Solid state periodic calculations

As already mentioned, in order to build a model system as close as possible to the one experimentally observed it is important to include in the calculations the gold surface on which the HAT molecule is adsorbed.

Electronic structure calculation for periodic systems

Crystalline solids and surfaces can be treated theoretically with the methods of solid state physics, in which advantage is taken from the spatial periodicity of the system under study. A solid sample is considered as a supercell obtained by replication of the crystallographic primitive cell along the three directions of its defining edges (figure 1). By application of the so–called periodic boundary conditions, the sample becomes in turn the "primitive" cell of an infinitely extended crystal. Thanks to this definition of the system, it is possible to obtain the description of the electronic structure of the solid sample free from any boundary effect and limiting the detailed ab initio atomic simulation to just the contents of the crystallographic primitive cell.

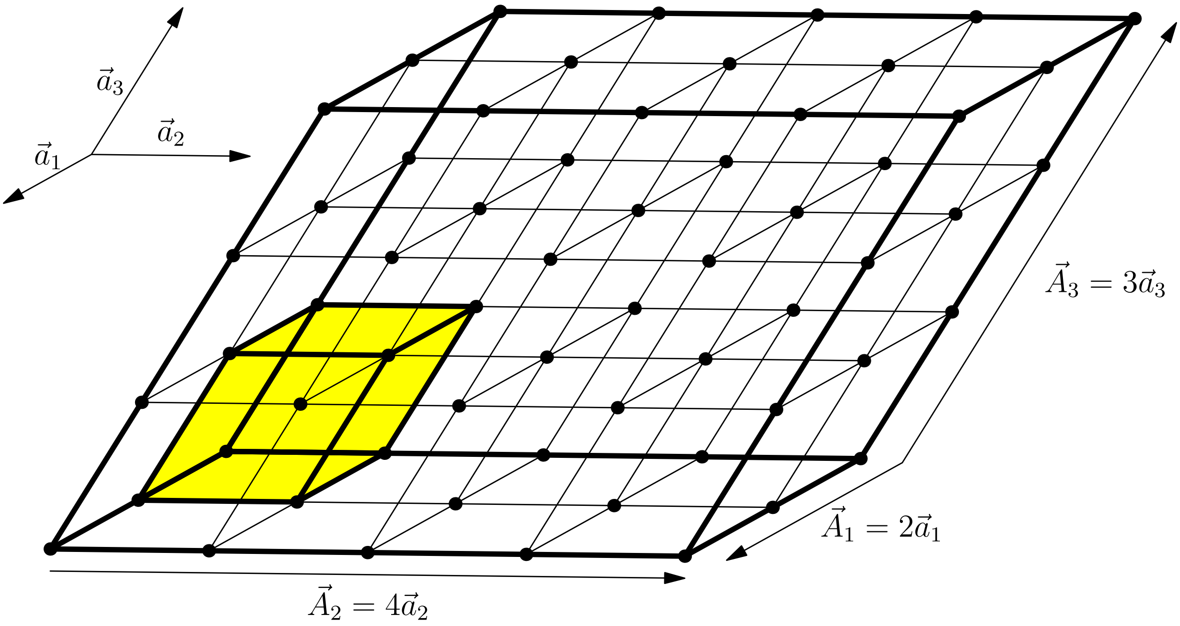

Figure 1: The definition of a solid cristalline sample (the "large" cell marked by bold black edges) as a supercell of the crystallographic primitive cell (the yellow cell). The supercell edges are integer multiples of the corresponding edges of the crystallographic primitive cell: $\vec{A}_i = N_i \vec{a}_i$. For the supercell in the figure we have $(N_1, N_2, N_3) = (2, 4, 3)$: of course, for a real solid sample, the N_i integers would be of the order of the Avogadro number. `fig:supercell`

In general terms, the procedure to solve the monoelectronic time independent Schrödinger equation for the i–th electron:

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V\left(\vec{r}\right)\right)\phi\left(\vec{r}\right) = \epsilon\phi_i\left(\vec{r}\right) \qquad \texttt{eq:TISE} \qquad (1)$$

for the case of a crystalline solid where the potential energy V is periodic can be summarized as follows.

