Modeling of Nanoscale Systems:
Electronic Properties and Self-Assembly

BY

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THESIS

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Dedication

To Ludmila Karyakina,
my dear friend and mentor who taught me to
be strong and whose wisdom and spirit I admire.
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### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Modeling of Nanoscale Systems</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Thesis Structure</td>
<td>2</td>
</tr>
<tr>
<td><strong>2</strong> THEORY AND METHODS</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2.2 Quantum Mechanical DFT Methods</td>
<td>7</td>
</tr>
<tr>
<td>2.3 DFT for Periodic Systems</td>
<td>19</td>
</tr>
<tr>
<td>2.3.1 Periodic Boundary Conditions and Bloch Theorem</td>
<td>20</td>
</tr>
<tr>
<td>2.3.2 Representation of Wavefunctions and Energy Cutoff</td>
<td>22</td>
</tr>
<tr>
<td>2.3.3 Core Electrons and Pseudopotential Approximations</td>
<td>25</td>
</tr>
<tr>
<td>2.3.4 Integrals in k-space and Sampling of the Brillouin Zone</td>
<td>27</td>
</tr>
<tr>
<td>2.3.5 The SIESTA method</td>
<td>28</td>
</tr>
<tr>
<td>2.3.5.1 Basis set</td>
<td>29</td>
</tr>
<tr>
<td>2.3.5.2 Pseudopotentials</td>
<td>31</td>
</tr>
<tr>
<td>2.3.5.3 Brillouin zone sampling</td>
<td>32</td>
</tr>
<tr>
<td>2.3.5.4 Electron Hamiltonian and matrix elements</td>
<td>34</td>
</tr>
<tr>
<td>2.4 Electron Transport Techniques</td>
<td>38</td>
</tr>
<tr>
<td>2.4.1 Non-equilibrium Green's functions</td>
<td>38</td>
</tr>
<tr>
<td>2.4.2 Landauer formalism</td>
<td>46</td>
</tr>
<tr>
<td>2.5 Self-Assembly Methods</td>
<td>50</td>
</tr>
<tr>
<td><strong>3</strong> ELECTRONIC STRUCTURE OF POROUS NANOCARBONS</td>
<td>51</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>51</td>
</tr>
<tr>
<td>3.2 Computational methods</td>
<td>53</td>
</tr>
<tr>
<td>3.3 Results and discussion</td>
<td>53</td>
</tr>
<tr>
<td>3.3.1 Porous graphene nanoribbons</td>
<td>53</td>
</tr>
<tr>
<td>3.3.2 Porous graphene</td>
<td>55</td>
</tr>
<tr>
<td>3.3.3 Porous nanotubes</td>
<td>59</td>
</tr>
<tr>
<td>3.3.4 Unified model of PNC conductivity</td>
<td>63</td>
</tr>
<tr>
<td>3.4 Conclusion</td>
<td>68</td>
</tr>
<tr>
<td><strong>4</strong> CHEMICAL SENSING AT GRAPHENE GRAIN BOUNDARY</td>
<td>69</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>69</td>
</tr>
<tr>
<td>4.2 Computational methods</td>
<td>70</td>
</tr>
<tr>
<td>4.3 Experimental results and discussion</td>
<td>73</td>
</tr>
<tr>
<td>4.3.1 Synthesis and characterization of graphene grain boundaries</td>
<td>73</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>PAGE</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>4.3.2</td>
<td>The graphene grain boundary sensitivity</td>
</tr>
<tr>
<td>4.4</td>
<td>Theoretical study of the graphene grain boundary sensitivity</td>
</tr>
<tr>
<td>4.4.1</td>
<td>Physisorption of DMMP molecules at graphene grain boundaries</td>
</tr>
<tr>
<td>4.4.2</td>
<td>Electron transport through graphene grain boundaries</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusion</td>
</tr>
<tr>
<td>5</td>
<td>CARBON DIOXIDE REDUCTION ON MOLYBDENUM DISULFIDE EDGES</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>5.2</td>
<td>Computational methods</td>
</tr>
<tr>
<td>5.3</td>
<td>Experimental results and discussion</td>
</tr>
<tr>
<td>5.3.1</td>
<td>MoS(_2) catalyst characterization</td>
</tr>
<tr>
<td>5.3.2</td>
<td>CO(_2) reduction performance of MoS(_2) catalyst</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Effect of ionic liquid on the CO(_2) reduction performance</td>
</tr>
<tr>
<td>5.4</td>
<td>Theoretical study of MoS(_2) catalytic activity</td>
</tr>
<tr>
<td>5.4.1</td>
<td>Electronic structure of MoS(_2) edges</td>
</tr>
<tr>
<td>5.4.2</td>
<td>Quantum molecular dynamic simulations of the hydrated (EMIM-CO(_2))(^+) complex</td>
</tr>
<tr>
<td>5.5</td>
<td>Conclusion</td>
</tr>
<tr>
<td>6</td>
<td>CORRELATED DISKOID-LIKE ELECTRONIC STATES</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>6.2</td>
<td>Two-electron diskoid-like states</td>
</tr>
<tr>
<td>6.2.1</td>
<td>Computational method</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Results and discussion</td>
</tr>
<tr>
<td>6.2.3</td>
<td>Mean-field solutions</td>
</tr>
<tr>
<td>6.3</td>
<td>One-electron diskoid-like states</td>
</tr>
<tr>
<td>6.3.1</td>
<td>Charge distribution on a metallic disk</td>
</tr>
<tr>
<td>6.3.2</td>
<td>Induced charge distribution and image potential</td>
</tr>
<tr>
<td>6.3.3</td>
<td>One-electron 1D diskoid-like states</td>
</tr>
<tr>
<td>6.3.4</td>
<td>One-electron 2D diskoid-like states</td>
</tr>
<tr>
<td>6.4</td>
<td>Conclusion</td>
</tr>
<tr>
<td>7</td>
<td>CLUSTERS AND LATTICES OF PARTICLES STABILIZED BY DIPOLAR COUPLING</td>
</tr>
<tr>
<td>7.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>7.2</td>
<td>Computational methods</td>
</tr>
<tr>
<td>7.3</td>
<td>Results and discussion</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Planar arrangements of dipolar particles</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Multilayers of honeycomb plaques</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Planar lattices built from particle plaques</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Tubular arrangements of dipolar particles</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>PAGE</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>7.4 Conclusion</td>
<td>154</td>
</tr>
<tr>
<td>8 SELF-ASSEMBLY OF MAGNETITE NANOCUBES INTO HELICAL SUPERSTRUCTURES</td>
<td>155</td>
</tr>
<tr>
<td>8.1 Introduction</td>
<td>155</td>
</tr>
<tr>
<td>8.2 Experimental results and discussion</td>
<td>157</td>
</tr>
<tr>
<td>8.2.1 Experimental setup and synthesis of magnetite nanocubes</td>
<td>157</td>
</tr>
<tr>
<td>8.2.2 Self-assembly of magnetite nanocubes at different surface concentration regimes</td>
<td>160</td>
</tr>
<tr>
<td>8.3 Theoretical model and computational methods</td>
<td>167</td>
</tr>
<tr>
<td>8.4 Theoretical study of self-assembly of magnetite nanocubes</td>
<td>175</td>
</tr>
<tr>
<td>8.4.1 Semi-analytical modeling of small magnetite nanocube aggregates</td>
<td>176</td>
</tr>
<tr>
<td>8.4.2 MC study of self-assembly of nanocubes</td>
<td>182</td>
</tr>
<tr>
<td>8.5 Conclusion</td>
<td>190</td>
</tr>
<tr>
<td>9 CONCLUDING REMARKS</td>
<td>192</td>
</tr>
<tr>
<td>CITED LITERATURE</td>
<td>196</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>224</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>225</td>
</tr>
<tr>
<td>VITA</td>
<td>226</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Correspondence rule for GNRs and CNTs. $N$ - number of dimers forming GNR, $p$ - index for the chirality vector in GNR and CNT; cond. - conductivity property (semiconducting (s) or metallic (m)); geometry defines the symmetry with respect to the mirror plane perpendicular to the ribbon and containing its axis: symmetric (s), asymmetric (a). Examples of AGNRs for $N = 7,...,14$ and ZGNRs for $N = 5,...,12$ are illustrated.</td>
<td>60</td>
</tr>
<tr>
<td>II</td>
<td>The energy eigenvalues (a.u.) for orbitals of the 2D hydrogen atom $(Z = 2)$ confined in the disk of radius $a = 1$ nm. The red line separates energy states with $E &lt; 0$ from those with $E &gt; 0$.</td>
<td>114</td>
</tr>
<tr>
<td>III</td>
<td>Energy spectrum of diskoid-like states (meV).</td>
<td>135</td>
</tr>
<tr>
<td>IV</td>
<td>The energy factor per particle, $\bar{\varepsilon}$, in multiple layers of identical honeycomb plaques with different orientations of dipoles. (top) The horizontally arranged numbers show the circumcircles (particles) in these clusters. (side) The numbers (1-4) gives the number of layers and the mutual dipole orientation in the neighboring layers. The bold numbers show dipole orientations with minimal energies.</td>
<td>144</td>
</tr>
<tr>
<td>V</td>
<td>The energy factors per particle, $\bar{\varepsilon}$, in honeycomb plaques with different orientation of dipoles: antiferromagnetic (electric) vertical (AV), antiferromagnetic (electric) horizontal (AH) and circular. AV and AH double-layers with the $sh$ and $hcp$ lattices are considered. Bold numbers show the dipole orientations with a minimal energy.</td>
<td>147</td>
</tr>
<tr>
<td>VI</td>
<td>Binding energies between honeycomb plaques calculated per particle at the boundary. Different sizes and mutual orientation of circulating dipoles are considered (same/opp. = dipolar circulation of neighboring plaques).</td>
<td>152</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Examples of porous nanocarbons: porous armchair nanoribbon, porous graphene, porous armchair CNT. ........................................ 52</td>
</tr>
<tr>
<td>2</td>
<td>Band structure of: a) pristine 11-AGNR, b) 11-AGNR with centered SP, c) 11-AGNR with shifted SP, e) pristine 10-ZGNR, f) 10-ZGNR with centered SP, g) 10-ZGNR with shifted SP. The energy scales for (b, c, f, g) cases are the same. Density of states: d) centered and shifted SP in 11-AGNR, h) centered and shifted SP in 10-ZGNR. Insets: Unit cells for 11-AGNR and 10-ZGNR with the standard pore ........................................ 54</td>
</tr>
<tr>
<td>3</td>
<td>(top) Band structure of a) a honeycomb SP-superlattice in e) and three rectangular SP-superlattices with b) (N_A = 15, N_Z = 4), c) (N_A = 7, N_Z = 2), and d) (N_A = 7, N_Z = 8). (bottom) e) honeycomb SP-superlattice, f) rectangular SP-superlattice characterized by (N_A, N_Z), g) rectangular superlattice with triangular-shape pores ........................................ 57</td>
</tr>
<tr>
<td>4</td>
<td>(top) Effective replacing of porous N-AGNR by “daughter” pristine (N_1)- and (N_2)-AGNR ((N = 14, N_1 = 5, N_2 = 6)). (bottom) Effective replacing of rectangular SP-superlattice with (N_A &gt; N_Z) by set of pristine AGNRs ((N_A = 15, N_Z = 4)). ........................................ 58</td>
</tr>
<tr>
<td>5</td>
<td>Band structures in pristine CNTs: a) ACNT ((10,10)), b) ZGNT ((9,0)), c) ZGNT ((10,10)); d) DOS. Porous CNTs: e) ACNT ((10,10)), f) ZGNT ((9,0)), g) ZGNT ((10,10)); h) DOS. The energy scales for (b,c) and (f, g) cases are the same. ........................................ 61</td>
</tr>
<tr>
<td>6</td>
<td>Cutting of: (top) ((10,0))ZCNT into ((19,1))AGNR and (middle) ((9,9))ACNT into ((18,0))ZGNR (opening of the GNRs is schematically shown). (bottom) Removal of atoms from porous ((10,10))ACNT leading to ((17,0))ZGNR 62</td>
</tr>
<tr>
<td>7</td>
<td>(top) Dependence of the band gap in the pristine and porous AGNR on the number of dimers (the central position of the SP). (bottom) The same dependence in ZCNT on the chirality index. ........................................ 65</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>8</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>68</td>
</tr>
<tr>
<td>10</td>
<td>72</td>
</tr>
<tr>
<td>11</td>
<td>76</td>
</tr>
</tbody>
</table>

Band structures of nanocarbons with periodic 55-77 Stone-Wales defects: a) 11-AGNR, b) 10-ZCNT, c) graphene superlattice with $N_A = 7$ and $N_Z = 4$, d) graphene superlattice with $N_A = 9$ and $N_Z = 4$. Figures (e-h) show unit cells for the respective cases.

Edge magnetism. The alternation of spin imbalance as result of introduction of 55-77 SW defects.

Characterization and sensing properties of individual grain boundary (GB). (a) False color SEM image of the fabricated GB sensing platform (scale bar-5μm). A corresponding electrical circuit is also shown. (b) D-band and (c) 2D/G ratio mapping of the synthesized graphene (Scale bar-5μm). (d) Selected area electron diffraction (SAED) patterns obtained from left (GL), right (GR) grains and GB region. Sharp and single hexagonal shape evidences the single crystalline structure of grains. A pattern with two discrete sets of rotated spots appears in the merging region indicating the imperfect stitching of the two graphene grains which results in the origination of grain boundary (GB). (e) Sensing signal for the dimethyl methylphosphonate (DMMP) and 1,2-dichlorobenzene (DCB) gas molecules. (f) Fabricated multi-electrodes single GB sensing platform (scale bar-5μm) and the sensitivity of the GB devices with respect to the distance from the electrodes. (g) Sensitivity of the individual GB against DMMP molecules extracted from the real time sensing measurements. The inset magnifies the same curves.

Extracted sensitivity for individual GB. The SEM image is the same image as shown in Figure 10 a. The sheet resistances of the left and right grains were calculated using the I-V characteristics of device ($R_{2-3}$ for left grain and $R_{4-5}$ for right grain) and considering the geometry of the flakes using the equation ($R = R_0 \cdot W_{Avg}/L$). For each flake, $L$ is the distance between corresponding electrodes and $W_{Avg}$ is the geometric mean of the sample width, calculated from $\frac{1}{W_{Avg}} = \frac{1}{L} \int_0^L \frac{dx}{W_x}$. Using inverse approach, resistance of blue and red portion of the flakes (trapezoids) were calculated, and resistance of individual GB was extracted as ($R_{GB} = R_{3-4} - R_{Red} - R_{Blue}$). In our measurement setup, resistances of left, right and GB region were monitored simultaneously, and time-dependent resistance of isolated GB were plotted. The sensitivity for the isolated GB were calculated from $S = (\Delta R_{GB}/R_{GB})$. 

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<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Classical and quantum simulation studies. (a) The top and (b) side views of the modeled graphene grain boundary structure deposited on the defective amorphous SiO\textsubscript{2} substrate with physisorbed DMMP molecules. Two transmission regions with different translational vectors are highlighted by red (small gap) and blue (large gap) colors. (c) Two-dimensional electrostatic potential energy profile across the GB. (d) One-dimensional potential profiles (with and without DMMP molecules) obtained by averaging of the 2D potential along the direction normal to the GB. (e) Calculated transmission spectra (red curves) for the open GB region (highlighted in red in a) and the grain region (green dashed lines), shown both without and with homogeneous n-doping (shifted left) by DMMP molecules. The Fermi level, $E_f$, is shifted down (Dirac point of the grains) due to the p-doping by SiO\textsubscript{2}. Bias window intersects the spectra of certain transmission regions and opens the passage of electrons through them, while adsorbed DMMP molecules tend to close these passage regions. (f) Calculated sensitivity for the GB and graphene grain (inset) with respect to the applied voltage for DMMP molecules. (g) Maximum sensitivity calculated as a function of a DMMP-induced spectral shift over a thermal energy, $\Delta E/kT$.</td>
</tr>
<tr>
<td>13</td>
<td>Hybrid MD simulations. (a) Graphene with the GB between two grains with a mismatch angle of 18° (b-c) Representative regions: pristine and defective, respectively.</td>
</tr>
<tr>
<td>14</td>
<td>Supercells for electron transport calculations. (a-b) Unit cells with different defect topologies for nonconductive region (marked by blue in Figure 12 a). (b-d) Unit cells with different defect topologies for conductive region (marked by red in Figure 12 a).</td>
</tr>
<tr>
<td>15</td>
<td>Transmission spectra of GBs with different translational vectors of left and right grains with different defect topologies. Blue solid and dashed lines show the transmission coefficients for the GBs with supercell units shown in Figure 14 a-b (blue region in Figure 12 a). Red solid and dashed lines show the transmission coefficients for the GBs with supercell units shown in Figure 14 c-d (red region in Figure 12 a). Relative values of the transport gaps are shown.</td>
</tr>
<tr>
<td>16</td>
<td>Bias-dependent sensitivity trend for graphene GB sensors. The figure shows the experimental trend of molecular sensitivity to the source-drain bias. The experiments for different applied biases are carried out in similar conditions.</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>17</td>
<td>Illustration of the model for electron transport calculations. Model transmission spectra for an ideal conduction channel with $T r_0(E)$ is shown. $\Delta E$ is a shift of the transmission caused by the adsorption of the DMMP gas molecules.</td>
</tr>
<tr>
<td>18</td>
<td>Structural and elemental analysis of MoS$_2$, (a) Optical image of bulk MoS$_2$ used as catalyst (scale bar, 2 mm), (b) SEM images of the MoS$_2$ displaying the stacked layered structure and sharp edges of the MoS$_2$ flakes. Scale bars are 50 and 5 $\mu$m (for inset) respectively, and (c) high-angle annular dark-field (HAADF) images (scale bar, 5 nm) showing both the 1T (blue) and 2H (red) phases of MoS$_2$, along with their respective Fast Fourier Transforms (FFTs) (inset). (d) Higher magnification HAADF images show clearly distinct atomic configuration corresponding to the 1T (top) and 2H (bottom) type of MoS$_2$. The related schematic atomic models have also been shown on the right side. (e) Raw grayscale HAADF and false-color low-angle annular dark-field (LAADF) image (inset) of MoS$_2$ edges (scale bar, 5 nm) and (f) the line scans (red and blue towards edges) identifying Mo atoms to be the terminating atoms in the general case. In limited instances, an additional light atom (gray line scan) occupying what should be a Mo-position, most probably a carbon atom from the STEM substrate.</td>
</tr>
<tr>
<td>19</td>
<td>Scanning electron microscopic (SEM) images of bulk MoS$_2$. (a) The natural layered structure of bulk MoS$_2$ is simply visible (scale bar, 20 $\mu$m). (b) High magnification image (scale bar, 2 $\mu$m) more clearly demonstrates the sharp MoS$_2$ edges which are supposed to be more electro-chemically active sites for CO$_2$ reduction.</td>
</tr>
<tr>
<td>20</td>
<td>Vertically aligned MoS$_2$ nanoflakes. (a) ABF STEM images of vertically aligned MoS$_2$ (scale bar, 20 nm). STEM analysis (inset) shows the vertically aligned texture of MoS$_2$ nanoflakes (scale bar, 5 nm). (b) RGB added image of (G+B) high-angle annular dark-field (HAADF) (R) inverted ABF STEM images of vertically aligned MoS$_2$. High resolution HAADF STEM image of vertically aligned MoS$_2$ (scale bar, 2nm). Mo atoms are brighter and larger in size in comparison to sulfur atoms due to high atomic number. (c) Raman spectrum for vertically aligned MoS$_2$. (d) CO$_2$ reduction performance of bulk MoS$_2$ and vertically aligned MoS$_2$ represented by VA MoS$_2$.</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>21</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>CO₂ reduction performance of the bulk MoS₂ catalyst in the EMIM-BF₄ solution: (a) Cyclic voltammetric (CV) curves for bulk MoS₂, Ag nanoparticles (Ag NPs) and bulk Ag in CO₂ environment. The experiments were performed in 96 mol% water and 4 mol% EMIM-BF₄ solution by sweeping applied potential from +1 V to -0.764 V vs RHE. The vertical gray line indicates the low overpotential (∼54 mV) for CO₂ reduction at bulk MoS₂. (b) CO and H₂ Faradaic Efficiency (F.E) at different applied potentials. (c) The current density of CO₂ reduction (measured by Chrono-Amperometry) at -0.764 V vs. RHE as a function of water mole fraction in 4 mol% EMIM-BF₄ electrolyte. The pH value of the solutions was also monitored (SI file). (d) Chrono-Amperometry results of MoS₂ catalyst in different solutions (96 mol%, 90 mol% and 0 mol% water) showing negligible loss in current density even after 10 hours.</td>
</tr>
<tr>
<td>22</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>Overview of different catalysts performance at different overpotentials (η). Bulk MoS₂, Ag nanoparticles (Ag NPs) and Bulk Ag results were taken from the present study where electrochemical experiments were performed in similar conditions. CO₂ reduction performance curve of bulk Ag is not visible as it is unable to reduce CO₂ in experimental conditions.</td>
</tr>
<tr>
<td>23</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>MoS₂-nanoribbon structure. (a) A single layer nanoribbon. Mo-atoms are pink, S-atoms are yellow. In the unit cell bulk Mo-atoms are red, edge Mo-atom is blue, and S-atoms are orange. (b) Shifted double layer (side view).</td>
</tr>
<tr>
<td>24</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>Electronic structure of single and shifted double layer MoS₂-nanoribbon. (a) and (c) show the spin resolved band structures (red and blue curves for α- and β-channels, respectively) of MoS₂ single and double layers, respectively. (b) and (d) show the total DOS for the corresponding structures. I, II, and III figures show the wavefunction modulus at the corresponding metallicity points (Mo-edge (top), S-edge (bottom)) in the single layer MoS₂-nanoribbon.</td>
</tr>
<tr>
<td>25</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>DFT calculations of electron density. Projected density of states (PDOS) for spin up channel of: (a) the Mo atom at the edge and Mo atom within the lattice; (b) s, p, and d orbital of Mo-edge atom. (c) PDOS of d-band of Mo-edge atom compared to PDOS of d-band of Ag atom from bulk and from the surface of the Ag-slab of 8.32 Å thickness. Picture discloses that electron density on Mo-edge atom is significantly (∼11 times) higher than the electron density on Ag atom.</td>
</tr>
</tbody>
</table>
26 Projected Density of State (PDOS) for spin up channel of the edge sulfur (S) atoms in single MoS$_2$-nanoribbon: Contributions of s-, p-, and d-orbitals to DOS of the edge S atoms are shown. .................................................. 105

27 Formation and stability of (EMIM-CO$_2$)$^+$ complex. First row (complex near the C$_4$ proton): (a) Formation of (EMIM-HCO$_3^-$) complex in neutral conditions. (b) Formation of (EMIM-CO$_2$)$^+$ complex in acidic conditions. (c) Time dependence of the hydrogen bond length formed between CO$_2$ and EMIM$^+$ ion. Second row (complex near the C$_2$ proton in acidic pH): (d) Initial configuration of (EMIM-CO$_2$)$^+$ complex with H-bonds shown between the C$_2$ proton (highlighted by iceblue) and the oxygen (highlighted by orange) from CO$_2$. (e) Stabilization of the (EMIM-CO$_2$)$^+$ complex with an additional coordination of CO$_2$ and the water molecule (the oxigen is highlighted by orange). (f) Time dependence of the hydrogen bond length formed between CO$_2$ and EMIM$^+$ and between CO$_2$ and an adjacent water molecule. ............................. 108

28 Model (He-type) system with diskoid-like states, where one electron is confined within the 2D disk area in the $z = 0$ plane and the second electron is orbiting around the disk in 3D. ................................. 112

29 ME density $\rho_1\rho_2|\Psi_{\Sigma_g}(\vec{r}_1, \vec{r}_2)|^2$ ($\vec{r}_2$ fixed) when EE sits on the disk plane at a distance of $\rho_2 = 0.2a$ (cases a, b, c) and $\rho_2 = 2.5a$ (case d) from the center with $\phi_2 = 0$ for a) $N = 5$, b) $N = 29$, c) $N = 48$, d) $N = 120$. The coordinates are given in units of the disk radius, $a = 1$ nm. ..................... 117

30 (top) Evolution of the ME density $\rho_1\rho_2|\Psi_{\Sigma_g}(\vec{r}_1, \vec{r}_2)|^2$ ($\vec{r}_2$ fixed) for EE positioned in the disk plane ($z_2 = 0, \phi_2 = 0$) at different distances $\rho_2$ from the disk center for the $N = 29$ state. The snapshots correspond to $\rho_2 = 0.1a - 0.8a$ values separated by $\Delta\rho_2 = 0.1a$. The area $\rho_1 \leq a$ is shown. (middle) The same as in (top) for the $N = 120$ state. The snapshots correspond to $\rho_2 = 1a - 3.8a$ values separated by $\Delta\rho_2 = 0.4a$. The area $\rho_1 \leq a$ is shown. (bottom) Evolution of the EE density $\rho_1\rho_2|\Psi_{\Sigma_g}(\vec{r}_1, \vec{r}_2)|^2$ ($\vec{r}_1$ fixed) in the disk plane ($z_2 = 0$) for different distances $\rho_1$ of ME ($\phi_1 = 0$) from the center of the $N = 72$ state. The snapshots correspond to $\rho_1 = 0.1a - 0.8a$ values separated by $\Delta\rho_1 = 0.1a$. The area $\rho_2 \leq 4a$ is shown. The disk is gray. ......................... 118

xv
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>119</td>
</tr>
<tr>
<td>(top) The radial distributions $\rho_{ME}$ of ME, $\rho_1</td>
<td>R_{1l_1n_1}(\rho_1)</td>
</tr>
<tr>
<td>32</td>
<td>120</td>
</tr>
<tr>
<td>(top) Degree of delocalization of energy eigenfunctions in $N$ states over the basis wavefunctions, $\Delta_{loc}$, where $M = 160$ is total number of basis wavefunctions. (inset) The average number of states $\langle n / M \rangle$ whose variational coefficients exceed a threshold of $\epsilon = 0.05, 0.02$. (bottom) The average electron-electron distance $\langle r_{12} \rangle$ as a function of $N$.</td>
<td></td>
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<tr>
<td>33</td>
<td>122</td>
</tr>
<tr>
<td>Comparison of the mean-field potentials without $U^I(\rho_2, z_2 = 0)$ (solid lines) and with $U^{II}(\rho_2, z_2 = 0)$ (dotted lines) the ME polarization. The first is calculated for the states with $l_1 = l_2 = l$ with $n_1 = l + 1$.</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>128</td>
</tr>
<tr>
<td>(top) Induced image charge densities on a neutral disk for two axial positions $z = 0.3a$, and $z = 0.5a$ of an external point charge. (bottom) Induced charge density on a neutral disk for a point charge positioned above a disk at $\rho = 0.5a$, and $z = 0.5a$.</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>131</td>
</tr>
<tr>
<td>(top) Effective potentials $U(\rho, z = 0)$ formed in the disk plane for different angular momenta quantum numbers. (bottom) The lowest two states of an electron ($l = 8$) formed in the effective potential $U$.</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>133</td>
</tr>
<tr>
<td>The effective potential of a charged disk $(a = 1\text{nm})$ for $l = 6, 8, 9$ and 10. The black dashed line marks $U(\rho, z) = 0$. The red area is the repulsion centrifugal wall. Disk area is shown in black.</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>134</td>
</tr>
<tr>
<td>The contour plot for the diskoid state $</td>
<td>1, 1\rangle$ with $l = 8$ of a charged disk. Disk is shown by the red line $z/a = 0, \rho/a = 0 - 1$ middle left.</td>
</tr>
<tr>
<td>38</td>
<td>142</td>
</tr>
<tr>
<td>Honeycomb plaques of different sizes and orientation of dipoles, where $M$ is the number of circumcircles.</td>
<td></td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>39</td>
<td>Stable configurations of particles and dipoles in two parallel plaques. (left) The simple hexagonal lattice with dipoles circulating in opposite directions in adjacent layers. (right) The hexagonal close-packed lattice with dipoles circulating in the same directions in the layers. Top views and side views are given.</td>
</tr>
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<td>40</td>
<td>The phase diagram for magnetic NPs with a bulk vdW coupling plotted as a function of the NP-radius, $R_{NP}$, and the saturation magnetization, $m_s$. The NPs are arranged in two plaques with $M = 1$ and 3 circumferences and opposite orientations of dipole moments, which are positioned on the top of each other in the hcp and sh configurations. The solid lines represent the hcp/sh phase boundary of touching NPs, while the dashed lines give the phase boundary for NPs with the minimum separation of 1 nm (surfactants). When the temperature is raised to $T = 298$ K, the hcp/sh phase boundary shifts towards larger $m_s$ and $R_{NP}$ (stronger coupling), since the hcp configuration has a larger entropy.</td>
</tr>
<tr>
<td>41</td>
<td>The potential energy per particle, $\bar{\varepsilon}$, in a double layer of honeycomb plaques of different sizes, rotated one with respect the other by the angle $\alpha$; $M = 1$ (up), $M = 2$ (middle), $M = 3$ (bottom). The $\alpha = 0$ angle corresponds to the sh configuration. Solid and dashed curves correspond to the opposite and the same orientations of dipoles, respectively.</td>
</tr>
<tr>
<td>42</td>
<td>The total energy per particle (contour plot) of two systems of plaques shifted with respect to each other. In a) and b), we show the energy of equal-size plaques, $M = 1$, with dipoles circulating in the opposite (left) and (right) the same directions. In c) and d) the same is shown for plaques of different sizes, $M = 1$ and $M = 3$. The NP-diameter is chosen as the unit of shifts on the axes.</td>
</tr>
<tr>
<td>43</td>
<td>Two plaques connected by a) the s-type junction and b) the o-type junction. Lattices of connected plaques: c) 19 plaques of $M = 1$ plaques assembled with the s-type junctions, d) 7 plaques of $M = 3$ plaques assembled with the s-type junctions, e) 9 plaques of $M = 1$ plaques assembled by the o-type junctions, f) 9 plaques of $M = 2$ plaques assembled with the o-type junctions.</td>
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<td>FIGURE</td>
<td>PAGE</td>
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<td>------</td>
</tr>
<tr>
<td>44</td>
<td>Magnetic particles arranged in a variety of structures: a) tube with close-packing lattice, b) tube with simple cubic packing lattice, c) Möbius strip, d) conical close-packing structure, e) simple cubic lattice, f) chiral tube with close-packing structure with parallel circulation of dipoles, g) chiral tube simple cubic packing structure with anti-parallel dipolar circulation, h) hollow icosahedral structure, i) close-packing tube, j) simple tube, and k) chiral tube with close-packing structure with the circulation of dipoles shown.</td>
</tr>
<tr>
<td>45</td>
<td>Self-assembly of one-dimensional nanocube belts. (A) Schematic representation of the experimental setup. (B) Low- and high-magnification TEM images of the building blocks, ~ 13 nm Fe₃O₄ nanocubes. The [111], [110], and [100] crystallographic directions correspond to the easy, intermediate, and hard axes of magnetization, respectively. (C) Low- and high-magnification SEM images of belts₁₀₀. (D) Averaged orientations of dipoles in a nine-cube-wide belt₁₀₀ in the presence of increasing magnetic fields. (E) Orientations of dipoles in belts₁₀₀ of different widths and in a belt₁₁₀ under a relatively weak external field (H = 167 G). (F, G) Top- and side-views of belts₁₁₀ by SEM.</td>
</tr>
<tr>
<td>46</td>
<td>TEM and SEM (inset) images of Fe₃O₄ nanocubes at various magnifications. All TEM images shown in this manuscript were obtained on a Philips CM120 Super Twin microscope operating at 120 kV, unless noted otherwise.</td>
</tr>
<tr>
<td>47</td>
<td>SEM images of structures obtained from Fe₃O₄ nanocubes under a sub-monolayer (χ = 0.2) surface concentration of the particles. All SEM images shown in this manuscript were obtained on a SUPRA 55VP field-emission SEM (Carl Zeiss Microscopy, LLC), or on an ULTRA 55 field-emission SEM (Carl Zeiss Microscopy, LLC, both operating at 5 kV.</td>
</tr>
<tr>
<td>48</td>
<td>TEM images of chains of cubic magnetite NCs formed by applying an external magnetic field to a solution of NCs. The samples were prepared by rapid evaporation the solvent (hexane) from the TEM grid in the presence of a magnetic field.</td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
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</tr>
<tr>
<td>49</td>
<td>Self-assembly of helical nanocrystal superstructures. (A) TEM image of individual single-stranded helices. (B) SEM image of a large array of single-stranded helices. (C) Snapshots from Monte Carlo simulations of a one-dimensional belt folding into a helix. (D) SEM image of a well-defined double helix. Inset shows a TEM image of two belts wrapping around each another. (E) SEM image of an array of double helices. Blue arrows show the direction of the applied magnetic field. (F) An array of triple helices and (inset) the end of a triple helix. (G) SEM image showing self-healing of double helices (“chirality self-correction”). Yellow and red arrows indicate sites of chirality inversion. (H) Collective switching of chirality. Gray and green colors indicate patches of right- and left-handed helices, respectively.</td>
</tr>
<tr>
<td>50</td>
<td>Additional SEM images of double-stranded helices taken at various magnifications. The area indicated in yellow in (H) is expanded as (I).</td>
</tr>
<tr>
<td>51</td>
<td>Self-assembly of Fe₃O₄ nanocrystals of different shapes. (A) TEM images of truncated octahedra (top) and an SEM image of 1D belts as they assemble (bottom). (B) TEM images of rounded cubes (top) and an SEM image of the resulting helix (bottom). (C) TEM images of Fe₃O₄-Ag heterodimeric NCs (top) and an SEM image of an ensemble of helices (bottom).</td>
</tr>
<tr>
<td>52</td>
<td>Two cuboids. (Left) The face-to-face and (Right) the corner-to-corner configurations.</td>
</tr>
<tr>
<td>53</td>
<td>The average energy of two magnetite cubes as a function of anisotropy constant $K_1$ at 500 G (Left) and 2000 G (Right) for the corner-to-corner and face-to-face configurations.</td>
</tr>
<tr>
<td>54</td>
<td>(Left) Two cubes in $f-f$ configuration tilted by angle $\theta$ from $z$-axis. (Right) $\langle E_T \rangle$, $\langle M_z \rangle$ and $\langle M_x \rangle$ in two tilted cubes in $f-f$ configuration in “weak” and “strong” field at different anisotropy constants $K_1$. $\langle M_{z,x} \rangle$ are in the units of $M_s$.</td>
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<tr>
<td>FIGURE</td>
<td>PAGE</td>
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<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>55</td>
<td>(A) Two superparamagnetic nanocubes with side length $a$ positioned side by side and aligned face-to-face. (B) Field-dependent average magnetic energy $\langle E(R) \rangle$ of two nanocubes at temperature, $T = 300$ K. The magnetic energy of two isolated cubes is set as zero. Weak- and strong-field asymptotic dependencies are shown by dashed black lines. (C) Atomistic model of nanocubes coated with oleic acid ligands. (D) The effective vdW potential associated with bulk nanocube coupling. Top inset: surface elements (color scale from blue to red corresponds to the increase of the surface area per element) used in the repulsive part of the vdW coupling energy ($E_{W}^{rep}$ in Equation 8.5). Bottom inset: subdivision of a nanocube by 27 identical volume elements (colored for clarity) used in the attractive part of the vdW coupling energy ($E_{W}^{attr}$ in Equation 8.5).</td>
</tr>
<tr>
<td>183</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>(A) Typical configuration of two cubes in an external field, $H = 167$ G (vertical $z$-orientation at $T = 300$ K (bulk vdW coupling is reduced by $1/2$ with respect to the nominal value) (B) View along the cube axis reveals that the nanocube pair is (transiently) chiral. Magnetic dipoles are represented by red arrows.</td>
</tr>
<tr>
<td>184</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>Averaged orientation of dipoles in a thick filament under relatively weak external field ($H = 167$ G). The top two layers are purposely separated from the structure (left) to better illustrate the dipole arrangement.</td>
</tr>
<tr>
<td>185</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>Potential energies of self-assembled belts as a function of belt thickness, arrangement of cubes, and strength of the external field. Total magnetic energy, $E_{mag}$, is the sum of the Zeeman energy, $E_z$, dipole-dipole energy, $E_{dd}$, and anisotropy energy, $E_a$: $E_{mag} = E_z + E_{dd} + E_a$. Total potential energy, $E_{all}$, is the sum of total magnetic energy and the van der Waals energy: $E_{all} = E_{vdW} + E_{mag}$. All values are in kcal/mol per nanocube. Averaged orientations of dipoles in different belts (left) are shown for weak external field ($H = 167$ G). The belts comprise the following numbers of nanocubes, from left to right: 300, 284, 600, 564, 900, 846. All of the energy values and dipole configurations shown in the figure are averaged over 10,000 MC steps.</td>
</tr>
<tr>
<td>186</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Snapshots of nanocube assemblies during helix formation (left) and the contributing energies (right) ($E_z$, Zeeman energy; $E_{dd}$, dipole-dipole energy; $E_a$, anisotropy energy; $E_{mag} = E_z + E_{dd} + E_a$, total magnetic energy; $E_{vdW}$, van der Waals energy; $E_{all} = E_{vdW} + E_{mag}$, total potential energy). The curves in the plots were obtained from smoothing (window = 500 steps) the original data (shown as thin lines).</td>
</tr>
<tr>
<td>187</td>
<td></td>
</tr>
<tr>
<td>FIGURE</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>60</td>
<td>Potential energy dependence on the distance between two perfectly aligned and slightly disordered belts. In each case, total magnetic energy, ( E_{mag} = E_z + E_{dd} + E_a ), was averaged at each distance over 5,000 MC steps of two belts approaching each other as a function of their separation. ( E_{mag} ) of two isolated belts was set as zero. The cases of weak, intermediate, and strong external magnetic fields (( H = 167, 417, 688 ) ( G ), respectively) are shown for two ( n \times n \times 100 ) belts, where ( n = 2, 3, 4, 5, ) and 6.</td>
</tr>
<tr>
<td>61</td>
<td>Potential energy dependence on the distance between two helices approaching each other along the direction shown by the arrow. Zeeman energy, ( E_z ); dipole-dipole energy, ( E_{dd} ); anisotropy energy, ( E_a ); and total magnetic energy, ( E_{mag} = E_z + E_{dd} + E_a ) at each distance were averaged over 5000 MC steps.</td>
</tr>
</tbody>
</table>
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AIMD</td>
<td><em>ab initio</em> Molecular Dynamics</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>CHARMM</td>
<td>Chemistry at HARvard Macromolecular Mechanics</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>PNC</td>
<td>Porous Nanocarbons</td>
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<tr>
<td>SP</td>
<td>Standard Pore</td>
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<td>GNR</td>
<td>Graphene Nanoribbon</td>
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<tr>
<td>AGNR</td>
<td>Armchair Graphene Nanoribbon</td>
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<tr>
<td>ZGNR</td>
<td>Zigzag Graphene Nanoribbon</td>
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<td>PG</td>
<td>Porous Graphene</td>
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<td>Carbon Nanotube</td>
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<td>CSF</td>
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<td>Zigzag Carbon Nanotube</td>
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<td>GB</td>
<td>Grain Boundary</td>
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</table>

xxii
### LIST OF ABBREVIATIONS (Continued)

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DMMP</td>
<td>Dimethyl Methylphosphonate</td>
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<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
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<td>DFT-D</td>
<td>Density Functional Theory with Dispersion Correction</td>
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<tr>
<td>DOS</td>
<td>Density of States</td>
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<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<td>GROMACS</td>
<td>GROningen MAchine for Chemical Simulations</td>
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<td>MA</td>
<td>Magnetic Anisotropy</td>
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<td>OA</td>
<td>Oleic Acid</td>
</tr>
</tbody>
</table>

xxiii
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBC</td>
<td>Periodic Boundary Conditions</td>
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<td>Potential Energy Surface</td>
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<td>Particle Mesh Ewald</td>
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<td>Restricted Hartree Fock</td>
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<td>Scanning Tunneling Microscopy</td>
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<td>van der Waals</td>
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<td>Visual Molecular Dynamics</td>
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SUMMARY

In this thesis describe the modeling of nanoscale systems with two main focuses: 1) electronic properties including electron transport and 2) self-assembly of many-particle systems with coupled internal and external degrees of freedom. We use multiscale computational methods to study the conductivity, molecular sensing and catalytic activity of materials on the nanoscale. We apply analytical and numerical methods to analyze the formation of correlations in material systems, such as electron-electron correlations in polarizable nanostructures and self-assembly of magnetic nanoparticles. The thesis is based on 3 original papers, 3 submitted manuscripts, and 1 review chapter.

