special choice of the exchange and correlation functional. Making an explicit variation of this density functional with respect to density and not to the Kohn-Sham orbitals, we will obtain an equation for the density, and the variation of the density gives a relation between density and potential, letting the Poisson's equation arise from the Thomas Fermi system. Because in principle the demonstration of the N -representability of the general density is partially constructive there are cases in which this definition may drive to study the effective form of the exchange and correlation functional. However, because these is very difficult in practice, we need to search for different ways to express the exchange and correlation functional. As we know the first approximation for the exchange and correlation was found by Thomas and Fermi and, subsequently, corrected by considering local and non local corrections obtained from statistic and thermodynamic considerations. After these pioneering works many theoretical approaches were developed, including the linear response tools, the Green equilibrium and non equilibrium functions, scaling arguments. Other heuristic approaches following the hydrodynamic approach were thus restated in the more rigorous picture of the field theory. The study of the structure factor for the electromagnetic interactions has been related to the exchange and correlation functional determination. By separating the correlation terms from the exchange terms the question of the generalized statistics arising from the Pauli principle is natural, as it was pointed out in the works of Majorana, Gentile, and Weiszacker. On the other hand the Montecarlo methods allowed to test such theoretical investigations (see Ceperley and Alder) and to derive an in principle exact solution for homogenous jellium.

1.8 Explicit functionals, LDA, gradient corrections, HF and non HF non locality.

As we have seen the functional density Hohenberg-Kohn approach with the extension of the functionals, translated in the non interacting language, is exact, except for some very difficult and relevant technical open questions regarding the application to spin systems: the open point is the scaling properties for spin systems and the entanglement properties. All this scheme however is right but non very useful is we don't write down some explicit form for the exchange and correlation functional. In 1965 Kohn and Sham introduced the Local Density Approximation (LDA): they assume that the exchange and correlation functional depends only on the local density:

$$\frac{\delta E_{xc}}{\delta n(r)} = \mu_{xc}[n(r)] = \varepsilon_{xc}[n(r)] + n \frac{d\varepsilon_{xc}(n)}{dn} \quad (1.103)$$

For the $\varepsilon_{xc}[n(r)]$ term they used the same dependence on the density as for an homogenous electron gas. The first approach was based on the virial theorem application. In fact the virial theorem gives the exact scale law for the density variation and permits to relate the correlation scaling exponent to the exchange one. This power-law result may be applied to derive the right Hartree Fock exchange correlation term:

$$\int \frac{\varphi_i(r)\varphi_j^*(r)\varphi_i(r')\varphi_j^*(r')}{|r-r'|} d^3r d^3r' \cong k \int n^{1/3} n d^3r \quad (1.104)$$

Because we use the Kohn-Sham orbitals this isn't the Hartree-Fock exchange, but it is named Kohn-Sham exchange. The residual term, the so called kinetic term, leads to the Thomas Fermi term $k' \int n^{2/3} n d^3r$. The gradient expansion method is the simplest way to extract the non local coefficients and an exchange and correlation functional better than the simple local density approximation. This method gives us the Fermi Thomas term at the zero order: $T_{xc}^{TF} = \frac{3}{10m} (3\pi^2)^{2/3} \hbar^2 n^{2/3}$ and a full equations hierarchy depending on all orders of spatial derivatives of the density. So the variation of the density brings a hierarchy of corrections. These corrections are partially summable using a method developed by Wigner. The linearized potential approximation leads to Airy functions (the wave functions obtained by solving the uniform accelerated motion) and to a kinetic energy correction implicitly defined in terms of Airy function integrals: $T_{xc}^{lin} = T_{xc}^{TF} f\left(\frac{|\nabla n(r)|^{1/2}}{n(r)^{2/3}}\right)$. If we include the correlation the expression for the functional becomes more complex, and the most used form arises from fits of Montecarlo calculations.

This is in principle a non local hierarchy, just as the analytic function's Taylor series is global, however some problems may be related to summability. In a very different approach, we can proceed independently starting from the virial theorem and developing with the diagrammatic technique the full electron interaction. This is a compelling necessity when the LDA and GGA fail, as it happens in the calculation of the semiconductor band gaps. We come back later to this method.

The Gradient corrected Local Density approximation is a good tool for the calculation of atomic and molecular orbitals, so CPMD implements this type of exchange and correlation functional. However the Van der Waals - Casimir forces between closed-shell systems need a separate discussion. They arise from the non-local coulomb and exchange interactions between distant terms, and they need a good estimate of the retarded potential in order to obtain a well behaved asymptotic limit. The right setting is in the current-functional-density-theory because a full gauge invariance is required in order to avoid unphysical results and verify the sum rules arising from the Kramers Kronig theorem. When the change in time is relevant the time-dependent-functional-density-theory is required. However the local density approximation gradient corrected exchange correlation works and gives a very good estimate of the binding energy for simple systems. This is because the local density approximation overestimates the attractive potential coming from the overlap of the tails of the charge density, so a good balance between underestimates and overestimates results. A good discussion of this point is addressed in the field theoretical context.

The exchange correlation hole evaluated in the local density approximation is not an adequate estimate of the true exchange correlation hole. However as in the surprising case of the Janak objection to Kohn-Sham, in this case the LDA works better than this objection may suggest. This isn't a fortuitous event, but it is due to the same balance in the total charge as in the Von Barth-Gelatt correction: because the monopole term only for the exact exchange-correlation and the LDA exchange-correlation term is the same. This agreement is more difficult to obtain for the other multipole terms and so the gradient correction and an estimation of the non local terms is required. But this isn't all. Where are the problems? First in the virial theorem, because the long range correlation is not necessarily gaussian at atomic scale, and may be related to coherent non gaussian fluctuations in the fields. The virial theorem is predictive about long time scale if the ergodic hypothesis is verified. However, because the spin degrees of freedom are characterized by small energy differences, the characteristic time related to polarization dynamics is lower than other scales. Then the ergodic hypothesis becomes unphysical in the ordinary time of a simulation, and for

small systems the exchange and correlation separation is derived from long term expectation value. When the time scale is shorter than the spin fluctuation, symmetry breaking in the wave functions may occur. Moreover, the Hamiltonian does not include the spin coupling neither the minimal coupling, and the electromagnetic fields are included without their proper degrees of freedom. All these questions should be properly addressed in order to include the electronic polarization in the exchange and correlation explicit functional. However a first step consists in the inclusion of the field degrees of freedom, to take into account the fluctuation as a small perturbation in the linear response regime, and to take into account the Kramers Kronig relations, so that the time scale separation is accounted for. This procedure may lead to better functionals.

1.9 Field theory equations for exchange correlation

The steps following the one discussed at the end of last paragraph lead to the development of the field theory and to the exact solution of the quantum motions equations, and hopefully to a non perturbative approach. A lot of people have carried this out in all details for a lot of practical situations. Nowadays we know that the conclusion is a hierarchy of perturbation many-body equations leading to an exact solution for non relativistic and relativistic systems. The simplest approximations take the form of non perturbative integro-differential equations as in the Bethe Salpeter approach to the electron correlated systems. The non relativistic version useful in the exchange and correlation theory is based on the self consistent system:

$$\left(-\frac{\hbar^2}{2m}\Delta + V(r) + V_H(r) - \epsilon_i\right)\psi_i(r) + \int \Sigma(r, r', \epsilon_i)\psi_i(r')dr' \quad (1.105)$$

Here the wave functions are quasiparticle states, the ϵ are the energies of these quasi-particles, and the kernel of the integral is the self-energy, which is complex, non local, and energy dependent. In this function are contained all the necessary ingredients. However in the ground state we have the stationary equilibrium Green function, which describes the virtual interactions and permits to find the equilibrium linear response theory. In practice to extract the true self energy is very difficult, because a very large range of physical regimes is encrypted in this function and because of the divergences in the potential give divergent self-interactions integrals which are to be renormalized and regularized. Consequently, the linear response approximation is

replaced by effective equations which do not need to be linear. Whether the equations need to be linear or not is a very intriguing and fundamental question that involves all the recent developments of field theories. Some results point out that topological quantum field invariants are sometimes obstructing the linearity of fully developed perturbation series. This achievements arise from the the work of Atiyah and Singer, applied to the non-relativistic approximation. More information can be found in the Thouless work [22]. As an example of non linear corrections to linear equations, arising from perturbation treatment of the full quantum equations, we recall the quadratic correction to vacuum Maxwell electrodynamics. This correction is related to the two photon scattering predicted from the quantum field theory, and in the low frequencies regime leads to:

$$L' = \frac{2\alpha^2(\hbar/mc)^3}{(4\pi)^2 45(mc^2)} \left[(\epsilon_0 E^2 - \mu_0 H^2)^2 + 7 \frac{(EH)^2}{c^2} \right] \quad (1.106)$$

To discuss an example of the exchange and correlation determination in jellium, we recall that Nozieres and Pines [23] treated the problem of the divergence of the Coulomb potential, and solved the problem to determine the correlation energy by starting from the [24] Gell-Mann Brueckner series and determining its last two terms.

1.10 Pseudopotentials

As we have seen the occupation number of core electron is fixed in the Kohn-Sham system. The atomic DFT calculations are usually performed assuming a spherically averaged charge density. An atom is described as in elementary quantum mechanics by an electronic configuration, a molecule is obtained combining several atomic orbitals, LCAO, gaussian type orbitals, Slater type orbitals. Although a plane wave basis is more suitable for periodic systems, it can be used to study atoms and molecules, or regular homogeneous approximated systems like gases moving in a supercell. Thus even finite systems (molecules or clusters) can be studied with a plane wave basis using supercells provided enough empty space between the periodic replicas is left in order to guarantee a weak interaction between them. Because in the study of chemical configuration we can suppose only outer electrons contribute significantly to the bonding, a computational advantage can be gained by fixing the core states: this is the so called "frozen core approximation". In practice all we need is to map the all electrons Kohn-Sham system into a reduced problem. This may happen by fixing the electrons, their potentials and their charge in

a core region and leaving the outer electrons free to "move" in this "pseudopotential": this is what we do with the norm-conserving pseudopotentials. Another way to gain our goal is to go in the opposite direction: given a partial pseudo-wavefunction for the external wavefunctions we reconstruct, using a fixed completing projector which will contain prepackaged wave functions, the all electron configuration – this is the Projector augmented waves (PAW) technique. For a set of external wave functions $|\psi_l\rangle$, we will construct, for each pseudo-wave a complete wave $|\Psi_l\rangle$ the expansion of the pseudo-wave function, then completing to the full electron wave function:

$$|\Psi\rangle = |\psi\rangle + \left[\sum_l (|\Phi_l\rangle - |\varphi_l\rangle) \langle\beta_l| \right] |\psi\rangle \quad (1.107)$$

where $\langle\beta_l|\varphi_m\rangle = \delta_{lm}$ and $\sum_l |\varphi_l\rangle \langle\beta_l| = I$. When these definitions are inserted into the functional and the variation is made by varying with respect to $|\psi\rangle$, we will obtain the full equations.