Since V is periodic over the Bravais lattice $\mathcal{R}_\mu$ defining the crystal structure of the solid, it can be expanded in a Fourier series as:

$$V\left(\vec{r}\right) = \sum_{\vec{G}} V_{\vec{G}} \exp\left(i\vec{G}\cdot\vec{r}\right) \qquad \texttt{eq:V:expansion} \qquad (2)$$

where $\vec{G}$ is a vector of the reciprocal lattice $\mathcal{R}^*_\mu$ of $\mathcal{R}_\mu$ and:

$$V_{\vec{G}} = \frac{1}{v}\int_v V\left(\vec{r}\right)\exp\left(-i\vec{G}\cdot\vec{r}\right)d\vec{r} \qquad (3)$$

with v being the volume of the primitive cell of $\mathcal{R}_\mu$.

Due to the periodic boundary conditions, the eigenfunction $\phi\left(\vec{r}\right)$ is periodic on the Bravais lattice $\mathcal{R}_M$ defined by the supercell which represents the solid sample. Note that $\mathcal{R}_M$ is *commensurate* to $\mathcal{R}_\mu$, i.e. the primitive lattice vectors $\vec{A}_i$ of $\mathcal{R}_M$ are integer multiples of the primitive lattice vectors $\vec{a}_i$ of $\mathcal{R}_\mu$:

$$\vec{A}_i = N_i\vec{a}_i \quad i \in \{1,2,3\} \quad N_i \in \mathbb{Z} \qquad (4)$$

Being periodic over $\mathcal{R}_M$, also $\phi\left(\vec{r}\right)$ can be expanded in a Fourier series:

$$\phi\left(\vec{r}\right) = \sum_{\vec{k}} C_{\vec{k}} \exp\left(i\vec{k}\cdot\vec{r}\right) \qquad \texttt{eq:phi:expansion} \qquad (5)$$

where $\vec{k}$ is a vector of the reciprocal lattice $\mathcal{R}^*_M$ of $\mathcal{R}_M$ and:

$$C_{\vec{k}} = \frac{1}{V}\int_V \phi\left(\vec{r}\right)\exp\left(-i\vec{k}\cdot\vec{r}\right)d\vec{r} \qquad (6)$$

with V being the volume of the primitive cell of $\mathcal{R}_M$, i.e. the volume of the solid sample.

By plugging 5 and 2 into 1, this latter can be converted into an homogeneous system of algebraic equations for the unknown Fourier coefficients $C_{\vec{k}}$ and energy eigenvalues ϵ:

$$\left(\frac{\hbar}{2m_e}k^2 - \epsilon\right)C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0 \quad \vec{k} \in \mathcal{R}^*_M \quad \texttt{eq:central:equation} \quad \vec{G} \in \mathcal{R}^*_\mu \qquad (7)$$

$(k = |\vec{k}|)$

Since $\mathcal{R}_M$ is commensurate to $\mathcal{R}_\mu$, the lattice vectors of $\mathcal{R}^*_\mu$ are a(n infinite) subset of those of $\mathcal{R}^*_M$ and the primitive cell of $\mathcal{R}^*_\mu$ contains $N = N_1N_2N_3$ lattice points of $\mathcal{R}^*_M$.

Even if this would not be mandatory in principle, it is most convenient to take the first Brillouin zone, $\mathcal{B_Z}$, as the the primitive cell of $\mathcal{R}^*_\mu$ among all the infinite possible choices.

By taking advantage of the fact that $\mathcal{R}_M$ is commensurate to $\mathcal{R}_\mu$ it is possible to partition the system 7 into N independent subsystems indexd by the N lattice points of $\mathcal{R}^*_M$ inside $\mathcal{B_Z}$:

$$\left(\frac{\hbar}{2m_e}\mid \vec{k}-\vec{G}\mid^2-\epsilon\right)C_{\vec{k}-\vec{G}}+\sum_{\vec{G}'}V_{\vec{G}'}C_{\vec{k}-\vec{G}'}=0 \quad \vec{k}\in\mathcal{B}_{\mathcal{Z}} \quad \vec{G},\vec{G}'\in\mathcal{R}^*_\mu \qquad \texttt{eq:subsystem:k} \tag{8}$$