In the first part of the thesis, we have studied electronic properties of modern layered materials. In the first project, we have used DFT-based ab initio calculations to study the electronic structure of geometrically restricted nanocarbons and the modifications upon modulation of their lattices with periodic arrays of nanopores or defects. We have described how pores with different shapes and localizations can switch the material from a semiconductor to a metal. We also have built a unified model that can be used to predict the electronic properties of porous nanocarbons. In the second project, done in collaboration with Prof. Amin Salehi-Khojin (UIC), ab initio modeling of electron transport through defective regions in graphene revealed ultra-sensitivity to the molecular environment. This sensitivity originates from a simultaneous opening or closing of local electron transport channels passing through the grain boundaries by the adsorbed analytes. In the third project, done in collaboration with Prof. Amin Salehi-
Khojin, we have analyzed a carbon dioxide reduction process with the bulk molybdenum disulfide. We have found that its superior performance, compared to noble metals, originates from outstanding catalytic properties of the molybdenum terminated edges of MoS\textsubscript{2}. These edges with metallic properties are characterized by a high d-electron density and a low work function. Altogether, these features of molybdenum-terminated edges of MoS\textsubscript{2} provide a high current density and low overpotential in an ionic liquid.

In the second part of the thesis, we have investigated the build-up of electron correlations in extended electronic image states around highly polarizable metallic nanodisks. We have used both semi-classical and quantum approaches to describe the spatial properties and correlations of image electronic states in a model two-electron diskoid-like quantum system. We also developed semiclassical one-electron model of such diskotic systems and explain how the one-electron and many-electron solutions are related.

In the third part of the thesis, we have modeled the self-assembly of magnetic nanoparticles. In the first project, we have modeled the stabilization of clusters and lattices of spherical particles with permanent electric or magnetic intrinsic dipole moments and weak van der Waals coupling. We found the parameters of nanoparticles, such as the size and strength of dipolar coupling, at which these spherical particles form lattices with sh, fcc and hcp packing stable at room temperature. In the next project, done in collaboration with Dr. Rafal Klajn (Weizmann Institute), we have modeled the formation of unprecedented helical superstructures out of anisotropic supperlarmagnetic magnetite nanocubic particles at the liquid-air interface in the presence of external magnetic fields. In our modeling, we have considered the coupling of
intrinsic and external degrees of freedom associated with the fluctuating superparamagnetic
dipole moment and the motion of nanocubes, respectively. The formation of chiral assem-
blies is rationalized in terms of the interplay among van der Waals and magnetic dipole-dipole
interactions, Zeeman coupling, as well as entropic forces.
CHAPTER 1

INTRODUCTION

1.1 Modeling of Nanoscale Systems

The general theme of the thesis is the application of multiscale computational methods to the description of electronic properties and structural characteristics of novel metamaterials based on modified graphene, MoS$_2$, and self-assembled magnetic nanoparticles. To describe these systems we need to find an optimal compromise between accuracy and required computational resources. The scale of the system, its precision of description, and the studied phenomena determine the methods used. In practice, the phenomena that we describe are at the interface of the quantum mechanics of atoms and molecules, solid state physics, and statistical mechanics. It necessitates us to combine quantum mechanical calculations based on density functional theory along with semi-analytical methods and the application of specific techniques, such as classical and quantum molecular dynamics.

Despite the remarkable advances in experimental techniques, such as scanning tunneling microscopy (STM) [1], atomic force microscopy (AFM) [2], optical tweezers [3], providing us access to the events occurring in single molecules in real time, experiments can not often provide all the information necessary for understanding of the physical and chemical phenomena. This is where theory and computational modeling can provide the missing information and help in understanding of phenomena in nanoscale systems.
An unprecedented example of great strides in the development of computational methodology is density functional theory (DFT). “In the past decades DFT has made its way from a peripheral position in quantum chemistry to the center stage” [4, 5]. In these days, we witness how this seminal methodology gives rise to hybrid techniques allowing us to study not only classical problems of quantum chemistry but also more versatile electron transport phenomena. With the introduction of supercomputers and the development of appropriate codes, we can study complex phenomena. These novel computational tools provide a platform for designing and optimizing new nanoconstructs, studying their dynamics in realistic environments, and testing of new hypotheses.

In this thesis, we start from a single-electron description of electronic structures developed in DFT. Next we proceed with the description of open quantum systems out of equilibrium, with the focus on mechanisms of molecular sensitivity and catalytic activity, discuss the effects of electron correlations on the image states in polarizable nanosystems, and finalize with the description of cooperative self-assembly of chiral helical superstructures from achiral anisotropic magnetite nanocubes.

1.2 Thesis Structure

In chapter 2, we review the theoretical basis and principal ideas of quantum mechanical methods of calculation of electronic properties of the nanosystems studied. First, we show how nanosystems can be described quantum mechanically by density functional theory as a tractable method to describe many-electron and many-particle systems. We specifically highlight the application of DFT methods to infinite crystallic materials, predominantly studied in this thesis.
Next, we describe in more detail how DFT methods are implemented in the SIESTA code. We discuss the essential parameters for this computational approach and the origin of linear scaling of computational efforts with the number of basis wavefunctions. Finally, we discuss the theory of the electron transport based on the hybrid nonequilibrium Green’s functions (NEGF) and the Landauer formalism.

In Chapter 3, we describe the electronic structures of porous nanocarbons, such as porous graphene, porous nanoribbons, and porous carbon nanotubes. We disclose common features of these systems and develop a unified picture to systematically characterize metal-semiconductor transitions in porous nanocarbons.

In Chapter 4, we analyze the mechanisms of chemical sensing at graphene grain boundaries observed by the Salehi-Khojin group. The experiments show that the electric sensitivity of isolated grain boundary is $\sim 300$ times higher than that of a single grain and much higher than that of a polycrystalline graphene sensor. We theoretically investigate the gas sensing mechanism at grain boundaries using electron transport methods and QM/MM simulations. We found that the sensing mechanism is based on the adsorbed analytes closing or opening local conducting channels across the grain boundary.

In Chapter 5, we computationally study the carbon dioxide reduction on bulk molybdenum disulfide observed experimentally by the Salehi-Khojin’s group. First, we study the electronic structure of molybdenum-terminated edges of MoS$_2$. We analyze their spin-resolved band structures, local and projected density of states at the Fermi energy level, and characterize the spatial distribution of the electron density in the bulk and at the edges of MoS$_2$-ribbons.
First-principles modeling revealed that the molybdenum-terminated edges of MoS$_2$ are mainly responsible for a superior catalytic performance, due to their metallic character and a high d-electron density. Next, we study the role of the ionic liquid in facilitating the reduction reaction at the MoS$_2$-electrode. Using QM/MM simulations, we found that the hydrated 1-ethyl-3-methylimidazolinium (EMIM-CO$_2$)$_2^+$ complex forms in an acidic solution. This complex is believed to play a critical role in the CO$_2$ reduction process.

In Chapter 6, we study highly excited diskoid-like electronic states formed in the vicinity of charged and strongly polarizable molecules of diskotic shape, such as circular graphene flakes. We study the nature of such extended states in a simple two-electron model. The two electrons are attached to a point-like nucleus with a 2+ charge, where the material electron is forced to move within a 2D disk area centered at the nucleus, while the extended electron is free to move in 3D. Pronounced and complex correlations are revealed in the diskoid-like states. We also develop semiclassical one-electron models of such diskotic systems and explain how the one-electron and many-electron solutions are related.

In Chapter 7 we model stabilization of clusters and lattices of spherical particles with dominant electric and magnetic dipolar coupling, and weak van der Waals coupling. We consider different arrangements of ferromagnetic particles forming closed-flux structures and perform comparative analysis of the stability of such clusters and lattices. Our analytical results demonstrate that dipolar coupling can stabilize nanoparticle clusters with planar, tubular, Möbius, and other arrangements. We also explain for which parameters the nanoparticles can form lattices with $fcc$, $hcp$, $sh$, $sc$, and other types of packing. We illustrate that realistic magnetic
and semiconducting nanoparticles need to have certain minimum sizes to stabilize at room temperature into nanostructures controlled by dipolar coupling.

In Chapter 8, we present the results of computational and semi-analytical modeling of self-assembly of superparamagnetic magnetite nanocubes into chiral helical superstructures obtained at the liquid-air interface in the presence of external magnetic field. These systems were observed experimentally by our collaborator Prof. Rafal Klajn. Under carefully engineered conditions, cubic nanocrystals of magnetite self-assemble into arrays of helical structures. The modeling takes into account the interplay between van der Waals and magnetic dipole-dipole interactions, the magnetocrystalline and shape anisotropy of nanocubes, the Zeeman coupling, as well as entropic forces.

Semi-analytical approaches applied to a few cube systems revealed how the stability of a system formed by two nanocubes depends on a nanocube arrangement, parameters of magnetic anisotropy and the strength of the external magnetic field. We use classical Monte Carlo simulations to analyze the structures of many self-assembled magnetic particles. MC simulations reveal the formation of helical structures, explain the filamentations of helices and the emergence of other structures.
CHAPTER 2

THEORY AND METHODS

2.1 Introduction

Over the past two decades, analytical techniques and computational simulation methods have made great progress towards modeling of complex systems. Multiscale methods can be now applied to study systems that have size ranging from atomic scale to large bio-molecules and nanoscale materials. With these methods we are able to study processes that have timescales in the range from attoseconds (e.g., real time dynamics of electrons in molecular systems in response to ultra short laser pulse) to milliseconds (conformational transitions of large biomolecules).

This computational power allows us to simulate realistic molecular systems important for practical applications. Nowadays, we have fully developed quantum mechanical methods able to describe atoms, molecules and solids, and a variety of computational methods based on all-atom classical, coarse-grained, and quantum molecular dynamics. The modeling methods used depend on the studied properties, sizes of the systems and timescale of the phenomena that one wants to describe. The chosen methods have to be precise enough to capture the underlying physics of the crucial phenomena, without oversimplifying the system properties.

Kohn-Sham density functional theory is one of the most used methods to describe the quantum properties of matter [6]. Once hybridized with non-equilibrium Green’s functions
techniques (NEGF), the resulting combined techniques can be used to solve a variety of practical scientific problems, such as electro-optical properties of molecules, electronic structures of solids and molecular clusters, electron and heat transport in nanoscale systems, catalytic properties of different materials, and modeling of chemical reactions.

In the following sections, we will discuss first-principle quantum mechanical methods used for electronic structure calculations. Specifically, we will address density functional theory and its applications to periodic systems (solids). Since most of the calculations were done using localized atomic orbitals method implemented in the SIESTA code, we will discuss in more detail this computational method. This will be followed by the electron transport techniques that are applied here to the study of the electron transport in practical nanoscale systems.

2.2 Quantum Mechanical DFT Methods

According to P. Dirac [7], the main problem of quantum chemistry is the development of efficient approximative methods that would allow prediction of the electronic properties of many-electron systems without directly solving many-electron Schrödinger equation (SE) which definitely cannot be solved for realistic material systems. Dealing with the wavefunctions that solve the SE for any interesting number of electrons is also an extremely challenging problem. For example [5], representing a 5-electron wave function in single precision (4 bytes per number) on a mesh of 10 grid points for each direction would require \( \approx 4 \times 10^6 \) GB of memory. Therefore, efficient methods of describing quantum systems need to be found.

We can classify the methods of solving quantum mechanical problems into two major groups: wave-function-based methods [8] (where we can include the Hartree-Fock method and methods
beyond the Hartree-Fock approximations, such as diagrammatic methods, Green functions) and density-functional-based methods. Here, we briefly describe these methods and ways how to approximate them.

The time-dependent Schrödinger equation (SE) of a molecular system, containing $M$ nuclei and $N$ electrons, can be written as:

$$i\hbar \frac{\partial \Psi(\vec{R}, \vec{r}, t)}{\partial t} = \hat{H}\Psi(\vec{R}, \vec{r}, t),$$

$$(2.1)$$

where $\hbar$ is the reduced Planck constant, $\hat{H}$ is the Hamiltonian operator which is linear and second order differential operator. $\hat{T}_p$ is the nucleus kinetic energy operator, $\hat{T}_i$ is the single electron kinetic energy operator, $\hat{V}_{i,p}$ and $\hat{V}_{i,j}$ are electron-nucleus and electron-electron potential energy operators, for electrons $i, j$ and nuclei $p$, and $\hat{V}_{ext}$ is an external potential.

The exact time-dependent solution of SE Equation 2.1 is a many-body wave function $\Psi(\vec{R}, \vec{r}, t)$ which depends in general on variables of nuclei $\vec{R} = \vec{R}_1, ..., \vec{R}_M$, and space variable $\vec{r} = \vec{r}_1, ..., \vec{r}_N$, and spin variable of all electrons in the system.

Relativistic effects are important for core electrons of heavy elements. However, these electrons are chemically inert and are usually treated in a frozen core approximation. In this way, the core electrons are typically considered in a pseudopotential approximation in which the orbitals of these electrons are obtained from a scalar relativistic description of isolated atoms.
For the Hamiltonians that do not depend explicitly on time, the time-dependent solution of the Equation 2.1 can be obtained in the form, \( \Psi(\vec{R}, \vec{r}, t) = \sum_{n=1}^{\infty} \alpha_n \Phi_n(\vec{R}, \vec{r}) e^{-iE_n t/\hbar} \), where \( \Phi_n(\vec{R}, \vec{r}) \) are the eigensolutions of a stationary time-independent Schrödinger equation:

\[
\hat{H} \Phi_n(\vec{R}, \vec{r}) = E_n \Phi_n(\vec{R}, \vec{r}).
\] (2.2)

Here, \( E_n \) are the eigenvalues, corresponding to the eigenfunctions \( \Phi_n(\vec{R}, \vec{r}) \). When \( \hat{H} \) has a continuous spectrum of eigenvalues, the general solution of Equation 2.1 can be written as:

\[
\Psi(\vec{R}, \vec{r}, t) = \int \alpha(E) \Phi_E(\vec{R}, \vec{r}) e^{-iEt/\hbar} dE.
\]

Due to the large mass difference between nuclei and electrons \( (M_n/m_e \sim 10^3 - 10^6) \), we can often use the Born-Oppenheimer (BO) approximation, according to which the electrons adjust \emph{instantaneously} to much slower nuclear motions [9]. Within the BO approximation, the repulsion between the nuclei does not depend on time. Using the BO approximation, we can decouple the electronic degrees of freedom from the nuclear degrees of freedom. Then the wavefunctions of a molecule can be written as a product of separable nuclear and electronic wavefunctions:

\[
\Phi(\vec{R}, \vec{r}) = \psi_{nucl}(\vec{R}) \psi_{el}(\vec{r}; \vec{R}),
\] (2.3)

where the electronic motion depends explicitly on the electronic coordinates and parametrically on the nuclear coordinates \( \vec{R} \) (i.e., for different arrangements of the nuclei, \( \psi_{el}(\vec{r}; \vec{R}) \) is a different function of the electronic coordinates).
In the BO approximation, the Equation 2.1 is reduced into a pair of equations for electrons and the nuclei

\[ \hat{H}_{el}(\vec{r}, \vec{R}) \psi_{el}(\vec{r}, \vec{R}) = E_{el}(\vec{R}) \psi_{el}(\vec{r}, \vec{R}), \]
\[ \hat{H}_{nucl}(\vec{R}) \psi_{nucl}(\vec{R}) = (E - E_{el}(\vec{R})) \psi_{nucl}(\vec{R}) \] (2.4)

where the first one describes the motion of the electrons in a fixed nuclei configuration whereas the second one describes the motion of the nuclei in a potential \( E_{el}(\vec{R}) \), where the potential energy of nucleus-nucleus interaction is included.

The electronic Hamiltonian of a system containing \( N \) electrons and \( M \) nuclei is:

\[ \hat{H}_{el} = \sum_{i=1}^{N} \hat{T}_i + \sum_{p=1}^{M} \sum_{i=1}^{N} \hat{V}_{i,p} + \sum_{j=1}^{N} \sum_{i=1, i>j}^{N} \hat{V}_{i,j} + \hat{V}_{ext}. \] (2.5)

The SE with \( \hat{H}_{el} \) and its exact solution for the time-independent electronic wavefunction can be written as:

\[ \hat{H}_{el} \psi_{exact}(\vec{r}_1, ..., \vec{r}_N) = E_{exact} \psi_{exact}(\vec{r}_1, ..., \vec{r}_N). \] (2.6)

However, the term \( \hat{V}_{i,j} \) correlates different electron coordinates and significantly complicates the analytical solution for \( \psi_{exact} \).
In principle, the exact solution of Equation 2.6 can be sought in the form of a linear combination of Slater determinants (configuration state functions (CSFs)) which form a complete basis set of antisymmetrized wavefunctions. The CSFs can be written as:

$$\psi_{\text{exact}} = \sum_{s_1, s_2, \ldots, s_N} c_{s_1, s_2, \ldots, s_N} \begin{vmatrix} \phi_{s_1}(r_1) & \phi_{s_2}(r_1) & \cdots & \phi_{s_N}(r_1) \\ \phi_{s_1}(r_2) & \phi_{s_2}(r_2) & \cdots & \phi_{s_N}(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{s_1}(r_N) & \phi_{s_2}(r_N) & \cdots & \phi_{s_N}(r_N) \end{vmatrix}, \quad (2.7)$$

where $\phi_{si}(r_i)$ are one-electron spin orbitals, which are products of spatial orbital and spin functions, and $\phi_{si}$ belong to a complete basis set of one-electron spin orbitals [10]. Since the many-electron wavefunctions given of a practical many-electron system in Equation 2.7 contains a very large (infinite) number of basis set functions and CSFs, it is not feasible to get an exact solution. However, for a non-interacting electrons, which can be represented as a sum of single-particle operators $\hat{T} + V_{\text{ext}}$, the many-body function can be found in the form of a single Slater determinant which satisfies the Pauli principle [11]. In this case, a 5-electron wavefunction would require $4 \times 5 \times 10^3 = 19$ kB of memory only. Therefore, many attempts have been made to convert the interacting system into an approximative fictitious non-interacting system where the effective external potential is modified in such a way that the properties of the model system would emulate those of the interacting system.
The Hartree Fock (HF) theory is perhaps the simplest approximation method for solving the many-electron problem, which is based on finding the wavefunctions. In the Hartree approximation, we can write the many-electron wavefunction as a product of one electron wavefunctions:

\[ \psi = \phi_{a,\alpha}(1)\phi_{a,\beta}(2)\ldots\phi_{z,\beta}(N), \]  

(2.8)

where electron 1 occupies molecular orbital \( \phi_{a} \) with spin \( \alpha \), electron 2 occupies molecular orbital \( \phi_{a} \) with spin \( \beta \) and so on. However, many electron wavefunctions must satisfy the Pauli principle and be antisymmetric with respect to the exchange of electrons. This can be achieved by expressing the wavefunction of \( N \) electrons as a single Slater determinant:

\[ \psi_{HF} = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc} \phi_{a,\alpha}(1) & \phi_{a,\beta}(1) & \ldots & \phi_{z,\beta}(1) \\ \phi_{a,\alpha}(2) & \phi_{a,\beta}(2) & \ldots & \phi_{z,\beta}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{a,\alpha}(N) & \phi_{a,\beta}(N) & \ldots & \phi_{z,\beta}(N) \end{array} \right|. \]  

(2.9)

When this wavefunction is combined with the variation principle, the orbitals (corresponding to the lowest total energy) must satisfy the Hartree-Fock equation

\[ f_{1}\phi_{a,\sigma}(1) = \epsilon\phi_{a,\sigma}(1), \]  

(2.10)
where $\sigma$ is either $\alpha$ or $\beta$ (spin up or down). The Fock operator $f_1$ is given by

$$f_1 = h_1 + \sum_j \{2J_j(1) - K_j(1)\}, \quad (2.11)$$

where the core Hamiltonian can be written as

$$h_1 = \frac{\hbar^2}{2m_e} \nabla_1^2 + \sum_n \frac{Z_n e^2}{4\pi\epsilon_0 r_{ni}}, \quad (2.12)$$

the Coulomb operator is

$$J_i(1)\phi_a(1) = \int \phi_j^*(2)\phi_j(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi_a(1)d\tau_2, \quad (2.13)$$

the exchange operator is

$$K_i(1)\phi_a(1) = \int \phi_j^*(2)\phi_a(2) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi_j(1)d\tau_2, \quad (2.14)$$

where $\tau_2$ denotes the coordinates of the second electron.

In the computational schemes, we first prepare a trial Slater determinant $\psi_{HF}$ containing orbitals $\phi_{a,\sigma}(r)$ which are linear combinations of basis set functions $\chi(r)$ with trial coefficients $k_i$, $\phi_{a,\sigma}(r) = \sum_i k_i \chi(r)$. Next, we perform an iterative minimization process where we gradually minimize the energy $E_{HF}$ with respect to the coefficients $k_i$. The HF method gives the best single SD solution, which minimizes the energy $E_{HF} = \langle \psi_{HF} | H_{el} | \psi_{HF} \rangle$ [10].
The variational procedure results in the total wavefunction that is constructed from one-electron wavefunctions that are optimized in the average potential, or mean field, of all the other electrons (and nuclei) (see Equation 2.10). Thus, in the HF approximation, the electron correlations based on the use of many SDs (see Equation 2.7) are neglected and the only included contribution as compared to the non-interacting electron case is the exchange interaction energy originating from antisymmetrization of electron wavefunction.

Nowadays, the most popular way of constructing such an effective mean-field potential is Density Functional Theory (DFT). DFT gives the recipe of constructing the effective potential such that the non-interacting system produces the same ground state electron density as the interacting system. The theory offers, in principle, a way to determine the exact ground state energy and hence all the quantities that can be derived from it, such as equilibrium geometry, vibrational frequencies, reaction barriers, etc., but not two-electron properties, such as conductivity and optical adsorption.

In DFT approaches, the many-electron problem is solved by using a single SD wavefunction but incorporating the correlations in an effective Hamiltonian of non-interacting electrons. In contrast, in the HF approximation, the electron correlations are neglected already at the stage of constructing the probe wavefunctions as a single SD, whereas in the configuration interaction methods (standing between HF and the exact wavefunction) the electron correlations are treated in terms of linear combinations of multiple SDs [8].

Here, we give a short overview of DFT [8,12,13] which is based on two Hohenberg-Kohn (HK) theorems generalized by Levy and Lieb [14–16]. The first HK theorem says that the ground-
state energy is a unique functional of the electron density. The second theorem states that the electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation. Mathematical formulation of this theorem uses the Rayleigh-Ritz variational principle for the ground state energy \( E_0 = \min_{\Psi \to n(r)} \langle \Psi | \hat{H} | \Psi \rangle \) [17]:

\[
E_0 = \min_{n(r)} \{ \min_{\Psi \to n(r)} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int dr n(r) V_{ext}(r) \}.
\]

(2.15)

Here, the energy functional \( \langle \Psi | \hat{H} | \Psi \rangle \) is minimized with respect to the single-electron density constructed from the electron wavefunction. By expressing the first term explicitly as a density functional:

\[
F[n] \equiv \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle,
\]

(2.16)

we conclude that the ground state energy can be considered as a minimum of a functional \( E[n] = F[n] + \int dr n(r) V_{ext}(r) \) which depends on the density only, and \( n_0(r) \) that provides the extremum of \( E[n] \) is the ground state density of the system.

The constrained minimization in Equation 2.15 is achieved by solving the associated Euler-Lagrange equation:

\[
\frac{\delta F[n]}{\delta n(r)}_{n=n_0(r)} + V_{ext}(r) - \mu = 0,
\]

(2.17)

where the conservation of electrons is enforced by the Lagrange multiplier \( \mu \) such that \( \int dr n(r) = N \) is the chemical potential of the system.
Since the HK functional $F[n]$ is universal (i.e., system independent), the Equation 2.17 provides a one-to-one mapping between the external potential and the ground state density $n(r)$. All the other observables can be also considered as functionals of the ground state electron density. These two HK theorems provide the rigorous basis for DFT and pave the way for finding physical properties of molecular systems in terms of a function $n(r)$ which depends on only three spatial coordinates. Such a tremendous reduction of the complexity from a many-body wavefunction dependent on $3N$ coordinates to a single electron density function $n(r)$ constitutes the efficiency of DFT.

Within the framework of Kohn-Sham DFT (KS DFT), the intractable many-body problem of interacting electrons is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the exchange and correlation potential, representing the electron coupling.

Therefore, the electron density $n(\vec{r})$ can be determined from a single-particle picture of non-interacting electrons [18]. The corresponding Hamiltonian for the single-particle KS orbitals $\psi_i$ is expressed by the KS equations as [6]:

$$H^{KS}\psi_i(r) = \left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(r)\right]\psi_i(r) = \epsilon_i \psi_i(r) \quad (2.18)$$

where the effective potential $V_{\text{eff}}$ is:

$$V_{\text{eff}}(r) = \int dr' \frac{\rho(r')}{|r - r'|} + V_a(r; \{R_{ia}\}) + \frac{\delta E_{xc}[\rho(r)]}{\delta(r)}, \quad (2.19)$$
here, \( V_{\text{eff}}(r) \) explicitly depends on the density \( n(r) = \sum_i \psi_i^* \psi_i \) with the sum running over occupied KS orbitals. \( V_a(r, \{R_{ia}\}) \) is the external potential due to the nuclei at positions \( \{R_{ia}\} \). The exchange-correlation term \( E_{xc} \), in principle, accounts for all many-body effects. However, in practice, it can only be determined with a limited precision by approximative methods. Finally, the ground state energy of the interacting problem can be expressed as:

\[
E[\rho(r)] = T[n(r)] + \int dr n(r) V_a(r, \{R_{ia}\}) + \frac{1}{2} \int dr dr' \frac{n(r) n(r')}{|r - r'|} + E_{xc}[n(r)]
\] (2.20)

where \( T \) is the kinetic energy corresponding to the density \( n(r) \) (function of three coordinates). The KS equations Equation 2.18 are solved by SCF methods: starting with an initial density, the effective potential \( V_{\text{eff}} \) is computed together with the KS orbitals and the corresponding density, and this procedure is repeated until the convergence has been reached.

The exchange-correlation functional \( E_{xc}[n(r)] \) is a complicated quantity, which takes into account the electron-electron interaction effects. The problem is that even though the HK theorem guarantees the existence of such functional, it does not give a practical guidance or an iterative scheme how to find it and improve it. Therefore, a lot of efforts are put into the construction of ad hoc functionals of different levels of accuracy, complexity, and type of systems for which they are well suited.

In the local-density approximation (LDA) \([6]\) the energy is simply related to the local density in each point of space:

\[
E_{xc}^{LDA}[n] = \int n(r) \epsilon_{xc}(n(r)) dr
\] (2.21)
where “$\epsilon_{xc}(n(r))$ is the exchange-correlation energy per particle of a uniform electron gas of density $n(r)$” [19, 20]. The exact expression for the exchange part is well known from Thomas-Fermi-Dirac theory [21, 22] while the correlation part is fitted to different quantum Monte Carlo simulations of the spin paired uniform electron gas [23, 24]. The LDA is appropriate for a system where $n(r)$ varies slowly in space but it fails in situations where the electron density undergoes rapid changes, such as in molecules.

The LDA can be improved by adding a dependence on a local density-gradient

$$E_{xc}^{GGA}[n] = \int n(r) f((n(r), \nabla n(r)) dr, \quad (2.22)$$

which makes the xc-functional a semi-local functional of the electron density. Generalized gradient approximation (GGA)-functionals are reduced to LDA for the uniform electron gas and should meet the sum rule [25, 26]. Adding other ingredients into the functional besides local density and gradient of density provides a flexibility that can be used to to satisfy additional constraints. However, pure density-dependent functionals are more convenient as they are easily evaluated and more are suitable for constructing approximate functionals.

Another type of functional designed to keep the advantages of both LDA and GGA functionals is the class of hybrid functionals composed of an exact exchange term from Hartree-Fock theory with exchange and correlation terms from other sources [20, 27, 28]. B3LYP (Becke, 3-
parameter, Lee-Yang-Parr) is one of the most commonly used hybrid functional to study biology and chemistry related problems. It can be expressed as:

\[
E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA}),
\]

(2.23)

where \(a_0 = 0.20\), \(a_x = 0.72\), and \(a_c = 0.81\). \(E_{xc}^{GGA}\) is the Becke 88 generalized gradient approximation to the exchange functional [27]. \(E_{xc}^{LDA}\) is the Lee, Yang, and Parr generalized gradient approximation to the correlation functional [20]. \(E_{xc}^{LDA}\) is the local-density approximation to the correlation functional [28].

The merits and disadvantages of DFT are well known [8]. Neither HF nor more advanced methods (e.g. coupled-cluster method) scaling as \(O(N^4)\) and \(O(N^7)\) with respect to number of basis wavefunctions, can compete with DFT for relatively large systems of \(\sim 1000\) atoms. However, DFT is known to have a limited accuracy in the calculation of excited electronic states and the optical properties of materials. An accurate description of those is beyond a single-electron picture and requires a development of a time-dependent DFT. DFT also systematically underestimates the energy band gaps in semiconducting and isolating materials and neglects vdW interactions, so a special treatment of molecular complexes is needed within DFT [29].

2.3 DFT for Periodic Systems

The level of DFT is defined by the chosen exchange-correlation functional \(E_{xc}[n]\). However, in practical applications there is also a number of numerical approximations suitable for a given system of interest. There are two quite different in nuce types of systems: spatially
localized (molecules/atoms) and periodic systems. In isolated systems, the space region in
which KS equations should be solved is restricted by a finite region determined by the decay
of the effective potential (usually at infinity) and by the appropriate boundary conditions (e.g.
Dirichlet boundary conditions). In infinite systems (e.g. crystals) the space region for KS
equations is in principle unrestricted. Within this approach, a special treatment is needed to
describe localized phenomena (e.g. disordered systems [30, 31]). In the following sections we
will discuss the basic approximations and their parameters implemented for periodic systems.

2.3.1 Periodic Boundary Conditions and Bloch Theorem

“A real crystal is a finite macroscopic object made of finite, although extremely large,
number of periodically arranged atoms. However, the ratio of the number of atoms at the
surface to the total number of atoms in the crystal, $N$, is usually very small, and is proportional
to $N^{-1/3}$. When $N$ is large, and the surface is neutral, the perturbation caused by the presence
of the boundary is limited to only a few surface layers and, therefore, has no practical influence
on the bulk properties. Therefore, a macroscopic crystal mostly exhibits properties and features
of a bulk material, and unless the attention is focused on the crystal boundary, surface effects
can be neglected” [32]. In this case, an infinite and translationally invariant model of a crystal
can be applied to study the bulk properties of real crystal. However, this is not true for
nanocrystals for which the bulk model can often not be employed, and the whole crystallite
needs to be studied as is.

The mean potential $U(\vec{r})$ which acts on electrons in an infinite “crystal must be a periodic
function with the same periodicity as the lattice, so that for a translation by any direct lattice
vector” [32] \( \vec{g} \), the potential energy satisfies \( U(\vec{r} + \vec{g}) = U(\vec{r}) \). The kinetic energy is invariant with respect to translation by a lattice vector as well because of the symmetry requirements. Therefore, the SE \( \hat{H}(\vec{r})\Psi(\vec{r}) = E\Psi(\vec{r}) \) “must also be [translationally] invariant, which is equivalent to the requirement that, after a translation of the entire crystal” [32] by \( \vec{g} \) the solution of the equation \( \hat{H}(\vec{r} + \vec{g})\Psi(\vec{r} + \vec{g}) = E\Psi(\vec{r} + \vec{g}) \) coincides with \( \Psi(\vec{r}) \).

It has been shown [33] that eigenfunctions of electrons moving in such a potential \( U(\vec{r}) \) must obey the Bloch theorem, stating that the wave functions can be described by a product of a function with the same periodicity as the lattice \( u_\vec{k}(\vec{r}) = u_\vec{k}(\vec{r} + \vec{g}) \), and a phase factor (a plane wave)

\[
\Psi_\vec{k}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_\vec{k}(\vec{r}),
\]

where \( \vec{k} \) is a wave vector belonging to the first Brillouin zone (BZ) of the lattice. The fact that \( \vec{k} \) belongs to the first BZ is a consequence of the translational symmetry of Bloch wavefunctions in reciprocal space. The Bloch theorem provides the relation between the values of an eigenfunction at equivalent points in the lattice. It also says that the periodic boundary conditions imposed by Equation 2.24 imply that the wavefunction needs to be solved within the supercell defining the lattice.

“Another important property of Bloch wavefunctions is related to the evaluation of the integrals extended to the entire space, which involves a function \( f(\vec{r}) \) with the same periodicity as the lattice” [32] \( f(\vec{k}, \vec{k}') = \int \Psi^*_{n, \vec{k}}(\vec{r}) f(\vec{r}) \Psi_{n, \vec{k}}(\vec{r}) d\vec{r} \). Bloch wavefunctions are the eigenfunctions of translation operators \( T_{\vec{g}}\psi(\vec{r}) = \psi(\vec{r} + \vec{g}) \) and operators commuting with translation operators including the Hamiltonian. It can be shown that Bloch wavefunctions form the basis
of the irreducible representations of the group of the lattice translations corresponding to one wave vector $\vec{k}$. Therefore, the advantage of the Bloch wavefunction representation is that an effective single-electron Hamiltonian has a block-diagonal form with respect to the reciprocal lattice vectors such that the eigenstates can be determined separately for each $\vec{k}$-point. “Owing to the smooth change of the eigenvalues and the eigenstates with $\vec{k}$, it is possible to sample matrix $\hat{H}$ at a finite number of points and solve SE for a periodic system at different points in the first BZ. If a sampling is convenient, the number of $\vec{k}$-points to be considered is usually relatively small, and solving of SE in the reciprocal space becomes feasible” [32].

2.3.2 Representation of Wavefunctions and Energy Cutoff

As explained in the previous section, the representation of wavefunctions is an important element of the numerical DFT implementation since it defines the strategy for evaluation of matrix elements and finally the procedure of finding the eigenvalues and eigenstates. There are three main ways of representing the wavefunctions in periodic systems: 1) plane waves, 2) numerical atomic orbitals, and 3) real space grids. We briefly summarize the essential points for each of them.

Due to the periodicity of the Bloch wavefunctions $u_{\vec{k}}(\vec{r})$ (see Equation 2.24), the KS wave functions can be expanded in a discrete set of plane waves:

$$\Psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n,\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, \quad (2.25)$$
where \( n \) labels different bands, \( \vec{G} \) are reciprocal lattice vectors defined by \( \vec{G} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3 \) with integer values for \( m_i \) such that for any real space lattice vector \( \vec{a}_i, \vec{G} \cdot \vec{a}_i = 2\pi m_i \).

According to Equation 2.25, evaluating \( \Psi_{n,\vec{k}}(\vec{r}) \) at each point in \( k \)-space involves a summation over an infinite set of possible values of \( \vec{G} \). Note that the kinetic energy operator \( \hat{T} \) is diagonal in reciprocal space and has eigenvalues \( E_{n,\vec{k}} = \frac{\hbar^2}{2m_e} | \vec{k} + \vec{G}_n |^2 \). For large reciprocal lattice vectors, the kinetic energy contribution to the Hamiltonian is dominant. As a result, it is common to truncate the infinite sum above to include the solutions with kinetic energies smaller than \( E_{\text{cut}} = \frac{\hbar^2}{2m_e} G_{\text{cut}}^2 \). Then, the infinite sum is reduced to

\[
\Psi_{n,\vec{k}}(\vec{r}) = \sum_{|\vec{G}+\vec{k}|<G_{\text{cut}}} c_{n,\vec{k}+\vec{G}} e^{i(\vec{k}+\vec{G}) \cdot \vec{r}}.
\]

For different \( \vec{k} \) the sum in Equation 2.26 contains slightly different number of terms. It is easier to define \( E_{\text{cut}} \) than \( k \)-points as it is done for most of the numerical implementations in quantum mechanical packages.

The main drawback of the plane wave representation of KS wavefunctions is that a large number of plane waves is generally needed to achieve convergence. Within this approach, only periodic boundary conditions are supported. In calculations of spatially localized objects (e.g. surfaces or defects) within infinite systems, large supercells must be used to avoid spurious interactions between repeated images. Another problem is that the plane wave representation relies heavily on the use of a fast Fourier transform (FFT) [34], which is a non-local operation and difficult to parallelize efficiently. The kinetic energy operator is diagonal in reciprocal
space. It implies that both the diagonalization of the kinetic energy operator and solving Poisson equation for the Hartree potential are trivial problems in this space. However, a FFT of the xc-potential is a much more complicated problem [12].

Alternatively, the wavefunctions can be directly represented in a real space grid using a uniform mesh of grid points. In real space, the kinetic energy operator is represented by a semi-local finite-difference stencil, similar to that used in tight-binding methods where only near neighboring points in space are accounted for. The Poisson equation for the Hartree potential can also be solved using purely-grid based algorithms [35] requiring very little communications between computational processors. The flexibility of boundary conditions and systematic convergence by reduction of the grid spacing constitute the virtue of the real-space grid wavefunction representation that can be numerically implemented in codes which can be efficiently parallelized. However, the disadvantages are that this representation requires even more degrees of freedom than plane waves for the same accuracy, and the discrete grid gives rise to the so-called egg-box effect which consists in artificial variations in observables by shifting the grid [36].

Another natural choice of representation is to work with linear combinations of atomic orbitals (LCAO) in which the KS wavefunction is written as

$$\Psi_{n,\vec{k}}(\vec{r}) = \sum_{\vec{R}} \sum_{\nu} c_{n,\vec{k},\nu} e^{i(\vec{k} \cdot \vec{R})} \Phi_{\nu}(\vec{r} - \vec{R}),$$  \hspace{1cm} (2.27)
where $\vec{R}$ goes over set of all lattice vectors for which the atomic orbitals $\Phi_\nu(\vec{r} - \vec{R})$ overlap with the supercell in which $\Psi_{n_\nu}(\vec{r})$ is represented, and $\nu = a, n, l, m$ is the combined atomic orbital index for orbitals centered on atom $a$

$$\Phi_{n\lambda m}^a(\vec{r}) = \zeta_{n\lambda}^a(|\vec{r} - \vec{R}_a^a|)Y_{lm}(\vec{r} - \vec{R}_a),$$  

(2.28)

where $\zeta_{n\lambda}^a$ is a numerical radial function which vanishes beyond a certain cut-off radius, and $Y_{lm}$ is a spherical Harmonic.

