

Universiteit Utrecht

# **Physics and Astronomy**

# Quantum simulating electronic systems: elementary building blocks

# BACHELOR THESIS



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#### Abstract

Quantum simulators are devices that mimic quantum effects with the aim of acquiring knowledge about real systems. During the past decades, scientist have recognized the tremendous potential of these devices on a computational and fundamental level, leading to the discovery and development of new types. One of these new strategies of quantum simulation is via electronic systems: 2D surface structures in which electrons can be confined. This enables us to build artificial lattices, which paves the way for investigating a whole zoo of exotic material properties.

In this thesis the foundations of this field are explored. Gradually a framework is built, starting with the fundamental principles of both experiment and theory. After discussing the scanning tunnelling microscope and the iterative Arnoldi method, we start with investigating the smallest unit: the particle in a box, or artificial atom. For this we use the hexagonal form in particular. From this, we move on to the coupling of sites in a dimer, about which we make predictions using the tight binding model. This system is then manipulated, and theoretical results are compared with experiment. We report that most of the tight binding predictions are fulfilled. Most notably, the coupling indeed depends on the barrier between the sites, as well as their size.

Hexagonal artificial atoms fulfil a central role throughout the thesis. The cover therefore shows density plots of the first ten numerically obtained eigenfunctions  $(|\psi|^2)$  of a particle in a 2D hexagonal box. The number above each plot indicates the corresponding eigenvalue in eV.

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# 1 Introduction

In this chapter a brief introduction is given on the nature and background of quantum simulation, enabling the reader to place the rest of the thesis, which is more focused on the specific simulation of electronic systems, into a broader theoretical perspective. One might regard the subsequent chapters as a branch of the more general subject discussed here. Besides this relevance for the rest of the thesis, quantum simulation in itself also is a very promising field of research with an enormous potential, as this chapter will illustrate.

As for the structure of this chapter, a general top-down tendency will be followed: firstly the simulation of physics as a whole will be discussed, considering the different ways in which this can be done. From this broad concept the subject will be narrowed down to quantum simulation and then even further to simulating electronic systems, the main topic of this thesis. The chapter will be concluded with a brief statement of the structure of the chapters to follow.

#### 1.1 Simulating physics

Simulations have been at the heart of physics for centuries, since they enable us to gain information and clarity about a certain system. A somewhat artistic example is the orrery, a mechanical model of the solar system that can show relative positions of the planets, used frequently during the Scientific Revolution and the Enlightenment[1]. Using this example the general concept of simulation can be illustrated.

There exists a real physical system, the solar system in this case, that we want to understand. Based on observations, general rules can be proposed, mostly mathematical formulas, and all of these rules combined form a model; one can think here of the collective orbits of the planets. A simulator is then the device that puts the model into practice to generate output that can be attributed to the real physical system. An overview of this process is shown in Fig. 1 (if one ignores the 'quantum' part). In the example, the orrery is based on the orbits (the model) and subsequently used to find relative positions as output. Proposed as such, the simulator device can fulfil two distinct purposes: it can be used to gather new information about a physical system, but also to test the validity of a model. Should the simulation give results that contradict the behaviour of the real system, there might be issues with the model.

Of course the latter function can only be fulfilled adequately when a satisfying accuracy of the simulator device is established with respect to the model. This can be a challenge on its own. One might be inclined to compare the results of one simulator with those of another. While in practice this is done very often, it does not prove the accuracy of the device; all it does is not falsify it. Multiple simulators might have an error that cancel out when results are compared, or the simulator under investigation might only work properly in a specific regime. Although it is good to be aware of these obstacles, they do not render simulations obsolete, for the entirety of physics depends on falsifiability as well.



**Figure 1: Simulating physics.** Schematic overview of the process of quantum simulation. If one disregards the 'quantum' in the upper box, it can also be used to describe simulation in general. A real system is translated into a model, which is put in practice by the simulator device. The output it generates is then compared to the system[2].

Given the basic function of a simulator, one can make a distinction between the different varieties of simulators based on their method. Firstly, a simulator can be analogue or digital. An analogue simulator is a (real) approximation of the model, such as the orrery, where the relative positions of the planets can be found by moving them around. A digital simulator, on the other hand, can be seen as a logical or mathematical continuation of the model, generating output that follows unequivocally from the model itself. The digital version of the orrery would perhaps be computing the coordinates of the planets at a certain time, directly using the mathematical functions that describe the orbits. The device could then be something like a calculator[2].

Another distinction is whether the simulator is classical or quantum. At this point definitions tend to differ between sources as stated by Johnson et al., as generally two different possibilities can be identified[2]. In the first, the difference is with respect to the system of interest: whether this is to be considered classical or quantum, as noted by Feynman in his famous speech on simulation[3]. In the former, the system is governed by time. Simulating time is generally doable, because the world then behaves causal in most of its regimes, implying that a known position and momentum, together with physical laws, are sufficient to determine the past and the future. However, if the system is in the quantum regime, what we generally calculate are probabilities. Simulating probabilities is exponentially difficult, because - say we have discretised space and time into  $x_i$ 's and  $t_i$ 's, and maybe even the probability itself into  $k_i$ 's - to give the probability of a system would mean to give a probability  $k_i$  of finding a particle at position  $x_i$  at time  $t_i$ . This is all together an enormous amount of data, that, moreover, scales exponentially with the size of the system. Because of this, almost no quantum simulations are available to us in a classical way. Exactly this is where quantum devices are made relevant. The second possible distinction between a classical or quantum simulator, however, puts emphasis on the type of device that is used and not so much on the system. This means for example that when a classical system, governed by time, is simulated via a device that is based on quantum probabilities, one would identify this simulation as quantum, even though the system itself is not. The advantage of this definition is that this "cross-use" of classicalquantum is given more attention, which would surely be justified when a quantum device is more successful at simulating a classical system than a classical device. A disadvantage is that this distinction might feel more counter-intuitive. Above all it is worth noting that the aim of this section is not so much to argue for one method in favour of another, but more to give the reader some insight into the possible considerations concerning this subject.

Lastly, having covered the function and different types of simulations, it might be useful to emphasize more explicitly the relevance of these processes. One might identify two benefits of simulations, the first of which is necessity. Since large portions of physics have with time evolved into more complex and less directly observable regions, simulations can grant us access to knowledge that otherwise would have remained hidden. The second advantage is convenience: simulations and the models that accompany them can guide us in our research, as opposed to some trial-and-error method. Johnson mentions drug development as an example of a scientific process that, with suitable simulation techniques, could be made drastically more efficient[2].

#### **1.2** Quantum simulation: electronic systems

Attention will now be given to the more narrowed-down topic of quantum simulation, which in the field of condensed matter can currently be done in a variety of ways. To provide the reader with a representative overview, the three most renowned will be mentioned briefly, after which the last is explained in full detail.

The first strategy involves photonics, where single photons are being controlled and made to interact with one another to simulate quantum systems[4]. As an elegant example stated by Aspuru-Guzik, quantum aspects of the hydrogen molecule were simulated by two entangled photons. Other applications involve particle statistics and quantum walks. The second form of quantum simulation yet available is the research of ultracold atoms in an optical lattice. By letting several laser beams interfere, a fully tuneable lattice can be created, in which atoms can be trapped at low temperatures because of their polarizability. It is reported that this way many-body quantum systems can be investigated thoroughly, even enabling taking 'snapshots' of the system[5]. To extend the trend of controlling single nanometer-scale particles, the third option is the simulation of electronic systems using the confinement of electrons in lattices. This is the main focus of this thesis.

The foundation of this field was laid in 1993, when Eigler reported the successful creation of a quantum corral: a closed loop of atoms of arbitrary shape positioned on a surface[6]. In this case a ring consisting of 48 Fe adatoms was created on a Cu(111) surface, a transition metal with electrons on its surfaces (surface states). When comparing the electron eigenvalues and eigenfunctions within the corral to those of a two dimensional circular, closed box, great similarities were found. This led to the conclusion that the corral simulated a closed box, confining electrons inside.

This conclusion opened up a wide variety of possibilities. If these artificial boxes could be connected to each other, each of them confining electrons, a two dimensional lattice could be built, the centre of these 'boxes' functioning as an artificial lattice site. This was done successfully for multiple configurations, the first of which was molecular graphene by Manoharan<sup>[7]</sup>. This artificial lattice was built with CO molecules on a Cu(111)surface, which has a hexagonal symmetry, making it very suitable for graphene's honeycomb structure. Since CO molecules act as repulsive scatterers, and the centre of a 'box' functions as the lattice site, the CO molecules had to be positioned as the anti-lattice in order to simulate graphene. However, the hexagonal symmetry of Cu(111) does not restrict the building of artificial lattices to those with sixfold rotational symmetry only. An elegant and more recent realisation of the same principle is the creation of a Lieb lattice on a similar surface, again with CO molecules [8]. The Lieb lattice is a square depleted lattice with fourfold rotational symmetry, the general form of which is shown in Fig. 2. Building and imaging of these structures can be done with a scanning tunneling microscope (STM); images of both the corral and the Lieb lattice can be seen in Fig. 3.