1.11 Gradient correction in CPMD and the non gradient corrected quantum effects

As we said the exchange and correlation functional is the very challenging question in density functional theory. No-one knows which form it has, a lot of studies indicate a non local nature of its density dependence, so the exchange and correlation density functional is really a functional of the density, not a density function of the density. Non local correlation determination of the density functional is possible in principle by solving the entire problem, but this is obviously too expensive in terms of calculation resources. The more widely accepted form of pseudopotential annexes the simplest correction by including the best of the theoretical efforts: namely it uses a first order correction depending on the gradient of the density. We used a general gradient approximation to the exchange and correlation functional. The gradient-corrected functionals yield atomic energies and binding energies much better than LDA, with a modest additional computational cost. In particular they yield a good description of the Hydrogen bond. This type of functional can be written as:

$$E_{xc} = \int dr \varepsilon_{xc}(n, \nabla n) = \sum_G \varepsilon_{xc}(G) n^*(G) \quad (1.108)$$

where the second equation is valid because, in the CPMD code we used, the molecule is studied using a supercell with enough empty space between the

periodic replicas of the finite system, choosing extended, atomic-independent Plane Waves (PW) as basis set. The weak van der Waals and Casimir forces between closed-shells systems, that are responsible for physisorption, are still beyond the reach of DFT. The van der Waals and Casimir interactions have a non-local character due to the quantum entanglement of the electrons as well as to the quantization of the fields. Though the mean field part of these interactions can be accounted by using the Lifshitz self consistent linear theory, the self consistency relations are very strongly resistant to computational simplifications, until now. Related to the full quantized electromagnetic fields there is another effect not accounted in the Schroedinger equation we wrote down, though it can be included via iterated approximations in the Schroedinger approach and in the density functional: this is the self-interaction of the electron with the field it generates. Self interaction should cancel exactly in HF, by construction, but this doesn't occur in DFT. The self interaction affects finite systems, especially when the electrons are strongly localized, since it implies a short range behavior of the potential felt by an electron: where we expect a potential to decay following $V_{xc}(r) \rightarrow -1/r$, current functionals yield instead a potential that decays exponentially. Another limit in application of gradient correction is in the strongly correlated systems. Because of the one electron way of filling the Kohn-Sham orbitals, the addition of electrons to localized states, where there are also delocalized states nearby in energy, implies the overestimate of electron repulsion. Last but not least, the gradient correction isn't able to reproduce the correct band gap in semiconductors, though it can be demonstrated that the exact DFT verifies a Koopman's theorem and predicts the ionization energy from the highest occupied molecular orbitals.

1.12 Kohn-Sham orbitals in CPMD, cut-off and all that.

The Kohn-Sham formulation implies a self-consistent problem, the non linear problem to search the stationary points for the energy functional is transposed in iterative procedure. Here we briefly recall the existence of two methods.

The fixed point method:

I) A density guess is chosen. II) The KS equations are solved for those radial orbitals that correspond to occupied states; III) The charge density is recalculated; IV) If the convergence isn't achieved we go back to the first step

The direct minimization method:

I) A guess is made for the occupied orbitals coefficients II) The density is calculated III) The potential is calculated from the density IV) The gradient of the energy with respect to the coefficient variation is calculated V) If the convergence threshold for the gradient isn't achieved a new set of occupation coefficients is calculated VI) Go back to the second step

In the next chapter we briefly discuss the advantage arising from the Car-Parrinello method in the "on the fly" optimization. As we saw the Density Functional approach is simplified using the single electron Kohn-Sham basis occupation, arising from the given density in a given external potential with the interacting terms and the exchange correlation term, in the place of the full electron wavefunction:

$$E^{KS}[\varphi_i] = T_s[\varphi_i] + \int V_{ext}(r)n(r)dr + \frac{1}{2} \int V_H(r)n(r)dr + E_{xc}[n] \quad (1.109)$$

We need to minimize this functional using the variational approach with the constraint:

$$n(r) = \sum_i^N f_i |\varphi_i(r)|^2. \quad (1.110)$$

The kinetic term is given by:

$$T_s[\varphi_i] = \sum_i^N f_i \left\langle \varphi_i \left| -\frac{1}{2} \nabla^2 \right| \varphi_i \right\rangle \quad (1.111)$$

the external potential is:

$$V_{ext}(r) = - \sum_I \frac{Z_I}{|R_I - r|} + \sum_{I < J} \frac{Z_I Z_J}{|R_I - R_J|} \quad (1.112)$$

and the Hartree potential is:

$$V_H(r) = \int dr' \frac{n(r')}{|r - r'|} \quad (1.113)$$

The Poisson equation gives the inverse of the last relation:

$$n(r) = -\frac{1}{4\pi} \nabla^2 V_H(r) \quad (1.114)$$

and it is solved by the integral form. The last term we are going to write is the most relevant because it includes, in this one-particle scheme, the many body contributions:

$$E_{xc} = \int dr \varepsilon_{xc}(n, \nabla n) = \sum_G \varepsilon_{xc}(G) n^*(G) \quad (1.115)$$

Minimization leads to the Kohn-Sham equations:

$$H_e^{KS} \varphi_i(r) = \left\{ -\frac{1}{2} \nabla^2 + V_{ext}(r) + V_H + \frac{\delta E_{xc}}{\delta n(r)} \right\} \varphi_i(r) = \sum_j \Lambda_{ij} \varphi_j(r) \quad (1.116)$$

where the Lagrange multipliers derive from the constraint on the density. We shall obtain the standard Kohn-Sham system diagonalizing this system:

$$H_e^{KS} \varphi_i(r) = \varepsilon_i \varphi_i(r) \quad (1.117)$$

In actual calculation all these formulas are translated into plane wave expanded form. The infinite sums over G vectors and cells have to be truncated, and the points in the Brillouin zone are weighted. The truncation of the plane wave basis is based on the fact that the Kohn-Sham potential converges rapidly with increasing modulus of the inverse lattice index. For this reason at each k -point only G vectors with a kinetic energy lower than a given maximum cutoff are included in the basis.

$$\frac{1}{2} |k + G|^2 \leq E_{cut}^{KS} \quad (1.118)$$

So the number of plan waves for a given cutoff depends on the unit cell and the k -point. This number is estimated by:

$$N_{PW}^{KS} = \frac{1}{2\pi^2} \Omega (E_{cut}^{KS} / 1 \text{Hartree})^{3/2} \quad (1.119)$$

where Ω is the cell volume. The electron density calculation requires a basis bigger by a factor four, because the $(k - k')$ vectors occurring in the density expansion span a range of plane waves bigger by a factor two than the k vectors. So that we have generally the two relations:

$$E_{cut}^{density} = 4E_{cut}^{KS} \quad (1.120)$$

$$N_{PW}^{density} = 8N_{PW}^{KS} \quad (1.121)$$

1.13 Car-Parrinello equations integration in the CPMD Verlet dynamics

As we said before, the key point in the Car-Parrinello method is the definition of a fictitious dynamical system, associated with the physical system, whose potential energy surface E is an appropriate functional of both ionic and

electronic degrees of freedom The generalized classical Lagrangian of the fictitious system is defined as:

$$L = \sum_i^{occ} \int dr \mu_i |\psi_i(r)|^2 + \frac{1}{2} \sum_I M_I \dot{R}_I^2 - E[\psi_i, R_I] + \Lambda_{ij} \left(\int dr \psi_i^*(r) \psi_j(r) - \delta_{ij} \right) \quad (1.122)$$

The Euler equations associated with this Lagrangian are:

$$\mu \ddot{\psi}_i = - \frac{\partial E}{\partial \psi_i^*} + \sum_j \Lambda_{ij} \psi_j M_I \ddot{R}_I \quad (1.123)$$

The Hellman-Feynman theorem guarantees that the forces acting on the nuclei in the Born-Oppenheimer approximation can be calculated by differentiating with respect to the nuclear positions the potential energy in the ground state for the electronic configuration $\nu(R_I) = \langle \psi_0 | H | \psi_0 \rangle$. Generally these forces are different from the Car-Parrinello forces, but this difference can be controlled by setting the fictitious mass μ . The system is integrated by using the Verlet algorithm, which implements the symplectic decomposition in order to optimize the dynamic evolution saving the conserved quantities. Briefly we recall that the Hamiltonian formulation of dynamics permits to reduce the equations to an Hamiltonian couple of equations or briefly to $\dot{\Gamma} = Lx$, where L is the Liouville operator. The key point is to obtain an algorithm that is stable, so that it conserves the symplectic structure with the flow phase, and it also conserves a modified approximate Hamiltonian close to the original one. The Hamiltonian associated to the Car Parrinello Lagrangian in the plane wave system is constructed by introducing the Fourier coefficient $c_i(G)$ for electronic orbitals in an extended CP Lagrangian:

$$L(c, \dot{c}, R, \dot{R}) = \sum_{i,G} \dot{c}_i^*(G) \dot{c}_i(G) + \frac{1}{2} M_i \dot{R}^2 - E(c, R) + \Lambda_{ij} \left[\sum_G c_i^*(G) c_j(G) - \delta_{ij} \right] \quad (1.124)$$

which corresponds to the system:

$$\mu \ddot{c}_i(G) = - \frac{\partial E(c, R)}{\partial c_i^*(G)} + \sum_j \Lambda_{ij}(G) \quad (1.125)$$

$$M_I \ddot{R}_I = - \frac{\partial E(c, R)}{\partial R_I} \quad (1.126)$$

under the orthonormality constraints, and furthermore:

$$-\frac{\partial E(c, R)}{\partial c_i^*(G)} = \sum_G \langle G | H_{KS} | G' \rangle c_i(G') \quad (1.127)$$

$$-\frac{\partial E(c, R)}{\partial R_I} = \int dr^3 \frac{\partial v_{ext}(r)}{\partial R_I} \sum_i |\phi_i(r)|^2 \quad (1.128)$$