The main advantage of localized atomic orbitals is that they make the Hamiltonian matrix sparse, which can be convenient when developing low $O(N^k)$-methods of solving KS equations. Another advantage of this representation is the flexibility of the basis set of LCAOs, where one can easily include effects of polarization, etc. This means that a description based on a few atomic orbitals can be sufficient. At the same time, the use of a highly reduced basis set size implies that the Hamiltonian can be easily diagonalized, which is in contrast to plane wave and grid methods, where iterative minimization algorithms are needed to extract only lowest eigenstates. However, the drawback of LCAO representation is that there is no general systematic convergence of observables with respect to such basis sets. Therefore, a truly accurate representation is hard to obtain.

### 2.3.3 Core Electrons and Pseudopotential Approximations

The chemically inert core electrons in atoms forming molecules and solids are usually unaffected by bonds formed between the atoms. Therefore, they can be considered to be frozen
in the corresponding states of the isolated atoms. The KS equations are thus explicitly solved only for the valence states only. However, “the atomic wave-functions as eigenstates of the atomic Hamiltonian must all be mutually orthogonal. Since the core states are localized in the vicinity of the nucleus, the valence states must oscillate rapidly in this core region to maintain orthogonality with the core electrons. This rapid oscillation results in a large kinetic energy for the valence electrons in the core region, which roughly cancels the large potential energy due to the strong Coulomb potential. Thus the valence electrons are much more weakly bound than the core electrons. It is therefore convenient to attempt to replace the strong Coulomb potential and core electrons by an effective pseudopotential which is much weaker, and replace the valence electron wavefunctions, which oscillate rapidly in the core region, by valence pseudo-wavefunctions that vary smoothly in the core region” [19].

The projector augmented-wave (PAW) method is based on [12, 37] an auxiliary atomic basis set employed to project out the core electron states. In the real space grids and LCAO representations, the Vanderbilt ultra-soft pseudopotentials [38] and norm-conserving pseudopotentials [39–41] are used, respectively.

In a nutshell, in all these pseudopotential methods, the auxiliary basis set functions are set non-zero only in the core region and are well suited to describe the nodal structure of the valence states. The valence electrons can be then described by a different basis to represent the long range structure of the valence states. First-principle pseudopotentials are usually non-local, meaning that different angular momentum states feel different effective potentials. The
representation of the core electron states can in principle be exact, provided that the set of projector functions span a complete representation of the core region [42].

2.3.4 \textit{Integrals in k-space and Sampling of the Brillouin Zone}

Integration of all quantities over the BZ is essential for the numerical implementation of DFT in periodic systems, especially for metals. In practice, the matrix elements and expectation values related to the supercell, instead of being computed in real space, are determined by averaging over a discrete sampling of the first BZ. The efficiency of calculations of integrals in \textit{k}-space strongly depends on the type of studied quantity, representation of Bloch wavefunctions, etc.

The integrals of the form \( \frac{V_{\text{cell}}}{(2\pi)^3} \int_{BZ} g(\vec{k})d\vec{k} \) can be approximated by evaluating the function to be integrated over a set of discrete points while summing its values with appropriate weighting for each point. For a very large number of points, the summation converges to the exact result for the integral. However, different choices for the placement and weighting of the functional evaluation can result in dramatically different convergences.

The most efficient and common method of \textit{k}-point sampling of BZ was proposed by H. Monkhorst and J. Pack [43, 44]. In the Monkhorst-Pack sampling method, we need to specify how many \textit{k}-points are to be used in each direction in reciprocal space. However, this method is heavily based on the symmetries of the unit cell. Due to these symmetries the integrals in a reciprocal space can be evaluated in a reduced portion of the zone called the \textit{irreducible Brillouin zone} (IBZ) [8]. For highly symmetric materials, e.g., \textit{fcc} crystals, using just the IBZ greatly reduces the numerical efforts required to perform integrals in \textit{k}-space. For example,
in the $10 \times 10 \times 10$ sampling of the BZ, only 35 distinct points in $k$-space lie within the IBZ
(compared to the 1000 that would be used if no symmetry was used in the calculations).

In practice, the integrals $V_{\text{cell}} \frac{V_{\text{cell}}}{(2\pi)^3} \int_{BZ} g(\vec{k})d\vec{k}$ are performed in a finite, uniform grid of the BZ. The fineness of this grid is controlled by a $k$-grid cutoff $l_{\text{cut}}$ (a real space radius) which plays a role equivalent to the plane-wave cutoff of the real-space grid [45]. By changing the size of supercells and using an unconventional set of primitive lattice vectors, a drastic reduction in the mesh size and optimum sets of special points for the BZ can be often achieved. The origin of the $k$-grid may be displaced from Γ-point to decrease the number of nonequivalent $k$-points [44].

2.3.5 The SIESTA method

Most of the quantum mechanical calculations of electronic properties of systems in this thesis are performed with the DFT package SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [46, 47]. In order to provide a more detailed description of numerical implementation of DFT with LCAO basis sets, in this subsection we briefly describe the essential approximations, the procedure and peculiarities of SIESTA.

In a nutshell, the SIESTA code implements a fully self-consistent DFT, based on a flexible linear combination of atomic orbitals (LCAO) basis set, with essentially perfect linear $O(N)$ scaling. It allows extremely fast and easily parallelizable simulations using minimal basis sets and very accurate calculations with complete multiple-$\zeta$ and polarized bases, depending on the required accuracy and available computational power. Exchange and correlation functionals are treated within the framework of the KS version of DFT with both local (spin) density approximations and several possible parametrizations, and the generalized-gradient-corrections
approximation. SIESTA uses a real-space grid for calculations of electron density and standard norm-conserving pseudopotentials in their full non-local form to avoid explicit computations of core electrons and to smooth the valence charge density. SIESTA also includes scalar-relativistic effects and non-linear partial-core corrections to treat exchange and correlation in the core region. The main precision parameters that characterize the SIESTA method are: basis set (number of atomic basis orbitals), basis range (radius of the basis orbitals), the fineness of the real-space integration grid and the confinement radius of the Wannier-like electron states.

2.3.5.1 Basis set

Linear scaling $O(N)$ with respect to the number of the basis wavefunctions relies heavily on the sparsity of the Hamiltonian and overlap matrices. In the SIESTA method this high level of sparsity is achieved by the use of strictly confined basis orbitals, i.e. orbitals that are zero beyond a certain radius [48]. The orbital radii are the parameters that keep the energy strictly variational, thus facilitating the test of convergence with respect to the radius of the confinement. Within this radius, the atomic basis orbitals are products of a numerical radial function (easily tabulated) and a spherical harmonic. For atom $a$, located at $\vec{R}_a$,

$$\Phi_{n\ell m}(\vec{r}) = \zeta_{n\ell}(|\vec{r} - \vec{R}_a|)Y_{\ell m}(\vec{r} - \vec{R}_a).$$

(2.29)
The radial functions $\zeta_{nl}(|\vec{r}|)$ are defined by a cubic spline interpolation from the values given on a fine radial mesh. The method of generating the standard (single-$\zeta$, SZ) basis set [48] uses the eigenfunctions of the pseudo-atom within a spherical box:

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{2r^2} + V_l(r)\right)\zeta_{nl} = (E_l + \delta E_l)\zeta_{nl},$$  \hspace{1cm} (2.30)$$

where $V_l(r)$ is an atomic pseudopotential, and energy $E_l + \delta E_l$ is chosen so that the first node occurs at the desired cutoff radius $r_{cl}$. Therefore, the orbital radii depend on the atomic species and angular momentum. Another method of generating higher $\zeta$-orbitals is based on the “split-valence” method [47]. In that method, “the first $\zeta$-orbitals are fixed linear combinations of Gaussians, determined either variationally or by fitting numerical atomic eigenfunctions. The second $\zeta$-orbital is one of the Gaussians, which is “released” from the fixed combination. Higher $\zeta$-orbitals are constructed in a similar way by releasing more Gaussians” [49].

To achieve more variational flexibility, in addition to the atomic valence orbitals (where one can include empty orbitals, e.g., 4p-orbitals for Mo-atoms), it is generally necessary to include the polarization orbitals, to account for the deformation due to the chemical bond formation. In this case, the polarization orbitals are constructed using spherical harmonics with higher orbital angular momentum. Overall, the flexible LCAO basis sets used in SIESTA are far more efficient in terms of number of basis orbitals than the plane wave method and usually allow faster convergence with the same accuracy.
2.3.5.2 Pseudopotentials

The pseudopotentials are used not only to remove the core electrons, but also to allow for the expansion of a smooth charge density on a uniform spatial grid. The Trouiller-Martins [41] parametrization is used as a semilocal form of the pseudopotentials which is then transformed into the fully non-local Kleinman-Bylander [50] for improved simplicity and efficiency. In the framework of this approach, the total atomic potential which includes the core and valence electrons is split into the local and non-local part

\[ \hat{V} = V_{\text{local}}(r) + \hat{V}^{KB} \]  

(2.31)

\[ \hat{V}^{KB} = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \sum_{n=1}^{N_{KB}} | \Phi_{lmn}^{KB} \rangle v_{ln}^{KB} \langle \Phi_{lmn}^{KB} | \]  

(2.32)

\[ v_{ln}^{KB} = \langle \phi_{ln} | \delta V_l(r) | \phi_{ln} \rangle^{-1}, \]  

(2.33)

where \( \delta V_l(r) = V_l(r) - V_{\text{local}}(r) \) and \( \Phi_{lmn}^{KB}(\vec{r}) = \zeta_{ln}^{KB}(r) Y_{lm}(\vec{r}) \) is the KB projection functions, \( \zeta_{ln}^{KB}(r) = \delta V_l(r) \phi_{ln}(r) \), and \( \phi_{ln}(r) \) are the atomic pseudo-orbitals, i.e. the solutions of the radial Schrödinger equation with potential \( V_l(r) \) (without any cutoff radius). Since \( \delta V_l(r) \) is nonzero only inside a small pseudopotential core radius, \( r_c^l \), the functions \( \Phi_{lmn}^{KB}(\vec{r}) \) are zero outside this radius.
The functions $\phi_{ln}(r)$ are obtained from the eigenstates of the semilocal pseudopotential (screened by the pseudo-valence charge density) at energies $E_{ln}$ using the orthogonalization scheme [51]:

$$
\phi_{ln}(r) = \psi_{ln}(r) - \sum_{n'=1}^{n-1} \phi_{ln'}(r) \frac{\langle \phi_{ln'} | \delta V_i(r) | \psi_{ln} \rangle}{\langle \phi_{ln'} | \delta V_i(r) | \phi_{ln'} \rangle},
$$

(2.34)

$$
\left( -\frac{1}{2r} \frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_i(r) + V^H(r) + V^{XC}(r) \right) \psi_{nl}(r) = E_{ln} \psi_{nl},
$$

(2.35)

where $V^H(r)$ and $V^{XC}(r)$ are the Hartree and XC potentials for the pseudo-valence charge density.

The above described scheme allows generation of norm-conserving pseudopotentials in a non-local form, rather than “ultrasoft” pseudopotentials as in the plane-wave scheme. As the nonlocal part of the pseudopotential is a relatively computationally cheap operator, a large value of $l_{max}^{KB}$ in equation Equation 2.32 is used, usually larger than the $l_{max}$ of the basis functions.

**2.3.5.3 Brillouin zone sampling**

The SIESTA code is designed for large unit cells which means that the sampling is performed only at the Γ-point without using complex phases. However, SIESTA also allows performing efficiently the calculations for smaller systems. For each unit cell, an auxiliary supercell is defined in such a way that it contains all the atoms whose basis orbitals are nonzero at any of the grid points of the unit cell or which overlap with any of the basis orbitals in it. For this supercell, all the nonzero two-center integrals between the unit cell and the supercell orbitals without any complex phase factors are calculated. In this way, the grid integrals between all
the supercell basis orbitals $\phi_{\mu'}$ and $\phi_{\nu'}$ within the unit cell only are evaluated. The information is stored in the matrix elements:

$$
\langle \phi_{\mu} \mid V(\vec{r}) \mid \phi_{\nu'} \rangle = \sum_{(\mu', \nu')=(\mu, \nu')} \langle \phi_{\mu'} \mid V(\vec{r}) f(\vec{r}) \mid \phi_{\nu''} \rangle,
$$

(2.36)

where $f(\vec{r}) = 1$ for $\vec{r}$ within the unit cell and is zero otherwise. All the orbitals belong to the unit cell; $\phi_{\mu'}$ and $\phi_{\mu}$ are equivalent orbitals, related by a lattice vector translation. $(\mu', \nu'') \equiv (\mu, \nu')$ means that the sum runs over all pairs of supercell orbitals $\phi_{\mu'}$ and $\phi_{\nu''}$ such that $\mu' \equiv \mu$, $\nu'' \equiv \nu'$. Once all the real overlap and Hamiltonian matrix elements are calculated, at every $k$-point they are multiplied by the corresponding phase factors [47].

Once we find the Bloch-state expansion coefficients $c_{\mu n \vec{k}}$, the eigenfunction can be written as:

$$
\psi_{n, \vec{k}}(\vec{r}) = \sum_{\mu'} c_{n, \vec{k}, \mu'} e^{i(\vec{k} \cdot \vec{R}_{\mu'})} \phi_{\mu'}(\vec{r}),
$$

(2.37)

where the sum runs over all basis orbitals; $n$ labels the different bands. The electron density is then defined as:

$$
\rho(\vec{r}) = \sum_n \int_{BZ} f_n(\vec{k}) \mid \psi_{n, \vec{k}}(\vec{r}) \mid^2 \, d\vec{k} = \sum_{\mu' \nu'} \rho_{\mu' \nu'} \phi_{\mu'}^*(\vec{r}) \phi_{\nu'}(\vec{r}),
$$

(2.38)

where $f_n(\vec{k})$ is the population function for the $n$-band, and the density matrix elements:

$$
\rho_{\mu \nu} = \sum_n \int_{BZ} c_{\mu n}^*(\vec{k}) f_n(\vec{k}) c_{n \nu}(\vec{k}) e^{i\vec{k} \cdot (\vec{R}_{\nu} - \vec{R}_{\mu})} \, d\vec{k}.
$$

(2.39)
“Thus, to calculate the [electron] density at a grid point of the unit cell, the sum” [49] in Equation 2.38 is taken over all pairs of orbitals in the supercell that are nonzero at that point. In practice, the integral in Equation 2.39 is performed in a finite and uniform grid of the BZ. If the unit cell is large enough to perform Γ-point-only calculations, the multiplication by the phase factors is skipped.

2.3.5.4 Electron Hamiltonian and matrix elements

Within the nonlocal pseudopotential approximation, the standard KS one-electron Hamiltonian may be written as:

\[
\hat{H} = \hat{T} + \sum_a \hat{V}^{\text{local}}_a(\vec{r}) + \sum_a \hat{V}^\text{KB}_a + \hat{V}^\text{H}(\vec{r}) + \hat{V}^{\text{xc}}(\vec{r}), \tag{2.40}
\]

where \(a\) labels the atom in the unit cell. The elimination of the long range of \(V^{\text{local}}_a\) is performed by screening it with the potential \(V^{\text{atom}}_a\), created by the atomic electron density \(\rho^{\text{atom}}_a\) constructed by populating the basis functions with appropriate valence atomic charges. The screened “neutral atom” potential \(V^{\text{NA}}_a \equiv V^{\text{local}}_a + V^{\text{atom}}_a\) is zero beyond the pseudopotential cutoff radius \(r^*_a\). With these notations the actual total electronic Hamiltonian used in SIESTA can be written as

\[
\hat{H} = \hat{T} + \sum_a \hat{V}^{\text{KB}}_a + \sum_a \hat{V}^{\text{NA}}_a(\vec{r}) + \delta\hat{V}^\text{H}(\vec{r}) + \hat{V}^{\text{xc}}(\vec{r}), \tag{2.41}
\]

where \(\delta\hat{V}^\text{H}\) is the electrostatic Hartree potential generated by \(\delta\rho(\vec{r})\) - the difference between the self-consistent electron density \(\rho(\vec{r})\) and the sum of atomic densities \(\rho^{\text{atom}}_a(\vec{r})\).
The matrix elements of the first two terms of $\hat{H}$ involve two-center integrals which can be easily calculated in reciprocal space and tabulated as a function of interatomic distance. This is done at the beginning of the calculations with great accuracy with a small computational effort. The remaining three terms involve the potentials which are calculated in a real space grid [36, 46, 47].

The usual computational strategy for two-center integrals implies the transition from real space to Fourier space:

\[
S(\vec{R}) \equiv \langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(\vec{r})\psi_2(\vec{r} - \vec{R})d\vec{r} = \int \psi_1^*(\vec{k})\psi_2(\vec{k})e^{-i\vec{k} \cdot \vec{R}}d\vec{k} \tag{2.42}
\]

Using the expansion of $\psi(\vec{r})$ over spherical harmonics, the overlap integral in Equation 2.42 can be written in the form:

\[
S_{lm}(\vec{R}) = \sum_{l_1m_1} \sum_{l_2m_2} G_{l_1m_1,l_2m_2,l,m} S_{l_1m_1,l_2m_2,l}(\vec{R}) \tag{2.43}
\]

where $G_{l_1m_1,l_2m_2,l,m}$ are the Gaunt coefficients [48], and:

\[
S_{l_1m_1,l_2m_2,l}(\vec{R}) = 4\pi i^{l_1-l_2-l} \int_0^\infty k^2dk j_l(k\vec{R})i^{-l_1}\psi_1^{*l_1m_1}(\vec{k})i^{l_2}\psi_2^{l_2m_2}(\vec{k}), \tag{2.44}
\]

where $j_l(k\vec{R})$ are Bessel functions of $l^{th}$-order. The Gaunt coefficients are evaluated using a Gaussian quadrature. These coefficients are universal and can be calculated and stored once.
The kinetic matrix elements $\vec{T}(R)$ can be calculated in the same way
\[
T_{l_1 m_1, l_2 m_2}(\vec{R}) = 4\pi i^{l_1 - l_2 - 1} \int_0^{\infty} \frac{1}{2} k^4 dk j_l(kR)i^{-l_1} \psi_{l_1 m_1}^*(\vec{k})i^{l_2} \psi_{l_2 m_2}(\vec{k}). \tag{2.45}
\]

To obtain the accurate matrix elements, a fine radial grid is needed. A usual practice is to use grid cutoffs $\sim 2000$ Ry for this purpose. Such calculations are a relatively difficult task. For this purpose, a spatial fast radial Fourier transform was designed [47].

The matrix elements of last three terms in Equation 2.41 are evaluated on a real-space grid. The fineness of this grid is controlled by a grid cutoff $E_{\text{cut}}$ - the maximum kinetic energy of the plane wave that can be represented in the grid. The Hartree potential $\delta V^H(\vec{r})$ is calculated by solving the Poisson equation in a reciprocal space using fast Fourier transform. With that, the total grid potential $\sum_a V_{a}^{NA}(\vec{r}) + \delta V^H(\vec{r}) + V^{xc}(\vec{r})$ is calculated.

For the periodic system with the Hamiltonian matrix elements $H_{\mu\nu} = \langle \phi_{\mu} | \hat{T} + \hat{V}_{\text{eff}} | \phi_{\nu} \rangle$, one needs to include the coupling to the periodic mirrors of the unit cell:
\[
H_{\mu\nu}(\vec{k}) = \sum_{\nu'} H_{\mu\nu'} e^{i\vec{k}(\vec{R}_{\nu'} - \vec{R}_{\nu})}. \tag{2.46}
\]

An analogous equation can be written for the total overlap matrix $S(\vec{k})$.

For the $N$ basis wavefunctions in the unit cell (non-spin-polarized case) the resulting $N \times N$ generalized eigenvalue problem:
\[
\sum_{\nu} (H_{\mu\nu} - E_i S_{\mu\nu}) c_{\nu i} = 0. \tag{2.47}
\]
This is then solved at every sampled $k$-point. Once the KS eigenstates Equation 2.37 are found, then the density matrix Equation 2.39 can be evaluated. The electron charge density is the diagonal elements of the density matrix in the real space grid representation.

Using the LCAO basis set, the electron density is written as:

$$\rho(\vec{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi^*_\nu(\vec{r}) \phi_\mu(\vec{r}), \quad (2.48)$$

where:

$$\rho_{\mu\nu} = \sum_i c_{\mu i} f_{i\nu} c_{i\nu} \quad (2.49)$$

$c_{i\nu}$ are the basis set expansion coefficients $c_{i\nu} = \langle \phi_\nu | \psi_i \rangle$ and $f_c$ is the population (Fermi-Dirac) function. To calculate the electron density at a given real space grid point, one needs first to find all the atomic basis orbitals at that point (see Equation 2.29) by interpolating the radial part from the tabulated values and then to use Equation 2.48. Since only a small number of basis orbitals are nonzero at a given grid point, the calculation of the density can be performed in $O(N)$ operations. The storage of the orbital values at the grid points is the most expensive part of the code.

The total KS energy (the sum of band structure energy and correction terms [47]) can then be calculated. The overall procedure requires the self-consistent solution. A density matrix calculated at the $i^{th}$-step is then used to calculate the Hamiltonian matrix elements. This leads to a new density matrix. The procedure is repeated until the convergence criterion is satisfied, specifically, $||\rho^i - \rho^{i+1}|| < \delta$, where $\delta$ is the tolerance parameter.
2.4 Electron Transport Techniques

In atomic-scale transport problems we typically study devices consisting of two charge reservoirs (electrodes) bridged by a nanoscale object, usually a molecule or a molecular cluster. Historically, atomically small electron transport regions were called “quantum point contacts” [52]. The experiments with a two dimensional electron gas confined in a GaAs-AlGaAs heterojunction revealed that the conductance behaves as a step-function, and the values of these steps are near-integer multiples of $\sim 1/13 \, k\Omega$ [53]. These results had attracted a great deal of attention. The study of such phenomena lead to the development of a theory of electron transport in mesoscale systems. In this subsection, we give a brief overview of theoretical approaches used to describe electron transport in nanoscale systems.

2.4.1 Non-equilibrium Green’s functions

The most general formalisms that take into account all the quantum electron transport phenomena are based on non-equilibrium Green’s functions (NEGF) [54]. In the framework of this formalism, the central quantities are the correlation functions $G^<$ and $G^>$, called the lesser and greater Green’s functions, respectively, defined as the functional average (functional expectation value) over the grand canonical ensemble.

$$-i\hbar G^<(1, 2) = \langle \psi^*(2)\psi(1) \rangle,$$

$$i\hbar G^>(1, 2) = \langle \psi(2)\psi^*(1) \rangle,$$

(2.50)

where $i = (\vec{r}_i, t_i)$, $\psi^*$ and $\psi$ are electron field operators. From the definition, these correlation functions correspond to electron and hole propagation, respectively, where lesser (greater) cor-
responds to removing an electron (hole) from site $\vec{r}_1$ at $t_1$ and reinserting it in site $\vec{r}_2$ at $t_2$. The total single electron excitation spectrum is then determined by the spectral function:

$$A(1, 2) = i\hbar(G^>(1, 2) - G^<(1, 2)).$$ (2.51)

The central equation used in the Green’s functions formalism is the Dyson equation [55] for the causal Green’s function. In the matrix form it can be written as:

$$G(1, 2) = G_0(1, 2) + G_0(1, 3)\Sigma(3, 4)G(3, 2).$$ (2.52)

Using the Langreth-Wilkins rule [56, 57], analogous equations can be written for retarded and advanced Green’s functions:

$$G^{r,a}(1, 2) = G^{r,a}_0(1, 2) + G^{r,a}_0(1, 3)\Sigma^{r,a}(3, 4)G^{r,a}(4, 2).$$ (2.53)

where for the time-independent Hamiltonian of a system at equilibrium the Green’s functions $G^{r,a}_0$ are defined as follows:

$$[E - \hat{H}_0(\vec{r}_1) \pm \delta E]G^{r,a}_0(\vec{r}_1, \vec{r}_2; E) = \delta(\vec{r}_1 - \vec{r}_2)$$ (2.54)
and $\Sigma^{r,a}$ describes self-energies related to the particular mechanisms of electron scattering (e.g. electron-phonon scattering, impurities, defects, etc.). The retarded and advanced Green’s functions are related to the $G^<$ and $G^>$ by relations:

\[
G^r(1, 2) = \theta(t_1 - t_2)(G^>(1, 2) - G^<(1, 2))
\]

\[
G^a(1, 2) = \theta(t_2 - t_1)(G^<(1, 2) - G^>(1, 2)).
\] (2.55)

One can get an equation for $G^{<,>}$ (in matrix form) in a similar way as for $G^{r,a}$:

\[
G^{<,>}(1, 2) = G^r(1, 3)\Sigma^{<,>}(3, 4)G^a(4, 2),
\] (2.56)

where $\Sigma^{<,>}$ represents the in-scattering and out-scattering rates, respectively. Generally, $\Sigma^{<,>}$ are functionals of causal Green’s function and can be expressed through all Green’s functions.

To compute the correlation function $G^<$, one needs to solve the quantum kinetic equation (Equation 2.56) which reads in integral form [58] as:

\[
G^<(\vec{r}_1, \vec{r}_2; E) = \int d^3\vec{r} \int d^3\vec{r'} G^r(\vec{r}_1, \vec{r}; E)\Sigma^<(\vec{r'}, \vec{r}; E)G^a(\vec{r}_2, \vec{r'}; E),
\] (2.57)
where $G^r$ is the Green’s function of the Schrödinger equation describing the system out of equilibrium by using a nonlocal self-energy potential $\Sigma^r$ (e.g., the effect of the electrode on the scattering region):

$$
[E - H_0(\vec{r}_1)]G^r(\vec{r}_1, \vec{r}_2; E) - \int d^3\vec{r}' \Sigma^r(\vec{r}_1, \vec{r}'; E)G^r(\vec{r}', \vec{r}_2; E) = \delta(\vec{r}_1 - \vec{r}_2),
$$

(2.58)

where $H_0(\vec{r})$ is the Hamiltonian of the scattering region.

All the Green’s functions $G^{<,>}$, $G^{r,a}$ are related through the set of Equation 2.53 - Equation 2.58 and $\Sigma^{<,>}$ are the functionals of other operators $G^{<,>}$, $G^{r,a}$. $\Sigma^<$ represent the in-scattering rate from different energies, $G^r(\vec{r}_1, \vec{r}'; E)$ represent the wavefunction at $\vec{r}_1$ provided that an electron is injected at $\vec{r}_2$ with energy $E$ by scattering from a state with different $E$.

The kinetic equation Equation 2.57 states that the correlation $G^<(\vec{r}_1, \vec{r}_2; E)$ between points $\vec{r}_1$ and $\vec{r}_2$ is given by the product of three factors: in-scattering rate between state with energy $E$ and states with other energies, the correlation $G^r(\vec{r}_1, \vec{r}'; E)$ due to propagation from $\vec{r}'$ to $\vec{r}_1$, and the correlation $G^a(\vec{r}_2, \vec{r}''; E)$ due to propagation from $\vec{r}''$ to $\vec{r}_2$.

In the stationary regime, the system is translationally invariant on the time axis. Therefore, the Green’s functions can only depend on the time difference $t_2 - t_1$. Therefore, it is convenient to use the coordinates of center of mass and relative coordinates (for time and space coordinates)

$$
\vec{r} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2), \ t = \frac{1}{2}(t_1 + t_2), \ \vec{R} = \frac{1}{2}(\vec{r}_1 - \vec{r}_2), \ \tau = \frac{1}{2}(t_1 - t_2).
$$

Using the Fourier transform with respect to relative coordinates we can express $-iG^<$ in the Wigner coordinates $\vec{r}_1 - \vec{r}_2 \rightarrow$
\[ \vec{k}, t_1 - t_2 \to E. \] The function \(-iG^<(\vec{r}; \vec{k}; E)\) is then the quantum-mechanical analog of the classical distribution function.

Once we know \(G^r\) we can find the spectral function (Equation 2.51) through which the projected and total density of states characterizing the excitation spectrum and non-equilibrium population of energy states can be found:

\[
\begin{align*}
g_i(E) &= -\frac{1}{\pi} \text{Im} [G^r(\vec{r}', \vec{r}; E)]_{i,i}, \\
g(E) &= -\frac{1}{\pi} \text{Im} [Tr \left( G^r(\vec{r}', \vec{r}; E) \right)]. 
\end{align*}
\] (2.59)

The energy- and spatially-resolved electron density can be expressed as:

\[
\rho(\vec{r}; E) = \frac{-i}{2\pi} \int \frac{d^3\vec{k}}{(2\pi)^3} G^<(\vec{r}, \vec{k}; E). 
\] (2.60)

Note that the NEGF framework does not depend on the particular parametrization of the scattering region Hamiltonian. It can be a tight-binding Hamiltonian [59], a many-body Hamiltonian [60]. However, the KS Hamiltonian is a suitable form because the total energy and Hamiltonian in DFT are written in terms of the charge density and consequently the density matrix, quantities that are readily available in the NEGF formalism (see Equation 2.60). Besides this advantage, the Hamiltonian treated in the LCAO basis sets, as implemented in the SIESTA code, “takes the same form as in empirical tight-binding calculations, so the tech-
niques developed in this context can be straightforwardly applied" [61]. Using the local orbital
wavefunctions $\phi_i$, the retarded correlated Green’s functions $G^r$ and $G^<$ can be expanded [62]:

$$G^{r,\sigma}(\vec{r}_1,\vec{r}_2; E) = \sum_{i,j} G^{r,\sigma}_{ij}(E) \phi_i(\vec{r}_1) \phi_j^*(\vec{r}_2), \quad (2.61)$$

$$G^{<,\sigma}(\vec{r}_1,\vec{r}_2; E) = \sum_{i,j} G^{<,\sigma}_{ij}(E) \phi_i(\vec{r}_1) \phi_j^*(\vec{r}_2), \quad (2.62)$$

where $\sigma$ is the spin index. The retarded and correlated Green’s functions are obtained from
solving the Keldysh-Kadanoff-Baym equation in the matrix form:

$$G_{MM}^{r,\sigma} = [E S_{MM} - H_{MM}^\sigma - V_{MM}^{\text{ext},\sigma} - \Sigma_{L}^{r,\sigma}(E) - \Sigma_{R}^{r,\sigma}(E)]^{-1} \quad (2.63)$$

and:

$$G^{<,\sigma} = i[G^{r,\sigma}(E) \Gamma_{L}^{\sigma}(E)G^{a,\sigma}(E)]f(E - \mu_L) + i[G^{r,\sigma}(E) \Gamma_{R}^{\sigma}(E)G^{a,\sigma}(E)]f(E - \mu_R) \quad (2.64)$$

where the effect of the contact with electrodes is incorporated as the self-energy operator $\Sigma_{R/L}^{r,\sigma}$:

$$\Sigma_{L}^{r,\sigma}(E) = (E S_{ML} - H_{ML}^\sigma)G_{LL}^{0,\sigma}(E S_{LM} - H_{LM}^\sigma),$$

$$\Sigma_{R}^{r,\sigma}(E) = (E S_{MR} - H_{MR}^\sigma)G_{RR}^{0,\sigma}(E S_{RM} - H_{RM}^\sigma),$$

$$\Gamma_{L/R}^{\sigma} = i(\Sigma_{L/R}^{r,\sigma} - \Sigma_{L/R}^{0,\sigma}). \quad (2.65)$$
Here, indeces $L$, $R$, $M$ denote the regions of the two-probe setup, the left, right electrode and “molecule” in between, respectively. $G_{LL/RR}^{\sigma} = (E S_{LL/RR} - H_{LL/RR}^{\sigma})^{-1}$ are the surface Green’s functions of the left ($L$) and right ($R$) electrodes. $H_{MM}^{\sigma}$ represents the part of the Fock matrix contributing the charge distributions (nuclei and electrons) in the “molecule” region only, whereas $V_{\text{ext},\sigma}^{\text{eq}}(\vec{r})$ represents the long range Coulomb potential due to the equilibrium charge distribution in the contact region, which includes the linear voltage drop caused by the applied bias. $S$ stands for the the overlap matrices. Since the applied potential $V_{\text{ext},\sigma}^{\text{eq}}$ changes both the charge distribution and the potential in the sandwiched region, the whole computational procedure requires the self-consistent solution.

The self-energy operators $\Gamma_{L/R}^{\sigma}$ characterize the interaction between “molecule” and both electrodes. The real part of $\Gamma_{L/R}^{\sigma}$ describes an effective shift of the molecular levels. The imaginary part of $\Gamma_{L/R}^{\sigma}$ describes an effective energy-level broadening due to the finite probability of electrons escaping into the respective electrode. The density matrix in $\phi_i$-representation is the energy integration of the matrix correlation function $G_{ij}^{<,\sigma}$:

$$\rho_{ij}^{\sigma} = \frac{-i}{2\pi} \int dE G_{ij}^{<,\sigma}(E), \quad (2.66)$$

where integration over energy is performed in the complex energy plane [61,63].

In the framework of DFT-NEGF technique, the self-consistent procedure is as follows. First, a trial charge density $\rho_0(\vec{r})$ is used to compute the Hamiltonian $H_{MM}^{\sigma}$ from Equation 2.41 as $H_{MM}^{\sigma} = H_{MM}^{\sigma}[\rho]$. Then $\Gamma_{L/R}^{\sigma}$ and $G_{MM}^{\sigma}$ are calculated from Equation 2.63 and Equation 2.65.
These quantities are used to compute $G^{<,\sigma}$ in Equation 2.64, which is fed back into Equation 2.66 to find a new $\rho_1(\vec{r})$. The process is iterated until a self-consistent solution is achieved $||\rho_j - \rho_{j+1}|| < \delta$, where $\delta$ is the tolerance parameter. Transforming to the basis of molecular orbitals, the diagonal elements of the density matrix give the non-equilibrium electron occupation of the corresponding molecular levels.

A general formula for the current through a mesoscopic system with arbitrary interactions in contact with two non-interacting electrodes is:

$$I(V) = \frac{e}{\hbar} \int dE \sum_\sigma Tr\{[\Gamma_L^\sigma - \Gamma_R^\sigma](E,V)iG^{<,\sigma}(E,V)] + \left[ f(E - \mu_L)\Gamma_L^\sigma(E,V) - f(E - \mu_R)\Gamma_R^\sigma(E,V) \right] A^\sigma(E,V) \}, \quad (2.67)$$

where $A^\sigma = i(G^{r,\sigma} - G^{a,\sigma})$ is the spectral function. Since the only scattering mechanism in the coherent transport region is that by the electrodes, Equation 2.67 reduces to:

$$I(V) = \frac{e}{\hbar} \int dE \sum_\sigma T_\sigma(E,V)\{f(E - \mu_L) - f(E - \mu_R)\}, \quad (2.68)$$

where the transmission probability $T^\sigma$ through the molecular region is:

$$T^\sigma(E,V) = Tr[\Gamma_L^\sigma(E,V)G^{r,\sigma}(E,V)\Gamma_R^\sigma(E,V)G^{r,\sigma}(E,V)] \}, \quad (2.69)$$
In the simplified version of the Equation 2.68, the transmission is assumed to be the transmission in equilibrium $T^\sigma(E, V) = T^\sigma(E, V = 0)$. Then, within the coherent transport model the “tunneling” component $I_{tun}$ and the “thermionic emission” component $I_{th}$ can be separated

$$I(V) = I_{tun} + I_{th} = \frac{e}{\hbar} \left( \int_{\mu_L \leq E \leq \mu_R} + \int_{E < \mu_L, E > \mu_R} \right) \text{d}E T(E) \left[ f(E - \mu_L) - f(E - \mu_R) \right]. \quad (2.70)$$

### 2.4.2 Landauer formalism

The simplified formula for the electric current in the coherent ballistic regime (Equation 2.70) was obtained in the phenomenological theory of R. Landauer. Here, we briefly summarize the key ideas of this approach. In the pioneer works of Landauer and Büttiker [64], the conductance of a device is associated with the quantum mechanical transmission probabilities of the one-electron wavefunction as it approaches an arbitrary scattering potential.

Within this approach, to describe the electron transport in atomic-scale systems, we need to consider them as open quantum systems described by a grand canonical ensemble. The bias can be described by two leads at different electrochemical potentials (in local equilibria) connected to the system. The analysis of devices in molecular electronics requires the simultaneous self-consistent solution of electron transport equations and the Poisson equation which provides the potential which the charged carriers generate and move in. To obtain the equilibrium line-
up of levels (bands) of the transport region, one needs to solve the Poisson equation for the electrostatic potential \textsuperscript{[65]} self-consistently with the equilibrium electron density

\[
\nabla^2 \phi(\vec{r}) = \frac{e}{\epsilon} \left( N_D(\vec{r}) - n_{eq}(\vec{r}) \right), \quad (2.71)
\]

\[
n_{eq}(\vec{r}) = \int dE N_0(\vec{r}, E) f_0(E). \quad (2.72)
\]

where \( N_D(\vec{r}) \) is the density of the donors, \( N_0(\vec{r}, E) \) is the local electron density of states which determines indirectly the potential \( \phi(\vec{r}) \), and \( f_0(E) \) is the equilibrium Fermi distribution function. Next, one needs to solve electron transport equations subjected to the boundary conditions imposed at the contacts. Since these contacts are in local thermodynamical equilibrium, the external source of field shifts the electrochemical potential \( \mu \) of one electrode with respect the other. By solving the transport equation in the region between the contacts, we determine both the electron density and the current density within the device, i.e., the quantities in we are interested.

The calculation of transmission is then formulated in terms of incoming \( |\phi_{in}\rangle \) and outgoing \( |\phi_{out}\rangle \) electron wavefunctions propagating along a 1D wire and scattered by a potential connecting the two leads. These wavefunctions have the form of Bloch wavefunctions, and in the absence of scattering potential, each one contributes \( G_0 = \frac{2e^2}{h} \) to the total conductance. The conduction (scattering) channel is defined as the asymptotic part of the wavefunction deep inside the lead. If the \( i^{th} \) conduction channel in the left hand-side reaches the scattering region
it can be transmitted to any channel into the right hand-side lead or back scattered into any channels of the left hand-side lead.

Alternatively, the scattering process can be described in terms of the scattering matrix, $S$, which relates the wavefunctions of the incoming and outgoing electrons:

$$|\phi_{\text{in}}\rangle = S|\phi_{\text{out}}\rangle,$$

(2.73)

where

$$S = \begin{pmatrix} r & t' \\ t & r' \end{pmatrix},$$

(2.74)

and $t$ and $r$ are the transmission and reflection coefficients, respectively, for incoming waves from left whereas $t'$ and $r'$ are the counter parts for incoming waves from the right. In a general multi-channel problem, $t, r, t', r'$ are matrices.