Figure 2: Lieb lattice. Schematic image of the Lieb lattice, where the red and blue dots represent the lattice sites. The coloring corresponds to the amount of nearest neighbours a site has. The smaller black dots show the positioning of the CO molecules, which form an anti-lattice, and can be seen in more detail in Fig. 3b[8].

In recent years, the scientific community has shown a strong interest in the creation of artificial lattices such as the examples given above. Why is this the case? What are the benefits?

Mainly, the ability to create an electron lattice with a geometry completely of ones own choice further enables research into very specific material properties. To remain with the previous examples, both the Lieb lattice and graphene are known to have a Dirac cone[9]. The band structure of a material is a description of the energies that electrons within the material are allowed to have; a Dirac cone is a cone-like shape in such a band structure. It is known that such a shape can give rise to peculiarities, such as massless behaviour of charge carriers. Researching such a phenomenon is facilitated by the option of creating the lattice geometry in question. One might for example create the same structure multiple times while varying one parameter, and then compare the results as a function of this. Some other examples of interesting systems that are now more accessible include superconductors and, relevant exactly at the time of writing, fractal geometries[10].

Another system that can be investigated using this kind of electronic systems, is a topological insulator. Here the material acts as an insulator in the bulk (i.e. there exists a large enough gap between filled and unfilled bands) but as a conductor on the surface. These surface states are the result of some topological order, and are protected by symmetries in the system. These material properties are especially interesting for quantum computing purposes, and may turn out to be a valuable aid for progress in that field[11].



Figure 3: STM images of artificial electronic systems. (a) Circular quantum corral, consisting of 48 Fe adatoms, in which confinement of the surface electrons can be seen[6]. (b) Lieb lattice, in which the black spots mark the positions of the CO molecules that form the anti-lattice. The red and blue dots indicate the Lieb lattice sites, with the color corresponding to those in Fig. 2[8].

#### 1.2.1 Thesis structure

With this motivation in mind, elementary artificial electronic systems are investigated in this thesis. This is mostly done in a theoretical way, i.e. by digitally computing systems of interest. How this is generally accomplished, and how these computations can be related to experimental results, is discussed in the upcoming two chapters. Thereafter basic background knowledge of electronic systems is presented, on which chapter five will build: there the developed framework will be applied to a theoretical case study. In chapter six, finally, two systems will be investigated that have experimentally been realised as well, enabling a direct comparison between theory and experiment.<sup>1</sup> It is hoped that conclusions drawn from these efforts can deepen our understanding of the matter, and can be of aid in further research in the field.

Lastly, some confusion might be lurking about the terminology of the set-up, so to summarise: one can build a system of interest in which electrons are confined by surface structures. This can be used to (analogously) simulate another system, for example a lattice. However, information about this system is then gathered by modelling it in a computing programme, which in itself can be seen as a (digital) simulation of the built (analogue) one. To avoid unnecessary complexity, from now on the experimental system will be denoted by words linked to 'simulation', and the act of theoretically gathering information about this system by 'computing' and 'modelling'.

<sup>&</sup>lt;sup>1</sup> The experimental set-up is equivalent to that of the Lieb lattice construction, so with CO molecules on a Cu(111) surface.

# 2 Characterising surface structures experimentally

In this thesis artificial lattices are mostly investigated in a theoretical way. The question is, then: what do we wish to compute? Since ultimately the aim is to gather information about experimentally realisable systems, it would make sense to calculate results that can be measured experimentally. This enables a direct comparison between the two. For this reason this chapter deals with the experimental side of the quantum simulation. If we know which experimental results we can generate, we can determine what we are looking for theoretically. All the results that can be generated from experiments in this field are acquired with a scanning tunneling microscope (STM). As an STM measures the local density of states (LDOS) of a system, this concept will be discussed first, before moving on to further investigating the principles behind this technique.

#### 2.1 Density of states (DOS)

The concept of DOS is used widely throughout the field of condensed-matter physics. An electron in a material can generally be described by certain physical characteristics, such as wavenumber (**k**) and spin. However, the values of these that the electron can take are restricted by rules depending on the system. Each set of these values is referred to as a state and results in a certain energy. Since nature always strives to minimize the energy, the states are occupied from lowest to highest energy; the occupied state with the highest energy is referred to as the Fermi energy. Now, the DOS is the number of allowed states at an energy interval  $d\epsilon$ . Since it is a density, integrating it over all energies returns the total number of states. The DOS is mathematically defined as

$$D(\epsilon) = \frac{1}{(2\pi)^d} \int d\mathbf{k} \,\delta(\epsilon - E(\mathbf{k})),\tag{1}$$

where d is the dimensionality of the system (applying to **k** as well) and  $E(\mathbf{k})$  is energy as function of the wavenumber (also called the dispersion relation)[12].

The local density of states (LDOS) is a variation on this idea, and it incorporates the wave function corresponding to each energy into the definition

$$D(x, y, \epsilon) = \sum_{i} |\psi_i(x, y)|^2 \,\delta(\epsilon - E_i).$$
<sup>(2)</sup>

The definition here is given in 2D, because the systems of interest considered later in this thesis are as well. Note that the sum (instead of an integral) corresponds to the discrete eigenvalues (instead of a dispersion relation). Moreover, by including the squared modulus of the wave function, i.e. the probability density, the states available are weighted over space.

#### 2.2 Scanning tunnelling microscope (STM)

As the name suggests, an STM is a device that uses the concept of tunnelling to gather information about a surface. Tunnelling is a quantum mechanical property of subatomic particles, meaning that they have a non-zero probability of passing through a finite potential barrier. In contrast, this is fully impossible in classical mechanics, as illustrated in Fig. 4. In an STM, the surface acts as the first electrode of the tunnelling junction, and a scanning tip above the surface as the second [14]. A vacuum is created in between the two, acting as the barrier through which the electrons can tunnel. By applying a small bias voltage V, a tunnelling current is created that can be measured in the tip. The direction of the current depends on the bias applied: for a positive bias, the electrons tunnel from the tip into the surface and vice versa.

An important restriction on the tunnelling is that the electrons can only tunnel into their own state, meaning that this state has to be unoccupied on the other side of the junction. The voltage bias excites the highest-energy electrons first (those close to the Fermi energy), meaning that this restriction directly relates the tunnelling current to



Figure 4: Particle in a potential. Schematic image of a 'particle' under influence of a finite potential. In classical mechanics, the indicated turning points would be the boundaries of the bound state. In quantum mechanics, however, the image represents a scattering state, because the particle has a non-zero probability of tunnelling through the hill on the left, out of the local and into the global minimum.[13].

the LDOS close (within  $e \times V$ ) to the Fermi energy. For a positive bias, we measure the unoccupied states just above the Fermi energy being tunnelled into from the tip; for a negative bias, we measure the occupied states just under the Fermi energy tunnelling into the tip.

Besides the LDOS, the tunnelling current also depends on the height of the tip with respect to the surface, and of the bias applied. If both are kept constant, the tunnelling current is given by

$$I = I_0 \int_{-eV}^0 D(x, y, \epsilon) \, d\epsilon, \tag{3}$$

where  $I_0$  is a constant including the height, V the applied bias and  $D(x, y, \epsilon)$  the LDOS as defined in eq. 2[15]. Since the energy interval over which the LDOS is integrated fully depends on the applied bias V, we have that

$$\frac{dI}{dV} \propto D(x, y, \epsilon), \tag{4}$$

where we have found a direct proportionality to the LDOS. Fortunately the change of current as a function of a change in bias (called the differential conductance) can be measured directly by the STM. Eq. 4 thus is a crucial feat, because it presents an accessible, quantitative way of characterising electrons on a surface. Now, as we are searching for a way to compare theory with experiment, theoretically calculating the LDOS would enable exactly that. For that we need the theoretical eigenvalues and eigenfunctions of the surface states, considering the definition of the LDOS in eq. 2. The next chapter discusses how these can be acquired. Finally, with the LDOS two different image types can be generated. The first is already shown in Fig. 3 in chapter one: the energy  $\epsilon$  is kept constant and the LDOS is shown as a function of coordinates x, y. When originating from STM data, this is usually referred to as a (dI/dV) map; when calculated one often calls it a density plot. The second type is exactly opposite, i.e. the coordinates remain fixed and the LDOS is shown as a function of energy. This is often referred to as a (dI/dV) spectrum or plot, respectively.

