

Chapter 2

Theoretical Methods

Many of the properties of the solid state and chemical systems can be determined solving the Schrödinger equation for a given system. However, states of most of electrons and nuclei have to be accounted for. The solution to many electrons can be obtained by the Hartree Fock (HF) method, using the wavefunction of the electrons, or density functional theory (DFT) based methods, using the density function of the electrons instead of solving the Schrödinger equation. The former method is a base for other approaches used in the quantum chemistry community, whereas the latter method has been largely used in the physics community to study the electronic structure of solids. However, over the last 20 years due to the increased efficiency of computers and the accuracy of the DFT functionals, the number of systems studied using DFT method has increased. As a result of this expansion, systems typically studied using quantum chemistry methods, such as organic and inorganic molecules, are being increasingly often studied with DFT methods because of much better efficiency and high quality which is close to that of the quantum chemistry (QC) methods.

Another way to address many body problem is the classical molecular dynamics that is used to derive physical properties of the system from empirical potentials.

2.1 Solving the Schrödinger Equation

To understand the properties of chemical bonding in molecules and extended systems, we consider the Schrödinger equation, which, for a generic system with N_a nuclei of mass M_N and N_e electrons of mass m_e , leads

$$\hat{H}(\mathbf{r}, \mathbf{R})\Psi_a(\mathbf{r}, \mathbf{R}) = E_a\Psi_a(\mathbf{r}, \mathbf{R}) \quad (2.1)$$

where $\Psi_a(\mathbf{r}, \mathbf{R})$ is the system many-body wave function, the electronic coordinates are $\mathbf{r} = \{\mathbf{r}_i\}$ and the nuclear coordinates $\mathbf{R} = \{\mathbf{R}_i\}$.

The Hamiltonian operator in Eq. (2.1) is expressed by:

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_n + \hat{T}_e + \hat{U}_{n,n} + \hat{U}_{n,e} + \hat{U}_{e,e} \quad (2.2)$$

$$\hat{T}_e = \frac{-\hbar^2}{2m_e} \sum_{i=1}^{N_e} \nabla_i^2 \quad (2.3)$$

$$\hat{T}_n = \frac{-\hbar^2}{2M_N} \sum_{i=1}^{N_a} \nabla_i^2 \quad (2.4)$$

$$\hat{U}_{n,n} = \frac{1}{2} \sum_{j=1}^{N_a} \sum_{i \neq j}^{N_a} \frac{Z_i^* Z_j}{|\mathbf{R}_j - \mathbf{R}_i|} \quad (2.5)$$

$$\hat{U}_{n,e} = - \sum_{i=1}^{N_e} \sum_{j=1}^{N_a} \frac{Z_j e}{|\mathbf{R}_j - \mathbf{r}_i|} \quad (2.6)$$

$$\hat{U}_{e,e} = \frac{1}{2} \sum_{i=1}^{N_e} \sum_{j=1, i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|} \quad (2.7)$$

where Z_i and e are the charges of the nuclei and electron respectively, $\hat{T}$ represents the kinetic energy and $\hat{U}$ the potential energy of either nuclei or electrons. Solving Eq. (2.1) exactly for realistic systems is impossible, because of the high number of degrees of freedom involved. Thus, it is required to apply some approximations.

The most important approximation deals with the separation of nuclear and electronic degrees of freedom and it is known as Born-Oppenheimer approximation. In general, electronic and nuclear dynamics are not independent. However, usually their dynamics can be considered independently because of the difference between the mass of the proton and electron ($m_e \ll M_N$): due to this difference, the electrons are faster with respect to the nuclei and can instantaneously adapt their wavefunction to the current nuclear positions. If the electron system is much “faster” than ionic one, the nuclei can be treated “classically” and the nuclear kinetic energy can be neglected (or treated as a small perturbation, if necessary).

To implement this approximation one can expand the wave function $\Psi_a(\mathbf{r}, \mathbf{R})$ into a complete orthonormal set $\Psi_\zeta(\mathbf{r}, \mathbf{R})$ of the electronic wave functions of the whole system as follows:

$$\Psi_a(\mathbf{r}, \mathbf{R}) = \sum_{\zeta} X_{\zeta}(\mathbf{R}) \psi_{\zeta}(\mathbf{r}, \mathbf{R}) \quad (2.8)$$

where $X_{\zeta}(\mathbf{R})$ is a function of the nuclear coordinates only. By replacing the new form of the wave function, Eq. (2.8), in Eq. (2.1), and neglecting some electron-nuclei matrix elements arising from the nuclei kinetic energy, it is possible to write two equations: one for the electronic wave function $\Psi_{\zeta}(\mathbf{r}, \mathbf{R})$,

$$(\hat{T}_e(\mathbf{r}) + \hat{U}_{e,e}(\mathbf{r}) + \hat{U}_{n,e}(\mathbf{r}, \mathbf{R}))\Psi_\zeta(\mathbf{r}, \mathbf{R}) = \varepsilon_\zeta(\mathbf{R})\Psi_\zeta(\mathbf{r}, \mathbf{R}) \quad (2.9)$$

and another for the nuclear wave function, $X_\zeta(\mathbf{R})$, which is an eigenstate of the following Hamiltonian:

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_n(\mathbf{R}) + \hat{U}_{n,n}(\mathbf{R}) + \varepsilon_\zeta(\mathbf{R}) \quad (2.10)$$

Note that the wave function $\Psi_\zeta(\mathbf{r}, \mathbf{R})$ and the eigenvalue $\varepsilon_\zeta(\mathbf{R})$ depend parametrically on the nuclear coordinates $\mathbf{R}$. In practice, in many cases the nuclei equation is not solved, and nuclei are considered classically.