These equations conserve the CP Hamiltonian:

$$H(c, \dot{c}, R, \dot{R}) = \sum_{i,G} \dot{c}_i^*(G) \dot{c}_i(G) + \frac{1}{2} M_i \dot{R}^2 + E(c, R) \quad (1.129)$$

The Verlet algorithm can be implemented simply by translating the integration of the equations: $\dot{\Gamma} = Lx$ in the operatorial Trotter series and decomposing the potential part from the kinetic part of L : $L_U + L_K$ so that

$$\Gamma(t + \Delta t) = e^{(1/2)\Delta t L_U} e^{\Delta t L_K} e^{(1/2)\Delta t L_U}. \quad (1.130)$$

This leads simply to the well known velocity Verlet procedure. First step:

$$r_i(t + \delta t) = r_i(t) + \delta t v_i(t) + \frac{\delta t^2}{2m_i} f_i(t). \quad (1.131)$$

Second step: compute the forces $f_i(t + \delta t)$, gradient of the potential at the new position. Third step: update the velocities:

$$v_i(t + \delta t) = v_i(t) + \frac{\delta t}{2m_i} f_i(t). \quad (1.132)$$

Velocity Verlet is simple and stable. However other symplectic algorithms are suitable for particular purposes, particularly when we have fast varying forces and slowly varying ones. In these cases the only modification to introduce to the Trotter series consists in the splitting of the slow part and the fast part, and fixing the splitting number N .

$$\Gamma(t + \Delta t) = e^{(1/2)\Delta t L_{slow}} (e^{(1/2N)\Delta t L_{fast}} e^{(1/N)\Delta t L_K} e^{(1/2N)\Delta t L_{fast}})^N e^{(1/2)\Delta t L_{slow}} \quad (1.133)$$

After this brief survey of the Multiple Time Scale algorithms we pass to consider the role of the μ parameters in the dynamics. First: the electron mass "renormalizes" the nuclear masses, increasing them by a term proportional to μ and to the integral of the squared gradient. Second: the fictitious

electron mass dictates the time scale in the frequencies of motion. According to the Bohr energy formula, the typical time scales are like the $\sqrt{\mu/E}$ (note that E/m is the square of velocity, and the characteristic time is given by the characteristic atomic length divided by velocity). Here E is the energy interval, with mass, energy and time in atomic units. For example a mass of 400 a.u. and an energy of 2.7 eV = .1 a.u imply a time of 63 a.u. = $1.2 \cdot 10^{-15}$ s, or a frequency of order of 1000 THz. This should be compared with the highest ionic frequency, which in our case is the C-H stretch mode: $1000 \text{ cm}^{-1} * 3 \cdot 10^{10} \text{ cm/s} = 3 \text{ THz}$.

The smaller energy interval establishes with μ the longer dynamical time. These parameters are chosen such that the nuclear time scale is much slower than the electronic one, thus the electrons can effectively follow the nuclei, and we can speak of adiabatic decoupling. However the fictitious electron mass acts on the time step as well, because the cutoff of the plane waves fixes the maximum time step which is compatible with the accuracy $f_c = 1/(2\Delta t) = \sqrt{E_{cutoff}/\mu}$.

Chapter 2

The system studied

2.1 The origin of the problem

In the study of Self Assembled Monolayers (SAM) there is a lack of understanding about the coupling between the molecular vibrations and the substrate. A lot of work is often made by using standard quantum simulation. Our work is intended to outline the feasibility of the *ab initio* study of vibrational spectra with the PW method and the Car-Parrinello dynamics. The energy loss spectrum acquired from atomic or molecular scattering with and without Self Assembled Monolayers, the Hreels spectrum and the X-ray spectroscopy pose very difficult theoretical challenges, because a huge span of time and space scales occurs in this case. The case of Au(111)-Dimethyldisulfide (DMDS) surface coupling was our far reachable objective. However the DMDS molecule shows a very complex phenomenology when interacting with the Au surface. The protocol followed in the construction of the SAM may change the order of the molecules on the Au(111) surface and two phases were discovered in X-ray synchrotron radiation studies. In all this when the Dimethyl-thiolate is deposited on the surface the Hreels energy loss showed the molecule is broken and the sulphur is bonded on the Au(111) surface. Evidences for Au-S stretching mode and for C-S stretching mode were found in the vibrational spectrum. The Hreels scattering technique is based on the dipole interaction of electrons with the bonds. The study of the hyperpolarizability of the molecules on the surface is the primary aim in the reconstruction of these spectral data. This method is based on the dynamical matrix evaluation and the phonons are obtained by diagonalizing the dynamical matrix. However, the real molecules are very fast moving objects with complex dynamics. And so the Car-Parrinello dynamics may offer a deep insight in order to understand some phenomena.

2.2 The aim of this study

Because of the last argument, our goal was to study with CPMD the molecular dynamics of the simplest systems involved in the very rich phenomenology so far described. The unsplit DMDS molecule has been studied in a very large range of conditions, and a very good knowledge has been gained so far. Consequently, it is essential to test the effect of the approximations in the Car-Parrinello dynamics before one can address the other challenges. In the Car Parrinello dynamics the principal limitation, as we saw when speaking about the NH_3 molecule, is the semiclassical character of the dynamics. Thus quantum resonances, due to tunneling coupling between semiclassical configurations, are erased, and the rotational dynamics is not quantized.

The characteristic angular frequency ω for molecular vibrations is around 10^{14} Hz, corresponding to a photon in the infrared, and the quantum level spacing is simply $\hbar\omega$ (neglecting anharmonicity). The level spacing for molecular rotations is generally smaller than this, but increases linearly with the level number l , or, roughly, with the square root of the energy E_l . For a simple rotator this follows from $E_l = (\hbar^2/2I)l(l+1)$, which gives $E_l - E_{l-1} = \hbar^2 l/I$, where I the moment of inertia. Then, by the correspondence principle (valid at large l), the classical frequency of rotation is $\omega = \hbar l/I$. If we, recklessly, extend the correspondence principle to $l = 1$, we should say that the slowest angular frequency for molecular rotations, \hbar/I , is of order 10^9 Hz. In fact at ambient temperature we shall see appreciable velocity of rotation with more than one rotation for picosecond, though the density of states for the rotation levels is rarefied in this range of energies with respect to the microwave region. Though only the harmonic frequencies are in the range of the time window for Car Parrinello dynamics in a simple dual-core machine, classical rotation of the molecule can give a small contribution coupled to the anharmonic correction, like we shall see in order to explain the spectral dynamics of the kind we shall observe. So then the simple molecule is an ideal system to address the study of effects of approximation on the semiclassical vibrational predictions. As we said speaking about the Born-Oppenheimer approximation, the typical non adiabatic effects, such as the tunneling effects, are in the same range as the slowest rotational effects, so that a direct investigation of all these effects in their finest expression is out of reach for the pure Car Parrinello method.

2.3 The structure of the molecule

In this project the dimethyldisulfide molecule structure was investigated in the DFT approach by using Troullier Martins pseudopotentials [25], and with an exchange correlation pseudopotential of “BLYP” type, with the exchange correction of Becke and the correlation function of Lee, Yang and Parr [26]. The convergence cutoff of the plane waves was searched by studying the total energy at the variation of the cutoff, in the very large range, between 20 Ry to 80 Ry. The ionic dynamics was activated for three representative cutoffs. We have observed an increase of the bond length when the cutoff was increased, and a decrease of the total energy. Finally the “best” cut-off was set to 60 Ry. The electron system analysis via Kohn-Sham procedure was activated, in order to minimize the energy functional by using the steepest descent algorithms to optimize the configuration, fixing a threshold for convergence. The cell dimension was fixed at 23 Bohr (1 Bohr = 1 a.u.). As usual the first step was to stabilize the ground state of the Kohn-Sham system for a fixed initial configuration. Various attempts were exploited in order to achieve a reasonable convergence time. The principal problem was, at first, to find an initial configuration and a damping factor which didn't blow up after the ions were released. This is because, if the initial configuration is very far from the minimum, the forces acting on the nuclei are too strong, the acceleration perturbs the initial configuration and the system goes out of control. When all these problems were solved, the obtained minimum configuration was compared with the structure obtained using a gaussian code. The structure was then visualized by using Xcrysden. The structure is characterized by two angles: the S-S-C angle was 103° and the C-S-S-C torsional angle 87° . The S-S bond length is 3.93 a.u., the C-S bond is 3.46 a.u., and the C-H bond is 2.06 a.u. Using these data, the inertial tensor of the molecule can be evaluated.

The whole molecule has an elementary symmetry group whose symmetry element is the axis in the plane bisecting the C-S-S and S-S-C plane orthogonal to the S-S bond in the mid point. Partial symmetries are constructed from the two C_{3v} symmetries for each methyl group. In figure 2.1 we show the geometry of the molecule. The input used to simulate this structure is displayed in the following:

```
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  calculation = 'cp',
  restart_mode = 'from_scratch',
  pseudo_dir = '../..Pseudopotentials',
```

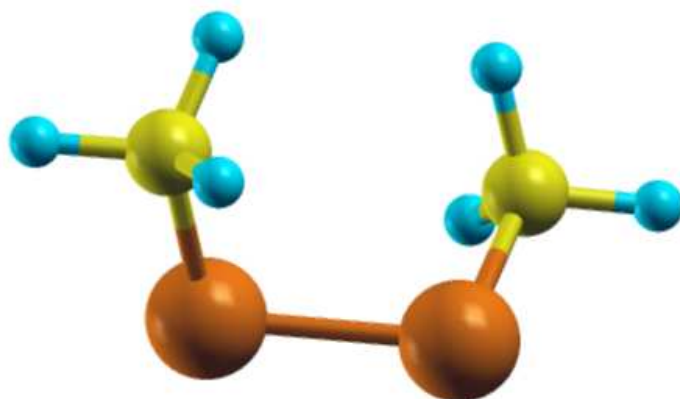


Figure 2.1: Geometry of the dimethyldisulphide molecule obtained in present calculations

```

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    ndw = 51,
    nstep = 1000,
    iprint = 10,
    isave = 100,
    tstress = .TRUE.,
    tprnfor = .TRUE.,
    dt = 5.0d0,
    etot_conv_thr = 1.d-9,
    ekin_conv_thr = 1.d-4,
    forc_conv_thr = 1.d-3
    prefix = 'dimethyl'
/
&SYSTEM
    ibrav = 14,
    celldm(1) = 23.0,
    celldm(2) = 1.0,
    celldm(3) = 1.0,
    celldm(4) = 0.0,
    celldm(5) = 0.0,
    celldm(6) = 0.0,
    nat = 10,
    ntyp = 3,
    nbnd = 13,
    nelec = 26,
    ecutwfc = 60.0,
    xc_type = 'BLYP'
/
&ELECTRONS
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    emass_cutoff = 2.5d0,
    orthogonalization = 'ortho',
    ortho_eps = 5.d-8,
    ortho_max = 15,
    electron_dynamics = 'sd',