# **3** Acquiring and adjusting theoretical results

Continuing from last chapter, we seek to compute the LDOS of an artificial electronic system. For this we need the eigenvalues and eigenfunctions of electrons in the system, as shown in eq. 2. This chapter discusses how this can be done in general, without specifying any actual system of interest. First the mathematical definition of the system is mentioned, after which the numerical method of solving the system is elaborated (Arnoldi). In the last section some points of attention are raised that have to be taken into account, if the comparison between theory and practice is to hold. Most notably this involves the broadening of the peaks in the LDOS spectra.

#### 3.1 Modelling an electronic system

Because we are interested in the eigenvalues and eigenfunctions of electrons, what we are actually looking for are solutions to the time independent Schrödinger equation,

$$\mathcal{H}\psi_i(x,y) = \epsilon_i \psi_i(x,y)$$
$$[-\frac{\hbar^2}{2\mu} \nabla_{x,y}^2 + V(x,y)]\psi_i(x,y) = \epsilon_i \psi_i(x,y), \tag{5}$$

where  $\mathcal{H}$  is the Hamiltonian, consisting of a kinetic and potential part, and the system is taken to be 2D (corresponding to surface systems). Note that  $\mu$  here resembles the effective electron mass of  $\mu = 0.4m_e[8]$ . The surface states on Cu(111) can accurately be described by a free electron gas (i.e. with only the kinetic part of eq. 5). This means that electron-electron interaction is neglected, and that with the potential V(x, y) we only have to account for the CO molecules. The next step, then, is to choose a suitable potential for this.

In this thesis the so called 'muffin tin' potential is used, as proposed in 1937 by Slater[16]. The original paper was introducing the augmented plane wave method (APW), with which wave functions could be found within a periodic potential such as a lattice. Although a different method is applied here, the same potential is used. Its form is spherically symmetric within a sphere around the atoms or molecules, and constant outside this sphere. An adaption of this principle is

$$V(r) = \begin{cases} V_0 & |r - r_0| \le r_0 \\ 0 & |r - r_0| > r_0, \end{cases}$$
(6)

where  $r_0$  is the radius of the sphere and  $V_0$  is the height of the potential. The motivation behind this choice originates in recent experiments, where this potential matched experimental results well[8]. Moreover, its structure is relatively simple, making calculations less time-consuming. For CO molecules on a Cu(111) surface the parameters best matching experiments are found to be  $r_0 = r_{CO} = 0.3$  nm and  $V_0 = 0.9$  eV. Owing its name to this potential, the computations done in this thesis may also be referred to as muffin tin calculations.

#### 3.2 Solving the system

Now that the system is defined, the next challenge is solving eq. 5 for the eigenvalues and eigenfunctions. In this thesis this is done entirely numerical, using the computing programme *Wolfram Mathematica*. While other programmes might suffice as well, the command that is used here in particular is *NDEigensystem*, which solves linear differential equations. It is mentioned here for completeness; its structure is

$$\{\epsilon_i, \psi_i\} = \text{NDEigensystem}[\mathcal{H}(\psi)), \psi(x, y), \{b\}, n], \tag{7}$$

with

 $\epsilon_i$  and  $\psi_i$  lists of electron eigenvalues and eigenfunctions, respectively,

 $\mathcal{H}(\psi)$  the linear differential operator, the Hamiltonian in this case, as a function of  $\psi$ ,

 $\psi(x,y)$  the function to solve for,

 $\{b\}$  the boundaries of the system,

n the number of solutions wanted.

For more detailed information on options and applications of the command, the reader is referred to the *Wolfram Documentation Centre*.

Because of the central role that the command fulfils in the computations, it is worth taking a closer look at its modus operandi. By default it utilizes the eigenvalue algorithm called Arnoldi, which is iterative, to solve the equation given. It is worth noting that, in order to use this method, the Hamiltonian is discretized automatically.

Being an iterative process, the accuracy of the results depends on the number of iterations allowed. Moreover, for the Arnoldi algorithm specifically, as it turns out, the number of iterations also determines the amount of solutions that can be generated. This amount is of great influence for the examination of some systems. For example, when investigating a system of sufficient size, the iteration number simply might not be enough to generate all relevant results.

One can alter this quite easily in terms of coding, but because of its relevance, it might prove useful to study the algorithm more profoundly. In what follows, the general method will be discussed, followed by emphasis on the iteration number near the end. To not deviate too far from the actual subject of this thesis, attention will only be paid to how the algorithm works, and not on proving why it works.<sup>2</sup>

<sup>&</sup>lt;sup>2</sup>A large portion of this section owes its content specifically to Ref. [17] and Ref. [18].

#### 3.2.1 Arnoldi algorithm

The goal of the Arnoldi method is to solve an eigenvalue problem in the form of

$$\hat{A}\mathbf{x} = \lambda \mathbf{x},$$
 (8)

with  $\hat{A}$  an operator of dimension  $\mathbb{R}^{m \times m}$  whose eigenvalues and vectors are  $\lambda$  and  $\mathbf{x}$ , respectively. In this case,  $\hat{A}$  is the discretised Hamiltonian, so that  $\lambda$  corresponds to  $\epsilon$  and  $\mathbf{x}$  to  $\psi$ . Solving this problem means finding both, which can be quite cumbersome for a large and dense operator, which a discretised Hamiltonian commonly is. The Arnoldi method reduces the problem to a simpler matrix, making solving easier.

Suppose there exists some matrix Q which is the orthogonal basis of some subspace, spanned by a collection of vectors  $q_n[17]$ . Also suppose then that the eigenvector  $\mathbf{x}$  is an element of this subspace

$$\hat{Q} = (q_1, q_2, \dots q_n) \in \mathbb{R}^{m \times n},\tag{9}$$

$$\mathbf{x} \in \operatorname{span}(q_1, q_2, \dots q_n). \tag{10}$$

Now there exists a  $\mathbf{z} \in \mathbb{R}^n$  such that

$$\hat{A}\hat{Q}\mathbf{z} = \lambda\hat{Q}\mathbf{z}.\tag{11}$$

The relevance of this step becomes obvious when one uses the fact that  $\hat{Q}$  is orthogonal, so that the previous expression can be rewritten as

$$\hat{Q}^T \hat{A} \hat{Q} \mathbf{z} = \hat{Q}^T \lambda \hat{Q} \mathbf{z},$$
  
$$\hat{H}_n \mathbf{z} = \tilde{\lambda} \mathbf{z}.$$
(12)

This is a very similar expression to eq. 8, but now with a different operator  $\hat{Q}^T \hat{A} \hat{Q}$ , which we denote  $\hat{H}_n$ , and where we solve for eigenvector  $\mathbf{z}$ . It is worth noticing that if the condition in eq. 10 is only met by approximation, the new eigenvalue of interest is only an approximation of the original  $\lambda$  as well. Because of this, the new eigenvalue is denoted with a tilde, to remind the reader that from this point on it can be inexact.

The general strategy just described, of rewriting an eigenvalue problem in this way, is called the Rayleigh-Ritz procedure. Accordingly, the new solutions  $(\tilde{\lambda}, \mathbf{z})$  are called Ritz pairs. What is left now is the choice of basis  $\hat{Q}$ , which is also the strength of this entire procedure: if chosen wisely, the new problem is easier to solve than the old one. The term Arnoldi refers to this choice of  $\hat{Q}$ .

In the Arnoldi method, the so called Krylov subspace is used, denoted by  $\mathcal{K}_n$  and known to be

$$\mathcal{K}_n(\hat{A}, q_1) = \operatorname{span}(q_1, \hat{A}q_1, \hat{A}^2q_1, \dots \hat{A}^{n-1}q_1).$$
(13)

Why exactly this subspace is chosen, and whether or not it fulfils the criteria of the Rayleigh-Ritz procedure, would require further elaboration, which is considered beyond the scope of this thesis. However, in Fig. 5 the algorithm used to construct such a subspace is shown

(where the  $q_i$ 's mentioned before have been renamed  $v_i$ 's). The power of the Arnoldi method lies within this algorithm. The vectors  $v_i$  each consists of all the elements  $h_{ij}$ ; in step (4-8) a summation over i until j + 1 can be seen. However, this means that for each new value of j, the summation over i is one element longer and thus  $v_i$  is one element longer. For this reason, subspace  $\hat{Q}$  is always an upper Hessenberg matrix, which has multiple advantages.<sup>3</sup> Firstly, it requires less memory to store on a computer than a denser matrix [19]. Most importantly, it makes the new operator of interest,  $H_n$  (eq. 12), much easier to calculate. This process of enlarging the matrix with each separate iteration is shown schematically in Fig. 6. This feature of the Arnoldi method is what makes the number of iterations so relevant: it is equal to the dimension n of  $\hat{H}_n$ . The solutions of the eigenvalue problem, which are the n Ritz pairs, are more often than not merely approximations of the original solutions (of eq. 8). Some of the Ritz eigenvalues converge to only one original eigenvalue, giving rise to the fact that typically only a small fraction of the n Ritz eigenvalues are distinct and useful. This means that to find a number of a eigenvalues, the amount of iterations n needs to be much higher than a. Should n be too small, either some original eigenvalues could be missing, or the convergence of Ritz values is not strong enough to find an accurate original value. This last problem is noted by Mathematica when the maximum amount of iterations is reached. "... without convergence to the specified tolerance, but the current best computed values have been returned.' Controlling the allowed number of iterations thus directly influences the accuracy of the results.