The original problem has thus been converted into N algebraic systems, one for each $\vec{k}$ point inside $\mathcal{B}_{\mathcal{Z}}$.
For a fixed $\vec{k}$ point inside $\mathcal{B}_{\mathcal{Z}}$, the solution of the corresponding system will give an infinite (in principle) set of eigenvalues ϵ and associated eigenfunctions $\phi\left(\vec{r}\right)$ (i.e. a set of Fourier coefficients C). The eigenvalues sorted in ascending order can be indexed by a single integer n (called *band index*) and a single solution of 1 is thus completely indexed by the $\vec{k}$ point inside $\mathcal{B}_{\mathcal{Z}}$ and the band index n:

$$\epsilon_{\vec{k}n} \qquad \phi_{\vec{k}n}\left(\vec{r}\right)$$

Limiting the number of $\vec{\mathbf{G}}$ vectors to be considered

The system 8 has as many equations as $\vec{G}$ vectors, i.e. an infinite number. To make it computationally affordable only the finite number of $\vec{G}$ vectors inside an energy isosphere in $\vec{G}$ space is usually considered:

$$\vec{G}: \quad \frac{\hbar\mid\vec{k}-\vec{G}\mid^2}{2m_e}\leq E_{\text{cutoff}} \qquad \texttt{eq:cutoff} \tag{9}$$

where E_{cutoff} is a predefined cutoff energy value.
Of course, the precision of the calculation will be related to E_{cutoff}, larger values implying more $\vec{G}$ vectors considered and hence a higher precision. On the other hand, increasing the cutoff value makes the computation more resource demanding, so a balance has to be found.

Pseudopotentials

Another crucial point regarding the computational implementation of the solution of system 8 is related to the potential energy $V\left(\vec{r}\right)$.
In the frame of density functional theory, V is written as:

$$V=V_{\text{nuc}}+V_H+V_{xc} \qquad \texttt{eq:total:potential} \tag{10}$$

where:

V_{nuc}	is the nuclear potential acting on the electron
V_H	is the Hartree potential
V_{xc}	is the exchange–correlation potential

Due to the $-\infty$ divergence of V_{nuc} at the nuclear positions ($V_{\text{nuc}}\approx -Ze^2/r$, Z=atomic number) the atomic core wavefunctions display wild high frequency oscillations when approaching the nucleus and these would require an enormous number of plane waves to be properly represented by the Fourier expansion.
Roughly, for a function oscillating with a length scale of δ, a Fourier expansion with wave vector components up to $2\pi/\delta$ is required.
As an example, the $1s$ atomic wave function of the C atom has an associated length scale of approximately $\delta\approx 0.1\,\text{a.u.}$. For C in the diamond polymorph

(volume of the primitive cell: $v = 76.5\,\text{a.u.} \implies$ volume of the reciprocal primitive cell (= volume per $\vec{G}$ vector in reciprocal space): $8\pi^3/v$) the number of required $\vec{G}$ vectors in the sum of 8 would be:

$$\frac{\text{volume of a sphere of radius } \dfrac{2\pi}{\delta} \text{ in reciprocal space}}{\text{volume per } \vec{G} \text{ vector}} = \frac{\dfrac{4}{3}\pi\left(\dfrac{2\pi}{\delta}\right)^3}{\dfrac{8\pi^3}{v}} \approx 320000$$

In order to cut the number of plane waves in the Fourier expansion of the potential to a manageable value, the so–called pseudopotential technology has been developed.

Basically, the pseudopotential is a smooth effective nuclear potential able to reproduce the effect of the nucleus plus core electrons on the valence electrons. The idea is that most of the properties one is interested in when doing an electronic structure calculation depend almost exclusively upon the behavior of the outermost (valence) electrons of the atoms, i.e. electrons far from the nucleus.

As far as this is assumed to be the case, then replacing real atomic orbitals with *pseudo-orbitals* matching the behavior of the real ones as closely as possible outside a given distance from the nucleus should not have any sizeable effect on the calculated properties.

On the other hand, if one is able to make these pseudo-orbitals behave smoothly inside a given core region (while maintaing their “faithful” behavior outside it), the number of Fourier terms needed to represent them can be dramatically reduced, thus making the system 8 computationally approachable.

