

Rian A.M. Ligthart, BSc. Master Thesis Thomas S. Gardenier, MSc. *Daily Supervisor*

Dr. Ingmar Swart Supervisor



October 28, 2019

"Ein rein verstandesmäßiges Weltbild ganz ohne Mystik ist ein Unding."

- Erwin Schrödinger [1]

Contents

1	Introduction	4
2	Theory 2.1 Scanning Tunneling Microscope 2.2 Atom Manipulation 2.3 Artificial Electronic Lattices 2.4 Muffin Tin	5 5 6 7 10
3	Methods	13
4	Results and discussion4.1Quantum Corral4.2Molecular Graphene	15 15 19
5	Conclusion	23
6	Outlook	24
7	Acknowledgements	25
Bi	bliography	26
A	ppendix 1	30
A	ppendix 2	31
Aj	ppendix 2	32

Abstract

With the advances in nanoscale technologies, experiments of well-known phenomena in quantum mechanics have swiftly become accessible. The technology of the Scanning Tunneling Microscope (STM) allows it to obtain atomic resolution and to manipulate atoms, enabling the design and construction of quantum simulators. Here, an electronic quantum simulator was created in the STM by confining the surface state of Cu(111) with CO molecules as repulsive scatterers. An experiment was conducted constructing artificial atomic sites in a quantum corral and in molecular graphene. The aim of this thesis is to study the effect of a perpendicular magnetic field on these electronic lattices. Results show a small shift in energy of the electronic states with an applied magnetic field of up to 4 T. A characteristic pattern was obtained when the differential conductance spectra taken at 1, 2, 3, 4 T were subtracted from the 0 T spectrum. Furthermore, muffin tin calculations were performed and compared with the experiments. The theoretical calculations corroborate the experimental findings as also the peaks in the distinct subtraction pattern matched. The magnetic flux in the experiments was too low to observe splitting into Landau levels or the integer Quantum Hall effect. Overall, the measurements performed here with a magnetic field show a new pathway to explore more magnetic quantum effects.

1 Introduction

Smaller, smaller and smaller, the size of the particles studied already reaches the atomic scale due to advances in technology. This opens an entire new world in which novel properties and phenomena in the quantum regime can be elucidated. One of the technologies is the Scanning Tunneling Microscope (STM) which can achieve sub-atomic resolution. The STM "feels" the electrons on the surface via a tunneling current between tip and sample. The STM is therefore a suitable technology to study the behaviour of electrons. Additionally, the STM tip can perform atom manipulations enabling it to tailor the structure of materials with atomic precision.[2–4]

By designing specific structures the physical properties of materials can be tuned, making them applicable as quantum simulators. A quantum simulator is a system used "to study quantum effects and to answer questions about model systems and, through them, real systems".[5] The need for quantum simulators was already stated by Feynman in 1959 as the systems can be engineered and manipulated at will to verify quantum effects.[6] Simulators that have served this purpose since are phononic crystals [7–9], photonic crystals [10, 11], cold atom lattices [12–14], and lattices on metal surfaces, i.e. electronic lattices [15–17]. The focus will be on the latter which serve as electronic quantum simulator.

A key electronic simulator was created by Crommie et al. in 1993 by building the first artificial "atom" on a metal surface.[18] A circular standing wave pattern was observed in a quantum corral by confining the Shockley surface state of Cu(111) with iron adatoms. Using the concept of artificial atoms, the group of Manoharan constructed an entire lattice by placing CO molecules on a Cu(111) surface.[15] In the STM, his group patterned the surface state into a honeycomb geometry creating the artificial electronic lattice of molecular graphene. A similar system using quantum well states was shown by preparing a chlorine monolayer on Cu(100) and patterning the individual vacancies into the desired lattice.[19, 20] By altering the geometry of the quantum simulator, the characteristics of electrons have been studied in chains, quasicrystals, fractal dimensions and in strained lattices (inducing a pseudo-magnetic field).[15, 17, 21, 22] With the CO on Cu(111) system, the nature of orbitals, topology and fractional charge have been further elucidated.[23–25] By tailoring the design, quantum phenomena which have been hard to exploit in real materials have suddenly become accessible.

Here, the aim is to use an artificial electronic lattice of CO on Cu(111) to study the effect of the magnetic field on electrons. The behaviour of electrons in different electronic lattices with a perpendicular magnetic field will be measured in the STM. To this purpose, the electrons are confined in a quantum corral and in a honeycomb geometry. Furthermore, a comparison between theory and experiment will be made by performing muffin tin calculations.

This thesis is organised as follows, Chapter 2 covers theory about the STM, atom manipulation, electronic artificial lattices and muffin tin calculations. Subsequently, the experimental methods are described in Chapter 3. Furthermore, Chapter 4 contains the results on the quantum corral with and without magnetic field. Additionally, the analysis of the molecular graphene lattice in magnetic field is presented in Chapter 4.

2 Theory

2.1 Scanning Tunneling Microscope

In 1981, Dr. Gerd Binnig and Dr. Heinrich Rohrer invented the STM for which they later received the Nobel Prize in Physics.[29] The STM is a surface sensitive technique which can obtain atomic resolution. This was first achieved on a reconstructed 7 x 7 Si(111) surface shown in Figure 1a. The STM has an atomically sharp tip which scans over a conducting surface and measures the tunneling current. The tunneling current between tip and sample closes the electrical circuit of the STM as seen in Figure 1b. Quantum tunneling is the process where a particle permeates through a potential energy barrier even though its energy is lower than the barrier, as displayed in Figure 1c. This classically impossible process, has a finite probability in quantum mechanics. The vacuum between tip and sample generates a potential barrier in the STM. The low probability of tunneling leads to a current in the nanoampere range when the tip is several nanometres away.

$$I \propto e^{-2\kappa d}, \qquad \kappa \approx \frac{\sqrt{2m\Phi}}{\hbar} \approx 1 \mathring{A}^{-1}$$
 (1)

The relation between the height of the tip (d) and the tunneling current (I) ensures the high resolution of the STM, see Equation 1. When the height changes with 1 Å, the current responds with high sensitivity, namely with a factor of 10. The high level of sensitivity enables the measurement of small distances in the STM. However, this principle only applies when the bias voltage is lower than the average workfunction (Φ) of the tip and the sample. During measurements, the tip scans the surface whilst the current is constant and regulated with a feedback loop. Subsequently, an image is created by determining the height of the tip at each pixel.



Figure 1: (a) First atomic STM image showing a reconstructed 7 x 7 Si surface made in 1983 by Binnig et al. [26] (b) The STM functions as a closed electrical circuit. The tunneling current between tip and sample is held constant with a feedback loop. Image obtained from [27]. (c) Schematical figure showing the tunneling current between tip and sample. The wavefunction of the sample tunnels through the potential barrier to the tip. The wavefunction loses amplitude exponentially as it passes through the potential barrier. Image taken from [28].

The probability distribution of the electron density, $|\Psi|^2$, at a specific energy can be visualised in a map. The feedback loop for the current is turned off to take maps which means a constant height is needed. Furthermore, scanning tunneling spectroscopy (STS) can be performed, plotting differential conductance versus voltage. A so-called dI/dV spectrum is taken at a single point by measuring the variation in current while applying a small modulation to the bias voltage. The bias voltage is swept over a certain energy range. The dI/dV is proportional to the local density of states (LDOS) and reflects the probability distribution of the electron density at a specific position. The electrons can tunnel from sample to the tip but also *vice versa*, the STM tip therefore probes the occupied and unoccupied electronic states of the sample. The tunneling in both directions also leads to a contribution of the wavefunctions of the tip to the measurements. In order to only observe the DOS corresponding to the lattice, a background correction should be made for the DOS of the tip. The correction can be performed by dividing the spectra by a clean Cu(111) spectrum.