Figure 5: Arnoldi algorithm. A detailed display of all eleven steps of the Arnoldi algorithm. Here the vectors  $q_i$ , as mentioned in the rest of the text, have been renamed  $v_j$ .[17].

Figure 6: Role of iterations. Schematic representation of the Arnoldi algorithm, in which the relation between iteration and the operator  $\hat{H}_n$  has been made explicit[18].

<sup>&</sup>lt;sup>3</sup>A Hessenberg matrix is a square matrix which has entry 0 for all elements above the first superdiagonal or below the first subdiagonal. 'Upper' here refers to the former.

#### **3.3** Caveats

Before the methods described so far can be performed, this final section covers some issues that have to be taken into account when comparing theory with experiment. Some are easy to gloss over, and can have a tremendous impact on the results.

#### 3.3.1 Units

Considering the Schrödinger equation (eq. 5), it is worth noting that the potential is defined in eV while the kinetic part generates results in joule. To illustrate the latter, the eigenvalues of an electron in an empty one dimensional box with length L, so without a potential, are given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2},\tag{14}$$

where  $[\hbar] = Js$ , [m] = kg and [L] = m. After cancelling terms in the fraction, one finds [E] = J, which is the case for other box types as well.

As a consequence the potential and kinetic part have to be adjusted to each other. Here the choice is made to add a conversion factor to the kinetic part, ensuring always [E] = eV. Moreover, a second conversion factor is used so that the box dimensions  $L_i$  can be given in nm without changing the results. Combined these two factors together are calculated to be  $c = 6.2415096 \times 10^{36}$ .

#### 3.3.2 System size & boundary conditions

One of the parameters that *NDEigensystem* requires in order to be operational, is the system size, i.e. where the boundaries are located. Closely connected to this are the boundary conditions: what happens with the wave function at the defined boundaries? Generally, there are three possibilities:  $\psi$  vanishes (closed or Dirichlet conditions), the derivative  $\psi'$  vanishes (open or Neumann conditions), or the wave function acts periodically (Born-von Karmann conditions). If nothing is specified, the command uses the second option by default.

Even though the necessity of these parameters is obvious from a theoretical point of view, in experimental reality the system has no boundaries. The size of the built structures is in the order of nanometers, while the entire copper surface typically has dimensions in millimeter range. Because of these proportions, the best way to model an experimental system would be by an infinite system size. Unfortunately simulations do not allow for this, and thus it is advised to define the system to be as large as the algorithm can cope with, without making the evaluation time completely unfeasible. Note that because of this mere approximation, there will almost certainly be an error in the theoretical results with respect to the experimental ones, due to unintended boundary effects.

Concerning the boundary conditions, one might opt for open conditions. After all, if the system size is somewhat appropriate for resembling experiment, the influence of the structure on the wavefunction is expected to have mostly decayed at the boundaries. This means we may expect  $\psi$  to be at least constant.

#### 3.3.3 Broadening

Given the definition of the LDOS (eq. 2), which has a delta function, one would expect the spectra measured by an STM to be a collection of vertical lines at allowed energies. However this does not turn out to be the case.

Further research has shown that the allowed energies are not as discrete as one would theoretically presume. As stated by Manoharan, the rigid distinction between surface and bulk states is only applicable without disorder in the crystal[7]. In the presence of disorder such as adatoms, there is a non-zero rate at which the surface electrons decay into bulk states via scattering. Upon decaying a surface state gains self energy, an energy contribution due to changes in its environment. Accordingly the allowed energies are not just the 'bare' ones denoted  $E_i$ , but also those wth this self energy contribution. This causes the peaks in the LDOS spectra to be broadened.

Since the extra energy is due to a decay, Fermi's golden rule can be used to calculate the decay rate. From this the linewidth or broadening  $\Gamma$  can be calculated as

$$\Gamma = 2\frac{V_0}{W} \left(\frac{a}{a_{Cu}}\right)^2,\tag{15}$$

where  $V_0$  is the CO potential height, W the copper bandwidth and  $a_{(Cu)}$  the CO (copper) lattice constant. It is in favor of relevance that the complete derivation is not given here explicitly, and that the reader is referred to the appendices of Manoharan and of the Lieb lattice for more detailed information[7, 8]. Nevertheless it is worth noting that the approximations made to arrive at eq. 15 have been made specifically for a system of CO molecules on a Cu(111) surface. This makes the formula relevant for this thesis but not applicable in general.

To adjust the calculated LDOS plots to the experimental spectra, the calculated  $\Gamma$  can subsequently be used to alter the LDOS definition. This way broadening is included. More concretely, the new function becomes

$$D(x, y, \epsilon) = \sum_{i} |\psi_i(x, y)|^2 \frac{\Gamma}{(\epsilon - E_i)^2 + \left(\frac{\Gamma}{2}\right)^2}.$$
(16)

For the Cu(111)/CO system  $\Gamma$  is reported to be 80 meV[8], using the parameters of a = 2.66 nm,  $a_{Cu} = 0.256$  and  $W \approx 1$  eV. However, eq. 15 is not the same in Ref. [7] as in Ref. [8]. With neither of them we have been able to reproduce this result successfully. Further investigation remains necessary to clear up confusing surrounding this topic, though this is considered beyond the scope of this thesis.

## 4 The fundamentals of electronic systems

In the previous two chapters, both the experimental and theoretical toolbox for researching artificial systems were developed. Moreover, they have been adjusted to each other, meaning the entire framework is now applicable to systems of interest. To re-emphasize, these systems involve electrons confined to certain structures (such as the quantum corral). For clarity, such a structure might be referred to as an artificial atom. Because an electron is confined in it, theoretically such an artificial atom can very well be described by an empty box with closed boundary conditions, or an infinitely deep well. It might prove insightful to first gain familiarity with these 'particle in a box' scenarios, so that we know what electron behaviour we can expect from the artificial atoms. This is done in the first section.

After establishing the foundations on these single sites, the focus is shifted to combining them into more advanced systems such as lattices. However, the behaviour of electrons in lattices is much more complex, as indicated by the existence of different models to describe them. In this thesis the tight binding model is used. This model will be discussed in the second part of this chapter.

#### 4.1 Particle in a box

Generally one of the least complicated quantum systems is the particle in a box. Starting with the simplest case of 1D, for a box with length L the system is defined by the Schrödinger equation (eq. 5), with the potential chosen to be

$$V(x) = \begin{cases} 0 & 0 < x < L\\ \infty & \text{otherwise.} \end{cases}$$
(17)

This ensures that the wave function  $\psi$  only exists within the box, and vanishes at the edges and outside of it. Consequently, within the box only the kinetic part of the equation has to be solved, which can be done analytically. One finds that the solutions of the eigenfunctions are

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right). \tag{18}$$

The corresponding eigenvalues are mentioned earlier in eq. 14. Given the theoretical toolbox presented in the previous chapter, these eigenfunctions can also be found numerically, of which the first three are plotted in Fig. 7. The figure matches eq. 18 nicely. Considering the structure of the solutions, a distinct feature is the number of nodes, which, if the points at the boundaries are not taken into account, equals n - 1.

Extending to 2D, options are now available concerning the shape of the box. One might think of a rectangle, as a variation on the square, but also the triangle, circle and hexagon can be chosen. It is at this point that not all shapes are analytically accessible any more, and those that are by no means have to be trivial, as the triangular case clearly illustrates[20]. However, the numerical procedure still works, and some results of this are shown in Fig. 9.



Figure 7: Eigenfunctions of the 1D box. Plot of the first three eigenfunctions of a particle in a onedimensional box with length  $L = \pi$ .