Unfortunately, solving Eq.(2.9) is still a complicated task and requires more approximations. Several methods are used to solve the Schrödinger equation approximately. In this chapter only the Hartree-Fock (HF) and the density functional theory (DFT) methods are considered.

2.2 The Hartree-Fock Method

The Hartree-Fock (HF) method allows solving the Schrödinger equation approximately. The starting point of this theory is the Pauli exclusion principle. From quantum mechanics it is known that the wavefunction depends on the position and spin of each electron and that the electrons are indistinguishable and the many-electron wavefunction is antisymmetric. That means that if two electrons switch their positions the wavefunction should change its sign. The probability density, defined as $\int d\mathbf{r} |\Psi_\zeta(\mathbf{r})|^2$, for both cases will be identical. Also the normalisation condition should be respected: the $\int d\mathbf{r} |\Psi_\zeta(\mathbf{r})|^2$ must be equal to unity. The simplest wavefunction which obeys these can be constructed as follows [1]. Each electron is given a one electron wavefunction $\psi_i(x)$, where $x = (\mathbf{y}, \sigma)$ contains both spatial and spin electronic coordinates:

$$\psi_i(x) = R_i(\mathbf{y})S_i(\sigma) \quad (2.11)$$

which is composed of a spatial part $R_i(\mathbf{y})$ and a spin part $S_i(\sigma)$, where σ has only two possible values α or β (spin up or spin down). In general for a system composed of N_e electrons the ground state wave function (the index ζ from here on will be omitted) may be given by the product of orbitals of each electron:

$$\Psi(x_1, x_2, \dots, x_{N_e}) = \psi_1(x_1)\psi_2(x_2), \dots, \psi_{N_e}(x_{N_e}) \quad (2.12)$$

However, this would be incorrect because the electrons are indistinguishable and the Pauli exclusion principle would not be respected.

If we take into account these principles, the simple product of the electron functions must be replaced by a Slater determinant [1]:

$$\Psi(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_{N_e}(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \psi_1(x_{N_e}) & \dots & \dots & \psi_{N_e}(x_{N_e}) \end{vmatrix} \quad (2.13)$$

In this approximation the one electron wavefunction is described by the Slater determinant, that gives the correct description because it is antisymmetric.

The Schrödinger equation, as defined in Eq.(2.1), is solved applying the variational principle: we have to minimise the energy and find the one-electron wavefunctions. The energy is:

$$\epsilon = \int \dots \int \Psi^* \hat{H} \Psi dx_1 dx_2 \dots dx_{N_e} = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.14)$$

where in the right hand side we introduced the Dirac bracket notation. Therefore, the total energy, ϵ , is expressed via the one-electron orbitals $\psi_i(x)$. Varying the total energy with respect to these functions, we obtain the Hartree-Fock (HF) equations for them:

$$\hat{F}(x)\psi_i(x) = \epsilon_i\psi_i(x) \quad (2.15)$$

where $\hat{F} = \hat{h} + \hat{J} - \hat{K}$ is the Fock operator with components [1]:

$$\hat{h}(x)\psi(x) = \left[-\frac{1}{2}\nabla_r^2 - \sum_{k=1}^{N_a} \frac{Z_k e}{|\mathbf{R}_k - \mathbf{r}|} \right] \psi(x) \quad (2.16)$$

$$\hat{J}(x)\psi(x) = \left[e^2 \int \frac{\rho_{HF}(x'|x) dx'}{|\mathbf{r} - \mathbf{r}'|} \right] \psi(x) \quad (2.17)$$

$$\hat{K}(x)\psi(x) = \left[e^2 \int \frac{\rho_{HF}(x'|x) \hat{P}_{xx'} dx'}{|\mathbf{r} - \mathbf{r}'|} \right] \psi(x) \quad (2.18)$$

where $\hat{J}(x)$ and $\hat{K}(x)$ are called Coulomb and exchange operators, respectively, and $\hat{P}_{xx'}$ is the permutation operator which changes x to x' in the function it acts upon. Finally,

$$\rho_{HF}(x|x') = \sum_{i=1}^{N_e} \psi(x)\psi(x') \quad (2.19)$$

is the one-electron density matrix.

To improve the HF method, it is necessary to take into account the difference between the exact and the HF energy, that is defined as the correlation energy. Higher level QC calculations are based on Moller-Plesset Perturbation theory (MP2) or Configuration Interaction method (CI). The latter is considered as exact as this method accounts for the correlation energy exactly. These methods, however, are not considered here because, due to their very high computational cost, they can only be

applied to small systems, under fifty atoms. For more detailed information about these methods, the reader is referred to [1].