To achieve a high resolution, a vast effort needs to be made to reduce the amount of noise in the system. Several elements are added to the microscope to achieve this, for instance the eddy current dampers, piezoelectric actuators, active vibrational dampers and springs lifting the stage. These parts all contribute to the reduction of vibrations.

2.2 Atom Manipulation

Besides imaging the surface, the STM tip can move adsorbates on the surface which was first shown by Eigler et al. in 1990 with single Xe atoms.[2] Manipulation, in vertical or lateral directions, allows the tailoring of nanostructures with high precision. The focus will be on adsorbed CO molecules on a Cu(111) surface. The CO adsorbs on top-sites and stands upright with the carbon atom faced towards the metal, see Figure 2a.[31] The CO molecule weakly chemisorbs to the surface, therefore, the temperature should remain below



Figure 2: (a) Graphic interpretation of a CO molecule on a Cu(111) surface with STM tip. The atomically sharp tip is depicted in grey, the red sphere represents oxygen and the black carbon. The atoms of the Cu(111) are coloured orange. Image created by Blender.[30] (b) A recorded trace of the height taken during a lateral manipulation of a CO molecule over the Cu(111) surface. The steps in the graph show the hops over the single Cu-atoms. The CO molecule is pulled over the surface.

40 K for adsorption. At the temperature of 4.5 K, the CO molecules have a low mobility on the surface allowing for manipulation as well as stability of the structure built.[32]

During controlled vertical manipulation, the CO molecule flips and attaches to the tip, the molecule is released later at a determined location.[31] The attachment of a single electron to the $2\pi^*$ orbital of CO causes the reversible transfer.[4] The CO molecule attaches to the tip by positioning the tip above a molecule and slowly lowering the bias voltage to zero.[33] When lowering the bias voltage the tip-sample distance decreases. The current should remain below 10 nA, otherwise the tip touches the surface at zero bias voltage. With a CO terminated tip the chemical contrast increases, e.g. another CO molecule is no longer depicted as a depression but as a protrusion.

During controlled lateral manipulation, the molecule is moved across the surface without breaking the bond with the surface. The occupied 5σ and the unoccupied $2\pi^*$ orbitals of CO bind to Cu(111) via the 3d band and partly the 4sp.[34] For lateral manipulation, the tip is brought close to the surface by increasing the current setpoint and decreasing the bias voltage. The small molecule-tip distance creates a highly localised potential well that traps the molecule under the tip. [35] Long range attractive Van der Waals interactions occur between tip and molecule. [32] Subsequently, if the tip is moved to the desired position, the CO molecule hops from one adsorption site to another. The CO molecule is either pulled, slided or pushed to the position. [33] Also a combination of these processes can occur during one manipulation, depending on the position of the tip relative to the molecule. In Figure 2b an example of a recorded manipulation trace is seen, the CO molecule is pulled in this case and the hops over single Cu(111) atoms are observed. At the end of the manipulation, the tip is retracted to the original height, lowering the intensity of the favourable interactions between tip and molecule. A successful manipulation relies on the strength of the interactions between the molecule with the surface and with the tip. Additionally, the shape of the tip, the bias voltage, the tunneling current and the speed of the manipulation play a crucial role in the process. [36]

2.3 Artificial Electronic Lattices

Atom manipulation enables the construction of artificial electronic lattices with high precision. The electrons are forced into a designed structure to study their properties and to verify quantum effects. In this section, the electronic quantum simulator CO on Cu(111)is discussed in more detail.

The electrons of the simulator are supplied by the Shockley surface state of Cu(111) which arises due to crystal termination. The surface state can be approximated as a twodimensional electron gas (2DEG) with an average density of 1 electron per 1.4 nm².[37] Figure 3a shows the surface state of Cu(111) which does not overlap with the bulk states between -0.45 and +0.50 V. As a result, the simulator is largely electronically decoupled from the bulk states of copper. The CO molecules act as scatterers and pattern the 2DEG creating an artificial electronic lattice. As the CO molecules are *repulsive* scatterers, the anti-lattice of CO molecules should be constructed. The CO molecules adsorb on top-sites of the Cu(111) surface, since Cu(111) has a hexagonal symmetry the designs for circles and squares are limited. Furthermore, a CO molecule cannot be placed on the



Figure 3: (a) A differential conductance spectrum on Cu(111) showing the surface state with an onset at -0.45 V. The surface state of Cu(111) is largely electronically decoupled from the bulk states of copper. Image obtained from [40]. (b) The radial wavefunction distribution of the *s* orbitals of hydrogen. The orbitals of the hydrogen atom can be compared to the wavefunction of the artificial atoms due to the same nodal plane character. (c) The electronic band structure of graphene showing a Dirac cone. Image taken from [41].

nearest-neighbour site of another adsorbed CO molecule due to repulsion between two molecules.[38] The CO molecules form a potential barrier of 0.9 eV as the bias voltage comes closer to the barrier the potential well will be more shallow. This results in less quantum confinement for the electrons at higher energies. A drawback of the CO/Cu(111) system is the incomplete decoupling of the surface state with the bulk states. This lowers the lifetime of the electrons in the surface state and therefore decreases the energy resolution. The finite lifetime of the electrons in the 2DEG is even further reduced by the use of CO as adsorbates. The CO scatterers couple the bulk states to the surface states, the final energy resolution comes down to approximately 80 meV.[39]

The name artificial "atom" is justified by comparing the probability distribution of the wavefunction $|\Psi|^2$ of an "atom" with a hydrogen atom. The lower orbitals of hydrogen show a high similarity in the shape of the spatial distribution with the wavefunctions of the artificial atoms.[39] Figure 3b shows the radial wave function distribution of the sorbitals of hydrogen. The artificial atom however lacks a positively charged core leading to a shift of the graph, e.g. for the 1s orbital placing the highest probability of the electron density exactly in the centre. The analogy is however less accurate for the p, d, forbitals. To demonstrate, the *p*-orbitals always have a defined angular momentum which is no fundamental property for the p - like wavefunctions of the artificial atom. For instance, the atoms in the quantum corral do have an angular momentum, but the atoms in the molecular graphene lattice do not. The comparison between the orbitals and the wavefunctions of the artificial atoms is mainly based on the nodal plane character of both. The artificial atom has the advantage of a higher versatility in comparison to the hydrogen atom as the on-site energy may be shifted by varying the size of the atom. When the artificial atom increases in size, the electronic states will be confined less and come near the bottom of the well where states might begin to overlap. Another advantage of the system is a minimal hybridisation of the orbitals of the artificial atoms, allowing to take a look at almost non-hybridised orbitals.

2 THEORY

The non-hybridised orbitals can lead to an increased understanding of the physics occurring in graphene. Graphene has hybridised sp^2 -orbitals with a half-filled $2p_z$ orbital. Graphene exhibits interesting electronic properties due to the perfect 2D structure and the honeycomb structure.[41] Figure 3c displays the electronic band structure of graphene, where the inset shows the Dirac cone. At the Dirac point a linear dispersion is present resulting in an effective mass of zero for the electrons. By investigating the physics of the Dirac cone in molecular graphene, the tunability of the system is extended. The artificial electronic lattice is therefore an adequate model to study the electronic band structure of graphene.