In this way, the simple explanation of the quantization of conductance in the point contact can be achieved. A voltage difference $V$ between the reservoirs induces a current $I$ through the scattering region, equally distributed among $N$ conduction modes. Even though the electrons at the Fermi level in each mode have different group velocity $v_n$, the difference in group velocities is canceled by the difference in density of states $\rho_n = 1/v_n$ so that each mode carries the same current $I_n = Ve^2/\rho_nv_n = Ve^2/h$. Summing over all modes in the wire, one obtains the conductance $G = I/V = Ne^2/h$. 
The quantized conductance of a point contact provides a firm experimental support for the
generalized Landauer formula, where the total conductance is defined:

\[ G = \frac{e^2}{\hbar} \sum_{\sigma} Tr[t_{\sigma}t_{\sigma}^\dagger] = \frac{2e^2}{\hbar} \sum_{n} t_n, \]  

(2.75)

where the numbers \( t_n \) are the eigenvalues of the product \( t_{\sigma}t_{\sigma}^\dagger \) of the transmission matrix \( t \) and its Hermitian conjugate, and \( \sigma \) stands for the spin index (\( \sigma = \uparrow, \downarrow \)). The sum runs over all the channels at the Fermi energy. Hence, the energy-dependent transmission probability for each spin channel is:

\[ T_{\sigma}(E) = Tr[t_{\sigma}(E)t_{\sigma}^\dagger(E)]. \]  

(2.76)

The electric current can be evaluated as follows:

\[ I(V) = \frac{e}{\hbar} \int dE \sum_{\sigma} T_{\sigma}(E,V)[f(E - \mu_L) - f(E - \mu_R)], \]  

(2.77)

where \( f(E) \) is the Fermi function, \( \mu_{L/R} \) are the electrochemical potentials for the left/right electrodes. Usually, the transmission coefficient \( T_{\sigma}(E) \) are computed from the Schrödinger equation, assuming coherent transport within the device. However, it was shown [66] that the Landauer formula, despite its simple physical interpretation, holds only in the limit of zero bias when the exchange and correlation terms in the Hamiltonian are local. Moreover, the direct generalization of Equation 2.77 is purely phenomenological and it does not tell how to evaluate \( T_{\sigma}(E) \). In this case, the theory based on NEGF is needed.
2.5 Self-Assembly Methods

Self-assembly is a spontaneous process of organization of building blocks (molecular units), driven by non-covalent interactions, into ordered structures. Depending on the type of building blocks (material, size and shape) and inter-block interactions, the self-assembly process may result in a large number of structures characterized by type of order, density packing, etc. In general, the self-assembly processes can be described by the (non)equilibrium statistical mechanics and thermodynamics, which means that the processes are driven by the minimization of the Gibbs energy, $G$. The process depends strongly on the competition of enthalpic forces generated by building blocks (vdW, dipole-dipole interactions, Coulombic forces), external fields and media (e.g. solutions), and the entropy associated with disordering as well as with depletion forces, communal and directional entropy [67–69]. Kinetics of self-assembly processes also play a significant role, especially if the assembly process is assisted by a continuous change of the system composition due to e.g., evaporation of the solution.

In principle, each self-assembly process requires an application of a unique combination of theoretical modeling and computational techniques. In the thesis we consider two projects related to the self-assembly of magnetic nanoparticles. We will discuss the details of computational approach in the corresponding chapters.
CHAPTER 3

ELECTRONIC STRUCTURE OF POROUS NANOCARBONS

3.1 Introduction

In this chapter, we use large scale \textit{ab-initio} calculations to characterize common features of band structures in graphene, nanoribbons, and nanotubes perforated with nanopores arranged in superlattices. We develop a unified picture, which permits us to analytically predict and systematically characterize metal-semiconductor transitions in nanocarbons with superlattices of nanopores of different sizes and types. These novel materials with highly tunable band structures have numerous potential applications in electronics, light detection, and molecular sensing. This research was conducted by myself. I performed all the simulations and analysis. The following contents are reproduced with permission from \textit{Sci. Rep.}, (1), 36, 2011. Copyright (2011) Macmillan Publishers Limited (see appendix).

Graphene [70] is highly promising for electronic, optical, and mechanical applications, due to its unique and potentially tunable parameters. It can be modified by doping [71,72], chemical functionalization [73], and geometrical restrictions, such as cutting and introduction of defects and pores [74–76]. Recently, graphene nanopores were used as selective sieves for hydrated ions [77], gases [78,79], and DNA [80,81]. In this work, we use large scale \textit{ab-initio} calculations to describe electronic structures of nanocarbons with superlattices of nanopores. We search for common principles allowing characterization of the electronic structures of porous nanocarbons.
Figure 1. Examples of porous nanocarbons: porous armchair nanoribbon, porous graphene, porous armchair CNT.

(PNC, see Figure 1), such as porous graphene (PG), porous nanoribbons (PGNR), and porous carbon nanotubes (PCNT). Although partial results for the electronic structures of PG [74–76] and other PNCs have been obtained [82–85], a broad picture that relates all their electronic structures had been missing until the present work.
3.2 Computational methods

We study the PNCs ab initio in supercells (of > 70 atoms), using SIESTA [46], and neglect spin degrees of freedom. We use the Perdew-Zunger LDA functional [23] and pseudopotentials with the cutoff energy of 400 Ry. The calculations are done within the eigenvalue tolerance of $10^{-4}$ eV, using the DZP basis (double-zeta basis and polarization orbitals, 13 and 5 orbitals for C-atom and H-atom, respectively). The Brillouin zones of the unit cells are sampled by the Monkhorst-Pack grid [44] with the spacing between the $k$-points of $\Delta k < 0.01 \text{ Å}^{-1}$. Geometry optimization is carried out for all the PNCs within the conjugated gradient algorithm, until all the forces are $F < 0.04 \text{ eV/Å}$ and the stress in the periodic direction is $\sigma < 0.01 \text{ GPa}$.

3.3 Results and discussion

The studied PNCs are perforated with pores of different shapes, sizes and localizations. Most of the results are obtained for the honeycomb-shaped pore (six C atoms excluded), called a “standard pore” (SP). SP preserves the sublattice balance and the symmetry of the unit cell, and it can be prepared experimentally [79, 86]. PNCs have their edges and pores passivated by hydrogen atoms.

3.3.1 Porous graphene nanoribbons

We begin by examining the band structures in porous armchair (AGNR) and zigzag (ZGNR) graphene nanoribbons. All GNRs are classified by the number of carbon dimers, $N$, that form the ribbon ($N$-GNR) [85]. First, we study the porous 11-AGNR and 10-ZGNR (both metallic when pristine), with the distances between SPs of 12.78 Å and 12.3 Å, respectively,
Figure 2. Band structure of: a) pristine 11-AGNR, b) 11-AGNR with centered SP, c) 11-AGNR with shifted SP, e) pristine 10-ZGNR, f) 10-ZGNR with centered SP, g) 10-ZGNR with shifted SP. The energy scales for (b, c, f, g) cases are the same. Density of states: d) centered and shifted SP in 11-AGNR, h) centered and shifted SP in 10-ZGNR. Insets: Unit cells for 11-AGNR and 10-ZGNR with the standard pore and elementary cells shown in Figure 2 (d, h). Figure 2 (a, b) shows that introduction of a periodic array of SPs in the center of 11-AGNR causes significant band gap opening (0.15 eV → 0.92 eV), whereas both pristine and porous 10-ZGNR have no energy band gap, as seen in Figure 2 (e, f). Their density of states (DOS) are depicted in Figure 2 (d, h). As the distances
between adjacent pores increases, the band structures of PGNRs monotonically approach their pristine forms. When the SP is displaced by one honeycomb towards the edge, the band gap shrinks $\approx 3.75$ times in 11-AGNR (Figure 2 b, c), while 10-ZGNR remains metallic (Figure 2 f, g).

The energy band gaps in ZGNRs and AGNRs arise from a staggered sublattice potential and a quantum confinement [87, 88], respectively, and they depend on the ribbon widths and functionalization [73, 89, 90]. The wave functions of the HOMO and LUMO bands in ZGNRs, which contribute directly to the area near $E_f$, are localized at the ribbon edges [73]. In contrast, in AGNRs these bands are localized at the center of the ribbons, keeping their edges chemically stable. Consequently, when the SP is positioned at the center of the ribbon, the band structure in 11-AGNR experiences more changes than in 10-ZGNR, as seen in Figure 2 (b, f). Shifting the pore closer to the edge of 11-AGNR decreases its influence on the band structure. As the SPs are shifted towards the edges in 10-ZGNR, its band structure is not changed much, as shown in Figure 2 (f, g).

3.3.2 Porous graphene

Next, we study PG lacking explicit edges. Graphene-based systems have a bipartite lattice [85], with $n_A$ and $n_B$ sites per unit cell in the $A$ and $B$ sublattices, leading to $n_A-n_B$ flat bands at the Fermi level [75]. Once these bands appear at the Fermi level, the system becomes metallic and highly stable to any perturbation (see Figure 2 (f, g)). Although, graphene has $n_A = n_B = 1$, introduction of pores or other defects may lead to $n_A \neq n_B$. Relationship between the edge-localized states, zigzag-like edges of GNR and flat bands at the Fermi level was first
disclosed in Ref. [91]. It was shown that even a small number of zigzag sites on the ribbon edge is enough to give rise to the highly edge-localized states and flat bands at the $E_f$. Further investigations disclosed that zigzag edges are characterized by the local sublattice imbalance leading to the unbalancing of pi-electron spin density. For a number of “anti-molecules” a set of simple rules which predict the net number of unpaired electrons and degeneracy of flat bands was proposed [71, 74, 75, 92–94]. Therefore, we might expect that although SPs keep the sublattice balance of the unit cell, their short zigzag-like rims locally break the balance and may still give rise to flat bands.

In Figure 3 (a-d), we show the band structures of edgeless PGs with one honeycomb and three different rectangular SP-superlattices, defined by $N_A$, $N_Z$, and displayed in Figure 3 (e, f). The size of the supercells (unit cells) used in our calculations varies between 12.3 × 8.52 Å, containing 40 atoms, and 22.13 × 21.3 Å, having 180 atoms. Figure 3 (g) also shows the studied rectangular superlattice with triangular-shape pores. The honeycomb SP-superlattice has flat bands around $E \approx -1.5$ eV, absent in the rectangular SP-superlattices (Figure 3 (b-d)). According to Ref. [75], the quasi-flat bands at non-zero energy, as in the case of honeycomb SP-superlattice, can be ascribed to local sublattice imbalance (while globally $N_A = N_B$). However, we cannot explain this fact as an effect of pore shape and have to relate it to the way how the SPs are organized. Due to the observed features of band structures of edgeless graphene SP-superlattices, we conclude that a small number of zigzag sites on the SP rim does not suffice to generate flat bands (neither at the Fermi level nor at its vicinity). In contrast, triangular-shape
Figure 3. (top) Band structure of a) a honeycomb SP-superlattice in e) and three rectangular SP-superlattices with b) $N_A = 15$, $N_Z = 4$, c) $N_A = 7$, $N_Z = 2$, and d) $N_A = 7$, $N_Z = 8$. (bottom) e) honeycomb SP-superlattice, f) rectangular SP-superlattice characterized by $N_A$, $N_Z$, g) rectangular superlattice with triangular-shape pores

pores break the sublattice balance, which leads to an unbalanced $\pi$-electron density [92] and appearance of rim- localized states giving rise to flat bands at $E_f$ (not shown).

We can now relate the band structures of PGNRs and PGs. Owing to the fact that SPs do not break the sublattice balance, they do not generate in the PGNRs any new flat bands at $E_f$ (see Figure 2). In contrast, we found that when GNRs are perforated with triangular-shape pores, their band structure always contains flat bands at $E_f$. Even though the SPs do
not create flat bands at $E_f$, they can still influence the sensitive band structure of AGNRs (Figure 2 (b, c)). On the other hand, the band structures of ZGNRs with flat bands at $E_f$, due to local sublattice imbalance caused by zigzag edges, can not be significantly modified by SPs. Therefore, we conclude that all porous ZGNRs are metallic, as we checked by calculations.

Figure 4. (top) Effective replacing of porous N-AGNR by “daughter” pristine $N_1$- and $N_2$-AGNR ($N = 14$, $N_1 = 5$, $N_2 = 6$). (bottom) Effective replacing of rectangular SP-superlattice with $N_A > N_Z$ by set of pristine AGNRs ($N_A = 15$, $N_Z = 4$).

Very interestingly, we found that rectangular PG-superlattices perforated with SP and larger pores of honeycomb symmetry can be metallic or semiconducting. In the first approximation, these superlattices can be seen as many parallel AGNRs or ZGNRs with effective widths $N_A$ or $N_Z$, respectively, depending on the ratio $\rho = N_A/N_Z$ (see Figure 4 bottom). This assumption
implies that when a wide nanoribbon is joined with a narrower nanoribbon (e.g. $N_A \gg N_Z$), the band structure of the wider nanoribbon in the vicinity of the Fermi level is almost not affected by electronic states of the narrower ribbon. This assumption is based on the results of \textit{ab initio} calculations. If $\rho \gg 1$, one can see the superlattice as being cut into separated $N_A$-AGNRs, while for $\rho \ll 1$ the same is true for separated $N_Z$-ZGNRs. Therefore, we might expect that the type of conductivity in these superlattices is the same as in the related GNRs. Our calculations largely confirm this picture. For $N_Z = 2$, the conductivity in the PGs is the same as in the corresponding AGNRs: PGs are metal for $N_A = 5, 11, 17...$ and semiconductor for $N_A = 7, 9, 13, 15...$ (see Table I). PGs with $N_A = 9, 15, 21, ...$ are semiconducting for all $N_Z$, with the band gap shrinking with increasing $N_Z$, signaling the transition to the ZGNR-dominated metallic conductivity. For PGs with $N_A = 7, 13...$, the metallicity appears abruptly at $N_Z \geq 4$. Also, PGs with $N_A = 5, 11, 17...$ and $N_Z \geq 4$ are metallic, as it should be, since all AGNR with $N_A = 5, 11, 17...$ (see Table I) are metallic. In general, we expect that the transition between the AGNR and ZGNR-type of behavior occurs somewhere around the “diagonal”, $\rho = 1$. The calculations also disclose that the metal-semiconductor transitions predominantly occur in two regions of the Brillouin zones, as seen in Figure 3 (b-d), and the bands can be partially flat in the $k_y$ direction ($N_A = 7, 13, ...$).

3.3.3 \textit{Porous nanotubes}

Since pristine CNTs are structurally analogous to rolled GNRs, it turns out that there is a clear correspondence between pristine CNTs and GNRs. While ZGNRs indexed by $\langle p, 0 \rangle$ are metallic for all $p$, only one third of AGNRs indexed by $\langle p, 1 \rangle$ are metallic. Since only one half
TABLE I. Correspondence rule for GNRs and CNTs. \(N\) - number of dimers forming GNR, \(p\) - index for the chirality vector in GNR and CNT; cond. - conductivity property (semiconducting (s) or metallic (m)); geometry defines the symmetry with respect to the mirror plane perpendicular to the ribbon and containing its axis: symmetric (s), asymmetric (a). Examples of AGNRs for \(N = 7, \ldots, 14\) and ZGNRs for \(N = 5, \ldots, 12\) are illustrated.

<table>
<thead>
<tr>
<th>AGNR (\langle p,1 \rangle)</th>
<th>dimers, (N)</th>
<th>(p)-index</th>
<th>cond.</th>
<th>geometry</th>
<th>ZGNR (\langle p,0 \rangle)</th>
<th>cond.</th>
<th>geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7, 8, 9, 10, 11, 12, 13, 14</td>
<td>5, 6, 7, 8, 9, 10, 11</td>
<td>m, m, m, m, m, m, m</td>
<td>a, s, a, s, a, s, a</td>
<td>ACNT (\langle p/2,0 \rangle)</td>
<td>m, m, m, m, m, m, m</td>
<td></td>
</tr>
</tbody>
</table>

The unambiguous relationship can be expressed in terms of the chirality index, \(p\), and the number of carbon dimers, \(N\) in the GNRs, as follows

\[
\text{ZCNT}\langle p,0 \rangle \Rightarrow N\text{-AGNR}, \quad \text{where} \quad N = 2p + 2,
\]

\[
\text{ACNT}\langle p,p \rangle \Rightarrow N\text{-ZGNR}, \quad \text{where} \quad N = 2p + 1.
\] (3.1)

Intuitively, we can look at this CNT-GNR correspondence as a consequence of CNT “cutting” (Figure 6 (top, middle)), which preserves the type of conductivity. The AGNRs and ZGNRs that do not match any CNTs are all semiconducting and metallic, respectively, as summarized in Table I.

Analogously, porous CNTs might have band structures similar to porous GNRs. Tight-binding calculations predicted [96] that a line of SP-pores (separated by \(\sim 12.8 \text{ Å}\) with supercells of 100 – 200 atoms) should cause band gap opening in ACNTs, whereas porous ZCNTs should be semiconducting regardless of the pore shape. These results are in contradiction with our ab-
Figure 5. Band structures in pristine CNTs: a) ACNT (10,10), b) ZGNT (9,0), c) ZGNT (10,10); d) DOS. Porous CNTs: e) ACNT (10,10), f) ZGNT (9,0), g) ZGNT (10,10); h) DOS. The energy scales for (b,c) and (f, g) cases are the same.

\textit{initio} calculations, which show that the metallicity of pristine ACNTs (Figure 5 a) is preserved in the porous ACNTs (Figure 5 e), even for triangular-shape pores with clear zigzag-like rims. In metallic ZCNTs, the SP-perforation causes band gap opening, as shown in Figure 5 (b, f), while in semiconducting ZCNTs, it causes band gap shrinking, as seen in Figure 5 (c, g).
Figure 6. Cutting of: (top) (10,0)ZCNT into $\langle 19,1 \rangle$AGNR and (middle) (9,9)ACNT into $\langle 18,0 \rangle$ZGNR (opening of the GNRs is schematically shown). (bottom) Removal of atoms from porous (10,10)ACNT leading to $\langle 17,0 \rangle$ZGNR
3.3.4 Unified model of PNC conductivity

The above observations allow us to build a unified model that can predict the type of conductivity in porous nanocarbons perforated with SPs and other pores that do not break the global sublattice balance. The model is based on the assumption that when NCs are perforated by a line of relatively close SPs, the type of conductivity in these PNCs is the same as in the (daughter) systems obtained from these NCs by removing all C atoms within a stripe going in the direction of the pores and having the same width as the pores (all dangling C bonds are H-terminated). We call these modified NCs the daughter systems of the original NCs (two GNRs for PGNRs, one GNR for PCNTs, and a GNR-lattice for PG). This rule predicts that: (1) Porous ACNTs are metallic as the (daughter) ZGNRs; Figure 6 (bottom) shows effective replacing of porous ACNT by pristine ZGNR. Perforating the resulting ZGNRs (and the other half of ZGNRs that can not be rolled up into CNTs) gives two metallic ZGNRs, preserving the ZGNR-metallicity. (2) Porous ZCNTs may give semiconducting or metallic AGNRs. Cutting all the AGNRs may give pairs of AGNRs with any conductivity. These results were all confirmed by \textit{ab initio} calculations.

We now use these rules to predict metallicity in porous AGNRs with SPs. We assume that their band gaps are $E_{BG} \simeq \min (E_{1BG}; E_{2BG})$, where $E_{1BG}$, $E_{2BG}$ are band gaps of their two daughter AGNRs (see Figure 6 (top)). With this inference, we can derive an analytical expression describing the dependence of the band gap on the width of the porous AGNRs. For simplicity, we consider SPs positioned in the middle of AGNRs of width $W = a \sqrt{3} (N - 1)/2$, where $a$ is the C-C distance and $N$ is the number of dimers. By evaluating the widths of the
pristine daughter AGNRs, we find that porous $N$-AGNRs are potentially metallic if the number of C-C dimers is given by at least one of these equations:

$$N = \left(6k + 11 + (-1)^k\right)/2, \quad N = 6k + 3 + 2(-1)^k,$$
$$N = 12k + 9, \quad (k = 0, 1, 2...), \quad (3.2)$$

i.e., if $N = 5, 6, 7, 8, 9, 12, 14, 17, 18, 19, 20, ...$

In Figure 7 (top), we compare the *ab-initio* energy band gaps in pristine $[97, 98]$ and porous AGNRs to validate the above model. In contrast to the pristine ribbons, where the metallic points emerge with the period of 3, ($N_{\text{met}} = 3m + 2$), the band gaps of porous AGNRs have a more complex dependence. Nevertheless, the positions of the band gap minima agree with Equation 3.2.

We can extend the assumptions used in Equation 3.2 to PNCs perforated with larger and shifted honeycomb-like pores. Their presence may still be reduced to removing from the AGNRs a layer of atoms of the width given by the pore size, where the minimum band gap of the two resulting AGNRs can determine the band gap of the porous AGNR. For example, when the SP is shifted in the 11-AGNR by one honeycomb from the ribbon center, the two daughter pristine 4-AGNRs are replaced by 2-AGNR and 6-AGNR (all semiconducting). This should lead to a band gap shrinkage, in agreement with our *ab-initio* calculations, presented in Figure 2 (b, c). Alternatively, we can replace the SP by a double-size hexagonal pore with 24 C-atoms excluded. If the 11-AGNR and 12-AGNR are perforated by such pores, they become
semiconducting, since their cutting leads to semiconducting 2-AGNRs and 2- and 3-AGNR, respectively. These results are in agreement with ab-initio calculations, giving in 11-AGNR and 12-AGNR the band gaps of 1.1 eV and 1.18 eV, respectively. We have also tested the triple-size hexagonal pore (54 C-atoms excluded) in order to check how its long rims affect band structure of GNRs. Our calculations show that no additional features (e.g., flat bands at the Fermi level) appear when the GNR are perforated by these pores. In contrast, when these AGNRs are perforated with SPs in the ribbon center, only the 11-AGNR is semiconducting.

![Figure 7](image)

Figure 7. (top) Dependence of the band gap in the pristine and porous AGNR on the number of dimers (the central position of the SP). (bottom) The same dependence in ZCNT on the chirality index.
Finally, we discuss porous ZCNTs that can have any conductivity. In Figure 7 (bottom), we present the energy band gap of porous ZCNTs as a function of the chirality index, \( p \). It exhibits similar periodicity as in the pristine ZCNTs. However, the model is not reliable in porous ZCNTs. For example, the porous ZCNT(7,0) and ZCNT(8,0) have band gaps similar to the daughter 11-AGNR and 13-AGNR, respectively. But the same is not true for the porous ZCNT(9,0) and ZCNT(10,0) paired with the daughter 15-AGNR and 17-AGNR, respectively. In principle, this failure might be caused by the fact that the AGNRs are not calculated deformed as the corresponding daughter ZCNTs [82,99]. However, our calculations show that the bent 17-AGNR has almost the same band gap as the pristine 17-AGNR. Therefore, a more quantitative approach needs to be used here.

It is of interest to see if other types of periodic modifications can also be used to tune the band structures of nanocarbons. To briefly examine this idea, we have replaced SPs by Stone-Wales 55-77 defects [100]. In Figure 8, we show the band structures of 11-AGNR, 10-ZGNR, and graphene superlattices modified in this way. The periodic array of SW 55-77 defect in 11-AGNR leads to small band gap opening, as shown Figure 8 (a), in analogy to 11-AGNR with SPs (Figure 2 b). The band structure of 10-ZGNR, shown in Figure 8 (b), is not sensitive to this perturbation, as in the SP-perturbations (Figure 2 f). On the other hand, when we replace in graphene superlattices SPs with the SW 55-77 defects, we can obtain qualitatively different band structures. In particular, the band structure of graphene modified by SW 55-77 defects in the array with \( N_A = 7 \) and \( N_Z = 4 \) (Figure 8 c) is similar to that of the SP-superlattice with the same \( N_A \) and \( N_Z \), but here we also observe opening of a small band gap. In Figure 8 (d),
we show the band structure of the SW-graphene superlattice ($N_A = 9$ and $N_Z = 4$), which is semiconducting, as the PG-superlattice with the same $N_A$ and $N_Z$. These observations show that periodic defects could also be used to tune band gaps in nanocarbons, but the rules might be slightly different.

For completeness, we have recalculated some of the above structures including spin polarization (we used a set of LDA and GGA functionals). It turns out, the band structures of NCs can be modified by spin polarization (zigzag edges) [71], but the presence of SPs does not introduce additional magnetic features beyond the changes described already in the non-magnetic calculations. Interestingly, the presence of arrays of SW (55-77) defects in ZGNRs can alternate...
Figure 9. Edge magnetism. The alternation of spin imbalance as result of introduction of 55-77 SW defects.

mutual orientation of the magnetic moments localized at the opposite edges, due to topological changes in the sublattices.

3.4 Conclusion

In this chapter, we have developed a unified picture of band structures in PNCs. Although, the proposed unified picture successfully describes band structures in many PNCs, it could be further refined to account for spin degrees of freedom, pore type, and chirality. We also have shown that the perturbation of nanocarbons by periodic SW defects leads to similar changes of their electronic structure as in the case of periodic array of pores. Precise knowledge of electronic structures of these materials is essential for their applications in electronics, optics, molecular sensing, and other fields.
CHAPTER 4

CHEMICAL SENSING AT GRAPHENE GRAIN BOUNDARY

4.1 Introduction

Grain boundaries (GBs) can dramatically affect the electronic [101–110], thermal [111], mechanical [112], and optical [113] properties of a polycrystalline graphene. While in many applications the presence of GBs in graphene is undesired, GBs may be an ideal structure for the detection of chemical analytes. Topological defects can improve the sensitivity of carbon-based molecular sensors, due to a selective physisorption of the gas molecules and an modified electron flow through the defect sites [114–120]. When such defects are formed within a single crystalline graphene lattice, they have a modest effect on its electronic properties. However, when GBs are formed between misoriented crystalline grains, they can potentially give rise to electronic transport gaps [106]. The emergence of transmission gaps in graphene GBs could be manifested in a switchable passage of charge carriers in the presence of gas molecules.

In this chapter we present the results of experimental and theoretical study of the GB sensitivity to the chemical analytes. In experiments it was observed that an isolated graphene GB has \( \sim 300 \) times higher sensitivity to the adsorbed gas molecules than a single crystalline graphene grain. Our modeling of the experimental system reveals that an ultra-high sensitivity of individual GBs to adsorbed gas molecules can be explained in terms of switchable charge carrier transport properties and originates from a simultaneous opening or closing of local
electron transport channels passing through the GBs by the adsorbed analytes. The results of this work can be used to design ultra-sensitive molecular detectors.

This is a collaborative research project with the Prof. Amin Salehi-Khojin’s group (UIC). The preparation of the samples, conduction of experiments, electric measurements are performed by Prof. Amin Salehi-Khojin’s group, namely by Mr. Poya Yasaei, Dr. Bijandra Kumar et al. I performed calculations of electronic structures, electron transport, analytical modeling of electron transport and related analysis. The classical and quantum molecular simulations of adsorption of analyte molecules on graphene grain boundaries were performed by the graduate student Mr. Nikita Repnin. Nikita Repnin and I analyzed the results of simulations. The paper “Chemical Sensing with Switchable Transport Channels in Graphene Grain Boundaries” by P. Yasaei et al. has been submitted to Nature Communications.

4.2 Computational methods

Computational study of the sensitivity performance of GBs is carried out in two steps. We first studied the adsorption of analyte gas molecules on the graphene GB. Towards this goal we use hybrid (classical and quantum) molecular dynamics (MD) simulations to model the graphene GBs deposited on a defective amorphous SiO$_2$. The classical MD simulations are performed with NAMD [121,122] and the CHARMM32 force field [123]. During our simulations, we keep the temperature fixed at $T=300$ K by Langevin dynamics with a damping constant of $\gamma_{\text{Lang}} = 1 \text{ ps}^{-1}$. The switching distance for non-bonded interactions is set to 8 Å, and the cutoff is set to 10 Å. The systems are simulated in an NVT ensemble, where the particle mesh Ewald summation [124] is used to describe long-range Coulombic coupling. In each classical
simulation, we first minimize the system energy and then equilibrate the system for $\sim 10$ ns at $T = 300$ K. In the quantum MD simulations, we use TeraChem [125–127] with energies and forces evaluated using the Becke, Lee, Yang, and Parr (BLYP) exchange-correlation functional with a 3-21g basis set and charges calculated with the Mulliken scheme.

Next, we studied electron transport properties of graphene GBs in the presence or absence of electron donor/acceptor molecules. We performed \textit{ab initio} electron structure and quantum transport calculations using SIESTA 3.1 and TRANSIESTA [46,61] DFT-based packages, respectively. We used the Perdew-Burke-Ernzerh parametrization of exchange-correlation functional [25] and the norm-conserving Troullier-Martins pseudopotentials [41] to describe valence electrons. The calculations were performed on a real-space grid with a mesh cut-off of 400 Ry within the eigenvalue tolerance of 104 eV, using a SZP (single-zeta basis and polarization orbitals) basis set. The distances between neighboring GBs are chosen to be $\sim 2.5$-3 nm to exclude their mutual elastic interactions in the superlattices. The geometry optimization was carried out with the conjugated gradient algorithm, until all the forces are $F < 0.04$ eV/Å and the stress in the periodic direction is $\sigma < 0.01$ GPa. The Brillouin zones of the unit super-cells were sampled by a Monkhorst-Pack grid with 3-5 $k$-points along the direction parallel to the GBs and 5 $k$-points along the electron transport direction. Convergence of the transmission spectra with respect to the $k$-points sampling was achieved.
Figure 10. Characterization and sensing properties of individual grain boundary (GB). (a) False color SEM image of the fabricated GB sensing platform (scale bar-5m). A corresponding electrical circuit is also shown. (b) D-band and (c) 2D/G ratio mapping of the synthesized graphene (Scale bar-5μm). (d) Selected area electron diffraction (SAED) patterns obtained from left (GL), right (GR) grains and GB region. Sharp and single hexagonal shape evidences the single crystalline structure of grains. A pattern with two discrete sets of rotated spots appears in the merging region indicating the imperfect stitching of the two graphene grains which results in the origination of grain boundary (GB). (e) Sensing signal for the dimethyl methylphosphonate (DMMP) and 1,2-dichlorobenzene (DCB) gas molecules. (f) Fabricated multi-electrodes single GB sensing platform (scale bar-5μm) and the sensitivity of the GB devices with respect to the distance from the electrodes. (g) Sensitivity of the individual GB against DMMP molecules extracted from the real time sensing measurements. The inset magnifies the same curves.
4.3 Experimental results and discussion

4.3.1 Synthesis and characterization of graphene grain boundaries

The graphene and GBs used in this study were synthesized using atmospheric pressure chemical vapor deposition (AP-CVD) technique with precise control over the growth time and environmental conditions [101,128]. In this approach, single crystalline hexagonal graphene grains grow discretely and subsequently coalesce together forming an individual GB. Figure 10 a shows a typical architecture of our individual GB-sensing platform. The fabricated structure can be classified in two different regions; single crystalline grains (further noted as grain) and GB region (area between electrodes 3 and 4 in Figure 10 a. The GB region of the device comprises an isolated GB and two trapezoid shaped grains on the sides. Figure 10 b shows the spatially-resolved Raman spectroscopy map obtained for the disorder-induced D band (wavenumber $\sim 1350$ cm$^{-1}$). An intense $I_D$ signal obtained in the merging region of the grains provides a strong evidence for the defective nature of GB region. The occasional $I_D$ signals at grains show some structural defects within the perfect lattice, which can be attributed to the nucleation points [101,129]. We also mapped the ratio of 2D-to G-band intensity ($I_{2D}/I_G$) where the high intensity ratio ($> 2.5$) allover the scanned area confirms the uniform existence of monolayer graphene. Figure 10 d shows selected area electron diffraction (SAED) patterns obtained from transmission electron microscopy (TEM) for both grains and GB regions. Identical and sharp hexagonal diffraction patterns recorded for the grains in different regions confirm their single-crystalline nature [130]. However, a twofold diffraction patterns was observed when the aperture was located exactly at the merging region, disclosing a crystallographic mismatch between the
grains, another evidence for the existence of GBs. In addition, the high intensity ratio of the $\{1100\}$ to the $\{2110\}$ diffraction peaks ($I_{1100}/I_{2110} \approx 1.4$) further verifies the existence of monolayer graphene.

4.3.2 The graphene grain boundary sensitivity

We study the chemical sensing characteristics of individual GBs by monitoring the resistance change of a GB region during exposure to gas molecules and comparing it with that observed in the gas-exposed grains. All the sensing experiments were performed at ambient conditions using a pulse injection method. Our sensing platform enabled us to record the simultaneous sensing response for the left grain, right grain, and GB region. A known concentration (50 ppb) of gas molecules (dimethyl methylphosphonate (DMMP) and 1,2-dichlorobenzene (DCB)) were injected over the sensing devices. DMMP and DCB analytes are purposefully selected due to their electron donating and accepting features, respectively. Figure 10 e shows the typical sensing response towards DMMP and DCB molecules for grains and GB region. Here, sensitivity ($S$) is defined as $S = (R - R_0)/R_0$, where $R_0$ and $R$ are the initial and final resistance (after gas exposure), respectively. Positive and negative signals upon injection of gas molecules were gained from all the fifteen devices tested against DMMP and DCB molecules, in agreement with their electron donating or accepting nature [131]. The sensitivity in the GB region (between electrodes 3 and 4) of all the devices is significantly higher compared to the grains sensitivity regardless of the type of gas molecules. For DMMP, the sensitivity of the GB sensors (39.5%) is more than one order of magnitude (14 times) higher than that of grain sensors (2.8%). A similar trend has also been observed for DCB molecules, where the sensitivity of GB sensors
(11%) is almost 5 times higher than in the grain sensors (2.3%). Clearly, the individual GB is responsible for the enhanced sensitivity in the GB region.

The experiment showed that the sensing response of a single GB is significantly improved as the GB is more isolated from its adjacent grains (i.e., the electrodes are patterned closer to the GB). Specifically, we fabricated a sensing platform having several electrodes located at different distances from the GB (see inset of Figure 10 f). As shown in Figure 10 f, GB region sensitivity increases from 17% to 70% (with 50 ppb of DMMP) as the distance between the active electrodes reduces from 43.6 μm to 2.8 μm. The extension of a fitted exponential curve reveals that a much higher sensitivity may be observed by minimizing the distance between the patterned electrodes. Note that the device level sensitivity of the GB-based sensor represents in fact the variation in the overall resistance of GB and the surrounding grain regions (two trapezoid shaped grains).

To exclude the contribution of adjacent graphene regions, a simultaneous sensing experiment were carried out on the left and right grains and GB regions (see Figure 11). We measured sheet resistances of the left and right grains ($R_{2-3}$ and $R_{4-5}$) to calculate the resistance of the adjacent trapezoid shaped grains ($R_{TL}$ and $R_{TR}$ in Figure 10 a). Then, we solved for the additional resistance in the GB region using an equivalent resistance model shown in Figure 10 a $R_{GB} = R_{3-4} - (R_{TL} + R_{TR})$ [107]. In absence of any gas molecules, the sheet resistance of $\sim 740 \Omega$ was observed for the GB region of the device shown in Figure 10 a (between electrodes 3 and 4) while slightly lower values of 680 Ω and 695 Ω were recorded for the left and right grains, respectively. The higher sheet resistance in GB region is due to enhanced scattering
Figure 11. Extracted sensitivity for individual GB. The SEM image is the same image as shown in Figure 10 a. The sheet resistances of the left and right grains were calculated using the I-V characteristics of device (R_{2-3} for left grain and R_{4-5} for right grain) and considering the geometry of the flakes using the equation \( R = R_0 \cdot W_{\text{Avg}}/L \). For each flake, \( L \) is the distance between corresponding electrodes and \( W_{\text{Avg}} \) is the geometric mean of the sample width, calculated from \( W_{\text{Avg}} = \frac{1}{L} \int_0^L \frac{dW}{dx} \). Using inverse approach, resistance of blue and red portion of the flakes (trapezoids) were calculated, and resistance of individual GB were extracted as \( R_{\text{GB}} = R_{3-4} - R_{\text{Red}} - R_{\text{Blue}} \). In our measurement setup, resistances of left, right and GB region were monitored simultaneously, and time-dependent resistance of isolated GB were plotted. The sensitivity for the isolated GB were calculated from \( S = (\Delta R_{\text{GB}})/R_{\text{GB}} \).
at GB defect sites [102]. In our devices, the calculated RGB (GB sheet resistance) before exposure to gas molecules are found in the range of $5 - 35 \Omega$. For the device shown in Figure 10 a, we observed that RGB changed from 15.3 to 142 $\Omega$ upon exposure to 50 ppb of DMMP gas molecules. Figure 10 g shows the time dependent-sensitivity of the isolated GB, demonstrating a maximum of 828% which is $\sim$300 times higher compared to the adjacent single crystalline grains under identical experimental conditions.

To investigate the role of GBs in large area polycrystalline graphene sensors, it is essential to understand the performance of GB sensors as the number of GBs increases. In this regard, we investigated the sensing response of a sequence of multiple GBs, naturally formed by the merging of the grains in the CVD growth. This study demonstrated the inherent limitation of the polycrystalline graphene sensors compared to an individual GB sensor with a high degree of isolation. In the case of an individual GB, the sensing response is amplified as the GB becomes more isolated, approaching the very large sensitivity shown in Figure 10 f. However, this is not the case in devices having more than one GB, since the resistance of the grain regions between two GBs cannot be avoided.

4.4 Theoretical study of the graphene grain boundary sensitivity

To reveal the microscopic nature of the observed ultra-high sensitivity we study computationally the graphene grain boundaries formed between two graphene grains to address two principal questions. (1) What is the geometrical structure, stability and physisorption of electron donor molecules (DMMP) on graphene grain and graphene grain boundaries with different defect topologies? Towards this goal, we used hybrid (classical and quantum) molecular dy-
namics simulations and study the equilibrium geometry, distribution of the gas molecules in vicinity of GB, the charge transfer between DMMP molecules and GB. (2) What are the electron transport properties of GBs, their modulation by the adsorbed analyte gas molecules, and the dependence of the GB sensitivity on the applied external bias voltage? Towards this goal, we performed *ab initio* calculations of electronic structure and quantum transport through the graphene GB in the presence/absence of analyte molecules and combine them with a simplified electron transport model to evaluate the dependence of the GB sensitivity on the applied external bias voltage.

4.4.1 **Physisorption of DMMP molecules at graphene grain boundaries**

We model a typical GB with an 18° mismatch angle (Figure 12 a-b). The GB model consists of a quasi-periodic meandered line of defects formed between two graphene grains (consistent with previous TEM studies [108]), which are deposited on an amorphous SiO$_2$ substrate to obtain their realistic doping. In our simulations, we first deposit the (uncharged) graphene system on amorphous SiO$_2$ (prepared by VMD) and run classical MD simulations for $\sim$5 ns. Once the system equilibrates, we cut from it two representative parts shown in Figure 13 and perform DFT calculations for each part separately. Then, we combine the results from different regions and use them in classical MD simulations of the DMMP molecules adsorption on the appropriately charged GB system. To calculate the charge transfer between the electron donor DMMP molecules and the graphene GB, we cut a representative part of the system and performed again the quantum MD simulations for $t \sim 1$ ps.
Figure 12. Classical and quantum simulation studies. (a) The top and (b) side views of the modeled graphene grain boundary structure deposited on the defective amorphous SiO$_2$ substrate with physisorbed DMMP molecules. Two transmission regions with different translational vectors are highlighted by red (small gap) and blue (large gap) colors. (c) Two-dimensional electrostatic potential energy profile across the GB. (d) One-dimensional potential profiles (with and without DMMP molecules) obtained by averaging of the 2D potential along the direction normal to the GB. (e) Calculated transmission spectra (red curves) for the open GB region (highlighted in red in a) and the grain region (green dashed lines), shown both without and with homogeneous n-doping (shifted left) by DMMP molecules. The Fermi level, $E_f$, is shifted down (Dirac point of the grains) due to the p-doping by SiO$_2$. Bias window intersects the spectra of certain transmission regions and opens the passage of electrons through them, while adsorbed DMMP molecules tend to close these passage regions. (f) Calculated sensitivity for the GB and graphene grain (inset) with respect to the applied voltage for DMMP molecules. (g) Maximum sensitivity calculated as a function of a DMMP-induced spectral shift over a thermal energy, $\Delta E/kT$. 
We found that the stress-relaxed structure forms a corrugation along the GB with different equilibrium heights from the SiO$_2$ substrate, giving rise to an effective $p - p' - p$ doping distribution (Figure 12 c). The presence of local doping has been demonstrated by calculating a two-dimensional (2D) electrostatic potential profile (Figure 12 c) in the GB region, revealing a potential well with large electric field gradients on its sides. Our simulations show that DMMP molecules with a permanent dipole are attracted to the regions of high electric field gradient present at the $p - p' - p$ interface. The accumulation of DMMP molecules at GB results in a local charge donation and modification of the doping distribution ($p - p'' - p$). These results are illustrated in Figure 12 d presenting a one-dimensional potential obtained by averaging of the 2D potential along the direction normal to the GB (with and without DMMP molecules).