2.3 Density Functional Theory

Density functional theory (DFT) [2] allows one to study the properties of complex systems of atoms by reducing the quantum mechanical problem for a many-body interacting system to an equivalent problem of non-interacting particles. This is achieved using as a fundamental variable the electronic density, instead of the many body wavefunction. Nowadays DFT is a well established and popular framework to study properties of many-body systems without using empirical parameters: hence it is considered as an ab-initio method.

The theory is advantageous for several reasons: the density is an observable that can be experimentally measured (e.g. X-ray diffraction) and the dimensionality is reduced from $4N_e$ (3 coordinate for each electron and a spin) to 4 (the coordinates x, y, z and a spin).

The theoretical basis of DFT are in the Hohenberg and Kohn theorems [2] that originally referred to an electronic system subjected to an external potential.

The first Hohenberg and Kohn theorem [2] can be formulated as follows:

- it exists a one-to-one mapping of the set of “densities” $\rho(\mathbf{r})$ onto the “potential” U_e
- all observable are functionals of these densities, and

Furthermore, the total energy can be written as:

$$E_U^{el}[\rho] = F[\rho] + \int U_e(\mathbf{r})\rho_e(\mathbf{r})d\mathbf{r} \quad (2.20)$$

where $F[\rho]$ is the universal functional independent of the external potential $U_e(\mathbf{r})$;

The second Hohenberg and Kohn theorem permits to determine the ground state of electronic systems by minimizing the energy with respect to the charge density, by means of the variational method.

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | (T_e + U_{ee}) | \Psi \rangle \quad (2.21)$$

The Hohenberg and Kohn theorem, which is true for each fixed electron-electron interaction $\hat{U}_{ee}$ can be used to construct an auxiliary “non-interaction” system, the Kohn-Sham (KS) system, with external potential leading to the same set of density as the original interacting system.

$$\left[-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r}) \right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i \psi_i^{KS}(\mathbf{r}) \quad (2.22)$$

The ground state density is:

$$\rho_e(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i^{KS}(\mathbf{r})|^2 \quad (2.23)$$

where the sum is over all occupied states. Equation (2.22) is known as the Kohn and Sham equation [3]. The term v_{KS} is:

$$v_{KS}(\mathbf{r}) = U_{\rho,e}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1 + v_{xc}(\mathbf{r}, \rho) \quad (2.24)$$

where v_{xc} is the exchange and correlation potential, which is an unknown functional of the electron density. The Kohn and Sham equations are solved in a self-consistent way with respect to the orbitals $\psi_i^{KS}(\mathbf{r})$ entering the charge density via Eq. (2.23).

The total energy of the electronic system has the following form:

$$\begin{aligned} E^{el}[\rho] = & -\frac{1}{2} \sum_{i=1}^{\text{occ}} \int \psi_i^* \nabla^2 \psi_i d\mathbf{r} + \frac{1}{2} \int \frac{[\rho(\mathbf{r})\rho(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ & + \int U_e(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho] \end{aligned} \quad (2.25)$$

Here $E_{xc}[\rho]$ represents the exchange and correlation energy. To solve the Kohn and Sham equations we need to determine the form of $E_{xc}[\rho]$ (or v_{xc}).

An approximation introduced by Kohn and Sham to solve the problem is known as the *Local Density Approximation* (LDA). It assumes that the exact exchange and correlation potential at the point $\mathbf{r}$ is equal to the exchange correlation energy of a homogeneous electron gas, which has the same density as in the real system at point $\mathbf{r}$. In this approximation the density is purely local, the corrections to the exchange and correlation energy at the point $\mathbf{r}$ due to nearby inhomogeneities in the electron density are ignored.

Another popular approximation is the *Generalized Gradient Approximation* (GGA), in which the correlation energy also depends on the density gradient. It takes account of the density inhomogeneities.

Both methods are very popular in practical calculations. One of the failures of the standard approximations is the incorrect description of weak vdW forces. The dispersion (van der Waals) interaction is inherently non-local, so that local (LDA) and semi-local (GGA) functionals fail to describe correctly interactions between two systems at distances from each other where their electronic densities do not overlap.

2.4 Technical Details of DFT Calculations

There are few practical issues to be faced with when one uses the DFT method. These concern the choice of the basis set, k-point sampling used for the description of the

electronic wavefunctions, the pseudopotential and the periodic boundary conditions (PBC).