```

```

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electron_velocities = 'zero',
electron_temperature = 'not_controlled',
/
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ion_velocities = 'zero',
ion_temperature = 'not_controlled',
/
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cell_velocities = 'zero'
/
ATOMIC_SPECIES
S 32.0d0 S.blyp-mt.UPF 4
C 12.0d0 C.blyp-mt.UPF 4
H 1.0d0 H.fpmd.UPF 4
ATOMIC_POSITIONS (bohr)
S 1.5136150 -1.2571350 -2.2362407 0 0 0
S -1.5136150 1.2571350 -2.2362407 1 1 1
C -3.6196687 -0.0268887 0.2070640 1 1 1
C 3.6196687 0.0268887 0.2070640 1 1 1
H -4.1496760 -1.9711330 -0.2367299 1 1 1
H -5.3099966 1.1668117 0.1886294 1 1 1
H -2.7494322 0.0648523 2.0772773 1 1 1
H 4.1496760 1.9711330 -0.2367299 1 1 1
H 5.3099966 -1.1668117 0.1886294 1 1 1
H 2.7494322 -0.0648523 2.0772773 1 1 1

```

2.4 The vibrational modes

After the molecule was studied in this conformation, we have simulated the dynamics of motion. In order to obtain an efficient thermalization the electron fictitious mass was set at 400 a.u. in order to accelerate the convergence of the electronic structure. After thermalization, the system was

allowed to move freely. We observe that this fictitious mass value is the right one in order to guarantee the adiabatic following of the nuclei by the electrons. However another effect, the renormalization of the masses of nuclei, is also relevant. In fact we remember that, to compute the correct acceleration, the masses of nuclei should be renormalized as follows: $M + \mu \int d^3x |\nabla\psi|^2$. This formula, which is intended in atomic units, estimates the upper bound for the electrons-nuclei coupling. A typical system in which this number is relevant is a system in an oscillating electric field. This effect was pointed out for a large class of systems by Scandolo and Tangney [27]. After thermalization, the free evolution of the system for 20000 time steps was analyzed by a self correlation Fourier analysis. In figure 2.2 is shown the velocity-velocity correlation function calculated combining the x,y and z velocity components of all atoms of the molecule.

2.5 Self correlation analysis

Though the problem of our interest is essentially the behavior of an electron system in an electric field, we shall not use an electrical field to predict the quantum electrodynamic response of the system. Rather, we shall study the response of the system in first order perturbation theory, and we shall reduce the quantum electrodynamics real problem to the semiclassical free vibrational modes, so that we will study a system in which the fictitious character of the electronic dynamics isn't very relevant and the coupling between the nuclei and the fictitious electrons is randomized. Thus the approach of Scandolo and Tangney [27] to the study of the effects of coupling between the nuclei and the electrons dynamics is very appropriate.

From the quantum mechanical point of view the problem is the connection of the semiclassical calculated quantities with the genuine quantum invariants, as predicted by Berry's approach to the quantum mechanics of adiabatic systems. This problem is related to the general problem of the definition of unbounded operators for periodic systems, in the cases in which the operator is not essentially self-adjoint in intervals. It arises especially for an infinite periodic system like in our case, because of the plane wave approach. In particular, for the quantum multiplicative operator associated with momentum, the periodicity breaks the translational invariance of the system, and a cyclic definition for position is needed. In a well thought work Resta [28] showed that this problem is overcome for the position operator with a simple gauge invariant definition. The approach is based on the observation that the position in a plane wave can be related to the expression $Im(Ln(e^{iX}))$. This permits to show that the usual perturbative prediction

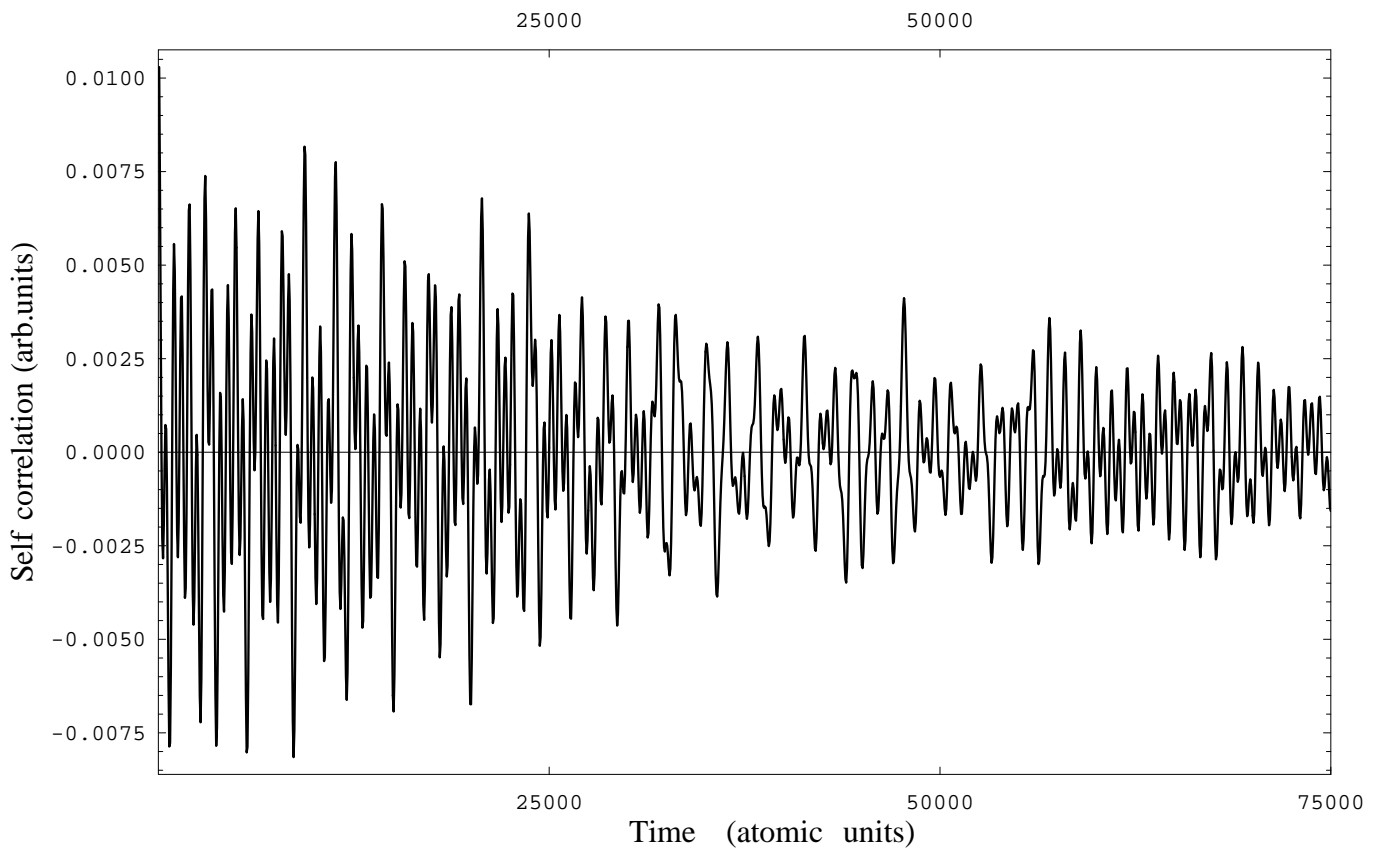


Figure 2.2: Free evolution velocity-velocity correlation function.

of the electromagnetic response:

$$I(\omega) = a \int dt \langle P(0)P(t) \rangle e^{i\omega t} \quad (2.1)$$

is well posed. Because the polarization is related to the current and the current to the velocity, it is usual to provide a simple way to a tentative assignment of the vibrational frequencies to molecular motion, by simply translating the above expression to the form:

$$P_I(\omega) = \int dt \langle v_I(0)v_I(t) \rangle e^{i\omega t} \quad (2.2)$$

The so called Berry's point phase (or open path Berry's phase), supplies a very useful tool in order to directly calculate the dipole moment and nowadays is implemented in many of *ab initio* codes, but was still untested when we made our calculation.

On the topic of Berry's phase we said, when speaking about the Jahn-Teller effect, that in systems in which there is a degeneracy we have a distortion. Restating the problem, in Resta's theory the degeneracy associated with the irreducible non null Berry's phase implies a static polarization gauge invariant. This phenomenon is shown for example by some ferroelectric systems, and *mutatis mutandis* by some magnetic systems like magnetite, where a deformation of the symmetric cubic structure is stable and implies a well defined magnetic order. The physical quantities indicated above are to be understood as tensors, of rank 2. The tensor in the last formula is immediately related to the covariance matrix. The complete calculation of the covariance matrix in a thermalized ensemble permits to find the normal mode matrix.