Figure 13. Hybrid MD simulations. (a) Graphene with the GB between two grains with a mismatch angle of 18° (b-c) Representative regions: pristine and defective, respectively.
4.4.2 Electron transport through graphene grain boundaries

A typical GB is known to be meandered consisting of short pristine regions separated by defective regions [108]. Due to this structure, the GB can be split into local regions with different transport properties, determined by the crystallographic orientation of the graphene grains, the local angle of GB with respect to the grains, and the local topologies of GB defects [106, 132]. Such regions can form individual electron transport channels with local transmission spectra (gaps) (see Figure 12 a). Depending on the local doping from the substrate (shift of transmission spectra), these transport channels can be initially either in opened or closed states. Upon adsorption of electron-donating or -accepting analytes at the GB, the transmission spectra of the channels can be shifted with respect to the $E_f (p - p'' - p)$. This can open or close some of the electron transport channels, with a potentially dramatic effect on the GB resistance.

To illustrate these phenomena, we have calculated the local electron transmission through two selected regions of the GB highlighted by red and blue colors in Figure 12 a with different local angles and defect topologies. In Figure 14 we show examples of unit cells of scattering regions with different defect topologies.

The transmittance reveals very different transport gaps ($\sim0.2$ eV, $\sim1$ eV) for the two GB regions (see Figure 15). We assume that only regions with the smallest energy gaps and energy onsets can significantly contribute to the molecular sensing. Figure 12 e shows the transmission spectrum through the low-gap (0.2 eV) region before (red curve) and after (red shadowed curve) adsorption of DMMP molecules. We used these two transmission spectra to calculate
an electron current passing through the GB region under bias (yellow area in Figure 12 e) in the presence and absence of homogeneously distributed DMMP molecules.

With transmission spectra calculated rigorously using \textit{ab initio} methods described in the \textbf{Theory and Methods} section, we describe the electron transport through the GB structure in the presence/absence of adsorbed gas molecules by a simple ballistic transport model [133], where the electric current density through the GB is given by (compare with Equation 2.70):

\[ J = \int Tr(E) \left( n_f(E - \mu_L) - n_f(E - \mu_R) \right) E, \]  

(4.1)

Here, \( Tr(E) \) is the zero bias transmission spectrum of the system with GB (shown in Figure 15) obtained from \textit{ab initio} quantum transport calculations, \( n_f(E - \mu_{L/R}) \) are the Fermi-Dirac
Figure 15. Transmission spectra of GBs with different translational vectors of left and right grains with different defect topologies. Blue solid and dashed lines show the transmission coefficients for the GBs with supercell units shown in Figure 14 a-b (blue region in Figure 12 a). Red solid and dashed lines show the transmission coefficients for the GBs with supercell units shown in Figure 14 c-d (red region in Figure 12 a). Relative values of the transport gaps are shown.
distribution functions (T=300 K) in the left/right grains, respectively, \( \mu_{L/R} = E_f \pm V/2 \) are the electrochemical potentials in the grains, \( E_f \) is the common Fermi energy, and \( V \) is the voltage applied between the grains.

We calculate the electric currents in the presence and absence of molecules at the GBs using Equation 4.1. In the presence of the DMMP gas molecules adsorbed at the GB, the transmissivity is shifted down. From these currents we calculate the bias-dependent device sensitivity

\[
S(V) = \frac{R_{gas}(V) - R_0(V)}{R_0(V)} = \frac{J_0(V) - J_{gas}}{J_{gas} + J_{noise}} \quad (4.2)
\]

where \( J_{noise} \sim 1 \mu A \) is a small noise current.

Figure 16. Bias-dependent sensitivity trend for graphene GB sensors. The figure shows the experimental trend of molecular sensitivity to the source-drain bias. The experiments for different applied biases are carried out in similar conditions.
Figure 12f presents the obtained bias-dependent sensitivity for DMMP analytes for both GB (channel region) and pristine graphene (see the inset) under similar doping conditions (0.05 eV) [134], showing a prominent sensitivity peak, in agreement with our experiments (see Figure 16). Because of the sharp transmission onset of the GB transport channel (Figure 12e), the calculated maximum sensitivity (250%) is 60 times larger than that of graphene (4%). However, due to the accumulation of analytes in the GB area (Figure 12d), one could expect even larger sensitivity (doping).

To quantify this effect, we have calculated the dependency of the maximal sensitivity of the GB on the transmission spectra shift $\Delta E$ caused by the local adsorption of analytes (Figure 12g). Towards this goal, we use a simplistic transmission model for an ideal conduction channel with an abrupt onset of transmission at $E = E_0$ defined by:

$$T_{r0}(E) = \begin{cases} 1, & E < E_0 \\ 0, & E \geq E_0. \end{cases}$$

Then, the electric current is given by the formula:

$$J_0(V) \sim \int_{-\infty}^{E_0} T_{r0}(E) (n_f(E - \mu_L) - n_f(E - \mu_R)) E = k_B T \times \log \frac{1 + \frac{E_{0+} + V/2}{k_B T}}{1 + \frac{E_{0-} - V/2}{k_B T}}, \quad (4.3)$$
where $E_f$ is set to zero. Upon the DMMP gas adsorption, the onset of transmission shifts by $\Delta E$ resulting in a current of:

$$J_{\text{gas}}(V) \sim k_B T \times \log \frac{1 + E}{1 + E} k_B T \times \log \left(1 + E \frac{E_0 - \Delta E + eV/2}{k_B T} \right).$$

(4.4)

Figure 17 illustrates the mechanism. The peak of sensitivity with respect to bias is observed when the bias window intersects the transmission spectrum of the system after DMMP adsorption. The value of this bias can be approximately calculated using the formula $eV_{\text{max}} = 2k_B T \cosh^{-1} \left( \cosh \frac{E_0 - \Delta E - E_f}{k_B T} - 2 \right)$.

Figure 17. Illustration of the model for electron transport calculations. Model transmission spectra for an ideal conduction channel with $T_{r_0}(E)$ is shown. $\Delta E$ is a shift of the transmission caused by the adsorption of the DMMP gas molecules.

According to this simplified model, the experimentally observed sensitivity ($\sim 800\%$) is achievable for a doping shift of $\Delta E = 3k_B T$ (0.08 eV), which is realistic due to accumulation of
molecules at the GB. It should be noted that the presented sensing mechanism has an inherent symmetry for electron donating and accepting analytes. To obtain maximum sensitivity for each case, the Fermi level should be tuned by gate doping close to below (above) the energy onset for the electron donors (acceptors), hence they can close (open) the electron transport channels.

4.5 Conclusion

In this research project we showed the results of experimental and theoretical studies of the gas sensing behavior at grain boundaries present in graphene. It was shown that the sensitivity of an isolated GB is \( \sim 300 \) times higher than that of a single graphene grain and much larger than that of polycrystalline graphene sensors. We have verified that the presence of local transport gaps in GBs together with the local accumulation of donating molecules plays a crucial role in the observed large chemical sensitivity of GBs, so the mechanism differs from the previously reported carrier density modulation in linear transport spectrum of graphene [119,120,134–139]. The sensing mechanism is based on a dramatic closing or opening of local conduction channels through the GB by the adsorbed analytes. This new sensing modality can be used to develop practical nanometer scale sensors with numerous potential applications.
5.1 Introduction

In this chapter we use \textit{ab initio} calculations and QM/MM methods to analyze the catalytic activity and a CO\textsubscript{2} reduction performance of molybdenum disulfide (MoS\textsubscript{2}). Experiments revealed a superior CO\textsubscript{2} reduction performance, compared to noble metals, with a high current density and low overpotential (54 mV) in an (EMIM-BF\textsubscript{4}) ionic liquid. Our first principle modeling in accordance with scanning tunneling electron microscopy (STEM) analysis discloses that the origin of such an outstanding catalytic activity is due to the molybdenum terminated edges of MoS\textsubscript{2} and their metallic character with a high d-electron density.

This is a collaborative research project with the Prof. Amin Salehi-Khojin’s group (UIC). The preparation of the samples, conduction of experiments, electric measurements are performed by Prof. Amin Salehi-Khojin’s group, namely by Mr. Mohammad Asadi, Dr. Bijandra Kumar et al. I performed calculations of electronic structures and related analysis. The classical and quantum molecular simulations of molecular complex formation (EMIM-CO\textsubscript{2})\textsuperscript{+} in aqueous acidic solutions were performed by the graduate student Mr. Nikita Repnin. Nikita Repnin and I analyzed the results of simulations. The following content is reproduced with permission.
As it was recognized, a large amount of carbon dioxide CO$_2$ in the atmosphere is one of the sources of unpredictable changes in the environment [140–143]. Many efforts have been devoted to the study of the CO$_2$ electrochemical conversion to renewable energy sources [134,144–147]. However, the CO$_2$ reduction by electrochemical processes is a far from being solved scientific and engineering problem due to high-cost and unsatisfactory conversion performance of existing catalytic systems [144]. Due to the high importance for industrial applications, numerous physical and chemical approaches have been proposed to improve the performance of existing CO$_2$ reduction systems [148–152] albeit without any great success.

Recently, MoS$_2$ have generated a great deal of scientific attention due to its low price and prominent catalytic features. MoS$_2$ became widely used as an efficient catalyst for hydrodesulphurization [153,154], oxygen reduction reactions [155], and hydrogen evolution reaction (HER) [154,156]. Moreover, it was demonstrated that MoS$_2$ has a noteworthy performance for water splitting, approaching that of Pt-group metals [156,157].

In this research project, we experimentally and computationally study layer-stacked bulk MoS$_2$ with Mo-terminated edges. The main focus is on the explanation of the highest reported CO$_2$ reduction performance in a diluted solution of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF$_4$) ionic liquid, i.e., 4 mol% EMIM-BF$_4$ and 96 mol% water. EMIM-BF$_4$ was purposely chosen due to its particular catalytic features which make the system more selective for CO formation rather than hydrogen (H$_2$) production [145–147]. Another function of the
EMIM-BF$_4$ ionic liquid is to capture CO$_2$ in hydrated form and increase its solubility. In our computational study we want to elucidate the role of the electronic structure of MoS$_2$ with Mo-terminated edges and the effect of the EMIM-CO$_2$ complex formation on the CO$_2$ reduction process.

5.2 Computational methods

We have performed spin-polarized DFT calculations using SIESTA 3.1 [46] with the Perdew-Burke-Ernzerhof exchange-correlation functional [25] and the norm-conserving Troullier-Martins pseudopotentials [41] to describe valence electrons. The calculations were performed on a real-space grid with a mesh cut-off of 400 Ry within the eigenvalue tolerance of 104 eV, using a DZP (double-zeta basis and polarization orbitals) basis set. The Brillouin zones of the unit cells were sampled by the Monkhorst-Pack grid with a spacing between $k$-points of $\delta k < 0.01 \text{ Å}^{-1}$. The geometry optimization was carried out within the conjugated gradient algorithm, until all the forces are $F < 0.04 \text{ eV/Å}$ and the stress in the periodic direction is $\sigma < 0.01 \text{ GPa}$.

Using TeraChem [126] we perform QM/MM simulations of the hydrated (EMIM-CO$_2$)$^+$ complex using the B3LYP functional with a 3-21g basis set and DFT-D corrections [127, 158]. We describe quantum mechanically one EMIM$^+$ ion, one CO$_2$ molecule and 99 water molecules, surrounding EMIM$^+$ and CO$_2$. The remaining (2,500) waters are described classically with the TIP3P force-field. The charges were calculated within the Mulliken scheme.
Figure 18. Structural and elemental analysis of MoS$_2$. (a) Optical image of bulk MoS$_2$ used as catalyst (scale bar, 2 mm), (b) SEM images of the MoS$_2$ displaying the stacked layered structure and sharp edges of the MoS$_2$ flakes. Scale bars are 50 and 5 μm (for inset) respectively, and (c) high-angle annular dark-field (HAADF) images (scale bar, 5 nm) showing both the 1T (blue) and 2H (red) phases of MoS$_2$, along with their respective Fast Fourier Transforms (FFTs) (inset). (d) Higher magnification HAADF images show clearly distinct atomic configuration corresponding to the 1T (top) and 2H (bottom) type of MoS$_2$. The related schematic atomic models have also been shown on the right side. (e) Raw grayscale HAADF and false-color low-angle annular dark-field (LAADF) image (inset) of MoS$_2$ edges (scale bar, 5 nm) and (f) the line scans (red and blue towards edges) identifying Mo atoms to be the terminating atoms in the general case. In limited instances, an additional light atom (gray line scan) occupying what should be a Mo-position, most probably a carbon atom from the STEM substrate.
5.3 Experimental results and discussion

5.3.1 MoS\textsubscript{2} catalyst characterization

The samples of the bulk MoS\textsubscript{2} were prepared and characterized by optical and electron microscopy tools. Shown in Figure 18(a-b) are optical and the scanning electron microscopy (SEM) images, respectively, of the layered structure [159,160] of our bulk MoS\textsubscript{2} sample (Figure 19). Such layered assemblies offer a large number of edges (inset of Figure 18 b), which are believed to be highly electro-catalytically active sites in electrochemical reactions [156,161]. To further detail the atomic arrangement, scanning transmission electron microscopy (STEM) analysis was performed on several mechanically exfoliated, mono- and multi-layer thick sheets of MoS\textsubscript{2} flakes. Since the STEM high-angle annular dark-field (HAADF) image intensity relies on the atomic number (Z), it delivers direct information about the arrangement of Mo and S atoms in the MoS\textsubscript{2} film. The results of the STEM structural analysis (Figure 18 c) show that the MoS\textsubscript{2} layers are made of two clearly distinct structural domains consisting of 1T (octahedral) and 2H (triangular prismatic). The magnified images (atomic resolution) of selected regions confirm the presence of both 1T and 2H atomic arrangements (Figure 18 d).

It is very important to identify MoS\textsubscript{2} edge atoms, as the Mo and S atoms possess entirely different electronic structures. Figure 18 shows the edge of a MoS\textsubscript{2} flake imaged in HAADF and 4 low-angle annular dark-field (LAADF) (inset) mode. The line intensity profiles (plotted towards vacuum) suggest that the edges of the MoS\textsubscript{2} flakes are Mo terminated (Figure 18 f). This finding is in agreement with the earlier work [162] where it was reported that the Mo-terminated edges have the lowest formation energy in free-standing single layer MoS\textsubscript{2}. In rare
Figure 19. Scanning electron microscopic (SEM) images of bulk MoS$_2$. (a) The natural layered structure of bulk MoS$_2$ is simply visible (scale bar, 20 µm). (b) High magnification image (scale bar, 2 µm) more clearly demonstrates the sharp MoS$_2$ edges which are supposed to be more electrochemically active sites for CO$_2$ reduction.

instances, a substitutional defect (atom) appears at the MoS$_2$ edge. Based on the LAADF image (inset of Figure 18 e) and the line intensity profile (gray line), it is clear that this is a lighter atom (compared to S), most likely a carbon atom (from the underlying holey carbon STEM grid). Hence, the STEM analysis undoubtedly validates the presence of Mo atoms on the edges of MoS$_2$ flakes.

The performance of the MoS$_2$ catalyst can be further improved by designing an atomic edge terminated surface via synthesizing vertically aligned (VA) MoS$_2$. In this vertical structure, we observed a twice as large CO$_2$ reduction performance. In brief, a 5 nm thick layer of molybdenum was deposited on glassy carbon substrate by electron beam evaporation, followed by sulfurization by exposing the film to a sulfur vapor stream at 700°. Figure 20 a presents a HAADF and annular bright field (ABF) image of the vertically aligned MoS$_2$ nanosheets. While the MoS$_2$ layers are generally aligned perpendicular to the substrate surface, only a few
Figure 20. Vertically aligned MoS\(_2\) nanoflakes. (a) ABF STEM images of vertically aligned MoS\(_2\) (scale bar, 20 nm). STEM analysis (inset) shows the vertically aligned texture of MoS\(_2\) nanoflakes (scale bar, 5 nm). (b) RGB added image of (G+B) high-angle annular dark-field (HAADF) (R) inverted ABF STEM images of vertically aligned MoS\(_2\). High resolution HAADF STEM image of vertically aligned MoS\(_2\) (scale bar, 2 nm). Mo atoms are brighter and larger in size in comparison to sulfur atoms due to high atomic number. (c) Raman spectrum for vertically aligned MoS\(_2\). (d) CO\(_2\) reduction performance of bulk MoS\(_2\) and vertically aligned MoS\(_2\) represented by VA MoS\(_2\).
select sheets can be found which are aligned parallel to the electron beam to allow for atomic resolution imaging (Figure 20 b). This image identifies the clearly-separated Mo and S atomic columns, as the Mo atoms are heavier and thus will appear brighter. The proposed atomic structure of the Mo and S layers is superimposed on the atomic-resolution image in Figure 20 b. While the nature of the terminating atoms in these MoS₂ nanosheets cannot be directly visualized in this orientation, previous results have shown that synthesized MoS₂ nanosheets are generally terminated by Mo atoms due to their low-energy state [162]. The vertically aligned MoS₂ samples were further characterized by Raman spectroscopy (Figure 20 c). Two essential peaks are clearly visible at 385 (in-plane Mo-S phonon mode - E₂g mode) and 408 cm⁻¹ (out-of plane Mo-S phonon mode - A₁g mode) respectively [159, 163–165]. The ratio of out-of plane A₁g phonon mode to E₂g mode is significantly high (∼3), which clearly supports the existence of vertically oriented nature of MoS₂ flakes [163].

5.3.2 CO₂ reduction performance of MoS₂ catalyst

The CO₂ reduction ability of bulk MoS₂ covered by flakes with exposed Mo-ended edges was first examined by performing cyclic voltammetry (CV). The applied voltage was swept between +1.0 and -0.764 V vs. reversible hydrogen electrode (RHE; in the present study, all potentials are reported with respect to RHE) with a 15 mV/s scan rate. The experiments were conducted in a 2-compartment three-electrode electrochemical cell using argon (Ar) or CO₂ saturated 96 mol% water - 4 mol% EMIM-BF₄ solution (pH ∼4) as an electrolyte. Figure 21 a represents the CV curve for the CO₂ reduction. It should be noted that the CO₂ reduction equilibrium potential is -0.11 V vs. RHE in the protic media [145, 148]. The CO₂ reduction
reaction initiates at -0.164 V confirmed by measuring CO as a product by gas chromatography (GC) system (CO Faradaic efficiency F.E. ∼ 3%). This suggests a very low overpotential (54 mV) for CO formation in our system. At -0.2 V (90 mV overpotential) approximately 7% CO formation F.E. was measured (see Figure 21 b). MoS$_2$ also exhibits a significantly high CO$_2$ reduction current density (65 mA/cm$^2$ at -0.764 V), where CO$_2$ is selectively converted to CO (F.E. ∼ 98%). In contrast, at the same potential (-0.764 V) the bulk Ag catalyst shows a considerably lower current density (3 mA/cm$^2$) (Figure 21 a). Ag NPs (average diameter of 40 nm) show only a current density of 10 mA/cm$^2$ with 65% selectivity for the CO formation under the same experimental conditions. In addition, the CO$_2$ reduction current density for MoS$_2$ is also significantly higher than the maximum current density (∼ 8.0 mA/cm$^2$) achieved when Ag NPs were used in the dynamic electrochemical flow cell using a similar electrolyte solution [151]. For all the cases, the current densities were normalized against the geometrical surface area [147, 148, 154, 156, 164, 166].

Figure 21 b shows the measured F.E. of CO and H$_2$ formation for a wide range of applied potentials between -0.2 and -0.764 V. Interestingly, depending on the applied potential, MoS$_2$ effectively operates as a catalyst for both CO$_2$ and HER reductions. CO$_2$ is converted by MoS$_2$ into a tunable mixture of H$_2$ and CO (syngas), ranging in each component from zero to ∼100%. The variation in F.E. of CO and H$_2$ as a function of the applied potential originates from the differences in the CO$_2$ and HER reduction mechanisms. In principle, the favorable thermodynamic potential for H$_2$ evolution is lower than CO$_2$ reduction. As the applied potential exceeds the onset potential of the CO$_2$ reduction (-0.164 V), this reaction is activated.
Figure 21. CO$_2$ reduction performance of the bulk MoS$_2$ catalyst in the EMIM-BF$_4$ solution: (a) Cyclic voltammetric (CV) curves for bulk MoS$_2$, Ag nanoparticles (Ag NPs) and bulk Ag in CO$_2$ environment. The experiments were performed in 96 mol% water and 4 mol% EMIM-BF$_4$ solution by sweeping applied potential from +1 V to -0.764 V vs RHE. The vertical gray line indicates the low overpotential (∼54 mV) for CO$_2$ reduction at bulk MoS$_2$. (b) CO and H$_2$ Faradaic Efficiency (F.E) at different applied potentials. (c) The current density of CO$_2$ reduction (measured by Chrono-Amperometry) at -0.764 V vs. RHE as a function of water mole fraction in 4 mol% EMIM-BF$_4$ electrolyte. The pH value of the solutions was also monitored (SI file). (d) Chrono-Amperometry results of MoS$_2$ catalyst in different solutions (96 mol%, 90 mol% and 0 mol% water) showing negligible loss in current density even after 10 hours.
Essentially, two H\(^+\) are consumed for a CO formation as a result of one CO\(_2\) molecule reduction [148,151,167–169]. Thus, a fraction of both the existing H\(^+\) (from the electrolyte) and the electrons (on the catalyst surface) are consumed in CO\(_2\) reduction reactions instead of HER reactions. In addition, the EMIM-CO\(_2\) complex works as an inhibitor for the H\(_2\) formation in HER [145].

We also compare the MoS\(_2\) catalyst performance with the existing results for noble metal catalysts (Figure 22 3). It should be noted that a current density represents the CO formation rate, whereas F.E. shows the amount of current density consumed to produce CO during the CO\(_2\) reduction reaction. Thus, we compared the catalyst’s overall performance by multiplying these two parameters at different overpotentials. Interestingly, we noticed that bulk MoS\(_2\) exhibits the highest performance at all overpotentials. At low overpotential (0.1 V), bulk MoS\(_2\) shows almost 25 times higher CO\(_2\) reduction performance compared to the Au NPs\(^{10}\) and \(~1.3\) times higher than the Ag NPs. As mentioned previously, bulk Ag is unable to reduce CO\(_2\) in the examined experimental conditions. Moreover, the Cu performance [149] remains below that of Ag NPs, Au NPs and bulk MoS\(_2\). These results clearly indicate that MoS\(_2\) exhibits the highest CO\(_2\) reduction performance reported so far.

As we mentioned before, the catalytic activity of bulk MoS\(_2\) can be significantly improved by making the vertically aligned edges of MoS\(_2\). Figure 20 d shows the CO\(_2\) reduction performance of the vertically aligned MoS\(_2\) obtained in similar experimental conditions (i.e., 96 mol% water and 4 mol% EMIM-BF\(_4\)). As expected, CO\(_2\) reduction reaction initiated at low overpotential (54 mV) similar to bulk MoS\(_2\). Additionally, further improvement has been observed within
Figure 22. Overview of different catalysts performance at different overpotentials ($\eta$). Bulk MoS$_2$, Ag nanoparticles (Ag NPs) and Bulk Ag results were taken from the present study where electrochemical experiments were performed in similar conditions. CO$_2$ reduction performance curve of bulk Ag is not visible as it is unable to reduce CO$_2$ in experimental conditions.

the entire applied potential range (Figure 20 d). In the low applied potential region, vertically aligned MoS$_2$ exhibits two times as high CO$_2$ reduction current density compared to the bulk MoS$_2$ as shown in inset of Figure 20 d. This trend remains also valid in the high potential region. At -0.764 V a remarkably high CO$_2$ reduction current density (130 mA/cm$^2$) was recorded for vertically aligned MoS$_2$. The high catalytic performance of vertically aligned MoS$_2$ is attributed to the high density of active sites, preferably Mo atoms, available for the CO$_2$ reduction reaction.

5.3.3 Effect of ionic liquid on the CO$_2$ reduction performance

Next, we investigated how the water mole fraction affects the catalytic activity of the MoS$_2$ catalyst for the CO$_2$ reduction (Figure 21 c). We observe that the CO$_2$ reduction current density largely grows above 90 mol% water solution densities (inset Figure 21 c) and reaches
a maximum in the 96 mol% water solution. The addition of water molecules can be used to
tune the pH value (i.e., H\(^+\) concentration) of the electrolyte [151, 170, 171] and consequently
affect the electrochemical reduction reaction rate. The pH of the electrolyte fluctuates due
to the hydrolysis of BF\(_4\)\(^-\), which produces anions (e.g. (BF\(_3\)OH)\(^-\)) and HF [151, 170, 171]. It
should be noted that the overall CO\(_2\)-to-CO conversion reaction requires both electrons and
protons [151].

We attribute the attained maximum rate of the reduction process to: (i) the high concen-
tration of H\(^+\) (pH ~4) in the reaction media and (ii) the low viscosity of the solution. It is
clear that the low viscosity allows for high diffusion rates of the reactants (EMIM-CO\(_2\)\(^-\) and
H\(^+\)) towards the catalysts active edge sites [167, 172–174]. A similar trend was observed for Ag
NPs catalysts in a dynamic electrochemical flow cell when the maximum current density (~8
mA/cm\(^2\)) was obtained in a 90 mol% water electrolyte [151]. Since the stability of catalysts is
a major issue, we examined the MoS\(_2\) stability for a prolonged period (10 hrs) in 96 mol%, 90
mol% and 0 mol% water solutions. As seen in Figure 21 d, the steady-state current densities
remained stable for the studied time (10 hrs), providing evidence of the long term stability and
efficiency of the MoS\(_2\) catalyst.

5.4 **Theoretical study of MoS\(_2\) catalytic activity**

To elucidate the origin of the high CO\(_2\) reduction rate on MoS\(_2\) catalyst, we study the
electronic properties of MoS\(_2\)-edges and address the effect of ionic solution of acidic pH on the
(EMIM-CO\(_2\))\(^+\) complex formation which supposedly plays a crucial role in the CO\(_2\) reduction
process.
5.4.1 Electronic structure of MoS$_2$ edges

In our DFT calculations, performed with SIESTA, we studied a single layer MoS$_2$ nanoribbon with zigzag edges (Figure 23 a), which were observed in our experimental structures; armchair edges are less thermodynamically stable [166]. We model the local electronic structures at the edge and bulk atoms in a MoS$_2$-nanoribbon, 5 zigzag lines (dimers) wide, with Mo- and S-terminated edges. After a full structural optimization, the MoS$_2$-nanoribbon has a lattice constant of $a = 3.111$ Å. To study more realistic systems, we also calculated a double layer MoS$_2$ strip with one layer shifted with respect to the other in a 2H-MoS$_2$ configuration [166] (Figure 23 b). The layers (neighboring S atoms) are separated by $\sim 2.97$ Å.

Figure 23. MoS$_2$-nanoribbon structure. (a) A single layer nanoribbon. Mo-atoms are pink, S-atoms are yellow. In the unit cell bulk Mo-atoms are red, edge Mo-atom is blue, and S-atoms are orange. (b) Shifted double layer (side view).
From the spin-resolved electronic structure of the single and double layer MoS\textsubscript{2}-nanoribbons (Figure 24 a-d), one can see that only spin-up bands cross the Fermi energy. We analyze the character of the (I, II, III) metallicity points in the single layer MoS\textsubscript{2}-nanoribbon by visualizing the corresponding wavefunctions forming one-dimensional metallic edge states. The wavefunctions at the metallic point I are localized at the S-edge of the strip, whereas the wavefunctions at the II and III points are localized at the Mo-edge, as observed in previous studies [175, 176]. In the presence of two MoS\textsubscript{2} layers, the bands associated with edge states split and become flatter, as highlighted in Figure 24 c. The accumulation and flattening of the bands leads to a higher DOS around the Fermi level (Figure 24 d), which can explain the high catalytic rates observed in our experiments. Additional layers in the bulk MoS\textsubscript{2} substrate could further enhance the DOS.

Further analysis of the band structure of MoS\textsubscript{2}-nanoribbon can be done by calculating its projected electron density (PDOS) per different Mo and S atoms [176–178]. The density of states (DOS) at the Fermi energy level ($E_f$) roughly determines the number of electrons available for a given reaction [177]. From Figure 24 (a-b) we see that near $E_f$ the electronic structure of MoS\textsubscript{2}-ribbons is formed by edge bands of only one spin polarization, originating from the Mo and S atoms exposed at both MoS\textsubscript{2} edges. In the vicinity of $E_f$, the spin-polarized PDOS for these Mo atoms is approximately twice as large as that of the bulk Mo atoms (Figure 25 a). Since the bulk Mo atoms, sandwiched between two S layers, are not directly exposed to the electrolyte, the MoS\textsubscript{2} catalytic activity should be primarily related to the edge states formed by Mo-edge atoms. In Figure 26, we present for the single layer MoS\textsubscript{2}-nanoribbon the calculated
Figure 24. Electronic structure of single and shifted double layer MoS$_2$-nanoribbon. (a) and (c) show the spin resolved band structures (red and blue curves for $\alpha$- and $\beta$-channels, respectively) of MoS$_2$ single and double layers, respectively. (b) and (d) show the total DOS for the corresponding structures. I, II, and III figures show the wavefunction modulus at the corresponding metallicity points (Mo-edge (top), S-edge (bottom)) in the single layer MoS$_2$-nanoribbon.
DOS for a spin-up channel of edge S-atoms projected on s-, p-, and d-atomic states. DOS of the edge S-atoms at the Fermi level is mostly due to p-atomic states, which are not expected to be electrochemically active in the CO$_2$ reduction. As it was confirmed by STEM, the S atoms possess less reactive p-orbitals and are not present at the catalytically active edge sites.

Next, we resolved the PDOS of the Mo-edge atoms into s-, p- and d-orbital electron contributions (Figure 25 b). The obtained data indicate that the PDOS is dominated near $E_f$ by d-orbital (Mo) electron states, which are known to actively participate in catalyzed reac-
The Mo $d$-electrons form metallic edge states [175], which can freely supply electrons to the reactants attached at the edges. To assess how the Mo-edge states are affected by the presence of additional MoS$_2$ layers, we performed the same analysis for a double-layer MoS$_2$ strip. Our calculations revealed that an interlayer coupling further increases the d-electron PDOS near $E_f$ (Figure 24 c-d). In the presence of an external bias all these d-electron states near $E_f$ can be accessed in the reaction, supporting the large observed MoS$_2$ activity. Finally, we compared our $d$-orbital PDOS in Mo-edge atoms to that in Ag atoms in two structures: a bulk Ag and a two-dimensional slab Ag (both $fcc$ lattice with a lattice constant of 4.09 Å) of a 8.32 Å thickness (after relaxation) (Figure 25 c). Interestingly, we found that the $d$-band center
for Mo edge atoms is closer to the Fermi energy level than that in both Ag structures. This supports the high catalytic activity of MoS$_2$, since the higher the $d$-band center is, the more reactive the metal is, due to a lower transition state energy. Moreover, the PDOS of Mo-edge atoms near $E_f$ is approximately one order of magnitude higher than the PDOS of Ag atoms, suggesting the large availability of $d$-electrons on the Mo-edge atoms. We believe that both factors are responsible for the high CO$_2$ reduction current density of MoS$_2$.

5.4.2 Quantum molecular dynamic simulations of the hydrated (EMIM-CO$_2$)$^+$ complex

We have performed quantum molecular dynamics simulations of an (EMIM-CO$_2$)$^+$ complex hydrated in quantum water (see for details Computational Method section). To properly model the current experiments, performed at pH=4, we have added one H$_3$O$^+$ ion and one more Cl$^-$ counter ion (for neutrality) in the quantum water region. In this way, we roughly have one H$_3$O$^+$ ion per 100 quantum water molecules (2,600 in total).

It is well known [179] that the solvation of CO$_2$ in water results in the formation of various species among which HCO$_3^-$ and CO$_3^{2-}$ are the dominant ones in neutral and basic conditions, respectively. Our simulations revealed that the EMIM$^+$ cation can form different complexes with CO$_2$ stabilized by hydrogen bonding (Figure 27), where CO$_2$ may be coordinated to EMIM$^+$ ion by hydrogen bond either through the most acidic proton at C$_2$ [180,181] or less acidic protons at C$_4$/C$_5$ (compare Figure 27 b and d). However, the stability of the complex depends on the pH of the electrolyte, temperature, and concentration of IL.

Using QM/MM simulations we found that when CO$_2$ initially is positioned around C$_4$/C$_5$ protons in neutral solution at room temperature, the (EMIM-CO$_2$)$^+$ complex forms but it
reacts within ~2 ps with water molecules and forms either the (EMIM-HCO$_3$) or (EMIM-CO$_3$)$^-$ complexes (Figure 27 a). In acidic environment, similar to our experimental conditions (pH< 4), the simulations show that the (EMIM-CO$_2$)$^+$ remains stable ($t \approx 10$ ps) (see Figure 27 b) and CO$_2$ stays in the linear configuration. The average length of the H-bond between the C$_4$ proton and O-atom of CO$_2$ is $\approx 2.4$ Å (Figure 27 c). However, the QM/MM simulations of EMIM$^+$ ion and CO$_2$ positioned around the C$_2$ proton (Figure 27 d) revealed that even in acidic environment the (EMIM-HCO$_3$) complex tends to form (Figure 27 e). The origin of this process is a higher polarizability of the C$_2$-H bond compared to, e.g., the C$_4$-H bond. The average length of the H-bond between the C$_2$ proton and the O atom of CO$_2$ is relatively long, $\approx 3.2$ Å (Figure 27 f). Therefore, this binding configuration might be less stable than the C$_4$/C$_5$ binding configuration. Moreover, since the reduction of the (EMIM-HCO$_3$) complex in the aqueous phase would lead the production of a formic acid, which is not observed in our experiment, we conclude that the (EMIM-CO$_2$)$^+$ complex most likely forms at the C$_4$ site.

Although we could not perform detailed simulations of the (EMIM-CO$_2$)$^+$ complex at the MoS$_2$ cathode, we think that the EMIM cations bring CO$_2$ to the negatively charged MoS$_2$ surface, where they physisorb (Coulombic and van der Waals coupling). Once CO$_2$ gets in contact with the MoS$_2$ surface, the positive charge of nearby EMIM ions could decrease the reaction barrier for electrons passing into CO$_2$, i.e., it acts as an electron pump. These observations suggest that the observed high-rate of CO$_2$ reduction is the result of a synergistic action of the MoS$_2$ catalyst and the EMIM-BF$_4$ ionic liquid. While EMIM-BF$_4$ plays a crucial role by
reducing the overpotential for the reaction, the CO₂ reduction rate is mainly governed by the intrinsic properties of the MoS₂ catalyst.

In addition, the work function (another signature of catalytic performance) of MoS₂ through the use of ultraviolet photoelectron spectroscopy was experimentally measured. The obtained
results indicate that the work function of MoS$_2$ (3.9 eV) is significantly lower than that of the bulk Ag (4.37 eV) and Ag NPs (4.38 eV) [147]. Due to the low work function of MoS$_2$, the abundant metallic-like d-electrons in its edge states can take part in the reactions, ultimately resulting in the superior CO$_2$ reduction.

5.5 Conclusion

In this chapter we showed that bulk MoS$_2$ as a non-precious catalyst and the most versatile member of TMDCs exhibits the highest observed catalytic performance for the CO$_2$ reduction. The significantly higher CO$_2$ reduction current density (relative to noble metal catalysts) is attributed to a high density of d-electrons in Mo-terminated edges, its low work function, and the supportive role of the EMIM ions. We propose that TMDCs can successfully replace expensive noble metal electrodes, with the promise of higher CO$_2$ conversion rates and selectivity and could be one of the most attractive catalysts for future CO$_2$ reduction applications.
6.1 Introduction

In this research project, we study highly excited diskoid-like electronic states formed in the vicinity of charged and strongly polarizable molecules of diskotic shapes, such as circular graphene flakes. Highly extended Rydberg-like electronic states in atoms and molecules [182, 183] bear semi-classical concepts developed in the Bohr model. Molecular Rydberg states can have extremely large permanent electric dipole moments [182] highly sensitive to their environment, which is useful in probing physical and chemical processes at the nanoscale [184, 185]. These extended states can provide unique information about light-matter interactions [186, 187] and particle entanglement [188, 189], with implications in quantum information and metrology sciences.

Similar extended electronic states were predicted to form [190–192] and have been observed [193, 194] above the surfaces of metallic carbon nanotubes (CNT). In these tubular image state (TIS), the electron is attracted to its hole image formed on a highly (longitudinally) polarizable CNT surface. In principle, analogous image-like states could be formed above highly polarizable diskoid-like molecules, such as graphene flakes. However, in contrast to TISs, the image hole is induced in a transversely polarizable disk, which means that it should be highly correlated with the orbiting electron. In this work, we introduce such highly excited diskoid-like states, discuss
their properties, in particular their correlations, and study also their one-electron solutions. First, we study the nature of such extended states in a simple two-electron model. The two electrons are attached to a point-like nucleus with a charge 2+, where the material electron is forced to move within a 2D disk area centered at the nucleus, while the extended electron is free to move in 3D. Pronounced and complex correlations are revealed in the diskoid-like states. We also develop semiclassical one-electron models of such diskotic systems and explain how the one-electron and many-electron solutions are related.

This chapter is organized as follows. In the first section, we introduce diskoid-like states, find their analytical solution in a simple two-electron model. We reveal their properties, in particular, their correlations, and discuss related mean-field potentials. In the second section, we study one-electron diskoid-like states of an electron moving around a perfectly conducting metallic nanodisk. Finally, in Conclusion section, we summarize the obtained results. This research project I conducted by myself and performed all of the simulations and analysis. The paper “Correlated Diskoid-like Electronic States” by A. Baskin, H.R. Sadeghpour, and P. Kral has been submitted in Scientific Reports.

6.2 Two-electron diskoid-like states

A fully quantum mechanical description of correlated electronic states formed above nanoscale metallic surfaces requires a proper accounting of many-body effects [195]. To simplify our treatment of correlated electronic states formed above large and polarizable diskoid-like molecules, we introduce a simple two-electron diskoid-like model. In this model, schematically shown in Figure 28, the two electrons move around a localized nucleus with a charge of $Z = +2$. The
Figure 28. Model (He-type) system with diskoid-like states, where one electron is confined within the 2D disk area in the $z = 0$ plane and the second electron is orbiting around the disk in 3D.