For completeness, some numerical results from 3D boxes are presented in the same figure as well. Since analytical solutions for those systems are often even more troubling, this only further illustrates the possibilities of the numerical procedure. It is worth noting that all solutions in Fig. 9 are for n = 2, and that all have one node, analogous to the 1D case. This demonstrates that the general structure of nodes in confined electrons is independent of the shape or dimensionality of the box.

Finally, the connection can be made explicit between on the one hand these theoretical cases of a particle in a box, and, on the other, the experimentally realisable artificial atoms. After all, it is the latter that caught our interest. Below, in Fig. 10, the eigenfunctions are presented of a circular box in 2D. This is followed by the corresponding eigenfunctions of an artificial atom in Fig. 11, completely based on Eigler's quantum corral<sup>[6]</sup>: 48 iron adatoms in a circle, modelled by a muffin tin potential. This potential is shown to the right in Fig. 8. Parameters such as the diameter of the ring, and of the adatoms generating the potential, are taken directly from the relevant paper. When comparing the eigenfunctions of the box and the corral, the similarities are obvious, supporting the conclusion that the corral acts as an infinite circular well.



Figure 8: Quantum corral model. Density plot of the muffin tin potential imitating Eigler's quantum corral. The white dots represent the 48 iron adatoms.



Figure 9: Eigenfunctions of varying boxes. Plots of the eigenfunctions for n = 2 of a) a 2D square box, b) a 2D triangular box, c) a 3D rectangular box, d) a 3D spherical box. The axes of the 3D contour plots represent the system boundaries; for 2D the z-axis represents the wave function amplitude. All solutions share the feature of having a single node.



Figure 10: Eigenfunctions of a circular box. Density plots of  $|\psi|^2$  of the first three solutions of a 2D circular box. It is worth noting that the middle and right solution are degenerate, and thus cannot experimentally be observed as portrayed here, but as a superposition of the two. However, the aim is merely a comparison with Fig. 11.



Figure 11: Eigenfunctions of the quantum corral. Density plots of  $|\psi|^2$  of the first three solutions of a modelling of the quantum corral. Again the middle and right solution are degenerate, but show striking similarity with 10. Closed boundary conditions were used.

#### 4.2 Tight binding model

Now that the general behaviour of electrons in single boxes has been established, it becomes interesting to study this behaviour when the boxes are combined to form a lattice. The tight binding model is frequently used for this, and is known to have a wide variety of applications throughout the field, one of which being the analysis of semiconductors[21]. The model is also closely related to quantum chemistry due to the similarities with LCAO theory.

The tight binding model can be thought of as a decomposition of the total electron wave function into a linear combination of atomic orbitals, which are wave functions corresponding to a single lattice site. In short one might write

$$\psi = \sum_{i}^{n} \sum_{j}^{m} c_{i,j} \phi_{i,j}, \qquad (19)$$

where  $\psi$  is the total wave function,  $\phi_{i,j}$  an atomic orbital, *n* the number of lattice sites, *m* the number of orbitals per site, and  $c_{i,j}$  are coefficients[22]. To avoid unnecessary complexity, in the following it is assumed that one orbital per site is taken into account. The key, then, is that interaction between all these sites is parametrized using integrals. Note that 'interaction' here refers to that between a single electron and the surrounding nuclei; and important part of the model is the neglect of electron-electron interaction. As stated before in section 3.1, copper surface states can be accurately described by a free electron gas, also neglecting electron-electron interaction. This makes the tight binding model particularly suited for our systems.

The expectation value of energy E is given by

$$E = \frac{\int \psi^{\dagger} \hat{H} \psi \, d\mathbf{r}}{\int \psi^{\dagger} \psi \, d\mathbf{r}},\tag{20}$$

with  $\hat{H}$  the Hamiltonian of the system, and where the denominator functions as normalization. Plugging in eq. 19 results in a sum of a variety of integrals, that can be renamed using

$$H_{i,j} = \int \phi_i \hat{H} \phi_j \, d\mathbf{r},\tag{21}$$

$$S_{i,j} = \int \phi_i \phi_j \, d\mathbf{r},\tag{22}$$

which are known as interaction integrals and overlap integrals, respectively. For  $i \neq j$ , the former is a measure of the energy shift of an electron due to the potential on neighbouring atoms. This is also referred to as coupling. The overlap integral contains no Hamiltonian and is thus a measure of the physical overlap between orbitals at different sites. For i = j, eq. 21 provides the on-site energy, while  $S_{i,i} = 1$ , because orbitals on the same atom are orthonormal.

After some algebra, combining eq. 20-22 gives a system of linear equations

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = \mathbf{0},$$
(23)

which can be solved for E using the determinant of the left matrix. Now, the true power of this method lies within this parametrization[22]. Some integrals can be calculated explicitly, some cannot, all depending on the system, but for a particular Hamiltonian and lattice constant, each integral is merely a constant. In line with this, one might set some of them to zero by approximation. Examples of this are neglecting the overlap between different sites, or only accounting for nearest-neighbour interaction. Accordingly, the left matrix can be reduced to a much simpler form, facilitating the calculation of eigenvalues and energy bands. In the next chapters, this model is used to make predictions on the eigenvalues of the systems in question.

## 5 Theoretical case study: splitting a hexagonal dimer

In this chapter we move on from single artificial atoms, and start combining two of them into a single system: a dimer of hexagons. However, it is not the complete dimer that we are interest in. Instead, it is split into two hexagonal monomers, which are gradually separated further from each other. A snapshot from this separation process, taken at an arbitrary distance, is shown in Fig. 12, together with the dimer. The motivation behind this particular set-up can be found in the tight binding model, which will be discussed first. After this the results will be presented and discussed.



Figure 12: Varying the hexagonal dimer. Contour plots of the system of interest in its initial state and an arbitrary excited state, respectively.

#### 5.1 Tight binding motivation

In the dimer, the two artificial atoms are directly connected to each other and are therefore expected to be coupled. Although there are only two, they can still be considered as a lattice with two sites, and thus eq. 23 is still applicable. In this case, it reduces to

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathbf{0}.$$
 (24)

In literature it is common to make a change of nomenclature at this point, renaming the onsite energy  $H_{11} = H_{22} = E_0$ , referring to the energy at which an electron is confined in a single hexagonal monomer. Furthermore, the interaction integral is often denoted  $H_{12} = H_{21} = t$ (notice the symmetry), where t is referred to as the hopping parameter. Orbital overlap between different sites (eq. 22) is neglected, because in this set-up the sites are separated, causing the overlap to decay quickly. All together, eq. 24 then becomes

$$\begin{pmatrix} E_0 - E & t \\ t & E_0 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathbf{0}.$$
 (25)

Solving for E results in

$$E_{\pm} = E_0 \pm t. \tag{26}$$

In other words, the energies at which an electron is confined within the dimer are shifted by a contribution of t with respect to the monomer. This can be shown when comparing monomer and dimer LDOS plots: when taken at the centre of a monomer, the plot would show a peak at the on-site energy. In contrast, when taken at one of the centres of the dimer, two peaks  $E_{\pm}$  should be visible with a difference 2t between them. Both these prediction based on the tight binding model can accurately be seen in Fig. 13.<sup>4</sup> The extra, smaller peaks are due to boundary effects, as mentioned in section 3.3.2.<sup>5</sup>



Figure 13: Monomer vs. dimer. LDOS plots taken in the centre of a hexagonal monomer and the centre of the left hexagon in a dimer, respectively. It can be seen that the  $E_{\pm}$  are nicely shifted around  $E_0 = 0.209$ , as predicted by the tight binding model.

Now, as the dimer is split into slowly separating monomers, the distance between the sites logically increases, thereby effecting the coupling. More specifically, there should be a finite distance at which the sites uncouple completely. In terms of the on-site energies, this would mean t = 0, and both sites regain the confinement energy of  $E = E_0$ . This corresponds to the transition of Fig. 13b into Fig. 13a. Concluding, the goal is to find this distance of uncoupling, and to research the coupling 2t as a function of the distance between the monomers. The results of this are presented in the next section.

#### 5.2 Results and discussion

In Fig. 14 2t is shown as a function of distance d, taken from centre to centre. Each hexagon has a circumradius of 1 nm (the distance from centre to the middle of a CO molecule). The distance d was varied between  $1.4\sqrt{3}$  and  $12\sqrt{3}$  with steps of  $0.05\sqrt{3}$ , and at each distance the LDOS was calculated at the centre of the left hexagon. Subsequently, the values for 2t were extracted from the energy difference between the two highes tLDOS peaks in the proximity of 0.2 eV ( $E_0$ ). The factor of  $\sqrt{3}$  in the distance variation was chosen because this is the centre-centre distance of the connected dimer. The factor 1.4 was chosen as starting point

 $<sup>^4{\</sup>rm The}$  parameters used in computing these LDOS graphs can be found in Appendix A, along with other figures.