However, if we are interested only to know the position of the absorption lines, we can consider the total self correlation of the system. In this case we shall use complex notation and the following definition for self-correlation:

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \sum_i v_i^*(t) v_i(t + \tau) dt \quad (2.3)$$

Now introducing the normal coordinates we obtain:

$$v_i(t) = \sum_j A_{ij}(i\omega_j) Q_j e^{i\omega_j t} \quad (2.4)$$

So that inserting this expression in the last equation 2.3 we shall obtain:

$$\begin{aligned} \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \sum_i \sum_{jk} A_{ij} \omega_j Q_j^* e^{-i\omega_j t} A_{ik} Q_k \omega_k e^{i\omega_k(t+\tau)} = \\ \sum_i \sum_{\omega_k = \omega_j} \omega_j Q_j^* A_{ij} A_{ik} Q_k \omega_k e^{i\omega_k \tau} \end{aligned} \quad (2.5)$$

where we used the property of the Euler function to be null in the mean when rotating in the unit circle with constant velocity (the mean value varies in time like the distance along an arithmetic spiral). The Fourier transform of this expression leads to:

$$\sum_i \sum_{\omega_k=\omega_j} \omega_j Q_j^* A_{ij} A_{ik} Q_k \omega_k \delta(\omega - \omega_k) \quad (2.6)$$

In the non-degenerate case, (one-dimensional case) for the k -th frequency this expression reduce to:

$$(A^T A)_{kk} (Q_k \omega_k)^2 \quad (2.7)$$

In order to search for a generalization of this result to a more general setting we need to remember the definition of A . We shall set the argument in the more general case in which the dynamics is described in generalized coordinates as follows:

$$L(q', q) = \frac{1}{2} q'^t T q' - \frac{1}{2} q^t K q \quad (2.8)$$

where T and K are symmetric positive matrices. Now the theorem of inertia permits to define U in order to diagonalize T by using the substitution $q = UN$, where N indicates a new set of coordinates and U is an orthogonal matrix. We shall obtain:

$$L(N', N) = \frac{1}{2} N'^t U^t T U N' - \frac{1}{2} N'^t U^t K U N = \frac{1}{2} N'^t M N' - \frac{1}{2} N'^t U^t K U N \quad (2.9)$$

where M is diagonal and positive like $U^t K U$ because UN is the transpose of the vector $N^t U^t$. Now we can define the new coordinates $N = \sqrt{M^{-1}} O$ so that:

$$L(O', O) = \frac{1}{2} O'^t O' - \frac{1}{2} O'^t \sqrt{M^{-1}} U^t K U \sqrt{M^{-1}} O \quad (2.10)$$

Now the third and last step consists in recognizing that the quantity $K_r = \sqrt{M^{-1}} U^t K U \sqrt{M^{-1}}$ is symmetric and positive because for each vector $U \sqrt{M^{-1}} O$ the vector $O^t \sqrt{M^{-1}} U^t$ is its transposed, so there exists an orthogonal matrix V diagonalizing K_r and coordinates P such that:

$$\begin{aligned} L(P', P) &= \frac{1}{2} P'^t P' - \frac{1}{2} P'^t V^t \sqrt{M^{-1}} U^t K U \sqrt{M^{-1}} V P = \\ &= \frac{1}{2} P'^t P' - \frac{1}{2} P'^t \Omega^2 P \end{aligned} \quad (2.11)$$

where Ω is a diagonal positive matrix containing the normal mode frequencies. Summarizing, we showed that there exist a matrix $G = U\sqrt{M^{-1}}V$ and coordinates P such that $q = GP$ and:

$$I = G^t T G \quad (2.12)$$

$$\Omega^2 = G^t K G \quad (2.13)$$

The connection with the standard normal coordinates is established by the relations:

$$P = \sqrt{M} Q A = G \sqrt{M} \quad (2.14)$$

In the special case we are considering the matrix T is diagonal and contains the positive masses of the nuclei, so that we can start from the second step and define $Z = \sqrt{M} A$. We obtain the relation: $Z^t Z = A^t \sqrt{M} \sqrt{M} A = A^t M A = I$, so that Z is orthogonal. The relation for the G matrix guarantees the possibility to rotate the axes in order to reduce a degenerate superposition of modes to a single new mode, with coordinate P_k . However because Z is orthogonal and $Z = \sqrt{M} A \sqrt{M^{-1}}$, A is not orthogonal (not with respect the ordinary scalar product which occurs in the self correlation function, but only with respect the scalar product induced by the matrix M).

$$\begin{aligned} \sum_i \sum_{\omega_k = \omega_j} \omega_j Q_j^* A_{ij} A_{ik} Q_k \omega_k \delta(\omega - \omega_k) = \\ \sum_i \sum_{\omega_k = \omega_j} \omega_j Q_j^* (A^t A)_{jk} Q_k \omega_k \delta(\omega - \omega_k) \end{aligned} \quad (2.15)$$

the degenerate case may show sum between diagonal and off diagonal terms. Generally speaking the population in the modes is related to their energy by the equipartition principle, and the energy of the modes is related to the frequency. What can we say about the sign of this expression? Because the complexity of the last expression regarding the possibility that two or more frequencies are degenerates, applying the argument that it is possible to define a rotation which reduces a general superposition of modes to a mode with a single coordinate P_k and observing that the matrix M relating the Q to the P coordinates is diagonal, we shall obtain, in the place of the last expression the simpler form:

$$\sum_k \omega_k Q_k^* (A^t A)_{kk} Q_k \omega_k \delta(\omega - \omega_k). \quad (2.16)$$

Finally then just the expression:

$$(\omega_k)^2 |Q_k|^2 (A^t A)_{kk} \quad (2.17)$$

contributes to the amplitude of the k^{th} peak. Now, because in the last expression only the diagonal terms of the $A^t A$ matrix appear we shall obtain a positive amplitude for each excited mode. In other words it doesn't occur in any case that the off diagonal and the diagonal terms in the original expression can cancel each other. Here in the following figure 2.3 we show the obtained frequencies.

The spectrum calculated from the velocity-velocity self correlation shows the stretching CH₃ mode at 3050 cm⁻¹. Really a closer look shows a shoulder near the principal peak at 3000 cm⁻¹. The symmetric and antisymmetric CH₃ bending modes are at 1330 cm⁻¹ and 1450 cm⁻¹, the CH₃ rocking mode at 950 cm⁻¹, the (S-C) stretching mode at 635 cm⁻¹ and the S-S stretching mode at 200 cm⁻¹. The last number indicates that the S-S stretching mode is soft: this indicates that when the molecule is adsorbed on a metallic surface such as gold, it is easy that the molecule will break into two methylic groups which stick separately to the surface. In different simulations, with different cutoff and different electron fictitious mass, it is possible to observe a shift of the peaks, and this appears to be, up to the order of 50 cm⁻¹. However, a finer analysis can be carried out. In fact, if we consider the Fourier Transform of the velocity of each atom of the molecule, we obtain the following finer information: $FT(v_i)[\omega] = \sum_j A_{ij} Q_j \omega_j \delta(\omega - \omega_j)$. So that if Q_j is chosen to be the normal coordinate for the single mode, we obtain $FT(v_i)[\omega_j] = A_{ij} Q_j \omega_j$. The absolute complex value of this expression gives us the single components for the vector. Furthermore, because the direct Fourier Transform for the velocities is made using all data, we have a better resolution of the peaks, because of the Nyquist's theorem. In this way we were able to resolve a finer structure shadowed in the self correlation spectrum. The sulphur atoms will move slower than the Carbon atoms because the Carbon is bonded to the Hydrogen atoms. The Carbon atom will show two principal peaks near in frequencies at the C-H stretching modes because the two antisymmetric modes break their degeneracy and cause transverse motion in the Carbon atoms. The Hydrogen atoms show three peaks very well resolved, one for the symmetric mode, the others for the antisymmetric modes degeneracy whose is broken.

In Figure 2.4 we show the superposition of all the spectra, in Figures 2.5, 2.6, 2.7 we show the single atom frequency analysis for Sulphur, Carbon, and Hydrogen.

This spectrum obtained by Fourier analysis of the velocity should be compared with the experimental data measured with IR-transmission technique for the gaseous phase, shown in figure 2.8, drawn from the NIST database. Notice that we have a very good agreement for the main peaks, both in position and in intensity. For what concerns the adsorbed molecule on metallic

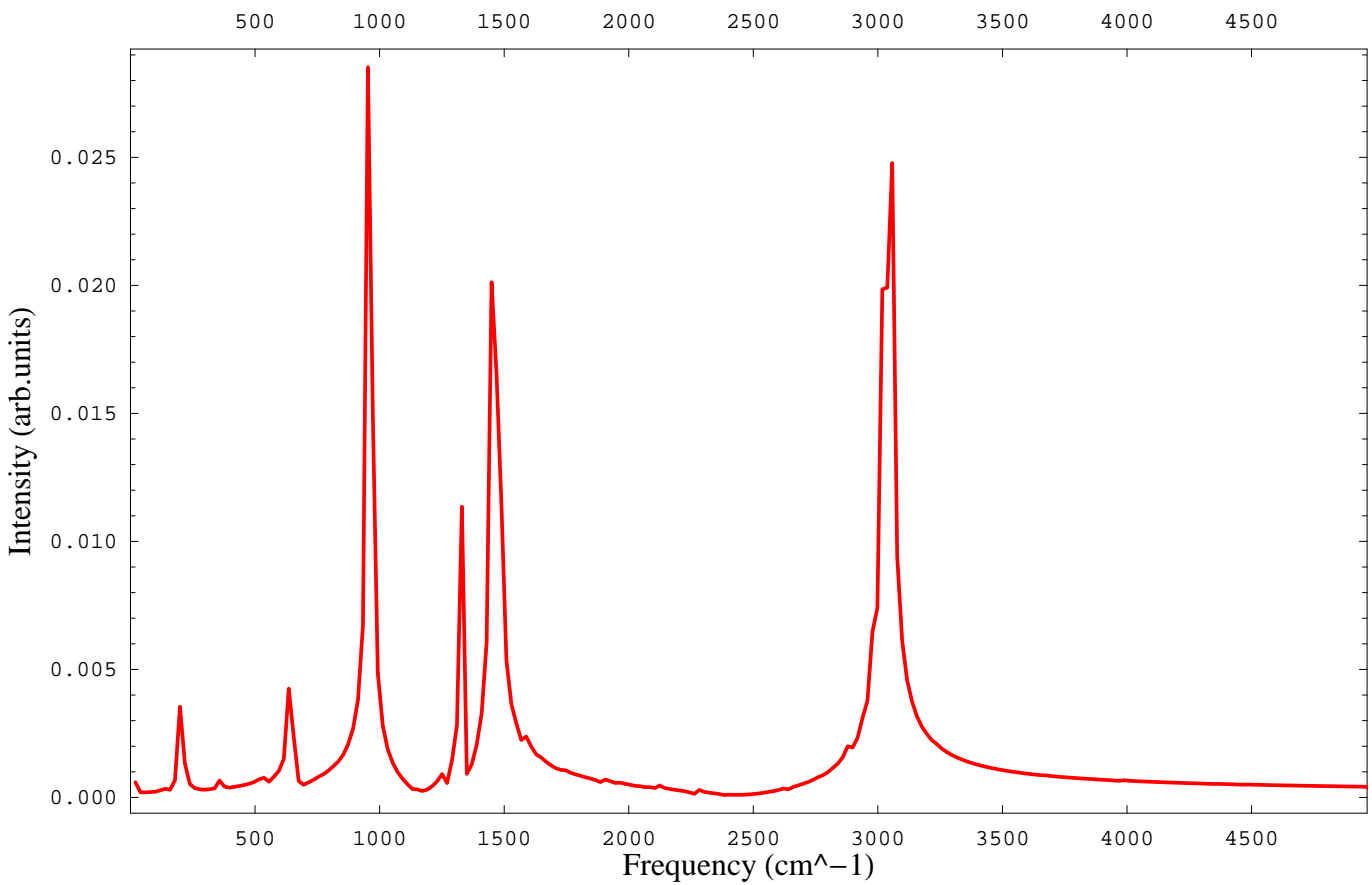


Figure 2.3: Vibrational frequencies of the molecule obtained in present calculations.