“material” (polarization) electron (ME) is confined in a 2D disk of the radius $a$ ($z = 0, \rho \leq a$), whereas the “external” electron (EE) is free to move in 3D space.

6.2.1 Computational method

The “hybrid” He atom in Figure 28 can be described by the Hamiltonian (a.u.):

\[
H = -\frac{1}{2} \left( \frac{\partial^2}{\partial \rho_1^2} + \frac{1}{\rho_1} \frac{\partial}{\partial \rho_1} + \frac{1}{\rho_1^2} \frac{\partial^2}{\partial \delta_1^2} \right) - \frac{Z}{\rho_1}
- \frac{1}{2} \left( \frac{\partial^2}{\partial \rho_2^2} + \frac{1}{\rho_2} \frac{\partial}{\partial \rho_2} + \frac{1}{\rho_2^2} \frac{\partial^2}{\partial \delta_2^2} + \frac{\partial^2}{\partial z_2^2} \right) - \frac{Z}{\sqrt{\rho_2^2 + z_2^2}}
+ \frac{L_z^2}{2(\rho_1^2 + \rho_2^2)} + \frac{1}{\rho_{12}},
\]

(6.1)
written in the relative and position-weighted angular coordinates [196], \( \delta = \phi_1 - \phi_2, \phi = \frac{\rho_1^2 \phi_1 + \rho_2^2 \phi_2}{\rho_1^2 + \rho_2^2} \), related to the two-electron coordinates, \((\rho_1, \phi_1), (\rho_2, \phi_2, z_2)\), where \( \rho_{12} \equiv \sqrt{\rho_1^2 + \rho_2^2 + z_2^2 - 2 \rho_1 \rho_2 \cos(\delta)} \) and \( Z \) is the nucleus charge. The first and second lines in Equation 6.1 are the one-electron \( h_1(\rho_1, \delta) \) (ME) and \( h_2(\rho_2, z_2, \delta) \) (EE) Hamiltonians in effective cylindrical coordinates, respectively. The third line represents the Coulombic coupling of the two electrons and their centrifugal term, with \( L_z^2 = -\frac{\partial^2}{\partial \phi^2} \).

We find the correlated two-electron eigenstates of \( H \) in Equation 6.1 by a configuration interaction (CI) method, using a variational technique with a one-electron basis set wavefunctions, which solve \( h_1(\rho_1, \delta) \) and \( h_2(\rho_2, z_2, \delta) \). The cylindrical symmetry of the Hamiltonian, associated with the point group \( D_{\infty h} \), prevent us from using the Hylleraas basis set [197, 198] (used in the He-atom problem). Moreover, the mixed dimensionality of our problem necessitates to consider ME and EE as distinguishable Coulombically coupled particles. Then, the CI eigenfunctions can be written in a separable form, \( \Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_\Lambda(\rho_1, \rho_2, z_2, \delta) e^{\pm i\Lambda \phi} \sqrt{2\pi} \), where \( \Lambda \) is an eigenvalue of \( L_z \). We will focus on \( \Sigma \) states with \( \Lambda = 0 \) and expand \( \Psi_0 \) in the eigenstates of \( h_{1,2} \).

As the Coulomb interactions of the ME and EE with nucleus do not depend on \( \delta \), this angle can be factored out in both \( (h_{1,2}) \) sub-systems, as \( \psi(\delta) = \frac{1}{\sqrt{2\pi}} e^{\pm i\delta} \). In the solution of the 2D
H-atom [199], described by \( h_1(\rho_1, \delta) \), the radial part of the eigenfunctions can be expressed in terms of confluent hypergeometric functions:

\[
R_{1nl}(\rho_1) = \, _1F_1(-n + |l| + 1, 2|l| + 1, \beta_n \rho_1) \\
\times \, A_{nl}(\beta_n \rho_1)^{|l|} e^{-\beta_n \rho_1 / 2}, \quad E < 0,
\]

\[
R_{1kl}(\rho_1) = \, _1F_1(i/k + |l| + 1/2, 2|l| + 1, i2k \beta_1) \\
\times \, C_{kl}(2k \beta_1)^{|l|} e^{-ik \beta_1}, \quad E > 0,
\]

where \( \beta_n = \frac{2Z}{n-1/2} \frac{1}{a_0} \), \( \beta = \frac{Z}{a_0} \), \( k = (\frac{2E}{Z^2 a_0^2})^{1/2} \), and \( a_0 \) is the Bohr radius. The confinement of the ME in the disk area can be resolved by applying a Dirichlet boundary condition, \( R_{1nl}|_{\rho_1=a} = 0 \) [200, 201], which selects and restricts the wavefunctions in Equation 6.2.

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<td>( E_{42} ) = 0.133351</td>
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<td>( E_{56} ) = 0.347205</td>
<td>( E_{65} ) = 0.650439</td>
<td>( E_{66} ) = 1.011136</td>
<td>( E_{67} ) = 1.430107</td>
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<tr>
<td>( E_{57} ) = 0.534240</td>
<td>( E_{66} ) = 0.880975</td>
<td>( E_{68} ) = 1.284670</td>
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<td>( E_{68} ) = 0.750451</td>
<td>( E_{75} ) = 1.140261</td>
<td>( E_{76} ) = 1.586679</td>
<td>( E_{77} ) = 2.090793</td>
</tr>
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**TABLE II.** The energy eigenvalues (a.u.) for orbitals of the 2D hydrogen atom \((Z = 2)\) confined in the disk of radius \( a = 1 \) nm. The red line separates energy states with \( E < 0 \) from those with \( E > 0 \).
Then, the allowed energies of ME can be found from $1F_1(-ζ + |l| + 1, 2|l| + 1, a) = 0$. For a given value of $|l|$, the first root corresponds to the ME energy of the lowest ($n = |l| + 1$) state and the successive roots are its excited states. The confinement also removes the $l$-degeneracy, leaving only the twofold degeneracy with respect to the sign of $l$, so the energy spectrum can no longer be expressed as in the free 2D H atom, $E_n = -\frac{Z^2}{2(n-1/2)^2}$. When the disk radius $a$ is decreased, the ME energy increases, passes through zero, and rapidly rises to large values.

In Table IV, we summarize the energies for 2D H-atom confined in the disk of radius $a = 1$ nm. The 3D H-atom Hamiltonian, $h_2(\rho_2, z_2, \delta)$, gives the solution for EE in the cylindrical coordinates, $R_{2nl}(\rho_2, z_2)$ [202].

Using these one-electron solutions, the combined CI wavefunctions can be expanded as

$$
\Psi^N_\Lambda(\rho_1, \rho_2, z_2, \delta) = \sum_{nkl} C^N_{nkl} R_{1nl}(\rho_1) R_{2kl}(\rho_2, z_2) \psi_l(\delta),
$$

where we omit the permutational spin symmetry, due to the distinguishability of ME and EE. However, these wavefunctions should have spatial symmetries belonging to the $D_{\infty h}$ group, i.e., the $i$ inversion in the force center and the $\sigma_v$ reflection in the plane containing $z$-axis.

These symmetry conditions can be satisfied by selecting certain $\Psi^N_\Lambda$-wavefunction components. We need to take into account that $R_1(\rho_1)$ is totally symmetric, $R_2(\rho_2, z_2)$ is gerade/ungerade with respect to $i$, and linear combinations of $\psi_l(\delta)$ can be either symmetric or antisymmetric with respect to $\sigma$. Then, considering $\Sigma^z_{g/u} (\Lambda=0)$, the allowed symmetry-adapted wavefunction products are $A^{N,\pm}_{g/u} R_{1nl}(\rho_1) R_{2kl}^{g/u}(\rho_2, z_2) \psi_l^\pm(\delta)$. Here, $\psi_l^+(\delta) = \frac{1}{\sqrt{\pi(1+\delta_0)}} \cos(l\delta)$ for $l = 0, 1, 2, \ldots$ and $\psi_l^-(\delta) = \frac{1}{\sqrt{\pi}} \sin(l\delta)$ for $l = 1, 2, 3, \ldots$ and $A^\pm_{g/u}$ are the normalization coefficients. For simplicity, we focus on the $\Sigma^+_{g}$ state and use a limited basis set which consists of all
the possible combinations of eigenfunctions of $h_{1,2}$, with $l = 0, 1, 2, ..., 9$ and $n = l + 1, ..., l + 4$ eigenvalues. Overall, the basis set contains 160 basis functions.

6.2.2 Results and discussion

First, we discuss the angular distributions in the two-electron wavefunctions (correlations) for ME and EE, caused by the electron-electron coupling. Figure 29 shows the spatial distribution of ME, $\rho_1 \rho_2 |\Psi_{\Sigma_g}(\vec{r}_1, \vec{r}_2)|^2$, in different excited $\Sigma_g$ states, when EE is positioned at a distance of $\rho_2 = 0.2 a$ and $\rho_2 = 2.5 a$ from the center and $\phi_2 = 0$ (the $x$-axis in the disk plane). We can see that all the considered states ($N = 5, 29, 48, 120$) have a significant angular asymmetry of the ME distribution. Moreover, the radial nodal pattern seems to be also altered in the moderately excited (b, c) states. In the higher excited state (d), one would expect that an opposite charge (hole) is accumulated close to the external electron in the disk (see Figure 34 (bottom)). However, since a single ME can not represent well a metal, this hole does not form.

Figure 30 (top) shows the evolution of the ME distribution in $N = 29$ for different radial positions of EE, $\rho_2 = 0.1 - 0.8 a$ ($\Delta \rho_1 = 0.1 a$), localized in the disk plane ($z_2 = 0, \phi_2 = 0$). As $\rho_2$ grows oscillations of the ME density can be observed (correlations with EE). Figure 30 (middle) shows the same for the $N = 120$ state, but $\rho_2 = a - 3.8 a$ and $\Delta \rho_2 = 0.4 a$. We can observe very interesting oscillations in the ME density even when EE is far away from the disk. Figure 30 (bottom) presents the EE distribution for $N = 72$ outside the disk area (gray), when the ME position is changing like that of EE in Figure 30 (top). This time, we observe oscillations of the EE density localized near the disk edge, where most of the EE population is largely present. However, the angular asymmetry is not seen farther from the disk.
Figure 29. ME density $\rho_1\rho_2|\Psi_{\Sigma}(\vec{r}_1, \vec{r}_2)|^2$ ($\vec{r}_2$ fixed) when EE sits on the disk plane at a distance of $\rho_2 = 0.2 \, \text{a}$ (cases a, b, c) and $\rho_2 = 2.5 \, \text{a}$ (case d) from the center with $\phi_2 = 0$ for a) $N = 5$, b) $N = 29$, c) $N = 48$, d) $N = 120$. The coordinates are given in units of the disk radius, $a = 1 \, \text{nm}$.

We also study the radial distributions in the same two-electron wavefunctions for ME and EE. Figure 31 (top) compares the one-electron density matrix for ME, $\rho_1|\bar{\Phi}_N(\rho_1)|^2 = \rho_1 \int \rho_2 |\Phi_N(\rho_1, \rho_2, z_2, \delta)|^2 \, d\rho_2 \, dz_2 \, d\phi_2$, with the one-electron distribution, $\rho_1|R_{l_1,n_1}(\rho_1)|^2$, where $l_1, n_1$ correspond to the basis function which has the largest variational coefficient in $\Phi_N(\rho_1, \rho_2, z_2, \delta)$.

In the middle excited states ($N = 29, 48$) the correlations significantly perturb the ME distribution. In these states, $\rho_1|\bar{\Phi}_N(\rho_1)|^2 \neq 0$ is largely spread over the whole disk, where even the nodal pattern is suppressed, as noticed in Figure 29. However, in contrast to angular cor-
Figure 30. (top) Evolution of the ME density τ_1τ_2|Ψ_Σ(⃗r_1, ⃗r_2)|^2 (⃗r_2 fixed) for EE positioned in the disk plane (z_2 = 0, \phi_2 = 0) at different distances \rho_2 from the disk center for the N = 29 state. The snapshots correspond to \rho_2 = 0.1 a - 0.8 a values separated by Δ\rho_2 = 0.1 a. The area \rho_1 ≤ a is shown. (middle) The same as in (top) for the N = 120 state. The snapshots correspond to \rho_2 = 1 a - 3.8 a values separated by Δ\rho_2 = 0.4 a. The area \rho_1 ≤ a is shown. (bottom) Evolution of the EE density τ_1τ_2|Ψ_Σ(⃗r_1, ⃗r_2)|^2 (⃗r_1 fixed) in the disk plane (z_2 = 0) for different distances \rho_1 of ME (\phi_1 = 0) from the center of the N = 72 state. The snapshots correspond to \rho_1 = 0.1 a - 0.8 a values separated by Δ\rho_1 = 0.1a. The area \rho_2 ≤ 4a is shown. The disk is gray.

relations (Figure 29), the radial correlations are suppressed in the low (N = 5) and highly (N = 120) excited states.

In Figure 31 (bottom), we perform the same analysis for EE. In particular, we compare τ_2|\Phi_N(\rho_2, z_2)|^2 = \rho_2 \int \rho_1|\Phi_N(\rho_1, \rho_2, z_2, \delta)|^2d\rho_1d\phi_1 with \rho_2|R_{2l_2n_2}(\rho_2, z_2)|^2, where we set z_2 = 0 (EE in disk plane) and pick l_2, n_2 for the largest variational coefficient in \Phi_N(\rho_1, \rho_2, z_2, \delta).

The radial distributions of EE are affected for all the chosen states, but for N = 29, 48 the correlations are substantially larger.
Figure 31. (top) The radial distributions $\rho_{ME}$ of ME, $\rho_1|R_{1l_1n_1}(\rho_1)|^2$ and $\rho_1|\Phi_N(\rho_1)|^2$, obtained from the one- and two-electron solutions. The blue- and red-fill areas show the localizations of ME which is free and perturbed by EE, respectively. (inset) $\rho_1|\Phi_N(\rho_1)|^2 - \rho_1|R_{1l_1n_1}(\rho_1)|^2$ for $N = 5$ is shown. (bottom) The radial distributions $\rho_{EE}$, $\rho_2|R_{2l_2n_2}(\rho_2)|^2$ and $\rho_2|\Phi_N(\rho_2)|^2$, of EE in the disk plane, obtained from the one- and two-electron solutions. The blue- and red-filled areas show the localizations of EE non-perturbed and perturbed by ME, respectively.
Figure 32. (top) Degree of delocalization of energy eigenfunctions in \( N \) states over the basis wavefunctions, \( \Delta_{\text{loc}} \), where \( M = 160 \) is total number of basis wavefunctions. (inset) The average number of states \( \langle n \rangle / M \) whose variational coefficients exceed a threshold of \( \epsilon = 0.05, 0.02 \). (bottom) The average electron-electron distance \( \langle r_{12} \rangle \) as a function of \( N \).
To analyze the electron correlations in more detail, we evaluate how the eigenstates \( \Phi_N \) are spread over the used basis wavefunctions, and compare these results with the average ME-EE distance \( \langle r_{12} \rangle \) in these states. In Figure 32 (top), we present the standard deviation of the variational coefficients for \( N = 1 - 160 \) states, normalized as \( \sum_i^M |c_i^N|^2 = 1 \). We evaluate the degree of delocalization from \( \Delta_{loc} = 1 - \sqrt{1 - \left( \sum_i^M |c_i^N| \right)^2 / M} \). For low and highly excited states the eigenfunctions are localized on a few one-electron wavefunctions, whereas the eigenfunctions in the middle part of the energy spectrum are more evenly distributed over the basis set. For each \( \Phi_N \), we also calculate the average number of states \( \langle n \rangle / M \) whose variational coefficients exceed a threshold \( \epsilon \). In Figure 32 (top, inset) the distribution shows how many basis wavefunctions contribute to the \( N \) state at a given threshold \( \epsilon \). For the chosen thresholds \( \epsilon = 0.02 \) and 0.05, the eigenfunctions have practically the same profiles of delocalization as when obtained through standard deviation of the variational coefficients.

In Figure 32 (bottom), we show that the \( \langle r_{12} \rangle \) dependence on \( N \) is almost linear; the quasi-periodic oscillations originate from the specific choice of the basis set. We found that \( \langle r_{12} \rangle \) has local maxima in the \( N \) states which are localized on a particular basis wavefunction and it has local minima in the \( N \) states which are more delocalized over the basis set.

These observations agree with the previous results, since in the \( N = 29, 48 \) states, where \( \langle r_{12} \rangle \) has a minimum, ME has a highly correlated radial distribution, seen in Figure 29 b-c and Figure 31. The suppressed radial correlations in the low excited stated can be related to the mixed dimensionality of this problem, where ME coupling to the nucleus can not be greatly disturbed by the electron repulsion with EE. In moderately excited states, \( \langle r_{12} \rangle \sim 1 - 2 \text{ nm} \)
and the mixed dimensionality becomes less relevant. In highly excited states, \( \langle r_{12} \rangle \simeq 3 - 5 \text{ nm} \), so the radial correlations largely disappear.

### 6.2.3 Mean-field solutions

Next, we discuss semi-classical solutions of the diskoid-like model in Figure 28, where the EE moves around a charged and polarizable (ME) disk (i.e., “Hartree hole” of an image charge). In principle, these semi-classical problems can be studied by asymptotic expansion methods [198,199,203–207] or perturbation methods, which can be used to obtain one-electron solutions of this mean-field problem [203,205].

![Figure 33](image_url). Comparison of the mean-field potentials without \( U^I(\rho_2, z_2 = 0) \) (solid lines) and with \( U^{II}(\rho_2, z_2 = 0) \) (dotted lines) the ME polarization. The first is calculated for the states with \( l_1 = l_2 = l \) with \( n_1 = l + 1 \).
We illustrate two approaches of finding effective mean-field potentials, $U_N(\rho_2, z_2)$, which could describe the interaction of EE with the nucleus and ME (affected by EE). In the first case, we evaluate the average potential that EE experiences, provided that its angular momentum quantum number is $l_2$ and ME is in the $|l_1, n_1\rangle$ state, $U_{l_1,l_2,n_1}^I(\rho_2, z_2) = \frac{l_2^2-1/4}{\rho_2^2} - \frac{2}{\sqrt{\rho_2^2+z_2^2}} + \frac{1}{2\pi} \int R_{l_1,n_1}^2(\rho_1) \frac{\rho_1}{\rho_2} d\rho_1 d\delta$. This potential does not include the polarization of ME, but the nucleus screening is accounted for. Alternatively, we can obtain the mean-field potential, $U_{N}^{II}(\rho_2, z_2) = \frac{l_2^2-1/4}{\rho_2^2} - \frac{2}{\sqrt{\rho_2^2+z_2^2}} + \int |\bar{\Phi}_N(\rho_1)|^2 \frac{\rho_1}{\rho_2} d\rho_1 d\delta$, where $|\bar{\Phi}_N(\rho_1)|^2 = \int |\Phi_N(\rho_1, \rho_2, z_2, \delta)|^2 \rho_2 d\rho_2 d\rho_2 d\phi_2$. This is an effective potential between EE, the force center, and ME with a distribution affected by EE.

In Figure 33, we present the $U^I$ and $U^N_{II}$ potentials. The $U_{l_1,n_1}^I(\rho_2)$ potential is calculated for different $l_1 = l_2$ and $n_1 = l_1 + 1$. It develops a well detached local minimum for $l_2 \geq 5$ at $\rho_2 > 1.5 a$. Small ripples in the potential form at $\rho_2 < a$ due to an inhomogeneous charge distribution on the disk. The ripples depend slightly on $n_1$, but vanish at $l_2 > 6$. The quantum numbers $l_1, l_2, n_1$ are extracted from the CI coefficients of the “exact wavefunction”. However, the correspondence between $|\Lambda = 0, N\rangle$ and $|l_1,l_2,n_1\rangle$ is approximate. Comparison of the potentials shows that polarization is important for $l_2 = 2, 3$. This is compatible with our exact two-electron solution where correlation effects are negligible for low excited states with $l_2 = 0, 1$ (Figure 31 a). Both mean-field and classical (Figure 35 (top)) potentials develop well detached minima for $l_2 \geq 5$ at $\rho_2 > 1.5 a$ and $l \geq 8$ at $\rho > 3.5 a$, respectively. For highly excited states, both the disk-electron distance and the average electron-electron distance are large, so the correlations are no longer seen.
6.3 One-electron diskoid-like states

Here, we describe the diskoid-like states in an one-electron approximation and evaluate the electron binding potential classically, rather than resorting to the semiclassical solutions discussed above. First, we calculate the electrostatic potential of an electron interacting with a perfectly conducting (isolated or grounded, charged or neutral) nanodisk. Then, we numerically solve the Schrödinger equation for the electron moving in this potential. Note that the system is somewhat different from that in the previous section, since the charge is freely distributed on the whole disk and the screening is ideal, rather than having a positively charged nucleus and one screening ME moving in 2D.

6.3.1 Charge distribution on a metallic disk

We start by finding the equilibrium charge distribution \( \sigma(x, y) \) of an isolated metallic disk (centered at the coordinate origin and oriented in the \( x - y \) plane) with a radius \( a \) and a charge \( Q \). The electrostatics of a perfectly conducting uniformly thin circular disk was first discussed by Lord Kelvin [208]. He derived the expressions for a surface charge density \( \sigma(\rho) \) on an equipotential disk using the formula for the gravitational potential of an elliptical homoeoid.

The Kelvin’s approach gives the surface charge density of an ellipsoid:

\[
\sigma(x, y, z) = \frac{Q}{4\pi abc} \frac{1}{\sqrt{\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2}}},
\]
By projecting this surface charge density on the plane $z = 0$, one can obtain the charge density of an ellipse:

$$\sigma(x, y) = \frac{Q}{4\pi ab} \frac{1}{\sqrt{1 - \frac{x^2}{a^2} - \frac{y^2}{b^2}}} ,$$

and a disk:

$$\sigma(\rho) = \frac{Q}{4\pi a} \frac{1}{\sqrt{a^2 - \rho^2}} , \quad \rho^2 = x^2 + y^2 .$$

In all these cases, the potential is constant over the particular geometrical objects.

The problem of finding the electrostatic potential generated by a charged equipotential disk can be reduced to the equations for the unknown function $f(k)$ (mixed boundary conditions):

$$V_\sigma(\rho, z) = \int_0^\infty dk \ f(k) e^{-k|z|} J_0(k\rho) ,$$

$$V_\sigma(\rho, 0) = V_0 , \quad 0 \leq \rho \leq a,$n

$$\frac{dV_\sigma}{dz}(\rho, 0) = 0 , \quad a < \rho < \infty \quad (6.3)$$

where $Q = V_0 \frac{2a}{\pi}$. These equations have the solution, $V_\sigma(\rho, z) = Q \int_0^\infty dk \frac{\sin(k\rho)}{k\rho} e^{-k|z|} J_0(k\rho) \quad [209]$, giving the same expression for the charge density as above.

### 6.3.2 Induced charge distribution and image potential

Next, we find the potential energy of a point charge above a metallic disk. When a metallic disk is present in a potential created by external charges, $V_{ext}(\rho, \phi, z)$, it develops an induced surface charge density, $\sigma(\rho, \phi)$, and a related potential, $V_\sigma(\rho, \phi, z)$, which makes the total potential $V_{total} = V_{ext} + V_\sigma$ constant on the disk. Depending, on the isolated or grounded character
of the disk, the total induced charge (integral of $\sigma(\rho, \phi)$ over disk) remains constant (zero) or not. For a neutral isolated disk, $\sigma$ and $V_\sigma$ originate solely in the disk polarization.

Due to the presence of disk edges, finding the potential $V_\sigma(\rho, \phi, z)$ can be a relatively complex task. Since Lord Kelvin’s solution, many sophisticated techniques have been developed. For example, Sommerfeld has shown [210] that such problems can be solved by image potential techniques. In this way, a Green’s function for a conducting disk and a point charge with Dirichlet boundary conditions could be found [211,212].

Alternatively, the electrostatic potential of a point charge above a disk [213] could be found from the Copson theorem [214]. The target is to find the electrostatic potential $V_\sigma(\vec{r})$ created by the induced charge density $\sigma(\rho)$ present on the disk, which can be expressed in the external space as:

$$V_\sigma(\vec{r}) = \int_{\rho' < a} \sigma(\rho') \frac{d^2r'}{|\vec{r} - \vec{r}'|}. \quad (6.4)$$

According to the central lemma, the potential generated by the external charge in the area of the disk can be expressed as:

$$V_\sigma(\rho) = \int_{-\pi/2}^{\pi/2} \lambda(\rho \cos \beta) \ d\beta, \quad (6.5)$$

where $\lambda(x)$ is a so called “strip function”:

$$\lambda(x) = \int \sigma(x, y) \ dy. \quad (6.6)$$
Equation 6.5 and Equation 6.6 form a pair of integral transforms equivalent to Equation 6.4. The physical meaning of the lemma is in the connection between the strip function \( \lambda(x) \) and the potential created on the disk surface. Once \( V_\sigma(\rho) \) is known, one can try to find the strip function which would generate the same (up to the additive constant) but opposite sign potential in the disk, and cancel \( V_\sigma(\rho) \). Thus, the total potential in the disk area would be constant. Along with the uniqueness of the Poisson equation solution, this provides the correct expression for \( \lambda(x) \) or \( \sigma(\rho) \) and, thus, for \( V_\sigma(\vec{r}) \).

In some cases the strip function can be easily guessed. A point charge, \( q_{\text{ext}} \), placed at \( \rho = 0 \) and \( z = z_0 \) creates on the disk the potential \( V_\sigma(\rho) = \frac{q_{\text{ext}}}{\sqrt{z_0^2 + \rho^2}} \). By inspecting this \( V_\sigma \), the strip function can be easily found as \( \lambda(x; z_0) = -\left( \frac{q_{\text{ext}}}{\pi} \right) \frac{z_0}{z_0^2 + x^2} \). We can use this strip function to compute the interaction potential energy between a point charge placed at the disk axis \( \rho = 0 \) at distance \( z \) above the disk, \( V_{\sigma,\rho=0}(z) = -\frac{q_{\text{ext}}}{\pi} \left( \frac{a}{z^2 + a^2} + \frac{1}{z} \arctan \frac{a}{z} \right) + \frac{2q_{\text{ext}}}{a^2} \arctan \frac{a}{z} \). For \( z \to 0 \), we obtain \( V_\sigma(z) \sim -\frac{1}{2z} \), while for \( z \gg a \), \( V_\sigma(z) \sim -\frac{8a^3}{4\pi^2z^3} \), as expected for a charge above an infinite conducting plane and for a point charge coupled to a quadrupole, respectively. In a similar way, we can also find the induced charge density, \( \sigma(\rho; z_0) = -\frac{1}{2\pi \rho} \frac{d}{d\rho} \int \sqrt{\frac{a^2 - \rho^2}{z_0^2 + \rho^2}} \lambda(\sqrt{a^2 + \rho^2}; z_0) \, dx = -\frac{q_{\text{ext}}}{\pi^2} \times \frac{z_0}{(z_0^2 + \rho^2)^{1/2}} \left( \arctan \frac{a^2 - \rho^2}{\sqrt{z_0^2 + \rho^2}} + \frac{z_0^2 + \rho^2}{\sqrt{a^2 - \rho^2}} \right) + \frac{q_{\text{ext}}}{a^{3/2}} \arctan \frac{a}{z_0} \right)

In Figure 34 (top), we show the charge distributions on a neutral disk induced by an external point charge positioned at two different distances above the disk center (\( \rho = 0 \)). The closer the point charge is to the disk plane, the more negative image charge the disk develops beneath it. The induced charge density diverges at the disk edges \( \sigma(\rho) \sim 1/\sqrt{a^2 - \rho^2} \). Given the disk neutrality, we have \( q = 2\pi \int_0^a \rho \sigma(\rho) \, d\rho = 0 \).
Figure 34. (top) Induced image charge densities on a neutral disk for two axial positions $z = 0.3a$, and $z = 0.5a$ of an external point charge. (bottom) Induced charge density on a neutral disk for a point charge positioned above a disk at $\rho = 0.5\, a$, and $z = 0.5\, a$. 
To find a general solution for the potential induced by a point charge in an off-axis position above the disk, we need to solve a Poisson equation with Dirichlet boundary conditions. This leads to a pair of dual integral equations involving Fourier components $f_n(\rho)$ of the external potential, $V_{\text{ext}}(\rho, \phi) = \sum_{n=0}^{\infty} f_n(\rho) \cos(n(\phi + \alpha))$, calculated in the disk area. Then, the Fourier components of the potential created by the induced charge on the disk, $V_{n\sigma}(\rho, z)$, can be calculated from the integral equations for the unknown function $\Phi(k)$:

\[
V_{n\sigma}(\rho, z) = \int_0^{\infty} dk \Phi(k) e^{-k|z|} J_n(k\rho),
\]
\[
\int_0^{\infty} dk \Phi(k) J_n(k\rho) = f_n(\rho), \quad 0 \leq \rho \leq a,
\]
\[
\int_0^{\infty} dk \Phi(k) k J_n(k\rho) = 0, \quad a < \rho < \infty. \quad (6.7)
\]

Instead, we consider the Fourier components $\sigma_n(\rho)$ of the induced charge density, which can be obtained with the help of the Abel’s integral equation:

\[
\int_0^{\rho} u \sigma_n(u) \, du \int_0^{2\pi} \frac{\cos(n(\theta + \alpha))}{\sqrt{\rho^2 + u^2 - 2\rho u \cos(\theta + \phi)}} \, d\theta = f_n(\rho) \cos(n(\phi + \alpha)). \quad (6.8)
\]

Using Copson’s theorem [214], we can find that:

\[
\sigma_n(\rho) = -\frac{2}{\pi} \frac{d}{d\rho} \int_0^{\rho} \frac{t S_n(t)}{\sqrt{t^2 - \rho^2}} \, dt,
\]
\[
S_n(\rho) = \frac{1}{2\pi} \frac{1}{\rho^{2n}} \frac{d}{d\rho} \int_0^{\rho} \frac{t^{n+1} f_n(t)}{\sqrt{\rho^2 - t^2}} \, dt. \quad (6.9)
\]
Then, the induced charge density in the disk can be found as
\[
\sigma(\rho, \phi) = \sum_n \sigma_n(\rho) \cos(n(\phi + \alpha)).
\]

In Figure 34 (bottom), we show the induced surface charge density, \(\sigma(\rho, \phi)\), on a neutral disk for a point charge located at \(r = 0.5 a, z = 0.5 a\). We can clearly see the induced negative charge beneath the point charge. The charge distribution also diverges at the disk edge.

The resulting potential created by the induced surface charge density \(\sigma(\rho, \phi)\) has the form:

\[
V_\sigma(\rho, z) = \int_0^a \int_0^{2\pi} \frac{\sigma(u, \theta) u d\theta du}{\sqrt{z^2 + u^2 + \rho^2 - 2u\rho \cos(\theta)}}. 
\] (6.10)

A grounded disk in an external field (of a point charge) gains beside its polarization also a nonzero induced charge, \(q\) (integral of \(\sigma\)). To calculate the induced potential when the disk has a net charge \(Q\), we need to add a term \(\frac{1}{4\pi \alpha}(Q - q)/\sqrt{a^2 - \rho^2}\) to \(\sigma(\rho, \phi)\) in Equation 6.10 (Kelvin’s formula for a total charge of \(Q - q\)).

One can easily find that \(V_\sigma(\rho, z)\) has a short-range asymptotic behavior \(-\frac{a}{\rho^2}|_{z=0, \rho \to \infty}\) (grounded disk), \(-\frac{a^3}{\rho^4}|_{z=0, \rho \to \infty}\) and \(-\frac{a^5}{z^6}|_{\rho=0, z \to \infty}\) (neutral disk). Therefore, \(V_\sigma(\rho, z)\) cannot support the formation of states localized outside the disk. To support such states, the long-range asymptotes should have a Coulombic character as well. Therefore, in the remaining calculations, we consider a metal disk (radius \(a = 1\) nm) bearing a charge of \(Q = |e|\), which can provide the necessary long-range asymptotic behavior.

6.3.3 One-electron 1D diskoid-like states

To capture the main features of the diskoid states, we consider first a quasi-1D motion of an electron in the plane \((z = 0)\) of the charged polarizable disk, using the potential obtained
Figure 35. (top) Effective potentials $U(\rho, z = 0)$ formed in the disk plane for different angular momenta quantum numbers. (bottom) The lowest two states of an electron ($l = 8$) formed in the effective potential $U$.

in the previous section. The Schrödinger equation for the radial part $R(x) = f(x)/\sqrt{x}$ of the wavefunction is ($x = \rho/a$):

$$-rac{\partial^2 f}{\partial x^2} + \left(\frac{l^2}{x^2} - \frac{1}{4} + \frac{1}{\epsilon} V_{a,z=0}(x)\right)f = \frac{E}{\epsilon} f,$$

(6.11)

where $\epsilon = \frac{\hbar^2}{2ma^2} = 38.1$ meV and $V_{a,z=0}$ is the total electrostatic potential in the disk plane.

In Figure 35 (top), we show the effective potentials, $U$, formed in Equation 6.11 by the attractive Coulombic and repulsive centrifugal terms. For $l \geq l_{\text{min}} = 8$, the potentials develop local wells, with minima rapidly shifting outwards with increasing $l$. For example, $\rho_{\text{min}} = 3.67a$.
for \( l = 9 \). In Figure 35 (bottom), we also show the ground \( n = 1 \) and the first excited \( n = 2 \) states for \( l = 8 \), with an energy difference of \( \Delta \varepsilon \approx 0.004 \) eV. To disclose the role of polarization in the formation of these extended states, we calculate the states when the disk polarization is removed. In this case, \( l_{\text{min}} = 5 \) and the effective potential has a minimum at \( \rho_{\text{min}} = 2.4a \), in contrast to \( \rho_{\text{min}} = 2.9a \) \( (l_{\text{min}} = 8) \) for the conducting disk. These results are similar to those for tubular image states [190–192].

### 6.3.4 One-electron 2D diskoid-like states

Next, we find the full solution of the diskoid-like system described by the 2D Schrödinger equation \( (x = \rho/a, y = z/a) \):

\[
- \frac{\partial^2 f}{\partial x^2} - \frac{\partial^2 f}{\partial y^2} + \left( \frac{l^2 - 1/4}{x^2} + \frac{1}{\varepsilon} V_a(x, y) \right) f = \frac{E}{\varepsilon} f. \tag{6.12}
\]

The energy factor is \( \varepsilon = \hbar^2 / 2m_e a^2 \) and \( V_a(x, y) \) is the 2D induced electrostatic potential. We solve Equation 6.12 using a finite difference method with the Hamiltonian matrix defined in a 2D square lattice with \((i, j)\) nodes:

\[
[\hat{H} R]_{x=i \Delta, y=j \Delta} = (V_{ij} + 4t) R_{ij} - t(R_{i+1,j} + R_{i-1,j} + R_{i,j+1} + R_{i,j-1}). \tag{6.13}
\]

Here, only the nearest neighbors are taken into account and \( t = \frac{\hbar^2}{2m_e a^2} \) is a “hopping” parameter. The effective potential \( U_a(x, y) \) has singularities at \( 0 \leq \rho < a, z = 0 \) and \( \rho = a, z = 0 \).
Figure 36. The effective potential of a charged disk \((a = 1\text{nm})\) for \(l = 6, 8, 9\) and 10. The black dashed line marks \(U(\rho, z) = 0\). The red area is the repulsion centrifugal wall. Disk area is shown in black.

In Figure 36, we show the effective potentials for different \(l\), where two distinct types of potential wells are seen to form. For \(l \leq 7\), the effective potentials develop local minima in the vicinity of the disk edges. An electron orbiting in states localized in these local minima overlap with the disk and easily fall onto its surface. At \(l \geq 8\), the competition between a long-range Coulombic attraction \((\sim -\frac{1}{\rho})\) and a centrifugal repulsion \((\sim \frac{1}{\rho^2})\) leads to the formation of an additional minimum (arrow) at \(\rho > 3a\) and \(-3a < z < 3a\), where an electron can only cause a negligible polarization of the disk. The formed potential wells are 0.085, 0.368, and 0.915 eV deep (along the path \(\rho, z = 0\)) for the \(l = 8, 9\) and 10 states, respectively. In Figure 37, we show one of the states \((l = 8)\) formed in these wells obtained in the one-electron approximation for a charged and polarizable disk. It has one node in each \((\rho\) and \(z\)\) direction.

In Table III, we summarize the energies of these diskoid-like states. Each state is characterized by a pair of quantum numbers \(n_\rho\) and \(n_z\). The calculations show that the binding energies
Figure 37. The contour plot for the diskoid state $|1, 1\rangle$ with $l = 8$ of a charged disk. Disk is shown by the red line $z/a = 0, \rho/a = 0 – 1$ middle left.

are approximately twenty to eighty times larger those of tubular image states [192]. At higher $l$ the states change their order.

We would also like to briefly explain the connection between the many-electron and one-electron diskoid-like states, discussed above. In principle, one could find highly excited many-electron (not just two-electron) wavefunctions of metallic nanodisks. In such states, the position of one of the electrons can be fixed and the rest of the many-electron wavefunction can be used to construct a one-electron density matrix. Then, one could find that as the position of the fixed electron is moved away from the disk axis, the density matrix produces electron densities similar to that in Figure 34 (bottom). This does not mean that hole is dynamically pursuing the
TABLE III. Energy spectrum of diskoid-like states (meV)

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In this chapter, we have studied extended diskoid-like states present in highly polarizable molecular or metallic nanosystems. We have studied the electron correlations and other properties in model two-electron diskoid states. Unique and complex correlations were revealed even in highly extended states, where the involved electrons are significantly separated. Mean-field and semiclassical solutions have also been discussed and compared to the correlated many-electron solutions. The diskoid-like states are of high fundamental and practical interest due to many existing nanoscale systems in which related states could be observed and applied.
CHAPTER 7

CLUSTERS AND LATTICES OF PARTICLES STABILIZED BY DIPOLAR COUPLING

In this chapter, we model stabilization of clusters and lattices of spherical particles with dominant electric and magnetic dipolar coupling, and weak van der Waals coupling. Our analytical results demonstrate that dipolar coupling can stabilize nanoparticle clusters with planar, tubular, Möbius, and other arrangements. We also explain for which parameters the nanoparticles can form lattices with fcc, hcp, sh, sc, and other types of packing. Although these results are valid at different scales, we illustrate that realistic magnetic and semiconducting nanoparticles need to have certain minimum sizes to stabilize at room temperature into nanostructures controlled by dipolar coupling.

This research was initially started by Mr. Wai-Yip Lo. However, I conducted by myself and performed all of the simulations and analysis. The following contents are reproduced with permission from ACS Nano, (6), 6083, 2011. Copyright (2012) American Chemical Society (see appendix).

7.1 Introduction

In recent years, colloidal nanoparticles (NP) of different materials [215, 216], shapes [217–220], and ligations [221–224] have been self-assembled into superlattices with many types of packing [225–236]. It is crucial to understand the principles underlying their self-assembly [237]
to predict and control the structures formed [238]. The interparticle forces that lead to these structures originate in the bulk and surface characteristics of the colloidal NPs [222, 239–242]. When the bulk forces dominate in the NP self-assembly, we might describe them by averaged force-fields acting between the NPs [235, 243–248]. Otherwise, we need to model the NPs atomistically and pay attention to their ligands [249].