2.4.1 Choice of the Basis Set

To solve the KS equation it is necessary to expand the electronic wavefunction in a basis set and there is a quite wide variety of basis sets used for constructing the electronic wavefunction. This can be obtained using a sum over atomic orbitals [1]:

$$\psi_{\lambda}(\mathbf{r}) = \sum_b C_{b\lambda} \phi_b(\mathbf{r}) \quad (2.26)$$

where $C_{b\lambda}$ are the expansion coefficients. These basis functions are usually constructed from atomic orbitals centred on atoms [1]:

$$\phi_b(\mathbf{r}) \rightarrow \xi_{nlm}(\mathbf{r} - \mathbf{R}_A) \quad (2.27)$$

where $\mathbf{R}_A$ is a vector of an atom A and n, l and m are the quantum numbers. The basis function ξ_{nlm} can be split into two parts, one radial and another angular, i.e. $\xi_{nlm} = R_{nl}(\mathbf{r}) S_{lm}(\mathbf{r})$ [1]. The angular part, S_{lm} , is a spherical harmonic describing the angular dependence while the radial part, $R_{nl}(\mathbf{r})$, describes the radial dependence. There are three main types for the orbitals which can be obtained following these principles [1]:

- Slater type orbitals where the radial part of the atomic orbital is a simple exponential which mimics the exact eigenfunctions of the hydrogen atom.
- Gaussian orbitals which are similar to the Slater type orbitals but the exponential terms in the radial functions are replaced by Gaussian functions.
- Numerical orbitals which have radial functions specified on a numerical grid which are more suitable for quick calculations.

The size of the basis set is important for the calculations: the larger the basis set, the more accurate the calculation should be. In this approximation the basis set suffers from being incomplete, with practical implications for the results, especially binding (or stabilisation) energies. Sometimes, adding more atomic orbitals may result in over-completeness problem as well, so one has to be very careful in reaching convergence with this type of basis set.

In fact, there are other ways to create the basis set where periodicity is present. It is possible to split the basis set into two main types [1]:

- Crystalline atomic orbitals where the atomic orbitals constructed using either of the atom based approaches given above are periodically repeated. The SIESTA code (see Sect. 2.5) uses crystalline numerical atomic orbitals.
- Plane waves [1]:

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}} \quad (2.28)$$

where $\mathbf{k}$ is a vector in the Brillouin zone, $\mathbf{G}$ is a reciprocal lattice vector and V is the volume of the crystal. These are not atom centred functions and they are completely analytic. They are also easy to use with periodic boundary conditions (PBC), especially for solids. However, with empty space in the system (e.g. a molecule on a surface in the slab model) they are very inefficient because the number of plane waves needed becomes very large.

2.4.2 Pseudopotential Method

Another important tool to solve the KS equation is the pseudopotentials method [1]. In general the number of electrons in a system is determined by summing up all core and valence electrons, where the latter are known to be most important for chemical bonding. This is due to their wavefunctions being further away from the nuclei and this also has the effect that they are shielded from nuclei Coulomb attraction by core electrons. The core electrons feel a very strong Coulomb attraction from the nuclei so that their wavefunctions are very localised around it and less affected by the surrounding of the atom.

In fact, the core electrons can be considered as frozen, i.e. in a molecular or periodic system they can be considered as having the same form as they have in the isolated atom. Therefore, only the valence electrons need to be considered variationally. However, valence electrons need to be orthogonal to the core electrons and therefore will oscillate rapidly in the core region. This requires many basis functions being required to properly describe the valence wavefunctions in the core regions [1].

This is where the introduction of pseudo-wavefunctions for the valence electrons becomes necessary. These pseudo-wavefunctions have unnaturally smooth behaviour inside the core regions, but still keep their natural form outside the core regions so that the chemistry is unaffected. Pseudopotentials incorporate the potential due to the nuclei and the core electrons into one effective potential. There are three general forms for the pseudo-potential [1]:

- Norm-conserving pseudopotentials which provide the correct normalisation for the pseudo-wavefunctions.
- Ultra-soft pseudopotentials which do not provide the correct normalisation for the wavefunctions, but are smoother in the core region. This complicates the KS equation but improves the efficiency overall.
- The Projector Augmented Wave method which takes explicit account of the frozen core electrons in a way which still provides good efficiency.

The radius of the core region is denoted by r_c . One must be careful in choosing r_c : if it is too large, the chemistry in the system may be unreliable; if it is too small, the

oscillating characteristics in the core region need to be described. This would destroy the reason for introducing the pseudopotential as larger basis sets would be needed.

2.4.3 Periodic Boundary Conditions and k -Point Sampling

Many physical systems have translational symmetry (for instance, solids, monolayers, chains etc.). However, even if this is not the case (e.g. isolated molecules, a point defect in a solid, an adsorbed molecule on a surface), periodicity in all the three dimensions is imposed artificially. When one system has only one or two-dimensional periodicity, the 3D periodicity can be easily implemented by introducing large vacuum gaps between the periodic systems so that one or two dimensional structures cannot spuriously interact with their periodic images.

The electronic structure of a system with PBC resembles a band structure of a perfect periodic crystal [1]. In this case the KS potential (2.24) is translationally invariant

$$v_{KS}(\mathbf{r}) = v_{KS}(\mathbf{r} + \mathbf{R}) \quad (2.29)$$

where $\mathbf{R}$ is the direct lattice vector. According to the Bloch theorem, this property will affect the form of the single-particle wavefunctions. One electron energies ε_λ and the wavefunction ψ_λ are counted using the band index n and the k point within the Brillouin zone, i.e. via λ which is the joint index ($n\mathbf{k}$):

$$\psi_\lambda(\mathbf{r}) = \psi_{n\mathbf{k}} = e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.30)$$

$$u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) \quad (2.31)$$

In practice, the number of $\mathbf{k}$ -points to be used depends on the size of the unit cell. When the unit cell is big, the number of $\mathbf{k}$ -points required is small because the corresponding Brillouin zone to sample is smaller [1]. The actual number of $\mathbf{k}$ -points required for given system can be chosen by checking the convergence of the energy and geometry while increasing the number of $\mathbf{k}$ -points.