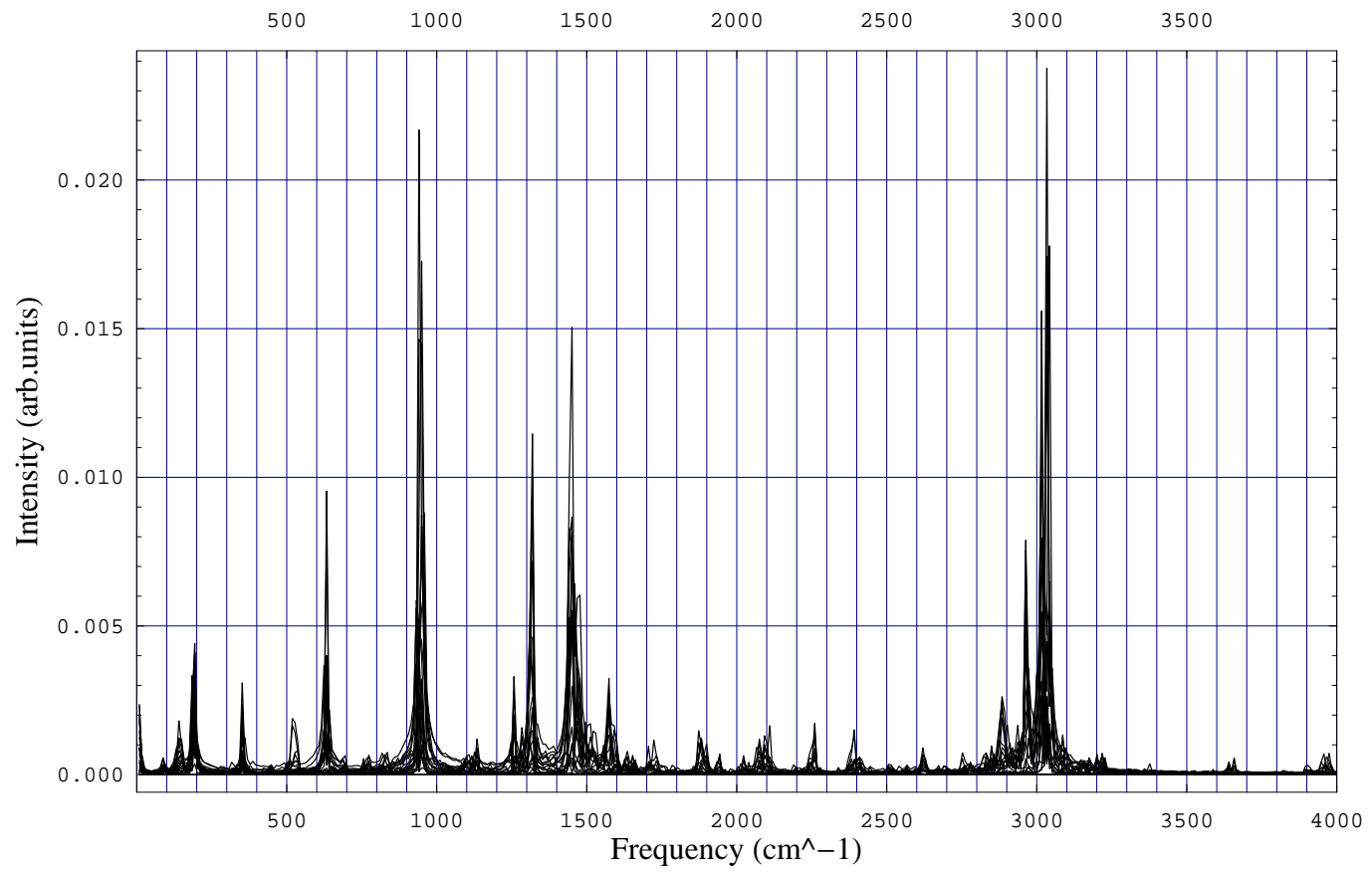


Figure 2.4: Superposition of all spectra

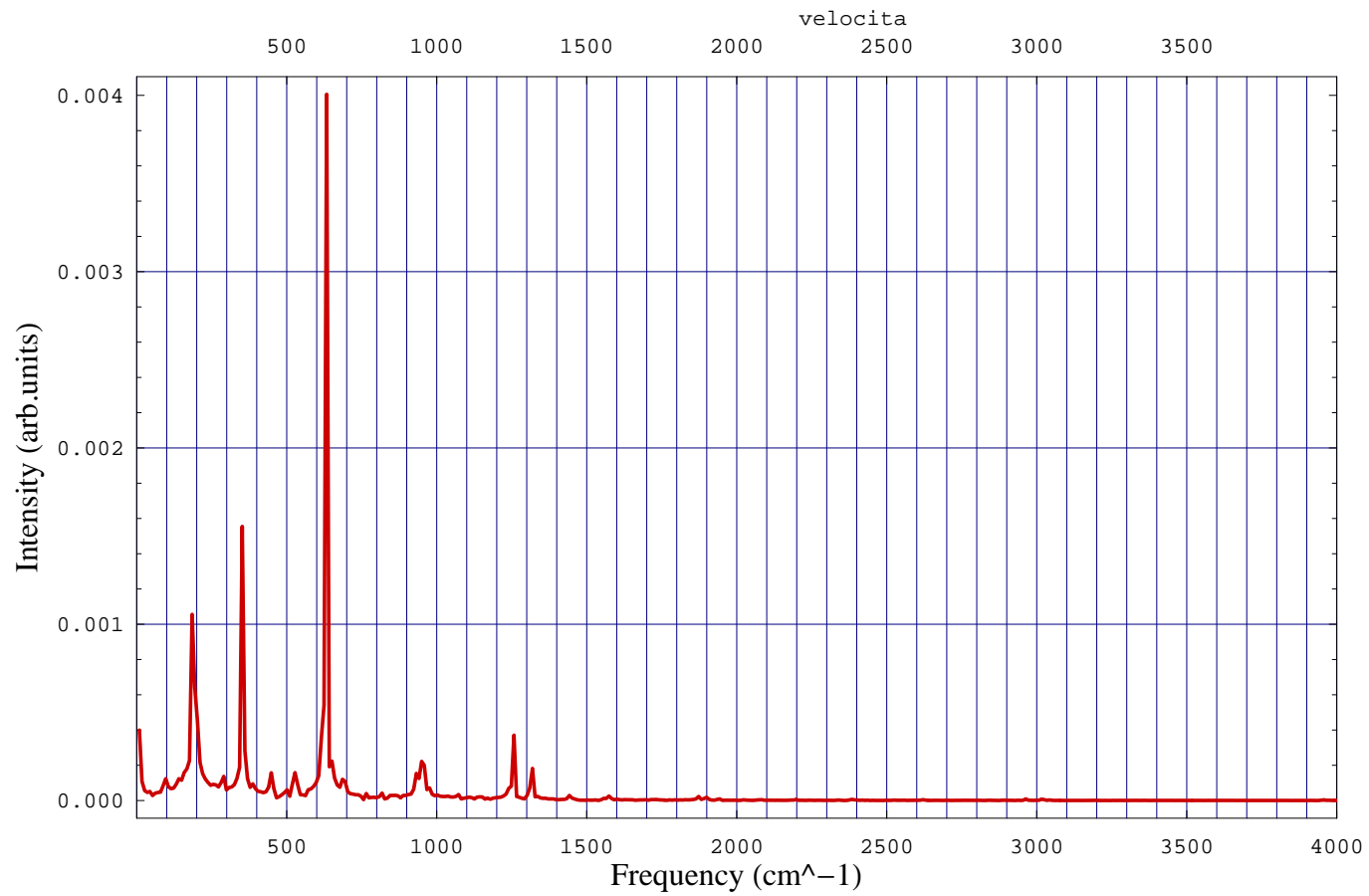


Figure 2.5: Spectrum of the Sulphur atom

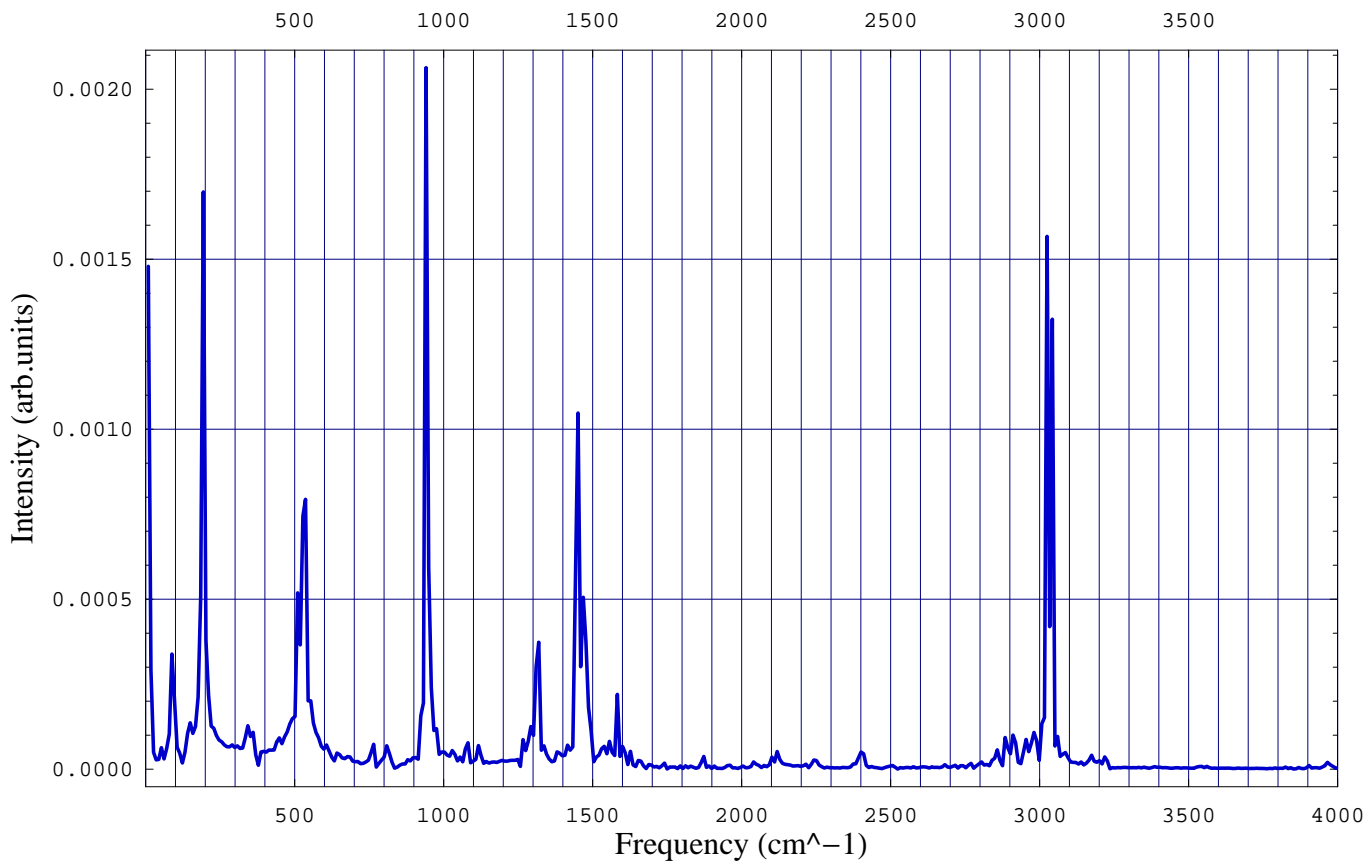
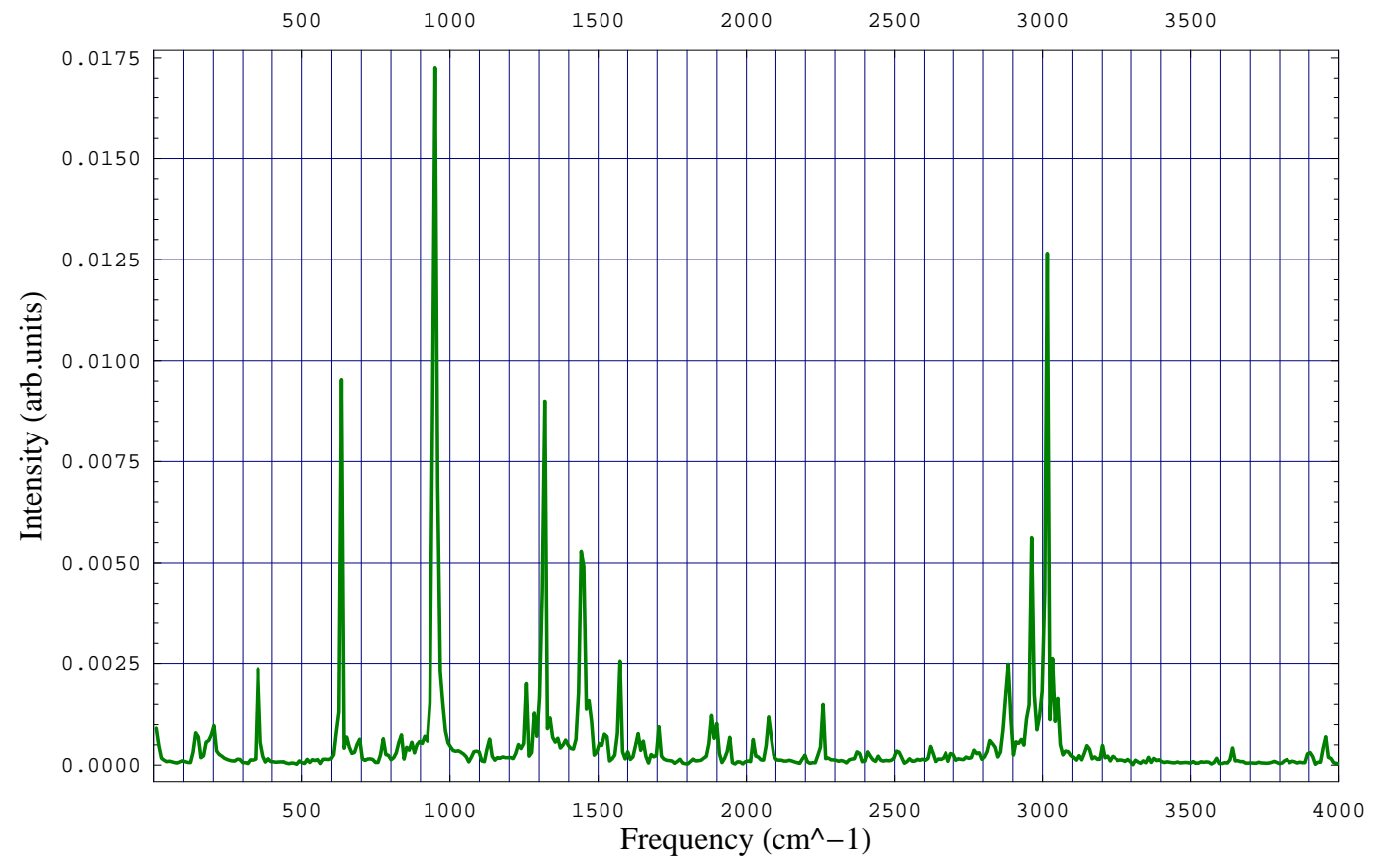


Figure 2.6: Spectrum of the Carbon atom

Figure 2.7: Spectrum of the Hydrogen atom



surfaces, such as gold, the HREELS spectra have been measured and these spectra show different frequency shifts of the Au-S modes in different experimental conditions, for different chains. In the case of the shortest chain, the methylthiolate, the asymmetric bending mode was observed at 1415 cm^{-1} , the symmetric mode at 1300 cm^{-1} , the Au-S mode at 230 cm^{-1} , the rocking CH_3 mode at 949 cm^{-1} , and finally the S-C stretching mode at 650 cm^{-1} [29]. Other experimental evidence regarding the methyl stretching and bending and rocking modes can be found in [30] for the dodecane molecule: the bending modes were found at 1450 cm^{-1} and 1378 cm^{-1} , the stretching modes were found at 2962 cm^{-1} and 2872 cm^{-1} . These results for the stretching modes are confirmed in more and more molecules containing methyl groups, so that we can assert that: the separation between the two stretching modes is underestimated by our DFT calculation (top-top interaction effect?)