Artificial electronic lattices in a magnetic field

The effect of a perpendicular magnetic field on artificial electronic lattices is still unexplored. A magnetic field can induce a shift in energy for the electronic states of the lattice. Nonetheless, the magnetic field cannot alter the total amount of states. The observed shift must therefore originate from a change in degeneracy, when a state becomes less degenerate another state must gain in degeneracy.[43]

The effect of the perpendicular magnetic field on real graphene has already been studied. The applied magnetic field leads to splitting of the electronic states into Landau levels.[44, 45] Landau levels exist in a magnetic field due to the quantization of the cyclotron orbits of charged particles. These so-called cyclotron orbits, see Figure 4a, arise due to the Lorentz force which causes the charged particles to orbit in circles anti-clockwise or clockwise. Landau levels are degenerate with the number of electrons per level, directly proportional to the strength of the magnetic field, B.[42]

The integer quantum Hall effect (QHE) is a second effect that can be induced by a perpendicular magnetic field. First the classical Hall effect is explained briefly. The set-up contains electrons constricted to move in the xy-plane, a current in the x direction and a



Figure 4: (a) Cyclotron orbits arise when a perpendicular magnetic field is applied. The electrons start to rotate clockwise/anti-clockwise due to the Lorentz force. At the edge no full orbit can be made resulting in edge modes. (b) A plot of resistance versus magnetic field strength showing the integer quantum Hall effect. The p_{xy} resistance contains different plateaux and the p_{xx} resistance peaks when there is a jump in the plateau. Image obtained from [42].

magnetic field in the z direction. The classical Hall effect states that this set-up induces a voltage in the y direction. The QHE is the quantization of the classical Hall effect.[43] In Figure 4b, magnetic field versus (p_{xy}) resistance is plotted, plateaux arise and at every jump between the plateaux the p_{xx} resistance peaks.[42] At each plateau, a Landau level is filled. Furthermore, the cyclotron orbits induce the existence of edge modes shown in Figure 4a. The orbit has a single direction and at the boundaries the complete orbit cannot be made due to the edge. The particle is restricted to move in a single direction along the boundary, the so-called chiral particle. At the boundary on the other side, the particles moves in the opposite direction as predicted by chiral anomaly. However, the net current vanishes as current in opposite directions takes place at the opposite edges. The robustness of the Hall state is clarified by taking the effect of impurities in the system into account.[42]

The magnetic field must be sufficiently strong to observe these effects. The strength of the magnetic field is measured in magnetic flux. Flux, ϕ , is defined as the amount of magnetic field per area or per unit cell, $\phi = \vec{A}\vec{B}_{\perp}$. To observe a change in the electronic structure the ratio of $\frac{\phi}{\phi_0}$ must be above a certain threshold, where ϕ_0 is the quantum of flux and equal to $\frac{h}{2e}$.[42] Theoretically for the Sierpinski triangle and carpet, the calculated ratio should be roughly higher than 0.20 to see a change in band structure.[46] The value of $\frac{\phi}{\phi_0} = 0.20$ will be used as an order of magnitude to see an effect of the magnetic field, since the ratio differs per lattice. Artificial electronic lattices are suitable quantum simulators to study magnetic quantum effects as the lattices provide a system with high versatility.

2.4 Muffin Tin

Two theoretical methods to describe the system of adsorbates on a noble metal surface are the muffin tin and tight-binding model. The muffin tin model is used to calculate electronic band structures and was proposed by J.C. Slater in 1937.[47] The adsorbates are interpreted as a potential barrier for the 2DEG for which the complex particle-in-a-box problem is solved. The muffin tin calculations coincide with the nearly free electron model and are described in this section. The tight-binding model calculates the band structure by regarding the lattice as a combination of artificial atoms. The tight-binding model is based on the Linear Combination of Atomic Orbitals (LCAO) approximation.[43]

Artificial electronic lattices created by depositing CO molecules on a Cu(111) surface enable to study electronic properties of new structures. Calculations are a practical tool to estimate if the structure is interesting enough to build in the STM. Additionally, the calculations also enable to optimize a specific design, for instance to see if the band structure of interest is in the energy range of the Cu(111) surface state. The type of lattice and the size of the unit cell have both a significant impact on the shape of the electronic band structure. To get a first prediction of the density of states shown in the STM, muffin tin calculations are performed. With muffin tin, the shape of the potential well in a lattice is approximated. The wavefunctions are found by solving the Schrödinger equation for a particle in a complex box. In this case, the calculations are performed for CO on a Cu(111) surface. The choice of CO and Cu(111) only influences the parameters that define the potential well.[48] Therefore, muffin tin can be used to a much broader extent



Figure 5: (a) Finite differences approximation of space. The xy-plane is divided into small boxes to approach the second derivative of the wavefunction. For each box, n wavefunctions and energies are calculated. (b) Simulated map made with muffin tin probing the LDOS. The calculations were performed on a square lattice of CO molecules on Cu(111) surface. The energy of the map is -0.31 eV and Dirichlet boundary conditions are used. (c) The same as (b), but the map is made with periodic boundary conditions.

by altering the parameters so they fit another system. In this section, the approach to perform a muffin tin calculation with the programming language Python is presented.

Muffin tin calculations can be compared by solving a complex particle-in-a-box problem. The problem is solved by using the Schrödinger equation. The Schrödinger equation consists of the wavefunction (Ψ) , the Hamiltonian operator (H) and the energies of the system (E), see Equation 2.

$$H\Psi(x,y) = E\Psi(x,y) \tag{2}$$

The Schrödinger equation is a so-called eigenvalue problem, the functions Ψ should return itself multiplied by a constant after the Hamiltonian operator has worked on it. By performing an eigenvalue decomposition, the eigenvalues and eigenfunctions are computed which correspond respectively to the energies and the wavefunctions of the system. The Hamiltonian contains a kinetic part and a potential part V, see Equation 3. The potential energy contains the potential barriers of the CO molecules. The location of the CO molecules create the complex box. The CO molecules are approximated as disks with a certain potential height, when two disks of the CO molecules overlap their energy is summed. The height of the disks is equal to the potential barrier created by the CO molecules, estimated to be 0.9 eV.

$$H = \frac{-\hbar^2}{2m_{eff}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x, y) \tag{3}$$

The kinetic part of the Hamiltonian consists of the second derivative of x and y of Ψ (in 2D), called the Laplacian. However when the wavefunction is unknown, the second partial derivatives cannot be determined exactly. In that case, the second derivatives can be solved numerically with the help of the finite difference matrix of the Laplacian. The range of x and y coordinates is divided into small boxes, see Figure 5a. The smaller the box size, the more accurate the results will be. In the ideal case the size of the boxes, dx or dy, is infinitely small leading to the exact solutions of the derivatives. For each box n eigenvalues/energy levels will be computed, n needs to be large enough to cover the

energy region of interest. To take the influence of the neighbouring boxes into account, a Lorentzian broadening of 80 meV is introduced. A LDOS plot is made when for all the boxes $|\Psi|^2$ values of one specific energy are shown. The LDOS plot is a theoretical image of a differential conductance map in the STM. Spectra are simulated by looking at all the energies of a wavefunction on a specific location.

The finite difference approximation of the second partial derivative results into two matrices, see Appendix 1: Muffin Tin Matrices Matrices 8 and 7. The matrices are composed via the recursion relation of the formal definition of the derivative. By altering the matrices, different boundary conditions can be applied such as the Dirichlet boundary conditions. The Dirichlet boundaries create an isolated system by placing a box around the entire region. Figure 5b shows that the outcome is inadequate for the CO/Cu(111) system as the box around the entire system influences the electronic band structure of the lattice. Additionally, periodic boundary conditions can be applied in which the right row of boxes "feels" the left row and the upper "feels" the lower boxes. The adapted matrices for the second derivative in x and y for the periodic boundaries are shown in Appendix 1: Muffin Tin Matrices Matrices 8 and 9. Figure 5c shows that the periodic boundary conditions are more reliable as the boundary conditions do not contribute to the electronic structure of the lattice. Therefore, the periodic boundary conditions will be used for all the calculations. The edge around the structure should be chosen large enough, so that scattering effects do not occur at the edges anymore.