As said above, the goal of smoothing the one electron orbitals inside the core region while keeping their original behavior outside it is achieved by replacing the true nuclear potential V_{nuc} with a properly designed pseudopotential.

The generation of atomic pseudopotentials is far from trivial and this technology has been (and is still being actively) developed over a long period of time. To better clarify the concept of a pseudopotential, figure 2 shows the all-electron and pseudo counterparts for the nuclear potential and $4s$ orbital of a Ti atom. The diverging behavior of the potential felt by the Ti $4s$ electron is replaced by a finite pseudopotential: the consequence is that the oscillations of the atomic orbital in the core region are eliminated, while maintaining the original behavior at distances $\gtrsim 2\,\text{bohr}$ from the nucleus.

Practical implementation of the calculations

We have performed the periodic calculations needed for this thesis using the Quantum Espresso (QE) [**FIXME**] suite of codes. This is an actively maintained and internationally recognized software for the practical implementation of the theoretical aspects outlined above.

The V_{nuc} contribution to the total potential V (eq. 10) is built with carefully designed atomic pseudopotentials, which are given as input quantities. The remaining two contributions, V_H and V_{xc} depend on the electron density $n\left(\vec{r}\right)$:

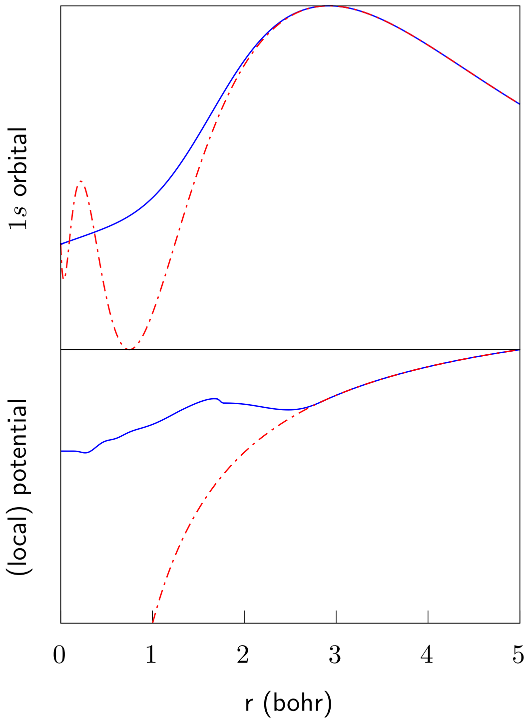

Figure 2: Lower panel: (local part of) the atomic potential for a $4s$ electron in the Ti isolated atom; dotted line is the true nuclear potential; full line is the pseudopotential. Upper panel: radial part of the $4s$ orbital; dotted line is the undumped behavior; full line is the pseudo orbital behavior.`fig:pseudopotential`

$$V_H = V_H\left(n\left(\vec{r}\right)\right) \tag{11}$$

$$V_{xc} = V_{xc}\left(n\left(\vec{r}\right)\right) \tag{12}$$

In turn, the electron density can be calculated only after the one electron orbitals have been obtained by the solution of the set of monoelectronic Schrödinger equations 1:

$$n\left(\vec{r}\right) = \sum_i^N \left|\phi_i\left(\vec{r}\right)\right|^2 \tag{13}$$

For this reason, as is usually the case in general, the set of monoelectronic Schrödinger equations 1 is solved self–consistently for a given set of $\vec{k}$ points given as input. For each $\vec{k}$ point:

- the V_{nuc} potential is constructed with the atomic pseudopotentials
- a starting guessed electron density is built up
- $V_H\left(n\left(\vec{r}\right)\right)$ and $V_{xc}\left(n\left(\vec{r}\right)\right)$ are calculated

- the monoelectronic orbitals $\phi_i\left(\vec{r}\right)$ are obtained by converting eq. 1 into the corresponding Fourier space version 8. A crucial computational point in this regard is the use of Fast Fourier Transform techniques for the generation of the $V_{\vec{G}'}$ Fourier coefficients on a grid defined by the cutoff energy condition 9.
- a new electron density can now be calculated: $n\left(\vec{r}\right) = \sum_i^N \left|\phi_i\left(\vec{r}\right)\right|^2$
- the process is iterated until the electron density at step j differs from that at step $j-1$ by less than a predefined convergence threshold

The whole process is represented in the flowchart shown in figure 3.