2.5 Siesta Method

The DFT code mainly used in this thesis for calculations of the electronic structure and geometry of various systems is the Spanish Initiative for Electronic Simulation with Thousands of Atoms (SIESTA) [4]. The code employs as the basis set a linear combination of numerical orbitals, uses periodic boundary conditions and the method of pseudopotentials. The core electron properties are simulated using scalar-relativistic norm-conserving [5, 6] Troullier-Martins [7] pseudopotentials factorised

in the Kleinman-Bylander form [8]. In this work the nonlinear core-valence exchange correlation scheme [9] is applied for all elements except for hydrogen.

In all our calculations, a double-zeta-plus polarisation orbitals (DZP) basis was used. DZP uses two functions for each atomic orbital plus polarisation orbitals. The energy cutoff used is between 160–200 Ry.

Perdew, Becke and Ernzerhof (PBE) [10] generalised gradient approximation (GGA) functional is used in this thesis for the exchange and correlation energy. This functional gives good description of the hydrogen bond formation of DNA pairs [11–14] as compared to quantum chemistry calculations.

The atomic relaxation in our systems was performed until the forces on atoms were no larger than 0.01 eV/Å for all the individual molecules and pair calculations. The exception were the monolayers and the molecules on the gold surface, where the precision was of 0.05 eV/Å or better.

In the calculations on single molecules and dimers, very large super-cells were used to avoid unphysical interaction between the images.

2.5.1 Definition of Useful Energies to Analyse Systems Stability

In order to analyse the stability of the studied systems, it is necessary to calculate a number of useful energies [15]. The first of these is the stabilisation energy, E_{stab} , defined as the total energy of the relaxed combined system (i.e. a pair of molecules) minus the total energies of all its individual components (two molecules) relaxed separately. The combined system is stable if the E_{stab} is negative. To describe the interaction between the single molecules, we define the interaction energy, E_{int} , as the total energy of the system minus the energies of each individual molecule calculated in the geometry of the relaxed combined system. This energy should also be negative for a stable system. Finally, we define the deformation energy, $E_{\text{def}} = E_{\text{stab}} - E_{\text{int}}$, which characterises the sum of losses in the total energies of the molecules due to their relaxation towards their geometry in the combined system. The E_{def} is positive because the energies of the individual molecules calculated in the geometry of the combined system are higher than when they are individually relaxed.

These energies are correct only if the complete basis set is used. Therefore, if a finite localised basis set is used, a Basis Set Superposition Error (BSSE) [16] correction is to be applied to calculate binding energies. Moreover, since we employ a localised basis set, these energies would only be correct after the application of the BSSE correction. Therefore, to simplify the analysis, the same BSSE correction was applied to the interaction and stabilisation energies ensuring that this exact relationship remains. These corrections have been calculated by the standard Boys-Bernardi counter poise correction method [16]. The BSSE correction for a pair is defined as:

$$E_{\text{BSSE}} = E_A + E_B - E_A^* - E_B^* \quad (2.32)$$

where E_A and E_B are the total energies of each monomer in the geometry of the pair, and E_A^* and E_B^* are the total energies of each molecule in the geometry of the pair with the orbitals of the other molecule also present. For this second group of energies the basis set is larger as more orbitals are available in the construction, implying a lower energy as the basis set is more complete (e.g. $E_A^* < E_A$), then the E_{BSSSE} is always positive. In the calculation the additional orbitals are considered as “ghost” orbitals because they are associated with atoms that do not exist in calculations of E_A^* and E_B^* .

2.5.2 Characterisation of the Hydrogen Bonds: “Kebab” Structures

A way of characterising the strength of the hydrogen bonding between two molecules is by analysing the electron density difference plots [11–14], $\Delta\rho = \rho_{ab} - (\rho_a + \rho_b)$, where ρ_{ab} is the electron density of the combined pair and ρ_a and ρ_b are the densities of the individual monomers calculated at the geometry of the pair. Hydrogen bonds are characterised by a “kebab” structure of alternating regions of charge excess and depletion, that represent the redistribution of the charge density due to the hydrogen bond formation Kelly et al. [11]. The stronger the bond, the more regular is the “kebab” structure. This concept can be easily generalised for complexes containing more than two molecules.

2.6 Diffusion Calculations

To investigate the corrugation of the surface potential for a single molecule or a cluster of molecules and hence calculate the corresponding diffusion barriers, we placed the molecules above the gold surface (the DFT optimum height) and translated it in steps of 0.1 Å along several directions across the surface ($[\bar{1}10]$, $[10\bar{1}]$ and $[11\bar{2}]$); during each relaxation the lateral position of one atom of the molecules was fixed, although it was allowed to move vertically. All other atoms of the system including the top layer atoms of the surface were allowed to relax. The bottom atoms of the surface slab were fixed in the bulk-like position.