<sup>&</sup>lt;sup>5</sup>As will be discussed in section 5.3, an unrealistically small system size influenced the results.

so that the hexagons were fully separate without any overlap between the CO molecules; the factor of 12 as ending point was chosen arbitrarily.



Figure 14: Hopping parameter as function of distance. Plot of the hopping parameter 2t, signifying the coupling between the two sites, as a function of their distance d. The distance was varied with steps of  $0.05\sqrt{3}$ .

Unfortunately, no clear relation between the coupling and the distance seems to be found. However, two features of the plot stand out distinctly, and finding an explanation for those might still be very insightful. The first is the oscillatory character of the data, most clearly seen between d = 4 and d = 7; secondly there is the abrupt jump around d = 9. Both features will be discussed below.

#### 5.2.1 Oscillations

In Fig. 15 LDOS graphs are shown of distances corresponding to a local minimum and maximum. The trend shown there actually manifests itself throughout the dataset: minima show a more dimer-like structure, whereas maxima seem to better resemble a trimer. Consequently, the relation between 2t and d is not stable, because not always the same peaks are chosen to calculate 2t. But then where does this trimer come from? When disconnecting the hexagons, a rectangular gap opens up in between the two, bounded by the vertices on the sides of the hexagons. This rectangular area also starts to function as a site, with electrons being confined there. The eigenvalues of a 2D rectangular box are given by

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2mL_x^2} n_x^2 + \frac{\hbar^2 \pi^2}{2mL_y^2} n_y^2, \tag{27}$$

where in this case  $L_x = d$ . Upon increasing the distance, the first term decreases and each eigenvalue lowers in energy. This means that those that are already in the energy frame (0.1-0.3 eV) gradually dissipate, while others 'move into' the frame. Thus peaks seem to come and go. At first a coming peak has a low amplitude, because its energy is too high for the dimer sites to couple with. Then as this peak approaches  $E_0$ , the rectangle actually starts to couple with the hexagons, resulting in trimer behaviour.



Figure 15: Trimer configuration. LDOS plots respectively taken at d = 5.5, a local minimum in Fig. 14, and d = 6.3, a local maximum. The latter seems to resemble a trimer.

#### 5.2.2 Discontinuity

The discontinuity in Fig. 14 is located at d = 8.75. To investigate this occurence, Fig. 16 shows a density plot of the eigenfunction corresponding to the highest peaks of the LDOS plot at d = 8.75 and d = 8.8. Comparison shows that the overall form of the wave function in between the hexagons changes shape: the 'envelope' around the yellow area in the middle is doubled. Upon generating similar plots for d < 8.75 and d > 8.8, it can be seen that the 'envelope' shapes in those ranges are also 'single' and 'double', respectively, matching Fig. 16. Thus this transition only happens at this distance, making it likely that this is the cause of the jump in Fig. 14. As a final argument, when extending the range of d beyond what is shown in Fig. 14, another jump is seen, showing a similar change in density plots ('double' to 'triple'). The only question, then, is what this change in 'envelope' means.

Reverting to the trimer hypothesis with the rectangular box in the middle, this could also explain the sudden shift here. Consider again the general structure of eigenfunctions of a particle in a box, as discussed in chapter four. There it was stated that there was a relation between the quantum number of the solution,  $n_i$ , and the number of nodes. Applying this to Fig. 16, not counting the nodes near the edges (close to the the hexagons), the 'envelope' seems to shift from zero nodes to one. This could very well correspond to an increase in  $n_y$  in eq. 27. After all, lower energy eigenfunctions come first, and generally here  $L_x > L_y$ . This means that it is more favourable to increase  $n_x$ , which apparently seems to happen until d = 8.75. Then for the first time it becomes energetically favourable to increase  $n_y$ , which is done, followed again by the raising of  $n_x$  until the position of the next jump.

Apparently this change in eigenfunction structure has influence on the LDOS spectra as well. Because of this sudden raise in energy, the relevant peaks are packed together more closely, resulting in a jump downwards in Fig. 14.



Figure 16: Eigenfunctions at the discontinuity. Density plots of eigenfunctions corresponding to the two highest peaks in the LDOS graphs of d = 8.75 and d = 8.8, respectively. The two bright spots on the sides resemble the hexagons. Above each plot the eigenvalue is shown in eV.

#### 5.3 Boundary effects

So far it can be concluded that finding a clear relation between the coupling of the sites and the distance between them, is obstructed by the formation of a third site in between the two. While this is true, it must be said that the size of the system has great influence on the results as well. When it comes to the trimer, a smaller system means that electrons are more easily confined to the area in between the hexagons, thereby amplifying the effects. To illustrate, all results in this chapter are gathered with a rather small system size:  $-2 < x < d\sqrt{3} + 2$ , -2 < y < 2. These boundaries were chosen such that the distance between boundary and hexagon would always be equal, but perhaps not enough attention was paid to the absolute size. It would be very interesting to repeat the experiment with a uniform, much larger system size, and compare the results.

In addition, the type of boundaries plays an important role as well. Thus far all results are gathered with open boundaries. However, while closer to experimental reality, this does allow for more solutions, as a vanishing wave function on the edges is a much sterner restriction. In general, these extra solutions tend to obscure the computations, especially with a relatively small system size. This feat is illustrated by the smaller peaks in Fig. 13. Density plots from their corresponding eigenfunctions show that they represent no real confinement, and they disappear when the boundary conditions are changed to closed. To demonstrate this effect, Fig. 17 displays the same 2t over d calculation as performed in Fig. 14, but with closed boundary conditions. Clearly the same oscillatory behaviour can be recognized, only much cleaner.



Figure 17: Hopping parameter with closed boundaries. Coupling 2t as a function of the distance d between two hexagons, with the boundary conditions chosen to be closed. The same oscillatory moves is seen as before, only cleaner this time.

Finally, exactly the same calculation was carried out once more (with closed boundary conditions), but now with only one hexagon. This was done to verify to extent to which the background effects of the box influenced the features in Fig. 14. The results are shown in Fig. 18. In comparison with Fig. 17, again the same characteristics are seen, supporting the first claim of this section, i.e. that the data in Fig. 14 and 17 are largely influenced by boundary system effects.



Figure 18: Hopping parameter for a monomer. Coupling 2t as a function of the distance d between two hexagons, with the boundary conditions chosen to be closed. However, this time only one site was used.

# 6 Comparing theory and experiment: monomers and dimers

In this chapter both theoretical and experimental results will be presented and compared, to see how well they correspond. The first system of interest is a hexagonal monomer, of which a relation is sought between the on-site energy and the confinement area. For this the 2D hexagonal box is used to make a prediction. Secondly attention is paid to the hexagonal dimer again, this time investigating how the coupling from tight binding is effected by changing the size and barrier strength. All experimental results are reported simultaneously by S. Borman in his own thesis.[23]

In order to justly compare theory with experiment, two minor adjustments are made with respect to previously shown results. The first concerns the calculated eigenvalues: they are calibrated with respect to the Fermi energy of copper. Recalling the principles of the STM from chapter two, the surface states that can be researched lie in close proximity to the Fermi energy. Furthermore, in the experimental dI/dV-spectra the x-axis resembles the applied bias V, of which V = 0 corresponds to the Fermi energy. For a clean comparison, it would thus make sense to ensure that in theoretical LDOS plots E = 0 corresponds to the Fermi energy as well. More concretely, from now on

$$E_i = \epsilon_i - E_f \tag{28}$$

with  $E_i$  the new energies and  $E_f = 0.445$  eV for Cu(111)[8].

Secondly, the geometry of Cu(111) needs to be considered. Since CO molecules can only be placed directly on Cu atoms, the nearest neighbour distance of copper applies to CO as well. This means that a = 0.256 nm is the minimum step size for varying structure lengths.

#### 6.1 On-site energy of a hexagonal monomer

In chapter four the link was established between an artificial atom and a particle in a box. Utilizing this once more, predictions can be made about the former by investigating the latter. In this spirit a plot was made of the 'on-site energy' of a 2D hexagonal box, which was chosen to be the first eigenvalue, as a function of the inversely squared circumradius  $(1/R^2)$ . The plot can be seen in Fig. 19, displaying an evident linearity, which should, then, also be visible in the results of the artificial atom.