To obtain an accurate result, a large number of boxes should be chosen as this determines the resolution of the spectra and maps. The matrices soon become gargantuan because the matrix size is equal to the amount of boxes in x times the amount of boxes in y. A lot of interactions between the boxes are zero as a box only feels its nearest neighbours. By using the large amount of zeroes in the matrix, a memory error from the computer is prevented. In Python this is done with sparse matrices which only store the location and value for non-zero inputs.

The magnetic field is introduced into the muffin tin calculations by adding extra terms to the Hamiltonian. The strength of the magnetic field can be described by $\vec{B} = \vec{\nabla} \times \vec{A}$. Nabla is the vector differential operator and A the gauge for the vector potential. By choosing an appropriate A, the Schrödinger equation with magnetic field potential is obtained. The final result of the calculation is gauge invariant, this arises as the magnetic field B is invariant under translational and rotational symmetry in the xy-plane. However, A does not necessarily have to be invariant with symmetry. The perpendicular magnetic field is applied via different gauges such as the Landau or the symmetric gauge. The Landau gauge, A = (0, Bx, 0), is the most straightforward in algebra and leads, in 2D, to Equation 4.[49]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{ie\hbar Bx}{m}\frac{\partial}{\partial y} + \frac{(eBx)^2}{2m} + V(x,y)\right]\Psi(x,y) = E\Psi(x,y) \tag{4}$$

The magnetic field gives rise to two terms, one term originating from the Lorentz force which couples x and y via the first derivative of y. The second term, described by a parabolic potential, leads to confinement of the wavefunction in the x direction.

3 Methods

The experiments were performed on the Sigma Surface Science POLAR SPM with a superconducting magnet generating a perpendicular magnetic field up to 5T, shown in Figure 6. The temperature in the microscope during measurements was 4.5 K with a base pressure in UHV around $1 * 10^{-10}$ mbar. A Cu-coated PtIr tip was used for all measurements.

First, a Cu(111) crystal was prepared for the experiments, the surface was cleaned in the preparation chamber of the SPM. The cleaning procedure consisted of dynamic sputtering at 1 kV with Ar-ions for 10 minutes with a pressure of Ar-ions of 8.5×10^{-6} mbar and annealing at 585 °C for 7 minutes. The cycle of sputtering and annealing was repeated three times, during the last step the temperature was lowered to 500 °C. After cleaning, the crystal had atomically flat terraces with an average size of 30 nm.

The CO molecules were evaporated in the SPM chamber with a direct access to the cold Cu(111) crystal in the head of the microscope. With a pressure of $5 * 10^{-8}$ mbar, CO molecules were leaked into the room for 5 minutes for a sufficient coverage.

Generally, the crystal was scanned at 1 nA with a bias voltage of 0.5 V. The k_i , a rate for the response sensitivity of the tip, ranged between 10 for flat surfaces to 50 for large overview scans. To design the lattice, electronic band structures were calculated with muffin tin considering different unit cell sizes. The on-site energy of the artificial atom site was chosen in the regime of the Cu(111) surface state between -0.45 and +0.5 V. The quantum corral and molecular graphene were built by laterally manipulating CO molecules with atomic precision to the desired locations. For atom manipulation, the current set point was 40 nA with a speed of 0.5 nm/s, a bias voltage of 0.01 V and a slew rate of 0.5 V/s.



Figure 6: The Polar SPM of Sigma Surface Science.

3 METHODS

Scanning tunneling spectroscopy was performed on the completed lattice at 273 Hz with a modulation amplitude of 10 mV. The range was set from -0.6 to +0.5 V with 551 points, an acquisition time of 250 ms and a time constant of 50 ms.

The images obtained with the STM were processed with the Gwyddion programme, version 2.52. The data was levelled by fitting a plane through three points of equivalent height. Furthermore, the lowest point was fixed to zero and a 2D fast Fourier transform filtering was applied to lower the noise.

The spectra analyses were performed with the help of a self-written script in Python. The spectra were averaged with 5 to 10 spectra. A correction for the background was made by dividing the spectra with a 25-times averaged spectrum of the bare Cu(111) surface. The correction was done to reduce features of the bulk states of Cu(111) and of the electronic states of the specific tip.

Another background correction to quantize the data was performed as well. The spectra were scaled by setting the jump of the surface state of Cu(111) equal to $G_{2D} = m^*/\pi\hbar^2 = 1.585 \text{ eV}^{-1}\text{nm}^{-2}$.[15] Subsequently, the spectra were normalised over the peak of the surface state. The spectra were plotted together with their background to check if the graphs have similar intensities, this should be the case as the spectra display the same surface state.

4 Results and discussion

4.1 Quantum Corral

The quantum corral was built to study its electronic band structure and to measure an effect of the magnetic field. The influence of the magnetic field is larger with a higher magnetic flux, the corral was therefore designed to have a large area. However when the corral size is too large, the electron confinement decreases and different electronic bands begin to overlap at the bottom of the potential well. An initial optimum was found with muffin tin simulations. The quantum corral designed with a radius of 5.9 nm and 36 CO molecules is seen in Figure 7a. First, the theoretical solution of the particle in a circle is explained, followed by the discussion of the experimental measurements with and without a magnetic field.

$$E_{n,m} = \frac{\hbar^2 k_{m,n}^2}{2m_{eff}} = \frac{\hbar^2 a_{m,n}^2}{2m_{eff} R^2}$$
(5)

The theoretical solution of the electron in a circle was calculated by the separation of variables method. The wavefunction was split into two functions, $\Psi = \Phi(\phi)R(r)$, which depend on the angle and the radius of the circle. The solution of the angular function has the form of an exponential and the radial function is given by the Bessel function $(J_m(k_{m,n},r))$. The Schrödinger equation was subsequently solved, leading to the following allowed energy levels seen in Equation 5. With the boundary condition that $J_m(k_{m,n}, R) =$ 0 with R the radius of the circle, the relation $k_{m,n} = a_{m,n}/R$ was found. As a result, the energy levels are shown to be inversely proportional to R^2 . The separation in two variables, due to a 2D problem, gives rise to two quantum numbers. The principal quantum number n, n = 1, 2, 3, etc., related to the number of radial nodes and the orbital quantum number m, $m = 0, \pm 1, \pm 2, etc$. The quantum numbers determine the degeneracy of the states. The m = 0 states are the only non-degenerate states and correspond to the s-orbitals of the hydrogen atom. All other states are two-fold degenerate, namely $\pm |m|$. The states, m = 1, 2, 3 could be compared to the p, d, f-orbitals of hydrogen respectively. The angular nodes created by m are not visible in the STM as $|\Psi|^2$ is measured. At the centre of the corral, a peak of $|\Psi|^2$ is only seen if m = 0 due to a peak in $J_m(k_{0,n}, 0)$. At higher m values $J_m(k_{m,n},0) = 0$ and therefore results in a node in the centre.

The experiments conducted in the STM showed the presence of peaks and dips in the constant-current images. A standing wave pattern was observed in the quantum corral. At -0.43 V, the first wave is observed in Figure 7b with the highest intensity in the centre. The black spot on the circle is a sub-surface defect and has limited influence on the wave pattern. At the higher energy of -0.11 V, Figure 7c, the amount of nodal planes increased in the quantum corral. A node was present in the centre, so $m \neq 0$. More images of the nodal planes together with the muffin tin LDOS plots are seen in Appendix 2: Quantum Corral Figure 11a-e.