2.7 Van der Waals Implementation in DFT Method

The standard approximations to the exchange-correlation energy in DFT, discussed in Sect. 2.3, are relatively cheap and can describe reliably many characteristics of systems of interest. However, LDA and GGA approximations to DFT are not able to describe a weak non-local dispersion interaction, also known as the vdW interaction, which is essential for many systems. The reason why the standard DFT functionals fail is due to an incorrect description of the electron correlation in sit-

uations where the electron densities of two parts of the system do not overlap and the vdW interaction becomes dominant. Indeed, the vdW interaction is non-local in character and is entirely missing in most of the GGA density functionals which are semi-local.

There have been attempts to solve the problem in several ways. One approach consists of adding to the standard DFT method additional semiempirical terms which take into account the dispersion interaction (DFT-D method) [17]. However, this method has a limited flexibility and is system dependent. The parameters are bound to work for the systems they were designed for and the use of these parameters outside that set of parametrisation may not be able to deliver reasonable results. Another approach includes accounting for the vdW interaction through effective atom-electron pseudopotentials [18]. Recently, a truly first-principles approach, which does not require any fitting parameters and is within the remit of the DFT method was developed (vdW-DF) [19–23] and successfully applied to many systems. In this method the exchange-correlation energy functional has the form:

$$E_{vdw-DF}[\rho] = E_{GGA}[\rho] - E_{GGA,c}[\rho] + E_{LDA,c}[\rho] + E_c^{nl}[\rho] \quad (2.33)$$

where ρ is the electron density, E_{GGA} is the GGA exchange-correlation energy corresponding to some flavour of GGA and $E_{LDA,c}$ is the LDA correlation energy. The E_c^{nl} represents a non-local contribution to the correlation energy and accounts for the dispersion interaction. The difference of correlation energies, $E_{LDA,c}[\rho] - E_{GGA,c}[\rho]$, serves to replace the correlation energy contained in GGA functional with that of the LDA. This particular form of the energy expression guarantees that for uniform densities (e.g. the uniform electron gas) the correlation energy equals exactly that of the LDA density functional as the non-local term $E_c^{nl}[\rho]$ vanishes.

This approach has been implemented in SIESTA [24, 25] and used in some calculation [24, 26]. It was shown that inclusion of dispersion interaction may result in substantial changes of the stabilisation energies of molecules on surfaces.

2.8 Super-Structure Modelling: A Systematic Method

The STM and AFM techniques which allow the imaging of the surface covered with molecules was mentioned in Sect. 1.3. Unfortunately, it is not possible to achieve atomic resolution with any of these techniques for most of the organic molecules. Therefore, a theoretical approach is required to determine the geometries of the observed supramolecular assemblies.

This subsection describes the approach employed to construct the supramolecular structures and the computational method used. In order to build all the possible structures, a systematic approach has been used [11], which consists of the following steps: (i) identification of all the peripheral sites of the molecule that can participate in a hydrogen bonding with another molecule; (ii) all possible dimers are constructed; (iii) by combining molecules, using dimer rules, all unit cells are constructed having

a predefined number of molecules; (iv) all possible one dimensional (1D) structures (chains) are constructed for every unit cell; (v) by attaching chains parallel to each other, all possible two dimensional (2D) structures are formed; (vi) the stabilities per unit cell of the assemblies predicted in this way are estimated by summing up all the dimer energies per cell; (vii) the most stable predicted structures are then fully relaxed using DFT. In this way, by assuming a certain number of molecules per unit cell, one can build up all the possible 1D and 2D structures. The gas phase calculation (i.e. without taking into account the surface) is a good approximation by considering that the molecules are quite mobile on the gold surface. This is because the surface potential, as will be demonstrated in Sect. 4.1.1 is flat. This approach is particularly useful because it allows considering all possible structures in the gas phase with a modest computational cost.

2.9 Modelling of STM Images

2.9.1 Tersoff-Hamann Method

The modelling of STM images could be a useful tool to gain an understanding of experimental images and as a means of identifying the actual system geometry.

The Tersoff-Hamann method provides an easy way to analyse this surface phenomenon.

According to the Fermi's golden rule one can write the current flowing from the tip to the sample using the Bardeen's expression [27]:

$$I_{t \rightarrow s} = \frac{2\pi e}{\hbar} \int |M_{ts}|^2 N_t(E - eV) N_s(E) f_t(E - eV) [1 - f_s(E)] dE \quad (2.34)$$

$f(E)$ denotes the Fermi-Dirac distribution for the tip and the sample, $N_t(E)$ and $N_s(E)$ denote their density of states. M_{ts} is the effective matrix element for the current between the tip and sample due to the states of energy E , and V is the applied voltage.

In order to model the STM image of the molecules on the surface the Tersoff and Hamann model has been used [28]. Tersoff and Hamann suggested replacing the unknown electronic structure of the tip by a simple model, where the wave function of the tip atom is assumed to be an atomic s -wave function. Since the tunneling current depends on the overlap of the wavefunction of the tip and sample, and the wavefunction decays exponentially into the vacuum, only the orbital localised at the tip will be involved in the tunneling matrix element.