In an effort to produce such results, monomers were modelled with a circumradius varying between R = 4a and R = 10a, with a the copper lattice constant. For each



Figure 19: Box eigenvalue over inversed area. The first eigenvalue of a 2D hexagonal box, plotted as a function of the inversely squared circumradius.

size an LDOS plot was made from the centre of the site, of which the first clear peak was taken to indicate the on-site energy. The area of the monomer was calculated as

$$A = \frac{3\sqrt{3}}{2}R^2 - 2\pi r^2, \tag{29}$$

with r = 0.3 nm the radius of the CO molecules. As such the first term gives the strict area of a regular hexagon with circumradius R, while the second term compensates for the area occupied by the six CO molecules. As a point of notice, this is a different quantity than shown on the x-axis in Fig. 19. However, this does not negate the prediction of linearity, since the differences merely act as a transformation by constants. At most this would only change the position and scaling of the function.

Experimentally, five different CO structures were built. Two completely match the theoretical dataset, with R = 4a and R = 5a. For the other three, R was (again) varied between 4a and 6a, but blockers were added. These are extra CO molecules around the initial structure that increase the confinement. Schematic images of the structures are shown in Fig. 20. On the theoretical side of the research, the choice was made at first not to include blockers, because they alter the shape of the site (as Fig. 20 shows). However, in experiment the blockers significantly increased the quality of the results (e.g. a more distinct peak in de LDOS because of better confinement), which was why they were chosen after all.<sup>6</sup>



Figure 20: Structures with blockers. Schematic representations of the experimentally built structures, making use of blockers to enhance the confinement within the hexagons. The red sites indicate the CO molecules. The size of each monomer is shown in the top left corners, as values of R.

Both the experimental and theoretical datasets are plotted and fitted in Fig. 21, which will be discussed here. First of all, the theoretical data accommodates the linear fit nicely, thereby matching the prediction from Fig. 19. It is worth noting, however, that the point most to the left (R = 10a) was omitted when finding the fit. At that point the second confinement energy was taken instead of the first, making it incompatible with the other data. The experimental results seem to constitute a linear function as well, although this is harder to say for a set of only five data points.

Concerning the difference between theory and experiment, this may not be as large as a first glance on Fig. 21 might indicate. Of both datasets two pairs of points are directly comparable, indicated in the figure by the black arrows. They give rise to two remarks. Firstly, even though their structures are the same, in the figure they do not have the same area. This is due to rounding. The lattice constant is taken to be a = 0.256 nm in the theoretical models (just as in the calculations for the Lieb lattice, see Ref. [8]), while for calculating the area of the experimental results, a = 0.255 was used. In reality the lattice constant lies somewhere

<sup>&</sup>lt;sup>6</sup>The used area values can be found in Appendix B.

in between. Secondly, for both pairs the difference between the experimental and theoretical point is almost the same: -0.0302 eV for the left pair vs -0.0297 eV for the right. This would indicate some systematic error between theory and practice, which is not wholly unexpected. All theoretical calculations are simply models of a perfect reality, which never truly exists. Experimental uncertainties could be, among others, the presence of impurities in the sample, the quality of the STM tip, calibrations in the measuring system or background vibrations. Moreover, theoretically the boundary effects remain, although it seems unlikely that these play a significant role here. When varying the system size, it was noted that an increase in size (i.e. better approaching reality) led to a decrease in on-site energy, thus only enlarging the difference with experiment.



Figure 21: Monomer on-site energy over inversed area. Theoretical (blue) and experimental (red) data of on-site energies of a hexagonal artificial atom, as a function of the inversed area. The points with the highest on-site energy (situated most right) correspond to R = 4a, with the on-site energy decreasing as R increases. The blue point on the left does not match this trend, because it shows the second confinement energy instead of the first. The two black arrows mark the two pairs from which theory and experiment are directly comparable: the blue one it is pointing to, and the red one immediately above it.

#### 6.2 Tight binding behaviour of different hexagonal dimers

Once more the hexagonal dimer is the subject of inquiry. Where in last chapter the 'barrier' between the two sites was manipulated by altering the distance, this time it is done by adding or removing a CO in between the sites. Concretely, three different barriers (denoted low, normal and high) are used for two different site sizes (R = 4a and R = 5a). In all structures blockers are present as well, both in theory and in experiment; the structures are shown schematically in Fig. 22.

Recalling the definition of the hopping parameter,

$$t = H_{1,2} = H_{2,1} = \int \phi_1 \hat{H} \phi_2 \, d\mathbf{r},\tag{30}$$

a higher barrier generally means the orbitals  $\phi_i$  will be decayed sooner. As a result, each site is less influenced by the other, i.e. the coupling decreases. This feature would be visible in LDOS spectra by a greater separation between the two dominant peaks. Consequently, one would expect the opposite for a lower barrier. Fig. 23 shows both the theoretical and experimental results on this, and will now be discussed in detail.

First and foremost, the theoretical results match the experimental ones nicely. Especially Fig. 23b and 23d look very much alike. Fig. 23a and 23c show some differences, in particular the clarity of the peaks. This can probably be attributed to the quality of the STM tip. While conducting the experiments, it was apparently already clear that the preparing procedure for the tip yielded a much better result for the measurements in Fig. 23b than in 23a. Differences aside, Fig. 23a and 23c still display the same general trends (as discussed further below). All together these results are a strong argument that the theoretical framework, as developed throughout this thesis, describes reality well.

Most notably, in all four spectra it is shown that as the barrier increases, the distance between the two peaks of the spectrum decreases. In three of the four spectra ((b)-(d)), the coupling for the high barrier even seems to be absent. All this directly matches the tight binding predictions described in the beginning of this section.

It is also shown that the measurements on the larger dimers, i.e. those with a larger area, all yield generally lower confinement energies. This is fully in line with the results from the previous section. Moreover, as the barrier increases for each size, the whole spectrum is seen to shift slightly to the right, so to a higher energy. This is a result of the same principle: a higher barrier means an extra CO in the structure, and thus a smaller area. This results in a higher on-site energy.

One of the structural differences between theory and experiment, that can be seen in both Fig. 23a and 23b, is the increase in LDOS at the right edge of the figure. Note that this happens only for the experimental results. This is most likely due to the second confinement energy (the p-orbital) that lies outside the frame. In the computations this feature is probably missing due to the amount of solutions being insufficient to also include the p-orbital. The number of solutions has great influence on the evaluation time, and was thus restricted to the energy frame of interest.



Figure 23: Experimental vs. theoretical spectra. LDOS spectra of six different dimer structures: three barrier types over two sizes. The colours of the plots are chosen such that theory and experiment directly correspond. Also they match the colour of the text in Fig. 22 (a) Experimental spectra of the three dimers with size R = 4a (top row in Fig. 22). (b) Experimental spectra of the three dimers with size R = 5a (bottom row in Fig. 22). (c) Discretised theoretical spectra matching (a). (d) Discretised theoretical spectra matching (b).

#### 6.2.1 Calculating tight binding parameters

One final way of supporting the conclusions above, is by making the coupling quantitative. This can be done by actually calculating the parameters from the tight binding model. For the hopping parameter t, this can be done the same way as in the previous chapter, i.e.  $E_+ - E_- = 2t$ . This method is indeed used for the theoretical results, where  $E_{\pm}$  are taken directly from Fig. 23. However, a second method is used for the experimental results, which might yield more accurate results. This method, along with the reason why this is not applied to theory, is discussed below. The results will be presented afterwards. Retracing our steps to eq. 24,

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \mathbf{0},$$
(31)

we wish to solve this for E. Last chapter we neglected the orbital overlap  $S_{21} = S_{12}$ , which was fairly accurate, because the monomers were drifted away from each other. In these systems, however, this is not the case, and thus the overlap integral becomes of more importance. Without neglecting this, eq. 31 becomes

$$E_{\pm} = \frac{E_0 \pm t}{1 \pm s},$$
(32)

with as before  $E_{\pm}$  the dimer on-site energy,  $E_0$  the monomer on-site energy (i.e. without coupling), t the hopping parameter and  $s = S_{1,2}$  the orbital overlap. The goal now is to calculate t and s. If  $E_{\pm}$  and  $E_0$  can be found, then eq. 32 becomes a system of two equations with two variables, which is solvable. The only matter at hand, then, is finding the energies.  $E_{\pm}$  can be deduced from the spectra in Fig. 23: they correspond to the two peaks of spectrum. However, because of the broadening mentioned earlier, the visible peaks are not the most accurate representations of the real energies. Instead, more precise would be to fit the spectrum as a sum of two Gaussians, which it in reality is. This way the effect of broadening is minimized, and the peaks of the Gaussians can then be taken to be  $E_{\pm}$ . This was attempted for all six theoretical plots, both by *Wolfram Mathematica*'s fitting options and by eye, but for only one plot were remotely acceptable results generated (for 4a low barrier, see Appendix C). Because of this,  $E_{\pm}$  is determined directly by the peaks in the LDOS plots after all.