To probe the occupied and unoccupied electronic states of the system a differential conductance spectrum was taken at the centre of the corral, seen in Figure 7. The peaks



Figure 7: (a) A schematical figure of the quantum corral with a radius of 5.9 nm. CO molecules, depicted as red (oxygen) and carbon (black) spheres, are adsorbed on a Cu(111) surface (orange). Image created with Blender.[30] (b) A constant-current STM image of the quantum corral showing a slight peak in the centre. The image is taken at -0.43 V and 1 nA. (c) Same as (b), but the image was obtained at -0.11 V which has given rise to more nodal planes and a dip in the centre. All the scale bars correspond to 2 nm in the figure. (d) An averaged dI/dV spectrum taken at the centre of the corral showing peaks which correspond to 1s, 2s, 3s, etc. The dashed line represents the muffin tin calculationz (e) A contour plot of 30 dI/dV specta along the diagonal of the corral visualising the spatial distribution of the electronic states. The orange line indicates the centre of the corral.

in the spectra are identified as m = 0 and correspond to 1s, 2s, 3s, etc. The experimental graph has a high resemblance to the muffin tin spectrum, only at higher energies the muffin tin model starts to slightly deviate from the experiment. In the experimental data, some smaller peaks between the s orbitals are observed. These low-intensity peaks likely arise by clicking a spot just off-centre. This is supported by the increase in off-centre peaks at higher energies when there are more nodal planes present. A position just off-centre would have the same shape at lower energies, but deviate more at higher energies.

The rise of nodal planes is particularly well visible in the spectra along the diameter of the corral, displayed as a contour plot in Figure 7e. The diagonal crosses the centre of the corral at a distance of 4 nm. Therefore, the spectrum at this distance is the same as the single spectra taken in the centre. The spatial distribution of the orbitals is visualised in the contour plot. All the peaks present at the centre correspond to m = 0 and can therefore be identified as s-orbitals. The other electronic states have a node in the centre and are localised in rings around the centre. Furthermore, at higher energies the distance between the s-orbitals increases.

In short, the theoretical solution was covered and the quantum numbers were related to the orbitals. The orbitals were subsequently visualised in the experimental spectra of the quantum corral.

Quantum Corral In A Magnetic Field

Perpendicular magnetic fields of 1, 2, 3 and 4 T were applied to the quantum corral to measure the effect on the artificial electronic lattice. At first glance, the differential conductance spectra taken in the centre show a minimal influence of the magnetic field on the electronic states of the corral, see Figure 8a. The spectra were quantitatively calibrated by setting the jump in the surface state of Cu(111) equal to $G_{2D} = 1.585 \text{ eV}^{-1}$ nm⁻². After the scaling and normalisation, the spectra on the corral and background overlap in intensity, see Appendix 2: Quantum Corral Figure 12. The intensities of the graphs should be comparable as they depict the same electron density of the surface state.

The spectra at different magnetic fields align to a large extent. The off-centre peaks are presumably due to an inaccuracy of the measurements and not the magnetic field. Nevertheless, the third and fourth peak show a trend of increased intensity at higher magnetic fields. Furthermore, the peaks broaden slightly with an applied magnetic field.

To focus on the differences between the dI/dV spectra, the spectra at different magnetic fields were subtracted from the spectrum at 0 T, seen in Figure 8b. By subtracting two quantized spectra, the electronic states of the tip were eliminated. A distinctive subtraction pattern of peaks and dips appeared which matched well with different magnetic fields and theory. The muffin tin calculations were translated with the onset of the experimentally determined surface state and then subtracted. At higher energies, the muffin tin pattern slightly deviates due to a lower alignment of the single muffin tin spectra with the experimental data at these energies. The subtraction reveals the smaller differences between the spectra. When a peak is present in the subtraction pattern, the 0 T spectrum has a higher intensity than the magnetic field spectrum and a dip indicates a higher intensity of the spectrum with magnetic field. At the energies of the s-orbitals, the pattern shows a peak followed by a dip and therefore indicate a shift to higher energies for the spectra obtained with magnetic field. The difference spectra have approximately an intensity of 10% of the original spectra, the effect is therefore rather small. As a result, when the individual differential conductance spectrum did not overlap considerably, the specific pattern changed. For instance for 1 T an off-centre peak is present at -0.10 V, at this particular point the difference spectrum matches less with the other magnetic fields. The same effect was observed for 4 T which for clarity reasons is not shown here.

To confirm that the characteristic pattern in the subtracted spectra arose due to the applied magnetic field, the difference spectra at various magnetic fields were compared. As the effect was slightly visible and the influence of clicking just off-centre was significant, the muffin tin calculations were used to make the comparison. With muffin tin, the spectra were calculated at the precise centre. Figure 8c illustrates that the amplitude of the peaks increases with an increased magnetic field. The pattern observed therefore appears to be



Figure 8: (a) dI/dV spectra taken at the centre of the corral at 0, 1, 2, 3, 4 T show a similar peak and dip pattern. The spectra are scaled with the jump in the surface state of Cu(111) which is equal to G_{2D} . (b) Subtracted dI/dV spectra of 0 T - 1, 2, 3 T taken at the centre of the corral showing a characteristic pattern. The subtracted muffin tin spectra (dotted graph) of 0 T - 3 T are shifted to match the onset of the surface state of the experimental data. (c) Subtracted muffin tin spectra of the LDOS in the centre of the corral showing an increase in amplitude of the peaks with increasing magnetic field.

an effect of the magnetic field and likely originates from a shift in energy of the electronic states. The applied magnetic field was not large enough to observe the splitting into Landau levels. To detect the Landau levels the ratio $\frac{\phi}{\phi_0}$ must be around 0.2. The flux was calculated for the corral by multiplying the magnetic field (4 T) with the area. Here $\frac{\phi}{\phi_0} = 0.05$ which is too low to observe the splitting.

To sum up, the magnetic field resulted in a characteristic pattern seen in the difference spectra due to an energy shift of the electronic states. The pattern matched with various magnetic fields and the calculations. The muffin tin model was used to show that the pattern originated from the magnetic field. Thereby, the muffin tin model corroborates the experimental effect of the magnetic field on the quantum corral.

4.2 Molecular Graphene

To explore the effect of the magnetic field on molecular graphene, a lattice was designed based on the work of Manoharan et al.[15] The unit cell of molecular graphene was enlarged to 3.86 nm to increase the magnetic flux. In order to keep enough electron confinement, more CO molecules were added to the design. The CO molecules were placed in a doubleringed hexagon, called a rosette. The rosettes were also placed in hexagonal symmetry. Figure 9a shows the lattice in the STM, two different sites are distinguished: The artificial atom site, from now on called site A, and the hopping site, the bridge site between two atoms, labelled B. The atomic A sites are in a honeycomb symmetry creating a lattice of molecular graphene. At the edges of the lattice blockers were placed at the same distance as the next rosette would have been placed. Blockers are used to partially extent the lattice and increase the effective size of the edge sites. Figure 9a was taken with a CO-terminated tip, increasing the chemical contrast and allowing to see the individual CO atoms.



Figure 9: (a) A constant-current STM image showing the molecular graphene lattice with the A and B site. The unit cell of the lattice is equal to 3.86 nm. The image is obtained with a CO-terminated tip at -0.40 V and 0.5 nA, The scale bar corresponds to 5 nm. (b) dI/dV spectra obtained at position A (orange) and B (green) of the lattice. The spectra show a s-Dirac cone, a p-type flat band and some features of a p-Dirac cone. The dotted lines show the calculated muffin tin spectra. The experimental spectra have a vertical translation for clarity. (c) A contour plot of dI/dV spectra taken along an A-B-A line showing the localisation of the A and B site. 21 spectra were taken along the line. The s-Dirac cone, the flat band and the p-Dirac cone are seen in the contour plot.