Within the approximation of zero temperature and low bias voltage the total current flowing from the tip to the sample will be:

$$I = \frac{2\pi e^2}{\hbar} V \sum_N |M_{ts}|^2 \delta(E_s - E_F) \delta(E_t - E_F) \quad (2.35)$$

where V represents the voltage applied and δ -functions ensure the energy conservation.

The effective matrix element M_{ts} is

$$M_{ts} = \frac{\hbar^2}{2m} \int (\Psi_t^* \nabla \Psi_s - \Psi_s \nabla \Psi_t^*) dS \quad (2.36)$$

where the integral is taken over a surface separating the tip and sample. To calculate the matrix element, the surface wave-function Ψ_s is written as a 2D reciprocal lattice expansion.

The main point of Tersoff-Hamann theory is that no choice of the wavefunction of the tip is needed. Since there is usually no knowledge of the exact tip structure, Ψ_t can be modelled as a solution in a locally spherical potential with curvature R about its center r . So asymptotically the tip wavefunction is chosen to have the form of an s-wave. By using this approximation the matrix element becomes proportional to the sample wavefunction evaluated at the tip center of curvature ($M_{ts} \propto \Psi_s(r_0)$). Then the total current flowing from Eq. (2.35) can be written as:

$$I \propto V N_t(E_F) \sum_s |\Psi_s(r_0)|^2 \delta(E_s - E_F) \quad (2.37)$$

In this expression, the sum represents the local density of states of the sample (LDOS) at the Fermi level evaluated at the tip center. Then Eq. (2.37) can be rewritten as

$$I \propto V N_t(E_F) \text{LDOS}(r_0, E_F) \quad (2.38)$$

This equation gives an easy way for the interpretation of the STM images.

SIESTA can output the LDOS integrated over a range of energies which allows one the calculation of simple STM images in the Tersoff-Hamann approximation.

2.9.2 Scattering Formalisms

The Tersoff-Hamann approximation is an easy way to analyse the surface phenomenon. However, this kind of approach does not take into account the effect of the tip.

We also used a new program called Nt_STM which is a graphical interface for “Green”, a code written by Cerda [29, 30]. This approach is based on the generalised Landauer theory [31], and the scattering matrix is determined by the Green’s-function techniques [29].

The junction is modelled by partitioning the system into three regions: two bulk regions for the substrate and the tip, and two principal layers that are involved in the scattering. The bulk region for the tip and the substrate is periodically repeated in the z direction away from the junction while the apexes involved in the scattering are composed by several atomic layers. The whole system is considered periodic in the x and y directions.

The tunnelling process is considered as a scattering mechanism for which the scattering matrix S is calculated from the electronic transmission and reflection amplitudes at the tunnel junction. The conductance is evaluated via the Landauer-Büttiker formula for the multichannel case¹ [31].

At the zero temperature limit, the current I is

$$I(V) = \frac{e}{\pi\hbar} \int_0^{-eV} T^\pm(E + \mu_T) dE \quad (2.39)$$

The $T^\pm(E)$ is the total transmission coefficient:

$$T^\pm(E) = \sum_{m,m'} T_{mm'}^\pm(E) \quad (2.40)$$

where $T_{mm'}^\pm(E)$ are the matrix elements that give the probability for an electron in the m channel to be transmitted to channel m' . The electron propagates from the channel m at the negative side of the tunnel junction to the channel m' at the positive side without dissipation. Each channel wavefunction has the current bloch-line asymptotic behaviour in the regions far away from the junction.

2.10 Classical Molecular Dynamics

Classical molecular dynamics uses empirical potentials (known as the “force field”) that either ignore quantum mechanical effects, or attempt to capture them in a limited way through entirely empirical equations. Parameters in the potential are fitted against known physical properties simulated in the system, such as the elastic constants and the lattice parameters, in order to reproduce the basic aspects of the intermolecular and intramolecular interactions.

In order to perform classical molecular dynamics calculations, the Sci-Fi code has been used [32]. The energy expression implemented in the code has the form:

$$U = V_{\text{cov}} + V_{vdW} + V_{el} \quad (2.41)$$

¹ At a given energy E the surface (s) and the tip (t) could be described by a certain number $N_s(E)$ or $N_t(E)$ of independent conductors that are defined as channels.

where in that energy, the effects of the covalent (V_{cov}), van der Waals (V_{vdW}) and the electrostatic (V_{el}) interactions are taken into account. The covalent term is used for describing internal energies of organic molecules and it consists of a number of terms:

$$V_{\text{cov}} = \sum_b^{Nb} k_b (b - b_0)^2 + \sum_{\theta}^{N_{\theta}} k_{\theta} (\theta - \theta_0)^2 + \sum_{\phi}^{N_{\phi}} K_{\phi} [1 + \cos(n\phi - \phi_0)] \\ + \sum_{\chi}^{N_{\chi}} K_{\chi} [1 + \cos(n\chi - \chi_0)] \quad (2.42)$$

The terms in the above expression apply to the many body interactions in the system and summations only apply to specified interactions, in this case only covalent interactions. These interactions are most conveniently specified via the internal coordinates of the system, not via the Cartesian coordinates of atoms as is the case for other interactions. These internal coordinates are: bond lengths b , angles between bonds ϑ , torsion angles about bonds φ and out-of-plane angles χ . The vdW energy is given via

$$V_{\text{vdW}} = \sum_{i < j}^{\text{atoms}} \left(\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right) \quad (2.43)$$

A_{ij} and B_{ij} are constants and R_{ij} is the distance between atoms i and j . It also includes short-range repulsion terms.