For finding  $E_0$  the previous section can be used. When we treat the dimer as two monomers, and the area of a single site is known, the fit from Fig. 21 can be used to determine the on-site energy. The only difficulty here lies in estimating the area of a single site, because a correction is needed for the fact that it is a dimer. Considering for example the higher barrier structures, one soon realises that a single site has less space available for confinement than in a regular monomer. Therefore the following approximation is made,

$$\begin{cases}
A_{\text{low}}^* = A + A_{CO} \\
A_{\text{normal}}^* = A \\
A_{\text{high}}^* = A - A_{CO},
\end{cases}$$
(33)

with  $A^*$  the corrected area and A the original monomer area.

With respect to theory, this method probably does not generate very reliable results. Most notably, all dimer constructions have been made with blockers, while the theoretical fit in Fig. 21 was based entirely on unblocked structures. Consequently, no trustworthy method of explicitly finding  $E_0$  could be established.

To conclude: in the theoretical approach s is still neglected, and the values of  $E_{\pm}$  are taken directly from the LDOS plots. In contrast, from the experimental side s was taken into account, and the spectra were decomposed into Gaussians. Because of this the general trends in each set of data can be considered, but directly comparing values between datasets is not realistic. Unfortunately there was no opportunity to correct for this lack of similarity, due to a shortage in time.

Finally, the results are presented in Table 1 and 2 below.

Dimer type	$E_+$ (eV)	$E_{-}$ (eV)	$t (\mathrm{eV})$
4a low	-0.169	-0.040	-0.0645
4a normal	-0.130	-0.049	-0.0405
5a low	-0.239	-0.157	-0.0410
5a normal	-0.219	-0.162	-0.0285

Table 1: Theoretical tight binding parameters, as calculated with eq. 32.

 Table 2: Experimental tight binding parameters.

Dimer type	$E_+ (eV)$	$E_{-}$ (eV)	$E_0 (eV)$	t (eV)	s
4a low	-0.181	-0.015	-0.160	-0.156	0.747
4a normal	-0.150	-0.021	-0.128	-0.121	0.659
5a low	-0.241	-0.138	-0.191	-0.057	0.029
5a normal	-0.235	-0.138	-0.191	-0.050	0.010

The values in both tables do show similar trends, supported by tight binding theory and the LDOS plots. To start, the hopping parameter (and orbital overlap) decrease as the dimer size increases, as can be seen most strongly for the experimental values. This can also be seen in Fig. 23, by the fact that the peaks in 23a and 23c are further apart than in 23b and 23d. This raises an interesting talking point: apparently the coupling of the sites can be tuned by varying their size. Consequently, since there is a minimum size a site can take, there also must be a maximum coupling. This result might be of aid in the manipulation of more complex systems in further studies.

Furthermore, in both tables the normal barrier has a smaller t (and s) than the low barrier of the same size. This aligns nicely with the tight binding theory: a higher barrier means less coupling.

# 7 Conclusion and outlook

In this thesis the foundations of quantum simulations via electronic systems have been explored. Firstly a framework was established on the experimental nature of the field as well as on the background of theoretical computations. In particular, the modus operandi of both the STM and the Arnoldi algorithm received due attention. Concerning the latter, the specific importance of the iteration number was established, greatly influencing the accuracy and number of the solutions.

After this the very basis of the concept of electronic systems was examined: the confinement of electrons in surface structures. To verify this concept, a particle in a box was modelled. If the results matched those of a surface structure with similar shape, confinement would be confirmed. Notably, the quantum corral was reproduced, and the results indeed matched with a closed 2D circular box. In addition, a variety of box shapes was modelled to concisely investigate the effect of the shape on the resulting eigenfunctions.

Subsequently, two hexagonal sites were connected into a dimer and gradually moved away from each other. Based on the tight binding model, a relation was sought between the hopping parameter and the distance between the sites. The results on this were disappointing, because a third, rectangular site was formed in between the hexagons, resulting in trimer behaviour. While this interfered with the research, it nevertheless became a valuable lesson for further research that new sites might form unintendedly. Furthermore, an insufficient system size amplified these trimer effects, while also adding highly influential boundary effects. It would be very interesting to study this set-up again, but in a much larger system, to see the displayed behaviour more clearly.

In the final part two systems were experimentally investigated as well, enabling comparison with theory. The first was a hexagonal monomer, for which a linear relation was established between on-site energy and site area. This again confirmed the expectation based on a particle in a box. However, the comparison was not as easy as we had hoped, because the experimental and theoretical sites did not completely match. Hence it could be very rewarding to repeat the comparison, this time with the experimental and theoretical structures exactly corresponding. Secondly the dimer was investigated again, only this time with a changing barrier in between the hexagons. LDOS plots from theory and experiment were compared and they matched remarkably well. Not only did this strongly support the entire numerical procedure of this thesis, but the plots also behaved in accordance with tight binding expectations. It was concluded that the higher the barrier was, the weaker the coupling; the bigger the dimer size, the lower the on-site energy; and the bigger the dimer size, the coupling also has a maximum. All together it is hoped that these conclusions can facilitate designing new systems.

At attempt was made to support these conclusions with quantified results. Unfortunately theoretical tight binding parameters could not be generated in the same way as the experimental ones. This made a direct comparison of values fruitless, but general trends could still be recognized in the separate datasets. Indeed the earlier conclusions were validated. However, it remains here that the biggest improvement can be made. By again making a fit of the on-site energy over area, but based on blocked hexagons only, it would be possible to process the theoretical results in a similar way as with experiment. Then orbital overlap could be calculated as well and values could be compared directly.

The overview of the foundations of this field, as laid here, can be used as a starting point for many research projects to come. Still in the spirit of the work done here, a trimer or tetramer might offer similar useful insights to the ones listed above. Thinking bigger, the principles stated might readily be extended to more complex systems. An example might be a topological defect: a hexagonal lattice with formed around a single pentagon. In such a way a lattice can still be formed, but with different hexagon sizes. Moreover, superconductors and topological insulators remain highly valued topics as well. The listing of these examples can by no means ever be exhausted, since there are so many promising systems about which we know so little. After all, the beauty of this entire field is captured right there: making accessible and manipulable what never was so before.

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# Appendix

#### A Parameters used for computation

When it comes to reproducing the results in this thesis, the numerical results and density plots follow relatively straightforward from the formulas and figures presented. LDOS plots, however, tend to hide the parameters with which they were made. Because of this, the relevant parameters for the computations are shown in Table 3 below.

**Table 3:** Parameters used in computations. When no discretisation value is given, the default value was used.

Figure	System size	Boundary condition	No. of solutions	Discretisation	
13a	-2 < x, y < 2	Open	40	-	
13b	$-2 < x < 2 + \sqrt{3};$ -2 < y < 2	Open	40	-	
14	$-2 < x < 2 + d\sqrt{3}; \\ -2 < y < 2$	Open	70	-	
20	-20 < x, y < 20	Open	800	0.1	
23	$-15 < x < 15 + \sqrt{3}; -15 - \frac{1}{2}\sqrt{3} < y < 15 + \frac{1}{2}\sqrt{3}$	Open	500	0.1	

#### B Areas of the hexagonal monomer (sec. 6.1)

For the theoretical areas of the data in Fig. 21, eq. 29 was used. The experimental areas are shown below in Table 4.

Table 4:	Experimental	areas	used	for	${\rm the}$	data	$\mathrm{in}$	Fig.	21.
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Dimer type	Area $(nm^2)$				
4a	2.14				
4a blocked	2.92				
5a	3.66				
5a blocked	3.58				
6a	3.85				

#### C Fitting the LDOS of dimers as the sum of two Gaussians (sec. 6.2.1)

Decomposing the dimer LDOS spectra intro separate Gaussians proved to be very difficult. Fig. 24 shows two attemps of this. The fit in the first plot has the same general structure as the original LDOS, but lacks the amplitude of the real peaks. In the second plot, the total fit does not even have two peaks, rendering it incorrect on sight. Efforts were made to



give constraints to the fitting programme, and also to crop the data, but the results harshly improved.

Figure 24: Fitting two dimer of LDOS plots. LDOS plots of the two low barrier structures, sized R = 4a and R = 5a respectively, together the found best fit. The fit was constrained to be a sum of two Gaussians. Blue dotted line: original spectrum as can be seen in Fig. 23. Red line: total fit. Orange and black striped lines: the two Gaussians, whose peaks can be taken to be  $E_{\pm}$ , if the accuracy of the fit is deemed high enough.