The local density of states of molecular graphene on site A and B were probed with differential conductance spectra. The spectra were averaged and obtained on different sites around the central rosette. Figure 9b shows the LDOS containing a s-Dirac cone (-0.30 V), a flat band (-0.11 V) and some features of a p-Dirac cone (0.07 V). The s-Dirac cone is also present in carbon-based graphene.[44] Dirac cones have unusual physics, such as effectively massless electrons. The flat band is an interesting feature as kinetic energy is absent making it sensitive to perturbations. The p-type flat band is localised on the B site. A flat band is localised in real space as the flat band is delocalised in reciprocal space. Theoretically the flat band should be infinitely narrow, the observed broadening is presumably caused by the finite lifetime of the electrons in the surface state. The experimental data show also a small peak from the flat band on the A site, likely due to the inaccuracy of the measurements which is further studied in Appendix 3: Molecular Graphene Figure 13.

The dI/dV spectra correspond well with the predictions from muffin tin. The double peak of the *s*-Dirac cone for muffin tin is less defined probably induced by a broadening which should have been less. The broadening of the flat band peak however matches adequately, indicating that the amount of broadening might depend on the energy as well.

The localisation of the atomic sites was studied in more detail with dI/dV spectra across an A-B-A line. The localisation was resolved at the energy of the flat band, seen in the contour plot in Figure 7c. The A site is present when there is a dip at the flat band energy and the B site is localised when there is a peak at this energy. Furthermore, the two peaks of the s-Dirac cone are seen around -0.30 V. The first peak can be assigned to the bonding s-orbital and the second peak to the antibonding orbital. The antibonding orbital is highly localised on the atomic sites with nodes in between and the bonding orbital is more spread with still some intensity on the bridge sites. This is observed in the spectra taken along the line, a lower intensity of the antibonding orbital at the B sites was measured in comparison with the bonding orbital. Additionally, grid spectra in Appendix 3: Molecular Graphene Figure 14a-b show the spatial distribution of the bonding and antibonding state of the s-Dirac cone. The p-Dirac cone which was slightly visible in the single spectra is observed more clearly in the contour plot in the two vertical lines around 0.07 V. The p-Dirac cone bonding and antibonding orbitals are less pronounced than the s-Dirac cone as they are higher in energy. The potential barrier is relatively lower at these higher energies.

In brief, the molecular graphene lattice was designed and constructed by placing CO molecules in anti-lattice positions. The differential conductance spectra display a *s*-Dirac cone, a *p*-type flat band and a *p*-Dirac cone. The spectra along an A-B-A line show the spatial localisation of the flat band on the B site.

Molecular Graphene In A Magnetic Field

A perpendicular magnetic field was applied to the molecular graphene lattice to study its effects. Figure 10a shows an image taken with a magnetic field which is more blurred, likely caused by noise induced from the magnet. The noise increased at higher magnetic fields. This had no noteworthy influence on the signal-to-noise ratio of the spectra.

The dI/dV spectra taken at 1, 2, 3, 4 T were subtracted from the 0 T spectrum in the same manner as was done for the quantum corral. Figure 10b shows the pattern arising after subtraction together with the muffin tin calculations. The characteristic pattern obtained



Figure 10: (a) STM images of a couple of rosettes from the molecular graphene lattice obtained at 0 T (left) and 4 T (right). The image taken at a higher magnetic field contains more noise. The images were made at 0.5 nA and -0.6 V. The scale bars correspond to 2 nm. (b) Subtracted dI/dV spectra of 0 T - 1, 2, 3, 4 T taken at position A and B. The spectra are scaled with the jump in the surface state of Cu(111). The dotted line represents the subtracted muffin tin graph of 0 T - 4 T which was shifted with the onset of the surface state of the experimental data. The spectra taken on site A have a vertical translation for clarity reasons. (c) Subtracted muffin tin graphs of 0 T - 1, 2, 3, 4 T showing an increase in amplitude of the peaks with increasing magnetic field. The spectra of site A have a vertical translation for clarity.

by experiments at different magnetic fields and theory align rather well. A different pattern was measured for the A and B sites, implying that the electrons feel the electronic structure they were confined to.

The effect of the magnetic field is quite modest as the individual spectra taken at 0 to 4 T on sites A and B overlap significantly. *Appendix 3: Molecular Graphene* Figure 14c shows the main difference which is present on the A site at the flat band energy. The flat band peak at -0.11 V has some intensity on the A site in all the spectra with magnetic field, however, without explicable trend. At the flat band energy of the subtracted spectra the experimental data on site A show a slight dip just like the B site. The muffin tin calculations on the A site however miss this dip. The magnetic field might not be the cause of this peak, but rather the inaccuracy of the measurement.

The experimental data provided no trend in the increasing strength of the magnetic field. To confirm that the pattern in the difference spectra was due to the magnetic field, subtracted muffin tin spectra were compared. The trend should be more pronounced in the muffin tin calculations as the location of the spectra is precisely the same between different magnetic fields. Figure 10c shows the subtracted pattern with an increased amplitude of the peaks at higher magnetic fields. Therefore, the pattern arises due to the magnetic field

and originates from a shift in energy of the electronic states. The spectra with magnetic field shift to a higher energy as the pattern displays first a peak followed by a dip. The shift is a result of the extra terms in the Hamiltonian when a magnetic field is applied. Furthermore, the magnetic flux was insufficient to observe the splitting into Landau levels or the integer QHE. The magnetic flux was calculated using the area of the unit cell and the largest applied magnetic field (4 T). For this lattice, $\frac{\phi}{\phi_0} = 0.025$ which is too low in comparison with 0.2 to notice these effects.

To summarise, the magnetic field led to a small shift in energy of the electronic states. The shift is observed when the spectra *with* magnetic field were subtracted from the spectra *without* magnetic field. The magnetic flux was too low to observe other effects. The theoretical outcome corroborated the experimental data as the individual spectra and the characteristic pattern matched.

5 Conclusion

Overall, two electronic quantum simulators were designed, built and analysed. The objective was to measure an effect of the magnetic field on the artificial electronic lattices of the quantum corral and molecular graphene. The results showed a characteristic pattern in the subtracted dI/dV spectra with a 10% intensity of the single spectra. The patten arose due to shift to higher energies of the electronic states when a magnetic field was applied. The magnetic flux was however insufficient to also observe splitting into Landau levels or the integer QHE. The theoretical muffin tin model corroborated the experimental data as the individual spectra and the characteristic pattern matched.

For the quantum corral the exact solution for a particle-in-a-circle was found and the quantum numbers m and n were related to the orbitals. The orbitals were identified accordingly in the dI/dV spectra taken in the centre, all the peaks coincided with the s-orbitals as m = 0. The spectra taken along the diagonal of the corral visualised the spatial distribution of the electronic states.

The molecular graphene lattice was realised and the local density of states was probed on the A and B site. The electronic structure consisted of a *s*-Dirac cone, a *p*-type flat band and a *p*-Dirac cone. The bonding and antibonding *s*-orbitals were distinguished in spectra along an A-B-A line. Additionally, the localisation of the flat band on the B site was observed.

Muffin tin calculations were performed for the quantum corral and molecular graphene. Muffin tin provided an adequate method to predict the electronic states of the systems given the experimental corroboration.

A perpendicular magnetic field was applied to the quantum corral and molecular graphene. The spectra obtained at different fields overlapped significantly. Nevertheless, smaller differences could be analysed when the dI/dV spectra with magnetic field were subtracted from the 0 T spectrum. The characteristic pattern that arose after subtraction matched with various magnetic fields and muffin tin calculations. Muffin tin showed that the peaks of the pattern increased in amplitude with higher magnetic fields, implying that the distinct pattern originated from the applied magnetic field. The pattern appeared due to a shift in energy of the electronic states caused by the extra terms present in the Hamiltonian for the magnetic field. The calculated ratio $\frac{\phi}{\phi_0}$ was well below the desired 0.2 and therefore insufficient to see the splitting in Landau levels and observe the states arising due to the QHE.