Among the many prepared systems, clusters and lattices of NPs stabilized by coupled electric [244, 248, 250] and magnetic [251–254] dipoles have been observed. It turns out that the type of structures formed depends on the number of particles and the relative strength of the anisotropic dipole-dipole coupling and the isotropic van der Waals (vdW) coupling. If the relative strength of coupling is fixed and the number of particles is increased, the Stockmayer model predicts the formation of perfect icosahedra, entangled knots, linear chains, and planar rings [255]. On substrates, colloidal magnetic NPs (MNPs) at low densities were seen to form lines and rings, while at high densities, they form chains and band-like aggregates [256–259].

The types of lattices stabilized should depend on the strength of dipolar coupling. At weak dipolar coupling, the vdW coupling dominates and leads to closed-packed fcc and hcp lattices [236, 248, 260–262]. As the strength of dipolar coupling increases, the dipoles can form ordered structures at room temperature [228, 263]. At large (dominant) dipolar coupling, the vdW coupling becomes irrelevant. Then, one should observe the formation of lattices with looser arrangement of NPs, such as simple hexagonal (sh) lattices of PbSe semiconducting NPs with electric dipoles [248] or nearly close-packed assemblies of Co nanocrystals and Rh₄H₂ atomic magnetic clusters [228, 264]. The stabilization conditions of particle clusters might also depend
on the substrate used for their deposition [265]. Various intricate spatial spin configurations were predicted to exist in ultra-thin films, such as the presence of magnetic vortices [266]. The question is if such complex dipolar arrangements can also be prepared in NP systems.

In this work, we systematically investigate clusters and lattices stabilized by electric or magnetic dipolar coupling of their particle constituents. Despite the formal similarity of NPs with electric and magnetic coupling, the absence of magnetic monopoles make them rather different [248, 267]. Typically, the self-assembly of colloidal NPs with electric dipoles can be largely influenced by screening in ionic solutions. On the other hand, magnetic dipolar interactions are relatively weak, but less spatially limited, due to lack of magnetic screening. MNPs can also have more complex coupling, since they interact at different length scales by dipole-dipole, magnetic anisotropy, and exchange mechanisms [221, 268–271]. The atomic exchange interaction acts at the length scale of 10 nm [256, 272], which is about the size of MPs for which this coupling matters [273]. The magnetic anisotropy and the MNP-shape are also important factors guiding the self-assembly [274]. However, magnetic anisotropy is of less relevance for freely rotating MPs. Thus, dipolar coupling dominates in the formation of structures with 10 – 100 nm MPs [275–280], with rich potential applications [281].
7.2 Computational methods

We will calculate the energies of assembled particles with dipolar coupling in different clusters and lattices. The dipole-dipole interaction energy between the $i$ and $j$ particles located at the $\vec{x}_i$ and $\vec{x}_j$ positions, and having the dipoles $\vec{\mu}_i$ and $\vec{\mu}_j$, respectively, is:

$$W_{ij} = \frac{\vec{\mu}_i \cdot \vec{\mu}_j - 3 (\vec{n}_{ij} \cdot \vec{\mu}_i)(\vec{n}_{ij} \cdot \vec{\mu}_j)}{|\vec{x}_i - \vec{x}_j|^3} = \Lambda_{m(e)} w_{ij}, \quad (7.1)$$

where $\vec{n}_{ij}$ is a unit vector in the $\vec{x}_i - \vec{x}_j$ direction. We can rewrite $W_{ij}$ as a product of the unitless geometric factor, $w_{ij}$, and the effective magnetic and electric dipole-dipole interaction strengths, $\Lambda_m = \mu_0 \mu_m^2 / 4\pi d^3$ and $\Lambda_e = \mu_e^2 / 4\pi \varepsilon_0 d^3$, respectively. Here, $\mu_{m(e)}$ is the magnitude of the magnetic (electric) dipole moment, $\mu_0$ is the magnetic permeability of vacuum, $\varepsilon_0$ is the dielectric constant for vacuum, and $d$ is the particle diameter.

The dipole moment of a spherical particle with homogeneous magnetization $m_s$ per unit volume or $\rho_s$ electric dipolar density is given by:

$$\mu_m = \frac{\pi}{6} d^3 m_s, \quad \mu_e = \frac{\pi}{6} d^3 \rho_s. \quad (7.2)$$

In our energy calculations, we will use the local dipole approximation, where we replace the material by point dipoles of the size, $\mu_{m(e)}$, located in the particle center. If its size scales as $d \rightarrow \alpha d$, the binding energy scales as $W \rightarrow \alpha^3 W$. This allows us to estimate the minimal size of the particles that form systems stable at room temperature.
In the following, we consider different dipolar and lattice arrangements with $N$ particles and calculate their total binding energies:

$$E_{tot} = \sum_i \sum_{j>i} W_{ij} = \Lambda_m(\varepsilon),$$
$$\varepsilon = \sum_i \sum_{j>i} w_{ij} = \sum_i \varepsilon_i = \varepsilon N . \quad (7.3)$$

We find the relative stability of different particle assemblies by evaluating the average energy factor per particle, $\varepsilon$, and disregard entropic effects.

The model in Equation 7.3 describes anisotropic dipole-dipole coupling between spherical particles. When the dipolar coupling is strong, such as in Co nanocrystals [228] and ionic colloidal microparticles [282], this coupling alone can determine the lattice structure. If other interparticle coupling mechanisms are relevant they can be added in the model as well [249]. Here, we estimate the effect of isotropic vdW interactions between the spherical particles using the formula [245, 283]:

$$W_{ij}^{vdW} = -\frac{A}{12} \left( \frac{R}{d_{ij}(1 + d_{ij}/4R)} + \frac{1}{1 + d_{ij}/R + d_{ij}^2/4R^2} + 2 \ln \left( \frac{d_{ij}(1 + d_{ij}/4R)}{R(1 + d_{ij}/R + d_{ij}^2/4R^2)} \right) \right). \quad (7.4)$$

Here, $R$ is the particle radius, $d_{ij}$ is the distance between the $i$th and $j$th nanoparticles, and $A$ is the Hamaker constant.
At finite temperatures, the stability of different particle arrangements (phases) is determined by their free energies. To find out which of the (two) possible phases is more stable at a given temperature $T$ and pressure $P$, we can evaluate the change of the Gibbs free energy associated with the transition between the arrangements, $\Delta G = \Delta U + P\Delta V - T\Delta S$, where $U$ is the potential energy ($E$ in Equation 7.3), $V$ the volume, and $S$ the entropy of each arrangement.

### 7.3 Results and discussion

#### 7.3.1 Planar arrangements of dipolar particles

Recently, superlattices of spherical colloidal PbSe NPs were observed to form loose $sh$ packing on conductive substrates, and explained by vertical antiferroelectric dipolar ordering [248]. However, the proposed dipolar organizations may not be the most stable. Moreover, other dipolar planar structures might allow stabilization of NPs with different lattice arrangements. We study planar systems with different dipolar and lattice structures, compare their energies using Equation 7.3, and check their stabilization with large magnetic particles (see Figure 44).

Magnetic structures with closed fluxes, such as rings and other more complex arrangements, tend to be highly stable [263,267,272,284,285]. Therefore, we will investigate first planar clusters and lattices with closed fluxes. In Figure 38 (top), we show closed-flux clusters which contain $M$ circumcircles of dipoles oriented along a tangent to the circumcircle. The central dipole points up or down. Even though we do not optimize the dipole orientations, the closed flux guarantees that their orientations are almost correct (for plaques of 2 and higher circumcircles.
Figure 38. Honeycomb plaques of different sizes and orientation of dipoles, where $M$ is the number of circumcircles.

the dipoles should not be exactly tangential). The clusters have a non-zero quadrupole moment and belong to the 6/mmm magnetic group symmetry.

Upon evaluation of the energy factor $\bar{\varepsilon}$ for the clusters in Figure 38 (top), we found that it is almost independent on $M$ and approaches $\bar{\varepsilon} \to -2.7$. In an infinite chain of NPs with a head-to-tail orientation of dipoles, we obtain the asymptotic dependence of $\bar{\varepsilon}(N) = -2 \left( \zeta(3) - \frac{\pi^2}{6N} \right) \to -2.404$, where $\zeta(x)$ is the Zeta function. It is useful to estimate at which sizes of NP the clusters in Figure 38 (top) are stable at room temperature, i.e., $\Lambda \bar{\varepsilon} \approx 10$ kT. For the saturation magnetization of $m_s = 425$ kA m$^{-1}$ in cobalt ferrite MNPs [209, 257, 286], we obtain $d_{\text{crit}} =$
Figure 39. Stable configurations of particles and dipoles in two parallel plaques. (left) The simple hexagonal lattice with dipoles circulating in opposite directions in adjacent layers. (right) The hexagonal close-packed lattice with dipoles circulating in the same directions in the layers. Top views and side views are given.

13.31, 11.97, 11.55 nm, while for CdSe NPs with the uniform dipolar density $\rho_s = 3.265 \times 10^{-3}$ C m$^{-2}$, we get $d_{crit} = 9.61, 8.62, 8.34$ nm ($M = 1, 3, \infty$) [287].

### 7.3.2 Multilayers of honeycomb plaques

Next, we study multilayers of coupled honeycomb plaques. In Figure 39, we show two stable arrangements of honeycomb plaques placed on the top of each other. The total dipole-dipole interaction energies per particle of these clusters are summarized in Table IV. It is very interesting that when the dipoles are oriented in the same way within the layers, they tend to get closer and form the $hcp$ ($fcc$) lattice, while if they are oriented in the opposite way, they tend to be further away and form the $sh$ lattice. Moreover, the stability of these clusters depends on the size of the plaques. When the number of circumcircles exceeds 4, the
hcp lattice becomes more stable than the sh lattice. This dipole organization might explain the experimentally observed lattices [248].

<table>
<thead>
<tr>
<th>layers</th>
<th>1 (7)</th>
<th>2 (19)</th>
<th>3 (37)</th>
<th>4 (61)</th>
</tr>
</thead>
<tbody>
<tr>
<td>orient.</td>
<td>sh</td>
<td>hcp</td>
<td>sh</td>
<td>hcp</td>
</tr>
<tr>
<td>1</td>
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<td>-1.81</td>
<td>-1.91</td>
<td>-2.26</td>
<td>-2.39</td>
</tr>
<tr>
<td>oppos.</td>
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<td>-1.81</td>
<td>-2.41</td>
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</tr>
<tr>
<td>alt.</td>
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</tr>
<tr>
<td>4</td>
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<td>-2.25</td>
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<tr>
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<td>-2.13</td>
<td>-1.79</td>
<td>-2.48</td>
<td>-2.20</td>
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</tbody>
</table>

TABLE IV. The energy factor per particle, $\bar{\varepsilon}$, in multiple layers of identical honeycomb plaques with different orientations of dipoles. (top) The horizontally arranged numbers show the circumcircles (particles) in these clusters. (side) The numbers (1-4) gives the number of layers and the mutual dipole orientation in the neighboring layers. The bold numbers show dipole orientations with minimal energies.

It is also of interest to find out when the looser sh structure, stabilized here by the anisotropic dipole-dipole coupling, becomes destabilized by the isotropic vdW coupling between the particles to the extent that the structure switches to the hcp lattice arrangement. We briefly study the transition between the hcp and sh configurations in the double layer of honeycomb plaques ($M = 1, 3$) with the opposite direction of dipoles in each layer. We combine Equation 7.3- Equation 7.4 to evaluate the total energy of the two arrangements as a function of the particle radius $R$ and the saturation magnetization $m_s$ (strength of dipolar coupling). We use this energy ($U$) to evaluate the difference of the Gibbs free energy of the two phases, $\Delta G$, where their
entropy is approximated by the values obtained in bulk lattices (see below) and the pressure term $P\Delta V$ is neglected.

Figure 40. The phase diagram for magnetic NPs with a bulk vdW coupling plotted as a function of the NP-radius, $R_{NP}$, and the saturation magnetization, $m_s$. The NPs are arranged in two plaques with $M = 1$ and 3 circumferences and opposite orientations of dipole moments, which are positioned on the top of each other in the hcp and sh configurations. The solid lines represent the hcp/sh phase boundary of touching NPs, while the dashed lines give the phase boundary for NPs with the minimum separation of 1 nm (surfactants). When the temperature is raised to $T = 298$ K, the hcp/sh phase boundary shifts towards larger $m_s$ and $R_{NP}$ (stronger coupling), since the hcp configuration has a larger entropy.

In Figure 40, we present the phase diagram of the two plaques calculated from $\Delta G$, where the vdW coupling is characterized by the average Hamaker constant (metals) of $A = 2.38$ eV [288]. At zero temperature, the hcp configuration dominates (lower $E$) when the particle
radius $R$ or magnetization $m_s$ are small, whereas the $sh$ configuration prevails elsewhere. At larger plaques, the $hcp$ arrangement becomes stable at larger $R$ and $m_s$. To roughly simulate the presence of surfactants on the particles [249], we also show by the dashed lines the results obtained for looser structures, where the distance between adjacent spherical particles is 1 nm. At higher temperatures, the larger entropy of the $hcp$ configuration becomes significant, causing the phase transition to shift towards particles with larger $R$ and $m_s$ (larger coupling).

In our calculation of $\Delta G_{sh\rightarrow hcp}$, we have estimated the entropy for the $sh$ and $hcp$ arrangements using the known bulk values (per particle) in hard sphere crystals [67, 289–291], and replacing for simplicity $\Delta S_{sh\rightarrow hcp} \rightarrow -\Delta S_{fcc\rightarrow hcp} \approx 0.001 k$ per particle. Using the enthalpy differences obtained in our systems, $\Delta H_{fcc\rightarrow hcp}$, and starting at $T = 0$ K in the $sh$ phase in the phase diagram from Figure 40, we can find the critical NP size that would keep the system in this phase at a given temperature. At room temperature, the NPs with $m_s = 425$ kA m$^{-1}$ must have the diameter $d > 5.2$, 5.8 nm for the plaques $M = 1$, 3, respectively, to prevent the transition to the more entropic $hcp$ arrangement. For $d = 10$ nm, the enthalpy is already ten times larger than the entropic term. If the vdW coupling is neglected, we can find that the critical size of NPs scales with temperature as $d_{min} \sim \sqrt{T}$.

We can extend the stability analysis to systems with honeycomb plaques of antiferromagnetic (electric) vertical (AV) and horizontal (AH) orientation of dipoles, shown in Figure 38 (bottom) [248]. Our results in Table V show that these dipolar open-flux arrangements are less stable than those discussed above, i.e., the total energy per particle is $\bar{\varepsilon}_{circ} < \bar{\varepsilon}_{AH} < \bar{\varepsilon}_{AV}$. A similar
situation holds for a double layer. We tested both \( sh \) and \( hcp \) lattices and found that the AH \( sh \) configuration is the most stable, while the AH \( hcp \) configuration is not stable.

<table>
<thead>
<tr>
<th>layers</th>
<th>circ.</th>
<th>1 (7)</th>
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<td>-1.72</td>
<td>-1.80</td>
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<tr>
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<td>-1.59</td>
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</tr>
<tr>
<td></td>
<td>AV, hcp</td>
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<td>-1.15</td>
<td>-1.21</td>
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</tr>
<tr>
<td></td>
<td>AH, sh</td>
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<td>-1.75</td>
<td>-1.86</td>
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</tr>
<tr>
<td>polarizable substrate</td>
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<td>-1.54</td>
<td>-1.59</td>
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<tr>
<td></td>
<td>AH</td>
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<td>-1.75</td>
<td>-1.86</td>
<td>-1.93</td>
</tr>
<tr>
<td></td>
<td>circular</td>
<td>-1.99</td>
<td>-2.41</td>
<td>-2.55</td>
<td>-2.62</td>
</tr>
</tbody>
</table>

TABLE V. The energy factors per particle, \( \bar{\varepsilon} \), in honeycomb plaques with different orientation of dipoles: antiferromagnetic (electric) vertical (AV), antiferromagnetic (electric) horizontal (AH) and circular. AV and AH double-layers with the \( sh \) and \( hcp \) lattices are considered. Bold numbers show the dipole orientations with a minimal energy.

We also calculate the energies of these clusters on an ideally polarizable substrate. Although the circular orientation of dipoles provides the largest coupling energy per particle, the AV structures gives the strongest binding to the substrate, as found experimentally [248]. Even though the clusters with circular orientation of dipoles stabilized on the surface have the largest total binding energy per particle, we need to deposit them on the substrate already assembled, since individual NPs deposited on the surface prefer the vertical orientation. Therefore, controlling the kinetics of self-assembly is important for the design of materials with tailored properties. The kinetics depends on the substrate polarizability, the speed of solvent evaporation, the speed of particle aggregation, and other factors. Strong NP attraction to the substrate may prevent relaxation of the formed structures, resulting in malformed aggregates [228, 292].
It is of interest to investigate how the energies of the double-layer systems change when the layers are rotated and translated with respect to each other. We examine first two identical honeycomb plaques with the same or opposite dipole circulations in the $sh$ configurations, and rotate them around the central particle. In Figure 41, we present the obtained potential energy profiles for different sizes of plaques. As the plaques rotate, they acquire intermediate states between $sh$ and $hcp$ lattices, some of which are locally stable. These configurations can be identified with the formation of the Moire pattern [293].

Figure 41. The potential energy per particle, $\bar{\varepsilon}$, in a double layer of honeycomb plaques of different sizes, rotated one with respect the other by the angle $\alpha$; $M = 1$ (up), $M = 2$ (middle), $M = 3$ (bottom). The $\alpha = 0$ angle corresponds to the $sh$ configuration. Solid and dashed curves correspond to the opposite and the same orientations of dipoles, respectively.
Figure 42. The total energy per particle (contour plot) of two systems of plaques shifted with respect to each other. In a) and b), we show the energy of equal-size plaques, $M = 1$, with dipoles circulating in the opposite (left) and (right) the same directions. In c) and d) the same is shown for plaques of different sizes, $M = 1$ and $M = 3$. The NP-diameter is chosen as the unit of shifts on the axes.

Next, we explore the potential energy profile as a function of a mutual shift of the two plaques. In Figure 42 (top and bottom), we visualize these profiles for two different systems. The first one is formed by two identical plaques ($M = 1$, Figure 38 (top)) sitting on top of each other, oriented in the same way, and mutually shifted in the common plane, while the distance between the plaques is constant. In the second system, the sizes of the two plaques are different ($M = 1$ and $M = 3$). The four insets show the potential energy when the plaques with the same (right) and opposite (left) circulations are shifted one with respect to the other (the coordinates are plotted in units of the particle diameter).
When the vertical axis of both plaques coincide, the plaques are in the \( sh \) configuration, corresponding to the \((0,0)\) center of coordinates in Figure 42 (a-d). This center is the most stable point for the opposite orientations of dipoles (left). For the same dipole orientation (right), the most stable configurations lie on the circle with the radius of \( r = 1/\sqrt{3} \), where we can find \( hcp \) (\( fcc \)) arrangements, except for the slightly larger distance between the plaques. Once we leave the area close to the \((0,0)\) center, a number of small local minima can be observed, depending on the system size. The magnetic vortices in both plaques break the translational symmetry of these systems at any plaque size.

\textbf{7.3.3 Planar lattices built from particle plaques}

We continue to study periodic systems assembled from the above plaques. In Figure 43 (a, b), we show two plaques in two stable configurations, with the same and opposite circulations of dipoles at the particle boundaries as in Figure 39, respectively. In Table VI, we give the binding energies between plaques per particle at the boundary for two plaques of different sizes and dipole orientations (for example, the \( M = 3 \) plaques have 8 particles at their boundary); the same and opposite orientations of dipoles in neighboring plaques favor different boundaries. As the plaques become larger, the binding energy per particle at the boundary should saturate.

We also extend this plaque binding to lattices. In Figure 43 (c, d), we show the lattices formed of \( M = 1 \) and \( M = 3 \) hexagonal plaques having the \textit{same} (s) and \textit{opposite} (o) circulations. When the magnetic fluxes circulate in the same direction, the plaque is the elementary cell of the 2D crystal. In this case, the \textit{s}-type junctions allow the formation of structures without vacancies. On the other hand, when the plaques are connected with the \textit{o}-type junctions,
Figure 43. Two plaques connected by a) the s-type junction and b) the o-type junction. Lattices of connected plaques: c) 19 plaques of $M = 1$ plaques assembled with the s-type junctions, d) 7 plaques of $M = 3$ plaques assembled with the s-type junctions, e) 9 plaques of $M = 1$ plaques assembled by the o-type junctions, f) 9 plaques of $M = 2$ plaques assembled with the o-type junctions.

as in Figure 43 (e, f), their magnetic fluxes circulate in alternating directions, so the elementary cell is formed by 4 neighboring plaques. the same-type junctions. The o-type junctions lead to lattices with (periodic) vacancies. One can also imagine 2D lattices with combined s and o-types of junctions. Some of them tend to form partially corrugated lattices.
TABLE VI. Binding energies between honeycomb plaques calculated per particle at the boundary. Different sizes and mutual orientation of circulating dipoles are considered (same/opp. = dipolar circulation of neighboring plaques).

<table>
<thead>
<tr>
<th>circ.</th>
<th>1 (7)</th>
<th>2 (19)</th>
<th>3 (37)</th>
<th>4 (61)</th>
</tr>
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<tbody>
<tr>
<td>orient.</td>
<td>same</td>
<td>opp.</td>
<td>same</td>
<td>opp.</td>
</tr>
<tr>
<td>$\bar{E}_{\text{boundary}}$</td>
<td>-0.24</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

7.3.4 Tubular arrangements of dipolar particles

Particles with dipolar coupling can also form various tubular structures, which can be assembled into lattices. Typically, tubular structures can form rings, where the dipoles circulate around the circumference. Again, these rings can be connected with the $s$ and $o$-type junctions, as shown in Figure 44 (a, b). The dipoles circulate in the directions shown in Figure 44 (i, j).

Other more exotic structures can also be formed. For example, we can assemble chiral tubular structures of dipolar particles, observed experimentally [294]. These helices can have different pitch, which can be equal integer numbers for the $s$-type junctions, as shown in Figure 44 (f, k), and even numbers for the $o$-type junctions, as shown in Figure 44 (g). The $s$-type tubular structures have nonzero fluxes oriented along their axes, proportional to the pitch, while the $o$-type structures have almost zero fluxes. One can even form knots based on a right-handed or a left-handed Möbius strip with the $s$ and $o$-type junctions, as depicted in Figure 44 (c). The dipolar particles might also be stabilized to form conical structures, as illustrated in Figure 44 (d). The dipoles circulate in a uniform direction spirally around the cone, similar to that of the close-packed chiral nanotube.
Figure 44. Magnetic particles arranged in a variety of structures: a) tube with close-packing lattice, b) tube with simple cubic packing lattice, c) Möbius strip, d) conical close-packing structure, e) simple cubic lattice, f) chiral tube with close-packing structure with parallel circulation of dipoles, g) chiral tube simple cubic packing structure with anti-parallel dipolar circulation, h) hollow icosahedral structure, i) close-packing tube, j) simple tube, and k) chiral tube with close-packing structure with the circulation of dipoles shown.

Apart from planar and tubular structures, other stable structures can be assembled from dipolar particles. In Figure 44 (e), we show a simple cubic crystallite. Within each layer of the lattice, the dipoles in each chain are antiparallel to the neighboring chains, as well as to those in the layers above or below it. The stabilization takes place in a similar way as in the structures discussed before. In Figure 44 (h), we also show a hollow icosahedral structure, which is formed
by hexagons and pentagons, with closed magnetic fluxes. The direction of dipole circulation in each face is the same, which makes the structure chiral.

7.4 Conclusion

We have described a rich spectrum of clusters and lattices that can be stabilized from particles with electric and magnetic dipole-dipole coupling. The dipolar coupling between large particles should be strong enough to control both their dipolar and lattice structures. We showed in a phase diagram the effect of inter-particle vdW coupling and entropic effects associated with different lattice arrangements stabilized at finite temperatures. The obtained results can provide guidance for the self-assembly of unique structures at different scales, but their formation might require careful control of the particle kinetics. The assembled particles can have applications as new materials for electronics, magnetism, and optics.
8.1 Introduction

Nanoscale particles often self-assemble into superstructures with unique spatial arrangements that are difficult to predict \textit{a priori}, based on the nature of their building blocks [159, 243, 295–301]. An important issue in the stabilization of such hierarchically self-assembled materials is a tight competition between forces of comparable magnitudes, originating in van der Waals (vdW), Coulombic, magnetic, and other types of particles interactions [242]. Although the structures of some systems are dominated by forces of a common origin, such as electrostatic interactions that govern the formation of open-lattice assemblies of peptide filaments [299] or colloidal crystals with a diamond-like lattice [296], it is typically the interplay between various nanoscale forces that leads to the formation of highly complex materials, such as nanocrystal superlattices exhibiting polymorphism [302, 303].

Self-assembly of nanoparticles by competing forces can result in truly unique structures, the diversity and complexity of which could be particularly striking if the building blocks were simultaneously coupled by short- and long-range forces of different symmetries. Such frustration could arise in ensembles of magnetic nanocrystals (NCs) whose axes of preferential magnetization (the so-called “easy” axes) do not correspond to any of the directions favoring close
packing. In the case of magnetite - the most abundant magnetic material on the Earth, also present inside multiple living organisms in the form of NCs [304] this condition is best fulfilled by cubic-shaped particles, whose easy axes (the [111] crystallographic direction) connect two diagonally opposite corners of each cube. However, despite the wealth of research on both natural and synthetic magnetite nanocubes, no complex superstructures resulting from the competition between the shape anisotropy (favoring face-to-face interactions) and the magnetocrystalline anisotropy (favoring corner-to-corner interactions) have been reported [305, 306].

In this research project, we investigate the self-assembly of magnetite NCs at the liquid-air interface in the presence of external magnetic fields. We study experimentally and computationally the self-assembly of magnetite NCs at different density regimes and identify different types of self-assembled superstructures, including unprecedented helical assemblies.

This is a collaborative research project with the Dr. Rafal Klajn’s group at the Department of Organic Chemistry in the Weizmann Institute of Science. The preparation of the samples, conduction of experiments were performed by Prof. Rafal Klajn’s group. Mr. Nikita Repnin and I derived all the equations describing the magnetite nanocubes motion in the external magnetic field. I performed all the semi-analytical modeling of stability of systems of few nanocubes. The Monte Carlo simulations were performed by Mr. Henry Chan. The results of simulations were analyzed by myself, Nikita Repnin, and Henry Chan.

The paper “Self-Assembly of Magnetite Nanocubes into Helical Superstructures” by G. Singh et al. has been submitted to Science.
8.2 Experimental results and discussion

8.2.1 Experimental setup and synthesis of magnetite nanocubes

The experimental setup is shown in Figure 45 A. Briefly, a drop of hexane solution of relatively monodisperse magnetite nanocubes [307–309] (average edge length 13.4 nm, see Figure 45 B and Figure 46) containing excess oleic acid (OA) was placed at the diethylene glycol (DEG)-air interface [310, 311] in the presence of a magnetizing field (whose strength, $H$, was regulated in the range of 0 to 700 G), and the solvent was allowed to evaporate within ca. 10 min. Our NCs are in the superparamagnetic (SPM) size regime, i.e. the collective dipoles of individual particles thermally fluctuate, and the directions of the dipole moments are randomized. When the NCs are exposed to an external magnetic field, the collective dipoles become partially aligned with the field direction, which allows for the magnetic dipole-dipole coupling between the NCs. The resulting chains of single particles further aggregate as the solvent evaporates, ultimately giving rise to higher-order superstructures at the solvent-air interface, which can be transferred onto a substrate of choice (e.g., a carbon-coated copper grid or a silicon wafer) for further inspection (Figure 45 A).

In a typical experiment, a hexane solution of NCs ($V = 20 \mu$L; $c = 2.5$ mg/mL) containing oleic acid ($1.25 \mu$L/mL) was placed on the surface of diethylene glycol (DEG) (Aldrich, 99%) ($\sim2$ mL) inside a polyethylene well (diameter$\approx 2$ cm; height 1.8 cm) placed between two neodymium magnets. The well was covered with a glass slide and left undisturbed until hexane has evaporated (up to 30 min). A small amount ($\sim200 \mu$L) of acetonitrile was very carefully applied onto the surface of DEG thereby lifting the NP film from the DEG-air interface to
Figure 45. Self-assembly of one-dimensional nanocube belts. (A) Schematic representation of the experimental setup. (B) Low- and high-magnification TEM images of the building blocks, \( \sim 13 \text{ nm } \text{Fe}_3\text{O}_4 \) nanocubes. The [111], [110], and [100] crystallographic directions correspond to the easy, intermediate, and hard axes of magnetization, respectively. (C) Low- and high-magnification SEM images of belts_{100}. (D) Averaged orientations of dipoles in a nine-cube-wide belt_{100} in the presence of increasing magnetic fields. (E) Orientations of dipoles in belts_{100} of different widths and in a belt_{110} under a relatively weak external field (\( H = 167 \text{ G} \)). (F, G) Top- and side-views of belts_{110} by SEM.
acetonitrile-air interface. Finally, the NP film was then carefully transferred onto a desired substrate (silicon wafer, carbon-coated TEM grid, etc.).

\( \text{Fe}_3\text{O}_4 \) nanocubes (Figure 46) were prepared by thermal decomposition of iron (III) oleate in the presence of sodium oleate according to a modified literature procedure [307]. First, iron oleate was prepared as follows: iron (III) chloride hexahydrate (Alfa Aesar, 98%) (5.40 g; 19.98 mmol) and sodium oleate (TCI, > 97%) (18.25 g; 59.95 mmol) were placed in a 250 mL round-bottom flask containing 30 mL of distilled water, 70 mL of hexane, and 40 mL of ethanol. The mixture was vigorously stirred at \( T = 70^\circ \text{C} \) under nitrogen atmosphere for four hours. The dark red organic phase was collected with a separatory funnel, washed three times with distilled water, and dried over magnesium sulfate. The solvent was evaporated in vacuo at \( 50 - 60^\circ \text{C} \) to yield viscous, dark brown liquid. The product was kept frozen at \( T \approx 5^\circ \text{C} \).

As-prepared iron oleate (1.57 g; 1.75 mmol), sodium oleate (TCI, > 97%) (0.53 g; 1.74 mmol), and n-docosane (6.0 g; 19.32 mmol, Aldrich, 99%) were placed in a 50 mL round-bottom flask containing 11 mL of 1-octadecene (Aldrich, 90%). The reaction mixture was heated to 120°C to dissolve all solids, and kept under high vacuum for 40 minutes. The reaction mixture was then heated to \( T = 325^\circ \text{C} \) with a heating rate of 3°C/min under nitrogen atmosphere, and left at this temperature for 26 minutes with vigorous stirring. The heating source was then removed and the reaction mixture was cooled down to \( T = 80^\circ \text{C} \). Nanocrystals were precipitated upon the addition of a mixture composed of 2 volumes of n-hexane and 3 volumes of ethanol (with respect to the original solution volume). The clear supernatant was discarded and the solids were redispersed in n-hexane and re-precipitated with a small amount of methanol with the
help of a neodymium magnet. Re-precipitating with a magnet was repeated two more times. Finally, the solid product was dried under vacuum, and finally redispersed in toluene. Yield = 60-70 mg. The resulting nanocubes had an average side length, $d = 13.37$ nm.

![Image](image_url)

Figure 46. TEM and SEM (inset) images of Fe$_3$O$_4$ nanocubes at various magnifications. All TEM images shown in this manuscript were obtained on a Philips CM120 Super Twin microscope operating at 120 kV, unless noted otherwise.

8.2.2 Self-assembly of magnetite nanocubes at different surface concentration regimes

Experiments show that the nature of the observed superstructures strongly depends on the surface concentration of the particles. For concentrations corresponding to less than 20% of the monolayer coverage (or $\chi < 0.2$, where $\chi = 1$ corresponds to a densely packed monolayer of nanocubes coated with interpenetrating monolayers of oleic acid), no long-range or well-defined structures were found (see Figure 47). When $\chi$ reached $\sim 0.2$, however, NCs assembled into parallel arrays of one-dimensional belts with high aspect ratios (2-3 NCs across and as long as 100 $\mu$m, see Figure 45 C), oriented parallel to the applied field. Individual cubes
within these belts had their [100] crystallographic axes oriented parallel to the long axes of the belts (Figure 45 C, inset). We refer to these assemblies as belts_{100}. This arrangement of the building blocks maximizes the cube-cube contact within the assemblies, i.e., the assemblies are dominated by the shape anisotropy of the particles. The widths of these belts grew with increasing $\chi$ and decreasing $H$ values.

Figure 47. SEM images of structures obtained from Fe$_3$O$_4$ nanocubes under a sub-monolayer ($\chi = \sim 0.2$) surface concentration of the particles. All SEM images shown in this manuscript were obtained on a SUPRA 55VP field-emission SEM (Carl Zeiss Microscopy, LLC), or on an ULTRA 55 field-emission SEM (Carl Zeiss Microscopy, LLC, both operating at 5 kV.

It is important to emphasize the critical role of OA in the formation of the highly ordered superstructures reported here. We found that in its absence under otherwise identical conditions, the resulting assemblies were shorter and irregular, similar to those reported previously [312, 313]. As a non-solvent for our NCs [314], OA induces attractive vdw [314] and/or depletion [315] interactions between the NC as hexane (the “good solvent”) gradually evaporates. In pure hexane, no attractive interactions beyond the magnetic dipole-dipole forces are induced until the volume fraction of the NCs is very high at which point aggregation commences
rapidly, giving rise to ill-defined assemblies, as confirmed by our control experiments. Because of the high boiling point (360 °C) of OA, the belts that formed were embedded in a thin film of OA (see Figure 48) and, interestingly, their structure could further be manipulated. Figure 49 A shows ensembles of belts wrapped together with their OA matrix. At the same time, the OA layer could be dissolved in methanol to leave behind OA-free belts on a solid substrate.

![Figure 48. TEM images of chains of cubic magnetite NCs formed by applying an external magnetic field to a solution of NCs. The samples were prepared by rapid evaporation the solvent (hexane) from the TEM grid in the presence of a magnetic field.](image)

In all experiments, the belt’s long axis followed the lines of the applied magnetic field. Consequently, we could induce the growth of belts tilted with respect to the liquid-air interface by modifying the direction of the applied magnetic field. In the presence of a field directed perpendicular to the liquid-air interface, the NCs assembled into arrays of pillars. Similar to the belts parallel to the interface, individual pillars repelled one another in the presence of the magnetic field, which resulted in their near-perfect hexagonal close packing.

As the surface concentration of NCs further grows and $\chi \in (1, 1.5)$, the structures made of NCs with their [110] axes parallel to the field direction (so called belt$_{110}$) were observed (see
Figure 45 F, G). These belt$_{110}$ are thicker which leads to the significant decoupling of magnetic dipoles from the external field due to the large induced field inside the structures. In this case, new arrangements are less favorable from the vDW interaction point of view (the belts are bound by corrugated sides). However, the magnetization along the [110] direction (“the intermediate” axis) occurs more easily than along the [100] axis $[316,317]$. Therefore, the MA takes over, leading to a new type of observed structures.

The most striking manifestation of this trend was observed at $\chi >\sim 1.5$, where the nanocubes tend to orient their [111] axes, the “easy” axes of magnetization along the magnetic field lines. As a consequence of this arrangement, the belts spontaneously fold, giving rise to single-stranded helices (see Figure 49 A). Similar to the belts discussed above, the helices are evenly spaced and spanned long distances of up to several hundred micrometers (see Figure 49 B). Interestingly, individual single-stranded helices tended to wrap around each other to form double- (Figure 49 D, E, Figure 50) or even triple- (Figure 49 F) stranded helices.

The relatively thin helices prepared at $1.5 < \chi < 2.0$ comprised equal populations of intermixed left- and right-handed structures (see a right-handed helix (top) neighboring a left-handed one (bottom) in Figure 49 A), all oriented parallel to the applied field. At higher ($\chi > 2.0$) coverages, however, long axes of the helices were tilted with respect to the external field, with the tilt increasing with increasing $\chi$ values. At the same time, we observed that the helices were mostly of the same handedness (e.g., Figure 49 E). The experiment shows the formation of ill-defined assemblies comprising both right- and left-handed helices (see Figure 49 F, G). These two types of helices assumed different directions, oriented at angles $+\theta$ and $-\theta$ with respect
Figure 49. Self-assembly of helical nanocrystal superstructures. (A) TEM image of individual single-stranded helices. (B) SEM image of a large array of single-stranded helices. (C) Snapshots from Monte Carlo simulations of a one-dimensional belt folding into a helix. (D) SEM image of a well-defined double helix. Inset shows a TEM image of two belts wrapping around each other. (E) SEM image of an array of double helices. Blue arrows show the direction of the applied magnetic field. (F) An array of triple helices and (inset) the end of a triple helix. (G) SEM image showing self-healing of double helices ("chirality self-correction"). Yellow and red arrows indicate sites of chirality inversion. (H) Collective switching of chirality. Gray and green colors indicate patches of right- and left-handed helices, respectively.
to the external magnetic field. However, to maximize packing within a given area, all the NC assemblies should be oriented in the same direction. Therefore, they should all assume the same handedness. We found that there was no intrinsic preference for helices of either handedness. Each experiment began with the nucleation of either right- or left-handed helices with equal probabilities. As the assembly progressed from one side of the dish to the other, however, the chirality of pre-formed helices determined those of their neighbor, and this process continued to yield large (up to 1 mm$^2$) patches (domains) of enantiopure helices.

However, defects were occasionally observed. In Figure 49 G, the red arrows in the ensemble of right-handed helices point to sites where chirality inversion took place, giving rise to segments
of left-handed structures. It is worth noting that segments of the “wrong” chirality were relatively short. The tendency to maximize packing leads the helices to “correct” their chirality, as denoted by the yellow arrows in Figure 49 G. In rare cases, however, we also observed collective switching of chirality. It happens when a critical number of helices changes their handedness, then a patch of inverted helices is stably propagated (see Figure 49 H).

To verify the key importance of magnetocrystalline anisotropy for forming helical assemblies, we performed additional assembly experiments using differently shaped magnetite NCs, including spheres, truncated octahedra, rounded cubes, as well as $\text{Fe}_3\text{O}_4$-Ag heterodimeric particles (Figure 51), all of which were in the same size regime (10-15 nm). With spherical and octahedral building blocks, we did not observe assemblies other than the one-dimensional belts even at $\chi$ values as high as 5 (Figure 51 A bottom, inset). These observations can be rationalized by the lack of competition between the magnetic interactions and close packing. In the case of octahedral NCs, the magnetocrystalline and shape anisotropy act cooperatively to align the particles with their [111] axes oriented parallel to the applied field, whereas the spheres possess no shape anisotropy.