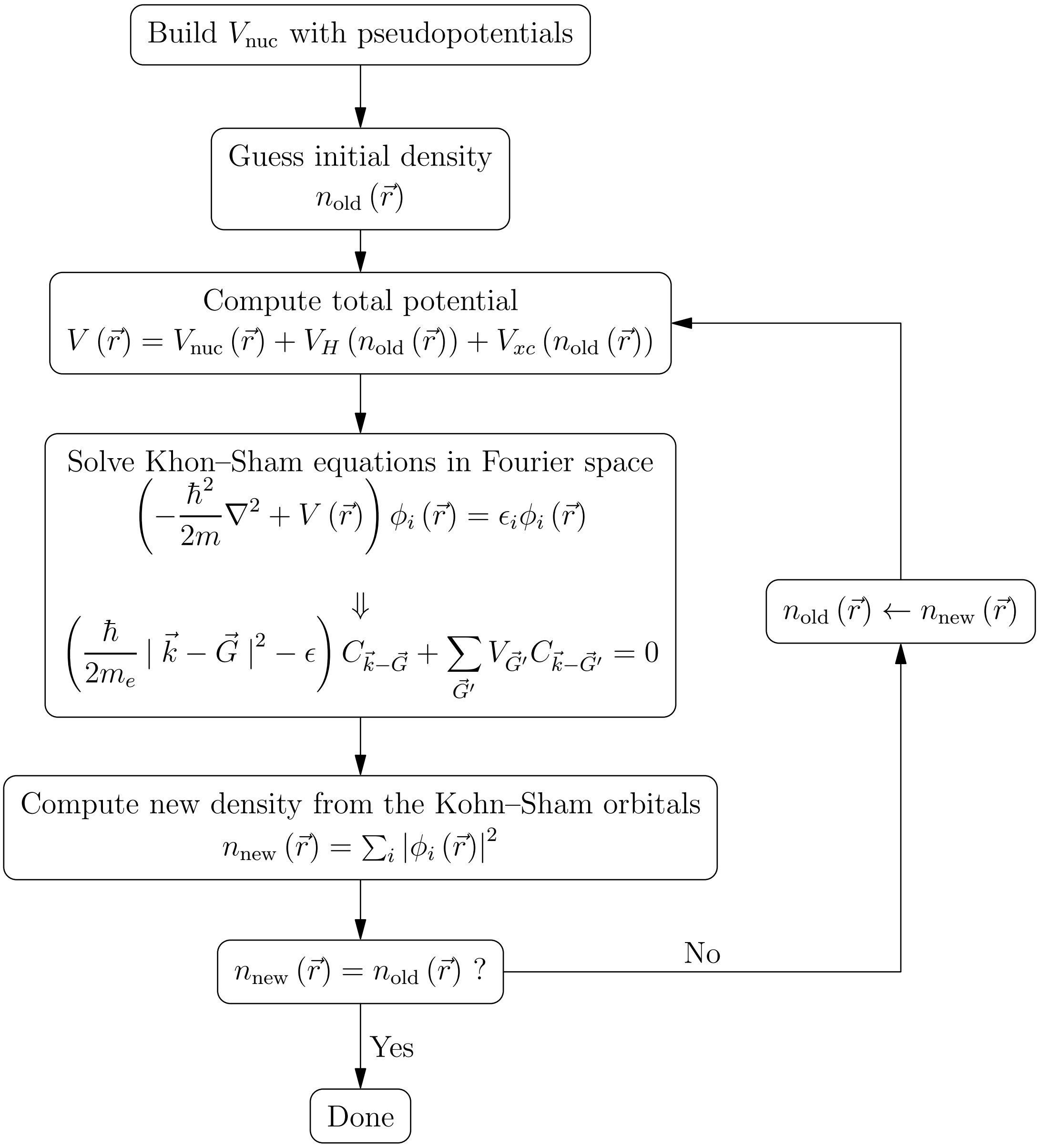

Figure 3: The self consistent field procedure as implemented in the Quantum Espresso code.fig:flowchart