Finally, the electrostatic energy V_{el} , in Eq. 2.41, describes electrostatic interaction between atoms.

Here, in a number of calculations we combined a DFT with a force field [33] developed by fitting results of the quantum chemistry calculations at the MP2 level of various groups of all DNA base molecules with gold clusters. Note that the force field includes all interactions between the bases and the gold surface, including vdW interactions. In these hybrid calculations only interaction between molecules and surfaces was supplemented by a force field. We have also done some calculations using the Sci-Fi code [32] we did not relax neither the surface, nor the melamine molecule, so that the total energy of the melamine-surface system represents directly the adsorption energy.

The following chapters review the results obtained. In Chap. 3, attention is paid to the assembly of molecules in the gas phase, considering the molecule-molecule interaction and disregarding the presence of the surface. Chapters 4, 5 include a more detailed characterisation of the interaction between molecules and surface.

References

1. Kantorovich LN (2004) Quantum theory of the solid state: an introduction. Fundamental theories of physics. Kluwer Academic Publishers, Dordrecht
2. Hohenberg P, Kohn W (1964) Phys Rev Lett 136:864B
3. Kohn W, Sham LJ (1965) Phys Rev Lett 140:1133A
4. Sanchez-Portal D, Ordejon P, Artacho E, Soler JM (1997) Density functional method for very large systems with lcao basis sets. Int J Quantum Chem 65:453
5. Kleinman L (1980) Phys Rev B 21:2630
6. Bachelet GB, Schluter M (1982) Phys Rev B 25:2103
7. Troullier N, Martins JL (1991) Phys Rev B 43:1993
8. Kleinman L, Bylander DM (1982) Phys Rev Lett 48:1425
9. Louie SG, Froyen S, Cohen ML (1982) Phys Rev B 26:1738
10. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
11. Kelly REA, Lee YJ, Kantorovich LN (2005) J Phys Chem B 109:22045
12. Kelly REA, Kantorovich LN (2006) J Mater Chem 16:1894
13. Kelly REA, Lee YJ, Kantorovich LN (2005) J Phys Chem B 109:11933
14. Kelly REA, Lee YJ, Kantorovich LN (2006) J Phys Chem B 110:2249
15. Spöner J, Leszczynski J, Hobza P J Phys Chem
16. Boys F, Bernardi F (1970) Mol Phys 19:553
17. Grimme S (2004) J Comput Chem 25:1463
18. von Lilienfeld OA, Tavernelli I, Rothlisberger U, Sebastiani D Phys Rev Lett
19. Dion M, Rydberg H, Schroeder E, Langreth DC, Lundqvist BI (2004) Phys Rev Lett 92:246401
20. Langreth DC, Dion M, Rydberg H, Schroeder E, Hyldgaard P, Lundqvist BI (2005) J Quantum Chem 101:599
21. Thonhauser T, Cooper VR, Li S, Puzder A, Hyldgaard P, Langreth DC (2007) Phys Rev B 76:125112
22. Cooper VR, Thonhauser T, Puzder A, Schroeder E, Lundqvist BI, Langreth DC (2008) J Am Chem Soc 130:1304
23. Langreth DC, Lundqvist BI, Chakarova-Draxl SD, Cooper VR, Dion M, Hyldgaard P, Kelkkanen A, Kleis J, Kong LZ, Li S, Moses PG, Murray E, Puzder A, Rydberg H, Schroeder E, Rydberg T, Thonhauser H (2009) Cond Matter 21:084203
24. Gulans A, Puska MJ, Nienminen RN Phys Rev B
25. Roman-Perez G, Soler JM Phys Rev Lett
26. Mura M, Gulans A, Thonhauser T, Kantorovich L (2009) Role of van der waals interaction in forming molecule-metal junctions: flat organic molecules on the au(111) surface. Phys Chem Chem Phys (submitted)
27. Bardeen J (1961) Phys Rev Lett 6:57
28. Tersoff J, Hamann DR (1985) Stm Theory Phys Rev B 31:805
29. Cerdá J, Van Hove MA, Sautet P, Salmeron M (1997) Efficient method for the simulation of stm images. i. generalized green-function formalism. Phys Rev B 56(24):15885–15899
30. Cerdá J, Van Hove MA, Sautet P, Salmeron M (1997) Efficient method for the simulation of stm images. ii. application to clean rh(111) and rh(111)+c(4x2)-2s. Phys Rev B 56(24):15900–15918
31. Büttiker M, Imry Y, Landauer R, Pinhas S (May 1985) Generalized many-channel conductance formula with application to small rings. Phys Rev B 31(10):6207–6215
32. Kantorovich LN, Trevethan T, Polesel-Maris J, Foster A Self consistent image force interaction + virtual AFM machine
33. Piana S, Bilic A (2006) J Phys Chem B 110:23467

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