We also study how cube corner bluntness affects the structure of the assemblies. To this goal, we prepared rounded cubes (Figure 51 B) by growing the NCs in the presence of a mixture of surfactants stabilizing the spherical and the cubic morphologies (oleic acid and sodium oleate, respectively). In this case, the superstructures obtained at high $\chi$ values exhibited helicity, although the helicity was not as prominent as in those superstructures obtained from the original cubes. This observation is consistent with the fact that building blocks have shapes
Figure 51. Self-assembly of Fe$_3$O$_4$ nanocrystals of different shapes. (A) TEM images of truncated octahedra (top) and an SEM image of 1D belts as they assemble (bottom). (B) TEM images of rounded cubes (top) and an SEM image of the resulting helix (bottom). (C) TEM images of Fe$_3$O$_4$-Ag heterodimeric NCs (top) and an SEM image of an ensemble of helices (bottom).

in between those of the spheres and the cubes. Finally, we synthesized novel heterodimers, each comprising a cubic Fe$_3$O$_4$ domain and a spherical Ag domain (Figure 51 C, top). The presence of the Ag particles hinders efficient dipole-dipole interactions between the magnetite domain. Nevertheless, well-defined helices were observed (Figure 51 C, bottom), although the belt-to-helix transition occurred at significantly higher ($\chi > \sim 5.0$) particle densities.

### 8.3 Theoretical model and computational methods

The subject of our theoretical modeling is the self-assembly process of magnetite nanocubes in the presence of an external magnetic field at different densities of NCs and subjected to changing composition of the system associated with evaporation of the solvent during the experiment.
The elementary units of assembled superstructures are magnetite NCs whose magnetic properties depend strongly on the temperature and size of NCs. At room temperature, small \(a < 26\) nm ([318]) magnetite nanocubes are superparamagnetic (SPM) for which no coercive fields [319] is observed. Each nanocube possesses a super-dipole (associated with its single magnetic domain), whose orientation fluctuates at room temperature so it exhibits a net magnetic moment only under an applied field \(H\).

In our simulations we model the cubes by an equation \(x^6 + y^6 + z^6 = (a/2)^6\) with an edge length of \(a = 13.37\) nm (see Figure 52) and volume \(V = \frac{2a^3}{\sqrt{\frac{7}{5}}}\left(\frac{7}{5}\right) \approx 0.9a^3\). This equation mimics the rounded corners and edges of the real magnetite NPs.

![Figure 52. Two cuboids. (Left) The face-to-face and (Right) the corner-to-corner configurations.](image)

In an external magnetic field, \(\vec{H}\), the dipole becomes partially locked to the field by Zeeman coupling, and its motion is further constrained by magnetocrystalline anisotropy (MA). For an
isolated nanocube, the total energy of such a dipole with a given orientation is given by the sum of its Zeeman and MA energies:

$$E_i = E_i^A + E_i^Z.$$  \hfill (8.1)

The Zeeman energy is given by:

$$E_i^Z = -K_z (\vec{H} \cdot \vec{M}_i), \quad \vec{M}_i = \begin{bmatrix} \sin \theta_i \cos \phi_i \\ \sin \theta_i \sin \phi_i \\ \cos \theta_i \end{bmatrix}, \quad 0 < \phi_i < 2\pi, \quad 0 < \theta_i < \pi,$$

where $K_z = 1.647 \times 10^{-2}$ kcal/mol ($2.77 \times 10^{-2} \text{kT}$ at 300K), $\vec{H} = [0, 0, H_0]$ is the external magnetic field vector (in Gauss units), $\vec{M}_i$ is the magnetic dipole unit vector, and $\cdot$ is the dot product. In these formulas both $\vec{H}$ and $\vec{M}_i$ are in the lab frame $(x, y, z)$.

Bulk magnetite ($\text{Fe}_3\text{O}_4$) belongs to the Fd3m crystal structure with a magnetocrystalline anisotropy energy characteristic of cubic crystals with anisotropy constants $K_1 \approx -1.1 \times 10^4 \text{J/m}^3$, $K_2 \approx -0.28 \times 10^4 \text{J/m}^3$ [319–321]. The bulk saturation magnetization of $\text{Fe}_3\text{O}_4$ is $M_s = 480 \text{kA/m}$ [318]. This leads to the amplitude value (per NP) of the intrinsic magnetic moment to be $m_s = M_s \times V = 1.174 \times 10^{-18} \text{A m}^2$, where $V$ is the NP volume. However, for cubic NPs the homogeneous magnetization approximation is no longer valid [267, 322]. The value of the saturation magnetization may be significantly smaller than its bulk value due to the disorder canting spins (spin-glass-like) on the surfaces and the coordination number imperfections [320]. For a realistic case we can assume that the saturation magnetization of a
magnetite NP is decreased as compared to its bulk value by 22% due to the disordered surface layer (typically $\sim 1$ nm [323,324]).

The magnetocrystalline anisotropy energy for cubic crystals includes quartic and sixth order term [318,325]:

$$E^A_i = K_1 \left( (\mathcal{M}'_{ix}\mathcal{M}'_{iy})^2 + (\mathcal{M}'_{ix}\mathcal{M}'_{iz})^2 + (\mathcal{M}'_{iy}\mathcal{M}'_{iz})^2 \right) + K_2 \mathcal{M}'_{iz}^4 \mathcal{M}'_{iy}^2 \mathcal{M}'_{ix}, \quad (8.3)$$

where $K_1 = -3.784$ kcal/mol and $K_2 = -0.963$ kcal/mol, $\mathcal{M}'_i$ is the magnetic dipole unit vector in the cube coordinate ($x', y', z'$). In the following we disregard $K_2$.

The quartic term is about four times larger than the sixth order term. Therefore, we just use this term to describe the MA energy. The reduced formula gives the orientation of the “easy” and “hard” axes of magnetization along the cube body diagonal and the face normal, respectively. The omitted correction does not lead to any significant change in the anisotropy energy and orientation of the magnetization axes. We neglect other corrections of the bulk magnetocrystalline anisotropy energy related to the cubic shape of the nanoparticles [267,322].

The nanocubes interact magnetically with each other by a dipole-dipole (dd) coupling which we describe using the local dipole approximation. For simplicity, we represent in our modeling the super-dipole of a single magnetic domain as a point dipole located in the center of each nanocube [242]. Then, the dd-coupling energy of dipoles in two cubes is given by:

$$E_{dd}^{ij} = K_d \left( \frac{\overset{\rightarrow}{M}_i \cdot \overset{\rightarrow}{M}_j}{|\overset{\rightarrow}{r}_{ij}|^3} - \frac{3(\overset{\rightarrow}{M}_i \cdot \overset{\rightarrow}{r}_{ij})(\overset{\rightarrow}{M}_j \cdot \overset{\rightarrow}{r}_{ij})}{|\overset{\rightarrow}{r}_{ij}|^5} \right), \quad (8.4)$$
where $K_d = \frac{\mu_0 m^2}{4\pi} = 7.923$ kcal/mol when $|\vec{r}_{ij}|$ is in $\text{a}$ units. This approximation neglects higher-order multipole interactions [209,242]. It can be corrected by direct computation of multipole magnetic moments or by calculating magnetic interactions via numerical integration over the surface of the two particles [273,326]. However, our more precise test calculations show that with the average interparticle distance $R_m = 28.23$ Å these corrections may be neglected.

In the absence of MA and dipolar coupling with neighboring nanocubes, the field-induced average magnetization of such SPM nanocubes can be described by the Langevin formula,

$$\langle M_i \rangle = m_s \left( \coth(\alpha) - \frac{1}{\alpha} \right),$$

where $\alpha = \frac{\mu_0 m_s H}{k_B T}$, $m_s$ is the material-dependent saturation magnetization, $H$ is the applied magnetic field, $\mu_0$ is the magnetic permeability of vacuum, $k_B$ is the Boltzmann constant, and $T$ is the temperature [286]. However, the MA and dipole-dipole coupling can significantly modify the magnetization.

In order to estimate the surface vdW coupling energy of two nanocubes (vacuum), we build an atomistic model of the nanocubes coated with oleic acid (OA) ligands (see Figure 55 C). This ligand-ligand coupling results in a high vdW energy of $\sim 700$ kcal/mol per nanocube surface. However, this large surface vdW coupling can only take part upon a complete evaporation of excess OA used as a co-solvent. Since evaporation of OA does not take place under experimental conditions, we cannot use this surface vdW coupling in our MC simulations. Instead, we describe the non-magnetic coupling between our nanocubes by an anisotropic potential (see Figure 55 D) which includes bulk vdW attraction of the nanocube cores in the OA solvent and the steric repulsion between the surface ligands:
\[ E_{ij}^{\text{vdW}} = E_{ij}^{\text{attr}} + E_{ij}^{\text{rep}}, \quad E_{W}^{\text{attr}} = -\varepsilon_1 \frac{A}{\pi^2} \int \int_{V_i,V_j} \frac{dV_i dV_j}{r_1^6}, \quad E_{W}^{\text{rep}} = \varepsilon_2 K_W \int_{S_i} \frac{dS_i}{(r_2 + \beta)^8}. \] (8.5)

The attraction term is a pairwise Hamaker expression (with a scaling constant \( \varepsilon_1 \)), in which the integral is taken over volumes of two interacting nanocubes. Each nanocube is divided into \( 3^3 = 27 \) identical volume elements over which the integral (sum) is performed, \( A = 3 \) kcal/mol is the Hamaker constant of magnetite in hexane, and \( r_1 \) is the distance between the centers of two volume elements in different nanocubes. The repulsion term is expressed as an integral (sum) over 386 surface elements that subdivide the cubes cuboid surface (the elements have different surface areas). Here, \( r_2 \) is the distance between the center of a surface element of a chosen nanocube and the surface element of the interacting nanocube. The shape of the vdW potential (Figure 55 D) is tuned by fitting parameters \( \varepsilon_1 = 130, \varepsilon_2 = 290, \) and \( \beta = 9.56 \) nm in a way that the energy minimum of the effective vdW potential is located at the average surface-to-surface distance of two face-to-face nanocubes, as in experiments (2.99 nm). The strength of the vdW coupling (depth of the potential curve) is defined by a constant \( K_W = \varepsilon_1 \frac{A}{\pi^2} \left( \frac{0.9a^3}{27} \right)^2 = 2.5105 \) nm\(^6\) kcal/mol, which gives a maximum vdW interaction energy of 2.33 kcal/mol per nanocube.

We add the above energy contributions to obtain the total energy of an ensemble of nanocubes:

\[ E_T = \sum_{i=1}^{N_P} E_i + \sum_{i=1}^{N_P} \sum_{j=i+1}^{N_P} \left( E_{ij}^{dd} + E_{ij}^{\text{vdW}} \right), \] (8.6)

where \( N_P \) is number of particles and the internal energy \( E_i \) is the sum of the magnetocrystalline anisotropy energy and the Zeeman energy given by Equation 8.1.
Overall, to simulate the self-assembly process we need to treat both material and magnetic degrees of freedom associated with the motion of NCs in Euclidean space and the rotation of superparamagnet dipole moments of each NC, respectively. Even for a simple system of a few interacting magnetically anisotropic NCs, such a treatment becomes an extremely challenging computational problem for a strict analytical approach. For this reason, in our simulations of the nanocube self-assembly we use the energy $E_T$ to perform a Markov Chain Monte Carlo (MCMC) algorithm based on the Metropolis scheme [327]. The algorithm uses pseudo-random numbers ("random walks") to generate configuration samples that form a Markov chain. The configuration chain represents a trajectory that should eventually converge to an equilibrium canonical ensemble of nanocube-structure configurations. The expectation values can be obtained by averaging over the equilibrated configurations in the stabilized trajectory.

In principle, the equilibrium configurations of the canonical ensemble can be generated in an arbitrary manner. To elucidate specifically magnetic structures for frozen nanocube positions, we performed separate semi-analytical simulations, where for a few NCs system we average magnetic energies over a phase space associated with magnetic degrees of freedom:

$$
\langle E_T \rangle = \frac{\int E_T e^{-E_T / k_B T} \Pi_i d\Omega_i}{\int e^{-E_T / k_B T} \Pi_i d\Omega_i} \quad (8.7)
$$

Here, $d\Omega_i = \sin \theta_i d\theta_i d\phi_i$, and $\theta_i, \phi_i$ are the spherical angles of individual magnetic dipoles in the lab system of coordinates.

In the MC simulations, we compute the total energy difference, $\Delta E_T$, between the system configurations before and after we perform the proposed nanocube or dipole movements. In the
Metropolis scheme, a new configuration is accepted when $\Delta E_T \leq 0$ or when a random number in the interval $[0,1)$ is smaller than $e^{-\Delta E_T/k_B T}$, otherwise the old configuration is kept and the MCMC algorithm proceeds to the next step. In one MCMC cycle, we first vary the values (position and orientation) associated with the mechanical degrees of freedom of every nanocube, and then we perform 10 magnetic steps (local magnetic dipole orientation sampled randomly) for all nanocubes in a random order. We introduce the nanocube translation by a randomly oriented vector and a random length shorter than $\delta s$. Likewise, nanocube rotation is performed by moving the nanocube around a randomly oriented axis by a random angle smaller than $\delta a$.

During the simulation, $\delta s$ and $\delta a$ can be changed by 5% (up or down) every 10 cycles in the first 2000 MC cycles and every 1000 MC cycles thereafter to maintain a 50% acceptance rate of the proposed configurations. We achieve uniform sampling in the orientation space by choosing our randomly oriented vectors from a $\mathbb{R}^3$ unit sphere [328]. This vector selection process is also used to prepare the randomized initial dipole orientation of our simulated systems.

In the simulations, we use the Gilbert-Johnson-Keerthi (GJK) algorithm [329] to efficiently determine if two nanocubes overlap. The GJK algorithm can be applied to any convex shapes, once a support function for the particular shape is given. To find the support function for our nanocubes, we apply the Lagrange multiplier method with a constraint equation $x^6 + y^6 + z^6 = (a/2)^6$. The support function for an axis-aligned cuboid-shaped nanocube is given by:

$$
supp(\vec{d}) = \frac{a/2}{\sqrt{d_i^{6/5} + d_j^{6/5} + d_k^{6/5}}} \cdot \left( d_i^{1/5}, d_j^{1/5}, d_k^{1/5} \right), \quad (8.8)
$$
The support function returns a point on the nanocube that is furthest along the direction $\vec{d} = (d_i, d_j, d_k)$. $\text{MinD}(\vec{d}) = \text{supp}_i(\vec{d}_i) - \text{supp}_j(\vec{d}_j)$ gives a boundary point on the Minkowski difference of nanocube $i$ and $j$, where $\vec{d}_i$ and $\vec{d}_j$ are $d'$ projected onto the coordinate of nanocube $i$ and $j$, respectively. Tetrahedron (3-simplex) formed by four points on boundary of the Minkowski difference will enclose the origin if overlap exists and the enclosure check is done by only a few dot product operations.

8.4 Theoretical study of self-assembly of magnetite nanocubes

To better understand the nature of the NC superstructures, we model the self-assembly of NCs by separate semi-analytical simulations and Monte Carlo (MC) simulations performed in a canonical ensemble [327]. We model the self-assembly of nanocubes functionalized with oleic acid ligands and solvated in hexane with an additional oleic acid, in the presence of external magnetic fields. The nanocubes have coupled mechanical and magnetic degrees of freedom. They interact with one another by van der Waals (vdW) coupling, originating in the NC bulk material, the NC ligands, and the solvent. The super-dipoles, associated with the single magnetic domains of the nanocubes, interact with the external field by the Zeeman coupling, the dipoles of neighboring nanocubes by a dipole-dipole (dd) coupling, the spatial orientations of the nanocubes are defined by shape anisotropy and magnetocrystalline anisotropy (MA).

The dynamics of a typical NC self-assembly experiment is controlled by varying competing forces due to changing composition of the system associated with hexane evaporation. Therefore, both thermodynamically and kinetically controlled processes take part in the self-assembly process. Initially, the ligated nanocubes are well soluble in hexane, and form only short chains
(Figure 48) when the magnetic field is applied. As hexane evaporates, the nanocubes start to coagulate in the remaining OA [314] due to vdW attraction and magnetic coupling. The coagulation is likely enhanced by depletion (entropic) forces and forces related to the gradient of hexane concentration (drying). Eventually, hexane evaporates completely and the self-assembled structures become frozen and partly fractured due to capillary forces from an OA film covering them.

The total energy of NC assemblies, $E_T$, is defined as the sum of energies related to the above interactions (equations Equation 8.1 - Equation 8.6). The Zeeman coupling tends to align the dipoles along the field, but MA prefers them to be oriented along the NC body diagonals. The dd coupling causes attraction between two parallel dipoles when they are within a cone with an azimuthal angle, $\theta < \cos^{-1}(1/\sqrt{3}) \approx 54^\circ$, otherwise, repulsion is expected. The dd-coupling can be combined with the external field to form an effective magnetic field, $H$ (magnetic susceptibility), which determines the outcome of the individual magnetic contributions and determines the types of formed structures. In the presence of a weak $H$, only short nanocube chains form (e.g. Figure 47). When $H$ is higher, the nanocubes form thin belts (belts100). At even higher $H$, wide, multilayered belts110 are observed; finally, when $H$ are the highest, the assemblies that form show helical features.

**8.4.1 Semi-analytical modeling of small magnetite nanocube aggregates**

First, we consider the individual cube case. The exact model which includes the Zeeman and anisotropy energy terms predicts that non-interacting superparamagnetic NPs align their body diagonals (easy axis magnetization) along an external magnetic field irrespectively on values
of magnetocrystalline anisotropy constants. The application of the external field leads to the precession of the superparamagnetic dipole moment around the field direction (z-axis) perturbed by magnetocrystalline anisotropy of nanocube. For the field $H = 500 \, G$ and $K_a = -6.34 \, kT$ the cone angle $\theta = 22^\circ$ and $\theta = 31^\circ$ for orientations of the cube along the easy- and hard-axis of magnetization, respectively. For the field $H = 2000 \, G$, the cones get narrower $\theta = 11^\circ$ and $\theta = 14^\circ$, respectively.

Next, we consider two cubes interacting via the dipole-dipole mechanism. We treat two NPs within the local dipole approximation and disregard the effects of non-local dipole and non-homogeneous magnetization. We also consider only magnetic forces and neglect vdW interaction. Within this model we take into account the spatial averaging of the magnetic moments, so that

$$E_T(\Omega_1, \Omega_2) = E_1^Z + E_2^Z + E_1^A + E_2^A + E_{dd}^{12}$$

and:

$$\langle E_T \rangle = \frac{\int E_T e^{-E_T/kT} d\Omega_1 d\Omega_2}{\int e^{-E_T/kT} d\Omega_1 d\Omega_2}, \quad d\Omega_i = \sin\theta_i d\theta_i d\phi_i.$$  \hspace{1cm} (8.9)

The results of calculations (Equation 8.9) are shown in Figure 53. One can see that the corner-to-corner (c-c) configuration (see Figure 52) becomes more stable than the face-to-face (f-f) one at larger anisotropy constant $K_1$. The threshold shifts towards smaller $K_1$ for stronger fields. The dipolar coupling narrows down the precession cones of magnetic moments due to local magnetic field ($\sim 500 - 700 \, G$) comparable to the external one. Qualitatively, the winning of the f-f configuration may be understood as follows. In “weak” field ($H_0 = 500 \, G$), the cone angles $\theta = 20^\circ$ and $\theta = 23^\circ$ for both configurations are small enough to treat dipoles
approximately as permanent ferromagnetic dipoles. Therefore, the dipolar coupling takes over the anisotropy energy difference simply because of the shorter distance between dipoles in $f-f$. In “strong” field ($H_0 = 2,000 \text{G}$), both cones become narrower in such a way that $\theta = 11.5^\circ$ and $\theta = 12.2^\circ$ for the $c-c$ and $f-f$, respectively. Therefore, the difference between dipolar coupling energies becomes smaller, and difference in anisotropy energies becomes more important leading to the more stable $c-c$ configuration.

Figure 53. The average energy of two magnetite cubes as a function of anisotropy constant $K_1$ at $500 \text{G}$ (Left) and $2000 \text{G}$ (Right) for the corner-to-corner and face-to-face configurations.

Next, we analyze in more detail the interplay between the anisotropy energy and dipolar coupling. The competition between these two contributions is believed to result in formation of helical structures in “weak” field and straight closely packed ribbons in “strong” magnetic field.

In Figure 54 we show how the average magnetic energy, $\langle E_T \rangle$, average $z$- and $x$-projections, $\langle \mathcal{M}_z \rangle$ and $\langle \mathcal{M}_x \rangle$, of individual dipole moments depend on the tilting angle $\theta$ around $y$-axis in
Figure 54. (Left) Two cubes in \( f-f \) configuration tilted by angle \( \theta \) from \( z \)-axis. (Right) \( \langle E_T \rangle \), \( \langle M_z \rangle \) and \( \langle M_x \rangle \) in two tilted cubes in \( f-f \) configuration in “weak” and “strong” field at different anisotropy constants \( K_1 \). \( \langle M_{z,x} \rangle \) are in the units of \( M_s \).

“weak” and “strong” magnetic field for different anisotropy constants. When no anisotropy term is included (the black solid line in Figure 54), the tilting is not energetically favorable due to the weakening of dipolar coupling between two magnetite cubes. Unlike a ferromagnetic dipole whose \( z \)- and \( x \)- projections would change monotonically with tilting angle as \( \cos \theta \) and \( \sin \theta \), a superparamagnetic dipole of each cube depends on \( \theta \) in a more complicated manner. When tilting, not only the axis of the procession cone tilts but the cone span changes as well. In a “strong” field, the cone span is small and, when tilting, the cone axis declines from \( \vec{H} \) resulting in decreasing \( \langle M_z \rangle \) (Figure 54 d). At the same time, due to the dipolar coupling the tilting leads to the decrease of local \( \langle H_z \rangle \). This results in the spanning of the procession cone so that when the tilting angle \( \theta \) runs from 0° to 90° \( \langle M_z \rangle \) first decreases due to the procession cone
declining and spanning, passes through the minimum, and then increases back to the smaller than \( \langle M_z(\theta = 0^\circ) \rangle \) value due to the straightening of the cone axis along \( \vec{H} \).

In “weak” field the cone span is larger, and the effect of the straightening of the procession cone back to \( \vec{H} \) on \( \langle M_z \rangle \) is washed out (see black solid line in Figure 54 c), so \( \langle M_z(\theta = 90^\circ) \rangle \) is much smaller than its initial value. Ultimately, in the absence of dipolar coupling we would have \( \langle E_T \rangle \sim -\sin^2 2\theta \), \( \langle M_z \rangle \sim \sin^2 2\theta \) and \( \langle M_x \rangle \sim -\sin 4\theta \). The larger anisotropy constant is, the closer we are to this extreme case. This can be seen in Figure 54: as we gradually increase the anisotropy constant, \( \langle M_z \rangle \) develops maxima and \( \langle E_T \rangle \) develops minima. As expected, the optima are more pronounced in “strong” field due to the smaller procession cone span (compare Figure 54 a and b).

The exact treatment of the two cube system revealed two principal features of interaction between magnetite cubes. First. The tilting of two cubes in \( f-f \) configuration leads to the more stable structure only if the anisotropy constant \( K_1 \) is larger than some critical value. The effect is more pronounced in “strong” field. With the realistic \( K_1 = -6.34 \text{ kT} \) the tilting is favorable neither in “weak” nor “strong” field. Second. The magnetization of each cube keeps track of the tilt, so that \( \langle M_z \rangle \neq 0 \). The extension of the exact model from 3 cubes up to an infinite chain of cubes in \( f-f \) configuration shows that the average dipole moment \( \langle M \rangle \) follows almost linearly the tilt of the chain. However, at \( \theta = 90^\circ \), \( \langle M \rangle \) becomes parallel to the field \( \mathcal{H} \), irrespective to its value as seen in Figure 54 e, f. This is drastically different from the approximate model of the infinite chain with ferromagnetic dipole moments where dipoles of each cube follows linearly the chain tilt, so in “weak” field at \( \theta = 90^\circ \) the dipoles are tilted
with respect to the field direction by 81° whereas in “strong” field they are tilted only by 55°.
It also shows that for large tilting angles, the approximate model overestimates the dipolar interaction, and only in “strong” field and relatively small tilting angles the exact model gives the same results as the approximate one.

Next, we analyze the effect of the external magnetic field on the dipole-dipole interaction between two superparamagnetic anisotropic nanocubes. Equation 8.4 gives the dd-coupling energy of two fixed dipoles. However, the average dd-energy can be obtained by statistical averaging of $E_{dd}^{ij}$ over thermally accessible dipole orientations (in MC simulations averaging over trajectories), as schematically shown for two nanocubes in a face-to-face arrangement in Figure 55 A. The distance dependencies of average dd-energy (Figure 55 B) obtained by these semi-analytical simulations shows the following. The average dd-coupling energy between two fluctuating dipoles positioned side-by-side and affected by the MA and the Zeeman coupling (see Equation 8.7) changes with distance from $-1/R^6$ (attraction) for randomly fluctuating magnetic dipoles (Keesom-like potential, weak-field regime of SPM nanocubes) to $1/R^3$ (repulsion) for strongly coupled ferromagnetic dipoles [330] (strong-field regime of SPM nanocubes). At medium field strengths (200-500 G) the $R$-dependence is non-monotonic with explicit repulsion and attraction regions. When the same calculation is done for nanocubes rotated by 45° with respect to field (cube edge on top) (corresponding to a diamond-like arrangement in Figure 45 E, right), the field dependence is similar, except that the repulsion starts at much lower fields ($\sim 50 - 100 G$). These results indicate that the simple-cubic lattice arrangement is
more reactive, since neighboring nanocubes can help each other to minimize MA by tilting the dipoles.

Another very interesting feature of a two superparamagnetic NC system is that it possesses intrinsic chiral properties. Figure 56 shows the formation of a transiently chiral nucleus formed by two NCs with vdW coupling in a magnetic field at room temperature. The NCs spend most of the time in configurations that possess either left or right chirality, where the angle between the cubes is around $\sim 10 - 30$ degrees. Both NCs are tilted with respect to the direction of the external magnetic field tending to align their easy axes of magnetization along the field. The chirality is the result of a competition between the magnetic and the spatial (cubic) symmetries. We propose that the propagation of these transiently chiral structures in the presence of many cubes leads to the formation of globally chiral helices.

8.4.2 **MC study of self-assembly of nanocubes**

For large systems comprised by hundreds of NCs we use MC simulations to evaluate the average values of different components of $E_T$. In the MC simulations we do not consider the solution or ligands explicitly. First, we study orientations of the magnetic dipole moments in different spatially fixed, perfectly aligned nanocube lattices (see Figure 45 E). In thin belts$_{100}$ under a relatively weak external magnetic field ($H = 167 G$), the (local) dipoles are on average largely oriented along the belts (Figure 45 E). Here, placing the dipoles above each other strengthens their parallel orientations (attractive dd-coupling). However, in wider belts (unfavorable side-by-side dd-interactions) under the same field, the dipoles tend to form a zigzag configuration, which is unlocked from the external field (as the effective field grows in magnetite), and increas-
Figure 55. (A) Two superparamagnetic nanocubes with side length $a$ positioned side by side and aligned face-to-face. (B) Field-dependent average magnetic energy $\langle E(R) \rangle$ of two nanocubes at temperature, $T = 300$ K. The magnetic energy of two isolated cubes is set as zero. Weak- and strong-field asymptotic dependencies are shown by dashed black lines. (C) Atomistic model of nanocubes coated with oleic acid ligands. (D) The effective vdW potential associated with bulk nanocube coupling. Top inset: surface elements (color scale from blue to red corresponds to the increase of the surface area per element) used in the repulsive part of the vdW coupling energy ($E_{\text{rep}}$ in Equation 8.5). Bottom inset: subdivision of a nanocube by 27 identical volume elements (colored for clarity) used in the attractive part of the vdW coupling energy ($E_{\text{attr}}$ in Equation 8.5).
Figure 56. (A) Typical configuration of two cubes in an external field, $H = 167$ G (vertical $z$-orientation at $T = 300$ K (bulk vdW coupling is reduced by $1/2$ with respect to the nominal value) (B) View along the cube axis reveals that the nanocube pair is (transiently) chiral. Magnetic dipoles are represented by red arrows.

...ing the contribution of MA. Note that the dipoles positioned near belt boundaries are aligned more vertically due to the dominant coupling to the external field. The effect of external field strength is illustrated in Figure 45 D, whereby a zigzag-to-parallel transition of dipoles in a relatively wide belt$_{100}$ is observed under increasing ($H = 167$, 417, and 668 G) external field. In multilayered stripes, the zigzag arrangement occurs in two dimensions, which leads to the formation of an onion-like dipole configuration, with counter-propagating fluxes in neighboring flux-closure rings [248, 287] (see Figure 57).

Next, we compare the relative stability of belt$_{100}$ vs. belt$_{110}$ by MC simulations. In general, the outcome of this competition is determined by the interplay between vdW interactions...
Figure 57. Averaged orientation of dipoles in a thick filament under relatively weak external field ($H = 167 \, G$). The top two layers are purposely separated from the structure (left) to better illustrate the dipole arrangement.

(disfavor belt$_{110}$ because of its corrugated sides), and magnetic interactions (favor belt$_{110}$ because of the arrangement of individual NCs enabling easy magnetization). Large thicknesses and heights of belts entail increasing induced magnetic field, and they favor belts$_{110}$ as observed experimentally. Quantitative analysis of the two types of belts of different thicknesses is shown in Figure 58.

Despite the favorable arrangement of dipoles in the direction parallel to the long axis of belt$_{110}$, the zigzag configuration is preserved in multilayered belts$_{110}$ in the direction perpendicular to the liquid-air interface. A smooth (non-zigzag) connectivity of the dipoles following the nanocubes easy axis can be resolved if the structures are further reconfigured by “side-stepping” of the nanocubes, which eventually leads to helical structures. Figure 59 shows snapshots from MC simulations of nanocube assemblies during helix formation, and the corresponding energies (Zeeman energy $E_z$, dipole-dipole energy $E_{dd}$, anisotropy energy $E_a$, total magnetic
Figure 58. Potential energies of self-assembled belts as a function of belt thickness, arrangement of cubes, and strength of the external field. Total magnetic energy, $E_{\text{mag}}$, is the sum of the Zeeman energy, $E_z$, dipole-dipole energy, $E_{dd}$, and anisotropy energy, $E_a$: $E_{\text{mag}} = E_z + E_{dd} + E_a$. Total potential energy, $E_{\text{all}}$, is the sum of total magnetic energy and the van der Waals energy: $E_{\text{all}} = E_{vdW} + E_{\text{mag}}$. All values are in kcal/mol per nanocube. Averaged orientations of dipoles in different belts (left) are shown for weak external field ($H = 167$ G). The belts comprise the following numbers of nanocubes, from left to right: 300, 284, 600, 564, 900, 846. All of the energy values and dipole configurations shown in the figure are averaged over 10,000 MC steps.
energy \( E_{mag} = E_z + E_{dd} + E_a \), van der Waals energy \( E_{vdW} \), and the total potential energy 
\( E_{all} = E_{vdW} + E_{mag} \). The loss of vdW coupling and, to some extent, the Zeeman and dd coupling in helices is compensated by the gain in \( E_a \) and the growth of entropy of the looser and more randomly organized NCs (Figure 59 also seen experimentally, e.g. Figure 49 D) (these simulations were performed with scaled parameters to yield helices despite the small widths of the filaments; helices formed by thick filaments should be less prone to entropic forces due to stronger effective magnetic fields).

Figure 59. Snapshots of nanocube assemblies during helix formation (left) and the contributing energies (right) \( (E_z, \text{Zeeman energy}; E_{dd}, \text{dipole-dipole energy}; E_a, \text{anisotropy energy}; E_{mag} = E_z + E_{dd} + E_a, \text{total magnetic energy}; E_{vdW}, \text{van der Waals energy}; E_{all} = E_{vdW} + E_{mag}, \text{total potential energy}) \). The curves in the plots were obtained from smoothing (window = 500 steps) the original data (shown as thin lines).
Figure 60. Potential energy dependence on the distance between two perfectly aligned and slightly disordered belts. In each case, total magnetic energy, $E_{\text{mag}} = E_z + E_{dd} + E_a$, was averaged at each distance over 5,000 MC steps of two belts approaching each other as a function of their separation. $E_{\text{mag}}$ of two isolated belts was set as zero. The cases of weak, intermediate, and strong external magnetic fields ($H = 167, 417, 688$ G, respectively) are shown for two $n \times n \times 100$ belts, where $n = 2, 3, 4, 5$, and 6.

Having discussed the magnetic and spatial structures of individual belts and helices, we examine the formation of their ensembles. The formation of wide ribbons in weak fields signifies the NC attraction perpendicular to the field direction [331,332]. Simulations (Figure 60) show that two parallel belts attract each other if their dipoles assume zigzag configurations, but they repel each other when the dipoles are largely parallel. Therefore, under weak fields, narrow
Figure 61. Potential energy dependence on the distance between two helices approaching each other along the direction shown by the arrow. Zeeman energy, $E_z$; dipole-dipole energy, $E_{dd}$; anisotropy energy, $E_a$; and total magnetic energy, $E_{mag} = E_z + E_{dd} + E_a$ at each distance were averaged over 5000 MC steps.
belts repel each other (parallel dipoles) whereas the wide ones attract (zigzag dipoles). As the external field grows, belts switch their magnetic arrangements from zigzag (attraction) to parallel (repulsion) (Figure 45 D), which stops their widening at high fields, in agreement with the experiments. However, at low fields the zigzag belts would widen without limitation, contrary to observations. In reality, introduction of a disorder within the belts observed experimentally causes the zigzag attraction to be overcome by a mean interfilament repulsion (Figure 60, right). We also modeled a potential energy dependence of two helices as they approach one another to explain the observation of parallel helices (Figure 50). Figure 61 shows that decreasing distance between the helices is associated with their magnetic repulsion. The nature of this interaction is such that it induces the same helicity in neighbors and keeps them in registry.

8.5 Conclusion

Organizing inorganic nanocrystals into complex architectures is challenging and typically relies on pre-existing templates, such as DNA origami or folded polypeptide chains. In this research project we show that under carefully engineered conditions, cubic nanocrystals of magnetite self-assemble into arrays of helical superstructures in a template-free, near-quantitative manner. Computer simulations revealed that the formation of helices is determined by the interplay between van der Waals and magnetic dipole-dipole interactions, Zeeman coupling, as well as entropic forces. Moreover, we found that neighboring helices within densely packed ensembles adopt the same handedness in order to maximize packing, thus revealing a novel mechanism for chirality amplification.
We envision that the diversity of self-assembled superstructures could be further expanded by i) decorating the surfaces of magnetite NCs with functional ligands [333], ii) choosing SPM NCs of different shapes and compositions (e.g. Ni, Fe, and CoFe$_2$O$_4$) as starting materials; iii) using mixtures of different NCs as building blocks (see Figure 57), and iv) employing complex / dynamic magnetic [334] fields during the self-assembly process.
CHAPTER 9

CONCLUDING REMARKS

The scope of the research projects described in the thesis encompasses a number of systems whose scale ranges from atomic to macroscopic sizes of several hundred microns. We have investigated the electronic properties and structural characteristics of these systems. Due to the quite different scale of the phenomena, we have implemented a vast variety of theoretical and computational methods combining heavy and extensive numerical calculations with analytical methods of mathematical physics. We have used \textit{ab-initio} DFT-based approaches, the Schrödinger variational principle mixed with semi-analytical methods of classical electrostatics, classical Monte Carlo methods to characterize the electronic and electron transport properties of graphene-based materials, electron correlations in quasi-atomic systems, stability and structural properties of the superstructures self-assembled out of magnetic nanoparticles systems. The computational models of the studied systems are sufficiently realistic to describe their chemical and physical properties and can potentially be used to investigate new phenomena. We have reproduced in many cases the experimental results both from a qualitative and quantitative points of view.

We have demonstrated by DFT-based electronic structure calculations that the perforation of graphene-based materials with nanopores can be used to tune their switching from semiconducting to metallic character. We found common features of electronic properties of porous nanocarbons and built a unified model that permits us to predict conductivity properties.
of superlattices without performing time-consuming quantum mechanical calculations. These complex nanostructures have a great potential for being used for molecular sensing, detection, separation and possess unique transport and optical properties.

Using a combination of ab-initio methods of electronic structure calculations with methods of classical and quantum MD we have shown that graphene grain boundaries (formed by merging two graphene grains) have an outstanding chemical sensitivity to electron donor/acceptor gas molecules. We have simulated the electron transport through individual graphene grain boundaries in the presence/absence of chemical analytes and explained the sensitivity mechanism in terms of closing or opening of local conduction channels through the GB by the adsorbed analytes.

We have used ab-initio DFT-based methods to evaluate the electronic properties and the CO$_2$ reduction capability of bulk molybdenum disulfide. Our first principle modeling revealed that the molybdenum terminated edges of bulk MoS$_2$ are mainly responsible for its superior catalytic performance, due to their metallic character, a high d-electron density and low work function. The outstanding catalytic activity of bulk MoS$_2$ is observed in an ionic liquid containing EMIM-BF$_4$. We have performed QM/MM simulations of the (EMIM-CO$_2$)$^+$ complex formation in water and showed the role of this complex in decreasing the potential barrier of the reduction reaction.

Using the Schrödinger variational technique we have studied extended excited diskoid-like electronic states formed in the vicinity of charged and highly polarizable molecules of diskotic shapes, e.g., circular graphene flakes. We have used a simple two-electron He-like Hamiltonian
with one electron locked in a 2D disk area and another one moving in 3D space to evaluate the electron-electron correlations. Pronounced and complex effects of correlated motion of two electrons were found even in highly excited states. We also developed a semi-classical one-electron model based on the rigorous solution of the Poisson equation to find a connection between one- and many-electron solutions.

The stabilization of clusters and lattices of spherical particles interacting by weak vdW coupling and possessing permanent electric or magnetic dipole moments was studied using semi-analytical modeling. We have considered a large variety of particle configurations with fixed orientation of dipoles corresponding to the closed-flux circulation of the dipolar field and explained for which parameters the nanoparticle can form lattices with \textit{fcc}, \textit{hcp}, and \textit{sh} types of packing. Our results demonstrate that dipolar coupling can stabilize clusters with planar, tubular, and other more complicated 3D arrangements.

Using mixed semi-analytical and classical Monte Carlo simulations we have modeled the formation of chiral helical nanoparticle superstructures during the self-assembly of magnetite superparamagnetic nanocubes at the liquid-air interface in the presence of the external magnetic field. The emergence of these and other assemblies was rationalized in terms of interplay between vdW and magnetic dipole-dipole interactions, Zeeman coupling, magnetocrystalline anisotropy, as well as entropic forces. We have studied the coupling between intrinsic and external degrees of freedom of nanocubes associated with rotation of superparamagnetic dipole moment and motion of nanocubes in 3D space and its effects on the assembling structures. We found that realistic coupling parameters lead to the formation of experimentally observed structures.
In all the above studies, we have shown a variety of multiscale methods of modeling of electronic properties and structural characteristics and dynamics of nanosystems. The studied systems can be used to perform molecular sensing, separation of gas/liquid mixtures, highly effective and low cost carbon dioxide reduction. The revealed mechanisms of self-assembly of isotropic or anisotropic dipolar nanoparticle/nanocrystals can be then used to design novel superstructures with unique material properties. The revealed electron correlations in extended image states formed around highly polarizable clusters can be used for probing electronic properties of surfaces of new materials at the nanoscale.
CITED LITERATURE


150. Hoshi, N. Electrochemical reduction of CO2 on single crystal electrodes of silver Ag(111), Ag(100) and Ag(110). *J. Electroanal. Chem.* **440**, 283 (1997).


APPENDIX

Title: Clusters and Lattices of Particles Stabilized by Dipolar Coupling
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APPENDIX

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