Another analysis we made consists in the study of the stability of the spectral density, analyzing the differences in the spectra obtained by dividing the total simulation time in three slices of equal duration. We see that the spectral density is not the same in the three pieces of the total history for some modes: energy exchange can be observed in the bending mode frequencies at 1500 cm^{-1} and in the stretching modes at 3000 cm^{-1} .

The variation at the higher frequency will not be discussed, because the resolution is poor when one third of the time is considered and doesn't permit to separate the peaks at this frequency, but the variation in the bending modes is interesting. In order to understand this variation we need to discuss the physical origin of these modes. The top of the molecules, the methyl groups, are symmetric, as we see in the structural analysis, and hindered in their rotation around the S-C bond. We estimated the barrier that the methyl group have to overcome in order to rotate, by calculating the constrained energy for a set of rotated geometry, obtaining the value of 0.1eV . This energy barrier corresponds to a frequency of 1000 cm^{-1} and the thermal energy at the temperature of 300K is near to 200 cm^{-1} . This means that the classical nuclei of our CPMD explore one fifth of the barrier, so that anharmonic effects could be relevant. Anyway this point deserves further study.

In 2.9 and 2.10 we show the Hydrogen and Carbon spectral evolution of the three history slices during the same free unperturbed evolution of the molecule.

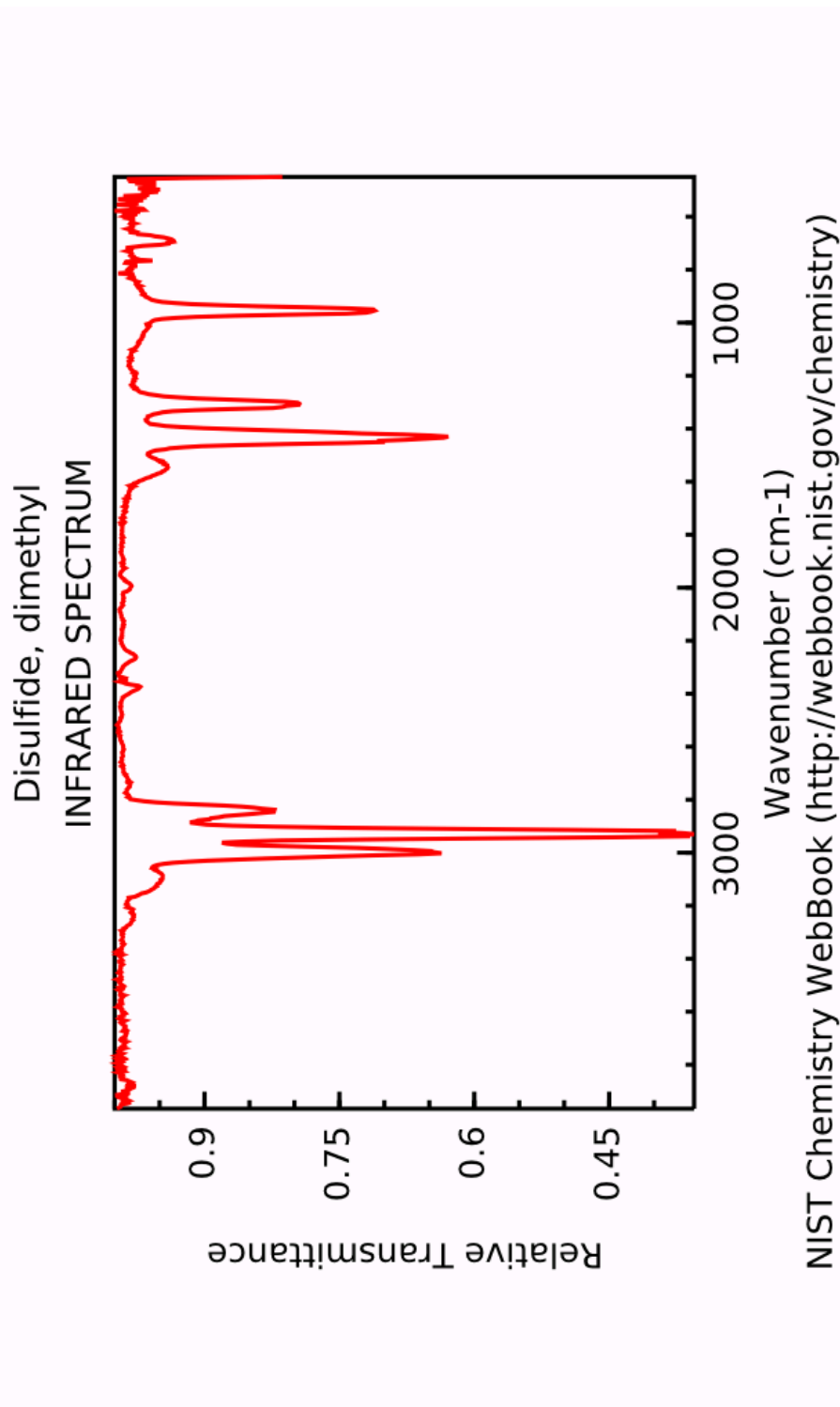


Figure 2.8: Spectrum measured with IR-transmission technique for the gaseous phase, from NIST database 60