6 OUTLOOK

6 Outlook

This section has been removed for the online version.

7 Acknowledgements

During this project, I received a lot of support from different members of the CMI-group at Utrecht University. My master thesis has been a great learning experience for which I am grateful to all who contributed in any way.

Especially I want to thank my daily supervisor *Thomas Gardenier* for explaining me all the ins and outs of the Gauss and his kind guidance during my thesis. Besides teaching me the incredible amount of practical and theoretical knowledge, you also showed me how to conduct proper scientific research. Apart from the scientific interaction, I appreciated the cheerful chats in the basement on a very wide range of topics.

Furthermore, I would like to thank *Ingmar Swart* for allowing me to do my thesis in your group. Your pragmatic approach and strong expertise in the field made our discussions a pleasure for me.

I am also grateful to *Stephan Zevenhuizen* for his contributions to the Python script. Another acknowledgement goes to the members of CMI and especially the members of Team Kelder. The people of Team Kelder were always available and ready to help which created an open and delightful working atmosphere. The past year would not have been as much fun without the CMI-master students, we laughed a lot and spent many amusing evenings together.

Finally, I would like to thank my family and friends for their support and patience with all my enthusiastic attempts to explain quantum mechanics.

Bibliography

- [1] E. Schrödinger. *Mein Leben, meine Weltansicht.* dtv Verlagsgesellschaft, München, 2006.
- [2] D. M. Eigler and E. K. Schweizer. Positioning single atoms with a scanning tunneling microscope. *Nature*, 344:524–526, 1990.
- [3] M. Emmrich, M. Schneiderbauer, F. Huber, A. J. Weymouth, N. Okabayashi, and F. J. Giessibl. Force Field Analysis Suggests a Lowering of Diffusion Barriers in Atomic Manipulation Due to Presence of STM Tip. *Physical Review Letters*, 114(14):1–5, 2015.
- [4] L. Bartels, G. Meyer, K.H. Reider, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, and G. Ertl. Dynamics of Electron-Induced Manipulation of Individual CO Molecules on Cu(111). *Physical Review Letters*, 80(9):2004–2007, 1998.
- [5] T. H. Johnson, S. R. Clark, and D. Jaksch. What is a quantum simulator? *EPJ* Quantum Technology, 1(1):1–13, 2014.
- [6] R. P. Feynman. There is plenty of room at the bottom. Caltech Engineering and Science, 23(5):22–36, 1960.
- [7] A. Khelif, B. Aoubiza, S. Mohammadi, A. Adibi, and V. Laude. Complete band gaps in two-dimensional phononic crystal slabs. *Physical Review E - Statistical, Nonlinear,* and Soft Matter Physics, 74(4):1–5, 2006.
- [8] X. Zhang and Z. Liu. Extremal transmission and beating effect of acoustic waves in two-dimensional sonic crystals. *Physical Review Letters*, 101(26), 2008.
- [9] S.Y. Yu, X. C. Sun, X. Ni, Q. Wang, X. J. Yan, C. He, X. P. Liu, L. Feng, M. H. Lu, and Y. F. Chen. Surface phononic graphene. *Nature Materials*, 15(12):1243–1247, 2016.
- [10] S. R. Zandbergen and M. J. A. De Dood. Experimental observation of strong edge effects on the pseudodiffusive transport of light in photonic graphene. *Physical Review Letters*, 104(4):9–12, 2010.
- [11] Y. Plotnik, M. C. Rechtsman, D. Song, M. Heinrich, J. M. Zeuner, S. Nolte, Y. Lumer, N. Malkova, J. Xu, A. Szameit, Z. Chen, and M. Segev. Observation of unconventional edge states in 'photonic graphene'. *Nature Materials*, 13(1):57–62, 2014.
- [12] D. Jaksch and P. Zoller. The cold atom Hubbard toolbox. Annals of Physics, 315(1):52–79, 2005.
- [13] C. Wu and S. Das Sarma. px,y -orbital counterpart of graphene: Cold atoms in the honeycomb optical lattice. *Physical Review B - Condensed Matter and Materials Physics*, 77(23):1–14, 2008.

- [14] L. Tarruell, D. Greif, T. Uehlinger, G. Jotzu, and T. Esslinger. Creating, moving and merging Dirac points with a Fermi gas in a tunable honeycomb lattice. *Nature*, 483(7389):302–305, 2012.
- [15] K. K. Gomes, W. Mar, W. Ko, F. Guinea, and H. C. Manoharan. Designer Dirac fermions and topological phases in molecular graphene. *Nature*, 483(7389):306–310, mar 2012.
- [16] M. R. Slot, T. S. Gardenier, P. H. Jacobse, G. C. P. van Miert, S. N. Kempkes, S. J. M. Zevenhuizen, C. Morais Smith, D. Vanmaekelbergh, and I. Swart. Experimental realization and characterization of an electronic Lieb lattice. *Nature Physics*, 13(7):672–676, apr 2017.
- [17] J. Girovsky, J. Lado, F. Kalff, E. Fahrenfort, L. Peters, J. Fernández-Rossier, and S. Otte. Emergence of quasiparticle Bloch states in artificial crystals crafted atomby-atom. *SciPost Physics*, 2(3):020, jun 2017.
- [18] M. F. Crommie, C. P. Lutz, and D. M. Eigler. Confinement of electrons to quantum corrals on a metal surface. *Science (New York, N.Y.)*, 262(5131):218–20, oct 1993.
- [19] R. Drost, T. Ojanen, A. Harju, and P. Liljeroth. Topological states in engineered atomic lattices. *Nature Physics*, 13(7):668–671, mar 2017.
- [20] M. N. Huda, S. Kezilebieke, T. Ojanen, R. Drost, and P. Liljeroth. Tuneable topological domain wall states in engineered atomic chains. (100):1–13, jun 2018.
- [21] L. C. Collins, T. G. Witte, R. Silverman, D. B. Green, and K. K. Gomes. Imaging quasiperiodic electronic states in a synthetic Penrose tiling. *Nature Communications*, 8(May):1–6, 2017.
- [22] S. N. Kempkes, M. R. Slot, S. E. Freeney, S. J. M. Zevenhuizen, D. Vanmaekelbergh, I. Swart, and C. Morais Smith. Design and characterization of electrons in a fractal geometry. *Nature Physics*, 15(2):127–131, feb 2019.
- [23] M. R. Slot, S. N. Kempkes, E. J. Knol, W. M.J. Van Weerdenburg, J. J. Van Den Broeke, D. Wegner, D. Vanmaekelbergh, A. A. Khajetoorians, C. Morais Smith, and I. Swart. P -Band Engineering in Artificial Electronic Lattices. *Physical Review X*, 9(1):11009, 2019.
- [24] S. N. Kempkes, M. R. Slot, J. J. van den Broeke, P. Capiod, W. A. Benalcazar, D. Vanmaekelbergh, D. Bercioux, I. Swart, and C. Morais Smith. Robust zero-energy modes in an electronic higher-order topological insulator. *Nature Materials*, pages 1–14, sep 2019.
- [25] S. E. Freeney, J. J. van den Broeke, A. J. J. Harsveld van der Veen, I. Swart, and C. Morais Smith. Edge-dependent topology in Kekule lattices. jun 2019.

- [26] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel. 7 x 7 Reconstruction on Si(111)Resolved in Real Space. *Chemistry Letters*, 50(2):1211–1214, 1983.
- [27] Parksystems. Nanotechnology Solutions Partner Scanning Tunneling Microscopy (STM) Probing the Local Electronic Structure of a Sample's Surface.
- [28] F. Trixler. Quantum Tunnelling to the Origin and Evolution of Life. Current Organic Chemistry, 17(16):1758–1770, jul 2013.
- [29] G. Binnig and H. Rohrer. Scanning Tunneling Microscopy. Surface Science, 126:236– 244, 1983.
- [30] Blender Online Community. Blender a 3D modelling and rendering package, 2019.
- [31] L. Bartels, G. Meyer, and K. H. Rieder. Controlled vertical manipulation of single CO molecules with the scanning tunneling microscope: A route to chemical contrast. *Applied Physics Letters*, 71(2):213–215, 1997.
- [32] G. Meyer, S. Zöphel, and K. H. Rieder. Manipulation of atoms and molecules with a low temperature scaning tunneling microscope. *Applied Physics A*, 63:557–564, 1996.
- [33] G. Meyer, L. Bartels, and K. H. Rieder. Atom manipulation with the STM: Nanostructuring, tip functionalization, and femtochemistry. *Computational Materials Science*, 20(3-4):443–450, 2001.
- [34] B. Hammer, Y. Morikawa, and J. K. Nørskov. CO chemisorption at metal surfaces and overlayers. *Physical Review Letters*, 76(12):2141–2144, 1996.
- [35] J. A. Stroscio and R. J. Celotta. Controlling the Dynamics of a Single Atom in Lateral Atom Manipulation. Science, 306(October):242–248, 2004.
- [36] W. Ko, C. Ma, G. D. Nguyen, M. Kolmer, and A. P. Li. AtomicScale Manipulation and In Situ Characterization with Scanning Tunneling Microscopy. *Advanced Functional Materials*, page 1903770, oct 2019.
- [37] G. A. Fiete and E. J. Heller. Colloquium: Theory of quantum corrals and quantum mirages. *Reviews of Modern Physics*, 75(3):933–948, 2003.
- [38] A. J. Heinrich, C. P. Lutz, J. A. Gupta, and D. M. Eigler. Molecule cascades. *Science*, 298(5597):1381–1387, 2002.
- [39] M. R. Slot. *Patterning atomic flatland: Electronic lattices crafted atom by atom.* PhD thesis, Utrecht University, 2019.
- [40] G. Hörmandinger. Imaging of the Cu(111) surface state in scanning tunneling microscopy. *Physical Review B*, 49(19):13897–13905, 1994.

- [41] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K. S. Novoselov, and A. K. Geim. The electronic properties of graphene. APS Physics, 81(1):109–162, 2009.
- [42] D. Tong. The quantum Hall effect. Number January. University of Cambridge, Cambridge, 2016.
- [43] J. R. Hook and H. E. Hall. Solid State Physics. John Wiley And Sons Ltd, The Manchester Physics Series, 2nd edition, 1991.
- [44] A. Luican, G. Li, A. Reina, J. Kong, R. R. Nair, K. S. Novoselov, A. K. Geim, and E. Y. Andrei. Single-layer behavior and its breakdown in twisted graphene layers. *Physical Review Letters*, 106(12):1–10, 2011.
- [45] D. L. Miller, K. D. Kubista, G. M. Rutter, M. Ruan, W. A. de Heer, P. N. First, and J. A Stroscio. Observing the Quantization of Zero Mass Carriers in Graphene. *Science*, 324(5929):924–927, may 2009.
- [46] M. Brzezińska, A. M. Cook, and T. Neupert. Topology in the Sierpiński-Hofstadter problem. *Physical Review B*, 98(20):1–9, 2018.
- [47] J. C. Slater. Wave functions in a periodic potential. *Physical Review*, 51(10):846–851, 1937.
- [48] S. Li, W. X. Qiu, and J. H. Gao. Designing artificial two dimensional electron lattice on metal surface: a Kagome-like lattice as an example. *Nanoscale*, 8(25):12747–12754, jun 2016.
- [49] J. H. Davies. The Physics of Low-Dimensional Semiconductors. Cambridge University Press, Cambridge, 1997.
- [50] V. D. Pham, K. Kanisawa, and S. Fölsch. Quantum Rings Engineered by Atom Manipulation. *Physical Review Letters*, 123(6):66801, 2019.
- [51] M. H. Liu, P. Rickhaus, P. Makk, E. Tóvári, R. Maurand, F. Tkatschenko, M. Weiss, C. Schönenberger, and K. Richter. Scalable tight-binding model for graphene. *Physical Review Letters*, 114(3):1–7, 2015.

Appendix 1: Muffin Tin Matrices

All the matrices shown here are valid for the situation with 3 boxes in x and 3 in y, creating a $9 \ge 9$ matrix. The matrix can be extended accordingly for larger systems.

The second derivative matrix of x: Dirichlet boundary conditions.

The second derivative matrix of y: Dirichlet boundary conditions.

.

The second derivative matrix of x: Periodic boundary conditions.

$$\frac{1}{(\Delta x)^2} \begin{vmatrix} -2 & 1 & 0 & \dots & \\ 1 & -2 & 1 & 0 & & \\ 0 & 1 & -2 & 1 & 0 & & \\ \vdots & & & & & \\ & & 0 & 1 & -2 & 1 \\ & & & 0 & 1 & -2 \end{vmatrix}$$
(8)

The second derivative matrix of y: Periodic boundary conditions.

$$\frac{1}{(\Delta y)^2} \begin{vmatrix}
-2 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 1 \\
0 & -2 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\
0 & 0 & -2 & 0 & 0 & 1 & 0 & 0 & 1 \\
1 & 0 & 0 & -2 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & -2 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & -2 & 0 & 0 & 1 \\
1 & 0 & 0 & 1 & 0 & 0 & -2 & 0 & 0 \\
0 & 1 & 0 & 0 & 1 & 0 & 0 & -2 & 0 \\
1 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & -2
\end{vmatrix} \tag{9}$$

Appendix 2: Quantum Corral



Figure 11: Constant-current STM images of 12 by 12 nm taken at 1 nA with corresponding muffin tin maps below. All scale bars are 2 nm. (a) -0.43 V (b) -0.34 V (c) -0.27 V (d) -0.20 V (e) -0.11 V.



Figure 12: Averaged dI/dV spectra taken at the centre of the quantum corral scaled with the jump in the surface state of Cu(111). The dash-dotted lines indicate the corresponding averaged background spectra on clean Cu(111). The spectra for different magnetic fields have a vertical offset for clarity. The spectra taken at the centre and their background show similar intensities as they represent the same surface state.

Appendix 3: Molecular Graphene



Figure 13: (a) An STM image taken at -0.35 V and 0.5 nA at 0 T showing the locations on which spectra were obtained. (b) dI/dV spectra of points 2 and 3 shown in (a), where the aim was to measure the A-site. The effect of a misclick, spectrum 2, results in picking up some intensity of the flat band.



Figure 14: (a) Grid spectroscopy performed on a quarter of the molecular graphene lattice. The energy shown, -0.326 V, corresponds to the bonding orbital of the s-Dirac cone. An STM image of a quarter of the lattice is shown in the background to guide the eye. The green points represent the 20 x 20 grid points where the spectra were obtained. (b) The same as (a), only at the anti-bonding energy of the s-Dirac cone, -0.270 V. Strong nodes between the atomic sites are seen. (c) Averaged dI/dV spectra taken on the A and B sites of the molecular graphene obtained at different magnetic fields. On the A site some intensity of the flat band is seen when a magnetic field is applied. The spectra of site A have a vertical translation for clarity.