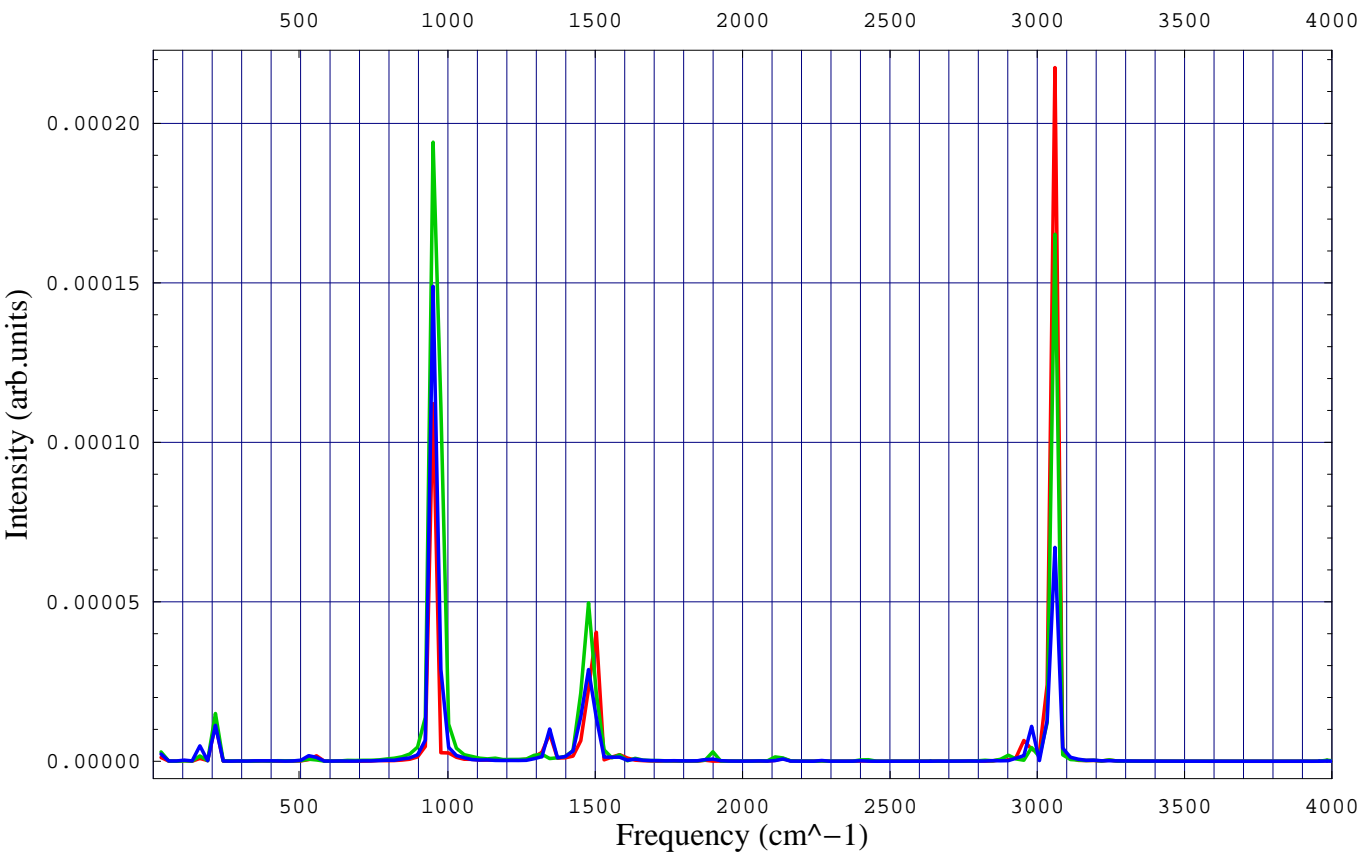


Figure 2.9: Hydrogen Spectrum Evolution: first slice of the history is depicted in red, the second one is drawn in green and the last in blue.

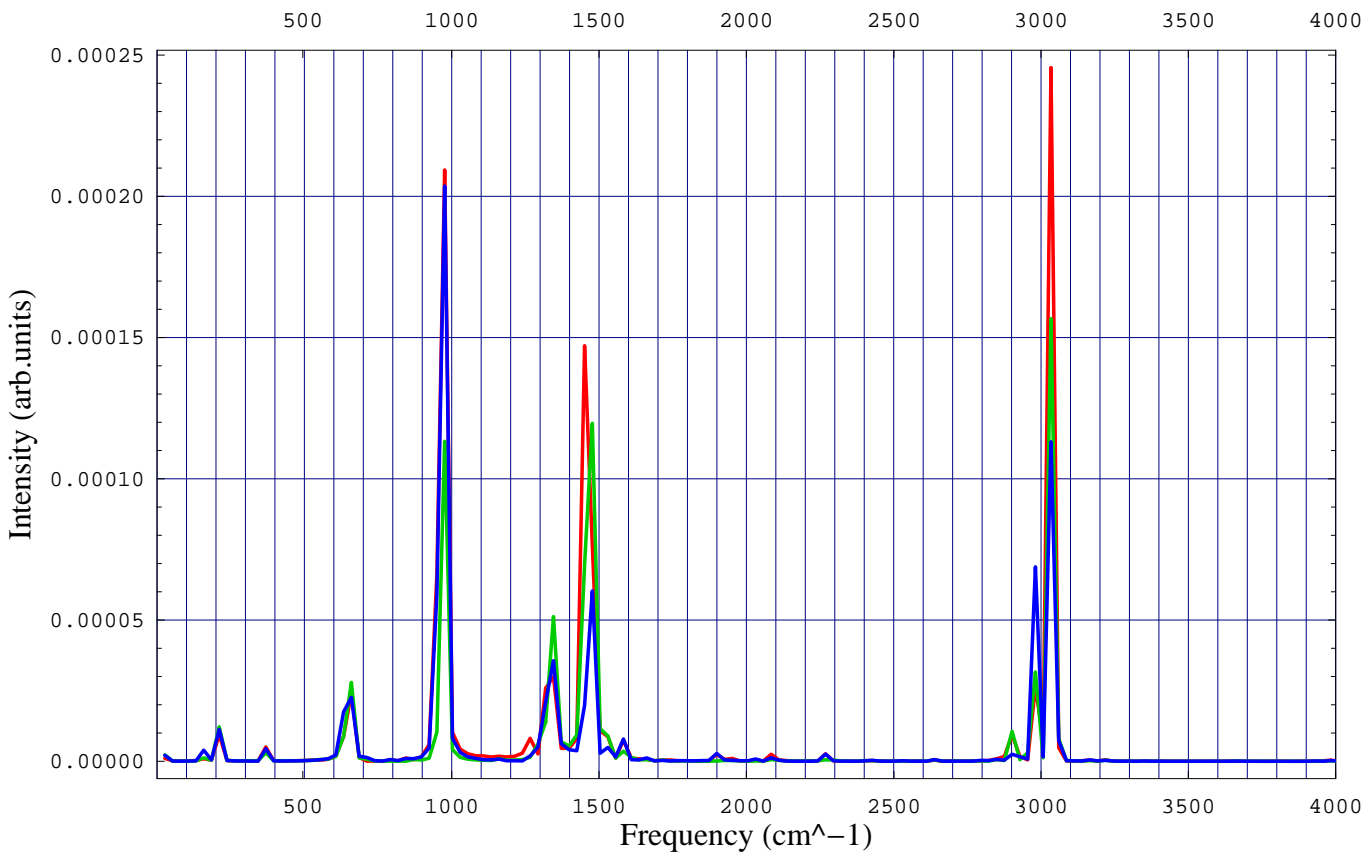


Figure 2.10: As in figure 2.9 for Carbon Spectrum Evolution

2.6 Conclusions and Perspectives

The analysis performed until now permits to observe that a systematic deviation of the vibrational modes is introduced by the DFT, and so a good interpretation of the dynamical modes in the case of adsorbates can be problematic. To complete the comparison with the experimental data we plan to study in the future the full system, which includes the Au(111) surface and the dimethyldisulfide molecule. The gold substrate influences dramatically the bonding energies, and the polarizability: in this case we could take a great advantage from an accurate description of the gold surface. The temperature reduces the frequencies, so that the frozen phonons approach isn't indicated for this kind of analysis. We should need to increase the simulation time scales in order to obtain good statistics from which we could get information about the temperature effect on the vibrational modes and on the gold influence. A qualitative study of the cooperative effects between the gold surface phonons and the molecular vibrations, in the inelastic scattering intensities of the neutral atoms will be addressed.

A finer analysis will be possible only after the full system simulation. We expect that the knowledge of the vibrational spectrum of the molecule adsorbed on the Au surface will be very important in order to understand the mechanism of the different surface reconstructions (of SAM and surfaces like the 3×4 or $\sqrt{3} \times \sqrt{3}$ shown in the experiments at different temperatures [1]).

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